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Titanium Dioxide Material for a Sustainable Environment

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TITANIUM DIOXIDE -MATERIAL FOR A SUSTAINABLE ENVIRONMENT

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Meet the editor



Dongfang Yang received his PhD degree in Physical Chemistry from the University of Guelph in 1995. He joined the National Research Council Canada in London, Ontario, in 2001 and is now a senior research officer. His current research interests include laser material processing; pulsed laser, sputtering, and e-beam deposition of thin films; new materials development for energy storage

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Contents

Preface XIII

| Section | 1 Synthesis and Characterization 1 |
|---------|--|
| Chapter | Hierarchical Nanostructures of Titanium Dioxide: Synthesis and Applications 3 Ramsha Khan, Sofia Javed and Mohammad Islam |
| Chapter | 2 Novel Two-Dimensional Nanomaterial: High Aspect Ratio Titania Nanoflakes 41 Yang-Yao Lee |
| Chapter | 3 Mesoporous TiO2 Thin Films: State of the Art 57 Francesca Scarpelli, Teresa F. Mastropietro, Teresa Poerio and Nicolas Godbert |
| Chapter | Pure and Nanocomposite Thin Films Based on TiO2 Prepared by Sol-Gel Process: Characterization and Applications 81 Nelcy Della Santina Mohallem, Marcelo Machado Viana, Magnum Augusto Moraes Lopes de Jesus, Gustavo Henrique de Magalhães Gomes, Luiz Fernando de Sousa Lima and Ellen Denise Lopes Alves |
| Chapter | 5 Novel TiO2 Photocatalyst Using Nonaqueous Solvent- Controlled Sol-Gel Route 99 Inderjeet Singh and Balaji I. Birajdar |
| Chapter | 6 Factor Affecting Geometry of TiO2 Nanotube Arrays (TNAs) in |

Aqueous and Organic Electrolyte 1102 Nanotube Arrays (TNAS) In Aqueous and Organic Electrolyte 117 Khairul Arifah Saharudin, Srimala Sreekantan, Rabiatul Basria S. N. M. Mydin, Norfatehah Basiron and Warapong Krengvirat

- Chapter 7 Recent Advances in TiO2 Nanotube-Based Materials for Photocatalytic Applications Designed by Anodic Oxidation 131 Phuoc Huu Le and Jihperng Leu
- Chapter 8 Synthetic Methods for Titanium Dioxide Nanoparticles: A Review 151 Pardon Nyamukamba, Omobola Okoh, Henry Mungondori, Raymond Taziwa and Simcelile Zinya
- Chapter 9 Innovation in the Electrophoretic Deposition of TiO2 Using Different Stabilizing Agents and Zeta Potential 177 Erick Barrios Serrano, Mercedes Teresita Oropeza-Guzmán and Eduardo Alberto López-Maldonado
- Chapter 10 Luminescence from TiO2 Nanotubes and Related Nanostructures Investigated Using Synchrotron X-Ray Absorption Near-Edge Structure and X-Ray Excited Optical Luminescence 191 Lijia Liu and Tsun-Kong Sham
 - Section 2 Photocatalytic Applications 209
- Chapter 11 Titanium Dioxide Films for Photocatalytic Degradation of Methyl Orange Dye 211 Rodrigo Teixeira Bento and Marina Fuser Pillis
- Chapter 12 **Preparation of Blue TiO2 for Visible-Light-Driven Photocatalysis 227** Jianmin Yu, Chau Thi Kim Nguyen and Hyoyoung Lee
- Chapter 13 Photocatalytic Degradation of Selected Organophosphorus Pesticides Using Titanium Dioxide and UV Light 241 Andreas S. Petsas and Maria C. Vagi

 Chapter 14 Photocatalytic TiO2: From Airless Jet Spray Technology to Digital Inkjet Printing 261
 Claudia L. Bianchi, Carlo Pirola, Marta Stucchi, Giuseppina Cerrato, Federico Galli, Alessandro Di Michele, Serena Biella, Wen-Fan Chen, Pramod Koshy, Charles Sorrell and Valentino Capucci Chapter 15 Influence of the Synthesis Method on the Preparation Composites Derived from TiO2-LDH for Phenol Photodegradation 281

Juan C. Contreras-Ruiz, Sonia Martínez-Gallegos, Jose L. García-Rivas, Julio C. González-Juárez and Eduardo Ordoñez

- Chapter 16 TiO2-Low Band Gap Semiconductor Heterostructures for Water Treatment Using Sunlight-Driven Photocatalysis 305 Raquel Del Angel, Juan C. Durán-Álvarez and Rodolfo Zanella
- Chapter 17 Silver Nanoparticle Incorporated Titanium Oxide for Bacterial Inactivation and Dye Degradation 331 Endang Tri Wahyuni and Roto Roto
 - Section 3 Solar Cell and Other Applications 349
- Chapter 18 Controlling the Microstructure and Properties of Titanium Dioxide for Efficient Solar Cells 351 Ahmed Esmail Shalan, Ahmed Mourtada Elseman and Mohamed Mohamed Rashad
- Chapter 19 One-Dimensional Titanium Dioxide and Its Application for Photovoltaic Devices 367 Norani Muti Mohammed, Robabeh Bashiri, Suriati Sufian, Chong Fai Kait and Saeed Majidai
- Chapter 20 Titanium Dioxide Modifications for Energy Conversion: Learnings from Dye-Sensitized Solar Cells 387 Hammad Cheema and Khurram S. Joya
- Chapter 21 **TiO2 Applications as a Function of Controlled Surface Treatment 421** Nika Veronovski
- Chapter 22 Nanostructured Titanium Dioxide for Functional Coatings 445 Indriana Kartini, Inna Yusnila Khairani, Chotimah, Kuwat Triyana and Sri Wahyuni
- Chapter 23 **Titanium Dioxide Nanotube Arrays for Biomedical Implant Materials and Nanomedicine Applications** 469 Rabiatul Basria S.M.N. Mydin, Roshasnorlyza Hazan, Mustafa Fadzil FaridWajidi and Srimala Sreekantan

Chapter 24 Investigation of Optical Properties and Radiation Stability of TiO2 Powders before and after Modification by Nanopowders of Various Oxides 485

Mikhail M. Mikhailov, Vitaly V. Neshchimenko, Semyon A. Yuryev and Alexey N. Sokolovskiy

Preface

Titanium dioxide is currently being used in many industrial products. It provides unique photocatalytic properties for water splitting and purification, bacterial inactivation, and organic degradation. In addition, due to its desirable optical, electronic, and mechanical properties, it has been widely used as the photoanode for dye-sensitized solar cells (DSSCs) and coatings for self-cleaning surfaces, biomedical implant, and nanomedicine. This book covers various aspects of titanium dioxide nanomaterials including their unique one-dimensional, two-dimensional, mesoporous, and hierarchical nanostructures and their synthetic methods such as sol-gel, hydrothermal, anodic oxidation, and electrophoretic deposition (EPD), as well as its key applications. Through these 24 chapters written by experts from the international scientific community, readers will have access to a comprehensive overview of the recent research and development findings on the titanium dioxide nanomaterials through original research studies and literature reviews. Chapter 1 provides a comprehensive overview on the preparation of titanium dioxide hierarchical nanostructures (HNSs) by various synthetic routes and summarizes the merits and demerits of those synthetic techniques. It also linked the applications of HNSs to the morphologies obtained from different synthetic techniques. Chapter 2 presents a one-step surface hydrolysis method to prepare high-aspect ratio TiO₂ nanoflakes, which shows enhanced photocatalytic activities for the degradation of methylene blue, better rate capabilities and excellent cycling stability as a negative electrode material for Li-ion batteries, and improved photon energy conversion efficiency in the DSSCs. Chapter 3 provides detailed experimental conditions for the preparation of mesoporous TiO_2 films and their physicochemical characteristics, as well as their photocatalytic applications. Chapter 4 reveals the effects of deposition parameters on the characteristics of the TiO_2 and doped TiO_2 thin films by sol-gel process, and it has been found that dopants were able to improve the mechanical, optical, and surface properties of TiO_2 thin films. Chapter 5 reports the nonaqueous solvent sol-gel route for the synthesis of metal ion (Zr⁺⁴ or Na⁺)-doped TiO₂ with improved photocatalytic properties due to small grain size, reduced electron hole recombination, and formation of oxygen vacancies in the TiO₂ structures. Chapter 6 investigates the effect of various electrochemical parameters such as applied voltage, anodization time, and electrolyte composition on the formation of TiO₂ nanotube arrays (TNAs) in aqueous and organic electrolytes by anodic oxidation. Chapter 7 presents the one-step and two-step anodic oxidation processes for making one-dimensional TiO₂ nanotube/nanowire arrays with various unique morphologies. It reveals the formation mechanisms through investigating several key synthetic process parameters and characterizes the photocatalytic and photoelectrochemical activities of these nanostructures through the degradation of methylene blue. Chapter 8 presents an overview on the different methods used for the preparation of titanium dioxide nanomaterials including nanoparticles. Chapter 9 investigates the influence of the stabilizing agents on electrophoretic deposition of TiO_2 , and it reveals the importance of monitoring and controlling zeta potential during the EPD process. Chapter 10 presents an original work on the characterization of the optical property of nanostructured TiO₂ by X-ray absorption near-edge structure (XANES) and X-ray-excited optical luminescence (XEOL). It demonstrates that the combined XANES-XEOL is an effective probing technique to reveal the relationship between nanostructures and optical properties of TiO₂ nanotubes with element specificity. Chapter 11 presents the use of the CVD process to deposit anatase-TiO₂ thin films of different grain size and thickness and evaluate their photocatalytic efficiency for the degradation of methyl orange dye under UV light irradiation. Chapter 12 provides an overview on the structure, properties, and synthesis of blue titanium dioxide, which has reduced bandgap energy, thereafter allowing better utilization of a wide region of solar light irradiant energy. Chapter 13 presents an original research work on using UV-TiO₂ and UV-TiO₂-H₂O₂ systems to photocatalytically degrade five selected organophosphorus pesticides. Chapter 14 reports the use of digital inkjet printing method to deposit TiO₂ photocatalyst films on porcelain grès, which exhibits superior photocatalytic performance for the removal of volatile organic compounds (VOCs) and NO_x from air. Chapter 15 presents an excellent, original work on the preparation, characterization, and performance evaluation of TiO₂-layered double hydroxides (LDHs) for phenol photodegradation. Chapter 16 presents the synthesis of visible light-driven photocatalysis that uses heterostructures obtained by combining low bandgap semiconductors with TiO₂. Through analysis, the photocatalytic performance of TiO₂-based heterostructures for the degradation of organic pollutants in water using visible light and sunlight explores the mechanisms leading to the increase of photocatalytic activities of such heterostructures. Chapter 17 presents a comprehensive overview on the fabrication and characterization of silver nanoparticles that incorporated TiO₂ and its photocatalytic performance for bacterial inactivation and dye degradation. It reveals the effect of fabrication methods, pH, light intensity, dose of photocatalyst, UV, and visible light intensity on the performance of the TiO_2 -Ag nanoparticles. Chapter 18 gives an overview on the synthesis of titanium dioxide nanostructures and the advantages of using nanostructures of titanium dioxide in dye-sensitized solar cell. Chapter 19 presents good strategies for bandgap engineering of one-dimensional TiO_2 to improve its optical properties, charge carrier separation, and transfer. It also gives examples of using 1D TiO₂ nanostructures in photocatalytic water splitting and dye-sensitized solar cells. Chapter 20 presents a comprehensive overview on various approaches used to modify TiO₂ material for dye-sensitized solar cells to enhance their electronic mobility, charge carrier generation and diffusion, conduction band shift, surface passivation, light harvesting, and long-term stability. Chapter 21 presents an overview on various surface treatments/coatings of titanium dioxide particles in order to satisfy different performance requirements in various applications such as paints and coatings, printing inks, plastics, and paper. Chapter 22 presents the synthesis of nanostructured titanium dioxides by hydro-/solvothermal-seeded technique and investigates its application as the photoanode for dye-sensitized solar cells, as photocatalysts for self-cleaning films on textiles, antibacterial coating on cotton, and antifouling coating on wood. Chapter 23 presents an overview on the applications of TiO₂ nanotube arrays (TNAs) for biomedical implants, nanomedicine in therapy, nanodiagnostics, and nanobiosensors and explains the mechanism of cell-TNA interactions, which is important for developing novel or improved nanomaterial products for medicine and health applications. Chapter 24 reports the optical properties and radiation stability of titanium dioxide powders after modification with nanoparticles of various other oxides. It reveals reasons that influence the radiation stability and methods to improve such stability.

This publication provides a comprehensive overview of current efforts on the synthesis and characterization of titanium dioxide nanomaterials mainly for environmental and energy applications. It will be useful for researchers and students who work in the areas of nanomaterials and green technologies. I gratefully acknowledge all the chapter authors for their enthusiastic and collaborative contributions, and I would like to thank Ms. Marijana Francetic, Author Service Manager, for her guidance and support in the preparation of this book.

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Synthesis and Characterization

Hierarchical Nanostructures of Titanium Dioxide: Synthesis and Applications

Ramsha Khan, Sofia Javed and Mohammad Islam

Additional information is available at the end of the chapter

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Abstract

This chapter covers different routes of preparation of hierarchical nanostructures (HNS) of titanium dioxide. Keeping the interest in developing modern and sustainable methods of materials chemistry, this chapter focuses on synthesis routes for TiO_2 HNSs reported by researchers from all over the world. The chapter includes the details of chemical reactions taking place during the synthesis and the effects of various process parameters like: type of surfactants, organic/inorganic titanium salts, temperature and pressure on products. The obtained TiO_2 HNSs from different synthesis routes are subsequently compared in terms of their morphology, crystallite size, surface area, particle size and phase. The merits and demerits of all synthesis techniques are also added for comprehensive information. At the end, various applications of HNSs are discussed and their performance is analyzed with respect to the morphologies obtained from different synthesis techniques.

Keywords: hierarchical nanostructures (HNSs), nanoflowers, $\text{TiO}_{2'}$ Titania, microwave synthesis

1. Introduction

Depletion of fossil fuels and environmental pollution has reached an alarming situation. New techniques are being searched now to overcome this situation by switching toward sustainable and renewable energy resources [1–4]. Severe pollution threats like global warming demand such materials and devices that are environment-friendly and green. The main idea is to fabricate materials that are not only cost-effective [5] but are also more capable to deal with energy crisis in the world.



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Recently, different renewable energy resources like wind, solar, bioenergy and geothermal energy have been deployed for energy production [6]. New materials are being explored and synthesized to harness energy from these alternate energy sources. The goal is to improve the competence of these devices by synthesizing materials that provide maximum energy harvesting and power control. For solar energy harvesting by photovoltaic devices, i.e., direct conversion of sunlight to electricity, different generations have been evolved depending upon materials and technologies used in device fabrication.

Various material types are employed for their use in renewable energy resources like organic, organometallic, metallic, semiconductors, etc. Wide band gap semiconductors have been exploited due to their substantial applications so far in cosmetics [7], drugs, electronics [8], photovoltaic devices [9], energy storage materials [10–12] and catalysis [13, 14] like photodegradation (**Figure 1**). The third-generation photovoltaics utilize nanomaterials that have attracted much attention recently due to their novel electric, photochemical, piezoelectric, mechanical and catalytic properties [15].

In PV devices [17], semiconductor materials are mostly chosen on the basis of many properties like band gap, electronic mobility, mesoporosity [18, 19], toxicity levels, robustness [20, 21] and high surface area. So far, many semiconductor oxides have been prepared and tested. Nanomaterials of transition metal oxides like $TiO_{2'}$ SnO_{2'} and ZnO are being further explored now because of their properties and applications. Titania [22] is the best material among all having distinguished optoelectronic and photochemical properties.

Titania is a promising material [12, 23] as it has high refractive index, biocompatibility and high dielectric constant. It exhibits redox reactions and has excellent optical transmittance in the visible and near IR regions. It is preferred because of its high performance as a photocatalyst for water splitting, oxidation capability [7] and degradation of organics [24]. **Table 1** highlights some of the properties of Titania.

Titanium dioxide also known as Titania exists in many crystalline forms among which rutile, anatase and brookite are of particular importance in nanomaterials. These forms can exist



Figure 1. Application of TiO₂ for photodegradation of organic pollutants [16].

| Properties of Titanium dioxide | | | | | |
|--------------------------------|---|--|--|--|--|
| Natural forms | Anatase, rutile and brookite | | | | |
| Crystal structure | | | | | |
| Anatase | Tetragonal | | | | |
| Rutile | Tetragonal | | | | |
| Brookite | Orthorhombic | | | | |
| Melting point | 1941 K | | | | |
| Boiling point | 3546 K | | | | |
| Thermal conductivity | 22Wm ⁻¹ K ⁻¹ | | | | |
| Band gap | 3.0 eV (rutile) | | | | |
| | 3.3 eV (anatase) | | | | |
| Solubility in water | Insoluble | | | | |
| Color | White-yellow | | | | |
| Molar mass | 79.8 g/mol | | | | |
| Density | 4.23 g/cm ³ (rutile), 3.78 g/cm ³ (anatase) | | | | |
| Flash point | Non-flammable | | | | |

Table 1. Physical properties of Titania.

individually as minerals but only rutile and anatase have been synthesized in their pure form yet [13, 25]. Both anatase and rutile phases have tetragonal, while brookite has orthorhombic crystal system [9] (Figure 2).

The properties of Titania depend on particle morphology, crystallinity, particle size and surface area. Titania has a band gap from 3.0 to 3.23 eV, which makes it photocatalytic only in ultraviolet radiation region [26]. It is desirable to shift its band gap [27] so that it may absorb radiations of the visible light spectrum to enhance its photocatalytic properties. Titania nanostructures offer a larger surface area for light absorption in solar cells and catalytic properties for dye and pollutant degradation [28].

Titania nanostructures can be synthesized using various techniques. Some of them are hydrothermal [26, 29–34], solvothermal methods [10, 11, 35], sol-gel synthesis [1, 15, 36], microwave irradiation [8, 24, 37, 38], physical and chemical vapor deposition [4, 32, 39], electrochemical methods [40, 41] and anodization [42-44].

Generally, anatase Titania shows superior properties to rutile Titania because of slow recombination of electron-hole pairs and higher potential energy of photogenerated electrons [45]. Nano-Titania exists in many forms like nanoparticles [15, 40–42], nanorods [10, 24, 46], nanowires [3, 31, 32, 47], nanotubes [43, 48], nanospheres [49], nanoflowers [8, 32, 46, 50], nanoforests [44, 50], etc. as shown in Figure 3. Nanotubes show enhanced charge percolation and direct electronic transport than nanoparticles because of their 1D structures [51].



Figure 2. Different crystalline forms of TiO₂ [9].



Figure 3. Different forms of TiO₂: (a) nanocubes [24], (b) nanospheres [24], (c) nanorods [24], (d) nanoparticles [52], (e) nanoflowers [8], (f) nanoforest [48].

1.1. Hierarchical nanostructures

Hierarchical nanostructures are composed of 3D self-assembly of primary structure (nanoparticle, nanorod, nanotube or nanosheets) in nanoscale. Recently, materials with hierarchical morphology have attracted great attention as compared to spherical nanoparticles. Many experiments have been done in order to perk up the efficiency of nanomaterials by synthesizing hierarchical structures and enhancing the specific surface area and porosity of these structures [8, 38, 40, 53]. These types of structures show utmost light harvesting due to maximum and efficient scattering (hence absorption) of incident light within [40]. Hierarchical TiO₂ nanostructures provide a significant improvement in properties due to enhanced porosity [54, 55] and many devices can be optimized using HNSs [43]. Hierarchical morphology can enhance the photon absorption capability [8] as compared to spherical nanoparticle as there is increased absorption of light due to scattering. The mesoporosity acts as distribution channels increasing adsorption of visible light sensitizers. It also creates an ideal environment for mass transportation [39] of electrons.

This chapter presents a compilation of different synthesis routes and control measures employed for the synthesis of "hierarchical nanostructures of TiO_2 " A brief overview of each synthesis route is provided. Investigation on the synthesis parameters and the correlation with the characteristic properties of the products are also discussed.

2. Synthesis of hierarchical nanostructures of TiO,

Various types of surfactants, organic/inorganic titanium salts, high temperatures and pressures may be used for the preparation of hierarchical nanostructures of Titania. Following are the reported methods for the synthesis of TiO₂ HNSs.

- Hydrothermal method
- Solvothermal method
- Microwave treatment
- Pulsed laser deposition
- Anodization
- Photolithography
- Vapor deposition method
 - Chemical vapor deposition
 - Physical vapor deposition

2.1. Hydrothermal synthesis

As the name indicates, the method involves heating in aqueous medium. Generally, in this method, sealed Teflon-lined steel autoclaves are used under controlled temperature

and pressure conditions. Sometimes, surfactants are also added to control the growth and morphology of target materials.

Internal pressure is set up by the amount of temperature and solution used. This process is mainly used for the preparation of small-sized particles for achieving enhanced surface area. Basically, this synthesis is used for preparation of crystalline TiO_2 from amorphous one. The morphology of the particles can be varied by changing crystallization temperature, time and concentration of etching chemicals. **Table 2** shows the various routes by which hierarchical TiO₂ structures have been prepared by hydrothermal route.

| Reference | Phase | Surface area (m ² g ⁻¹) | Particle size (diameter) | Precursor materials | Morphology | Used in application |
|----------------------|---------|--|--|---|---|------------------------|
| Lin et al. [56] | Rutile | 67 | 1–1.5 µm | Tetrabutyl titanate (TT) | Flower-like structures | DSSCs |
| Wang et al. [50] | Rutile | 75.53 | (4.4 μm length) 150 nm diameter | Titanium 1D/3D nanorods tetrabutoxide | | DSSCs |
| Qiang et al. [3] | Anatase | _ | NW trunk 95 nm, NR 5 nm | K ₂ TiO ₂ (C ₂ O ₄) ₂ and diethylene glycol (DEG) | Nanowire trunk on which nanorods are grown | DSSCs |
| Xiang et al. [57] | Anatase | _ | 300–600 nm | Dodecylamine and titanium isopropoxide | Nanoparticle-based HNs | DSSCs |
| Zheng et al. [60] | Anatase | 27.4 | 4–6µm | Primary Titania microspheres | Hierarchical microspheres | Photocatalysis |
| Shao et al. [58] | Anatase | 36.93 | 15–25µm | Ti foil | Flower-like structure formed from nanobelts | DSSCs |
| Zhu et al. [29] | Anatase | 170 | 350 nm | Titanocene dichloride | Flower-like shapes formed from nanosheets | Photocatalysis |
| Wang et al. [32] | Anatase | 64.8 | 1–1.5µm | Titanium powder | Radial nanoflakes | Gas sensing |
| Gao et al. [2] | Anatase | 116.6 | 3–4µm | Tetrabutyl titanate (TBT) and acetic acid | Overlapped subunits of nanoflakes | Lithium sulfur battery |
| Yang et al. [59] | Anatase | _ | 20–50 nm | Titanium sulfate (Ti $(SO_4)_2$) and urea (CO $(NH_2)_2$) | Nanothorn-like hierarchical structures | Gas sensing |
| Min et al. [59] | Anatase | 168.3 | 2–4µm | Titanium powder | Nanospheres composed of nanosheets | Photocatalysis |

Table 2. Hierarchical TiO, nanostructures produced by various hydrothermal routes.

2.1.1. Examples

Lin et al. have reported rutile TiO_2 hierarchical flower-like structures via hydrothermal synthesis without using any surfactant. Precursor tetrabutyltitanate (TT) is first mixed with HCl for acidification and is subsequently hydrolyzed using distilled water. To ensure complete hydrolysis, the reaction mixture is stirred for about one and a half hour. Next, the mixture is transferred to a Teflon-based autoclave and is placed in an electric oven for 5 h at 150°C for crystallization. Hierarchical nanoflower-like structures are obtained as an end product. By increasing the HCl concentration, the etching rate of TiO₂ structures is enhanced and symmetric flower-like structures are produced [56] (**Figure 4**). These structures are employed for DSSCs and 8.6% of conversion efficiency is achieved.

Wang et al. have prepared rutile Titania 1D/3D structures via hydrothermal treatment. The precursor Titanium tetrabutoxide (0.9 m) is acidified using HCl (16 ml) and then hydrolyzed using DI water (16 ml). The reaction mixture is subsequently heated to 150°C and kept at this temperature for 10 h for crystallization. The position of FTO substrates is varied to obtain different HNSs. 1D/3D HNSs are produced while the FTO substrate lied flat on the bottom of the reactor with the conductive side facing up. 3D nanorods are produced when the conductive side of substrate is placed downwards.

Rutile Titania 3D flower-like nanorods are grown on 1D nanorods with length in microns [50] (**Figure 5**). These structures are employed as a photo anode material in DSSCs and significant improvement in device performance is seen. 1D structure provides directed pathway for electron percolation and 3D morphology provides large surface area for light scattering and dyeloading. Also, the structures exhibit long life time due to less electron-hole recombination.

Qiang et al. have obtained hierarchical anatase TiO_2 nanowire trunks with short nanorod branch HNSs by facile one-way hydrothermal synthesis on FTO glass without using any surfactant/stabilizing agent. The solution is prepared using precursor K₂TiO₂(C₂O₄)₂ (0.002 mol)



Figure 4. FESEM images of TiO_2 structures. Change in morphology is produced from changing HCl conc. at (a) 1M (b) 2M (c) 3M (d) 4M (e) 5M (f) 6M (f) 7M (g) 8M [56].



Figure 5. (a,d) SEM images of 1D/3D nanorod structures (b) 1D nanorods (c) 3D nanoflower-like structures [50].



Figure 6. SEM images of hierarchical anatase nanowire trunk covered by short nanorod branches (a) Nanorods covering the nanotrunks (b) Enlarged image of nanorods (c) Nanotrunks covered by nanorods [3].

and diethylene glycol (DEG) (30 ml) as Titania precursor. About 10 ml H_2O is used for hydrolysis. The solution is then spin coated on FTO substrate for seeding of TiO_2 structures. The spin-coated substrate is immersed in Teflon-based autoclave, which is kept at 180°C for 1–12 h for crystallization of Titania structures. **Figure 6** shows nanotrunks produced having nanowire-like structures grown on them [3].

These structures are employed as a photo anode material in DSSCs and impressive power conversion efficiency of 7.34% is achieved. Hierarchical morphology aids in efficient electron transfer but these structures provide additional recombination sites so results are inferior to bare TiO₂ nanowires.

Xiang et al. have reported Ta-doped and -undoped hierarchical TiO_2 nanostructures. Dodecylamine (8 g) and titanium isopropoxide (TIP, 8 g) are used as precursor materials and are mixed with ethanol (360 ml) and DI water (120 ml) for hydrolysis under vigorous stirring at ambient room temperature. HNO_3 formed during reaction is removed from the reaction mixture and white powder of anatase Titania is obtained, which is then washed with water and ethanol to maintain the pH of particles at 7. After that, $TaCl_5$ is added in reaction mixture in different ratios. The solution is transferred to Teflon-lined autoclave, kept at 250°C for 12 h to dope Ta particles with TiO₂.

HNSs made up of symmetrically arranged interconnected spherical nanoparticles are obtained as a result of these syntheses [57]. These structures are employed as a photoanode material in this article. The large spheres can provide maximum scattering of sunlight for light-driven reactions like photocatalysis (**Figure 7**).

Shao et al. have prepared hierarchical TiO_2 flower-like structures on Ti foil by placing it in Teflon-lined autoclave at an inclined angle in 5 M NaOH solution for its reduction. Sodium titanate is formed as a result of this reaction. The temperature is maintained at 220°C for 24 h for complete reaction of converting Ti foil to TiO_2 nanostructures. The sample is then washed with water and ethanol to remove all the acidic content and to maintain its pH at neutral. The sample is then immersed in HCl solution so that all Na⁺ ions of sodium titanate would get replaced by H⁺ ion. After calcination, nanobelts (**Figure 8**) forming nanoflower-like structures are formed [58].

Reaction of TiO_2 nanoparticles with NaOH results in the formation of $\text{Na}_2\text{TiO}_{3'}$ which is a nanoporous structure. The reaction that takes place is as follows.

$$TiO_{x} + NaOH \longrightarrow Na_{2}TiO_{3} + H_{2}O$$
(1)

These Na⁺ ions can be replaced with H+ ions by washing them with deionized water or acid. It can be shown as:

$$Na_2 TiO_3 + H^+/H_2 O \longrightarrow H_2 TiO_3 + NaOH$$
 (2)



Figure 7. TEM images of hierarchical TiO_2 spherical structures composed of nanoparticles (a) Agglomerated TiO_2 nanoparticles (b) Dispered TiO_2 nanoparticles [57].



Figure 8. SEM images of nanoflower-like hierarchical TiO₂ structures produced after annealing at 500°C [58].



Figure 9. SEM images of hierarchical TiO₂ prepared by hydrothermal heating: (A) after 1 h, (B) after 2 h and (C) after 12 h. (D, E) Annealed powder of sample B [29].

By reduction of nanoparticles and increasing time duration of crystallization, nanoflower-like structures can be grown.

Zhu et al. have prepared HNSs of TiO_2 using titanocene dichloride $(\text{Ti}(\text{Cp})_2\text{Cl}_2)$ (20 mg) as precursor. DI water (10 ml) is added for hydrolysis, and ethylene diamine (EDA) (2 drops) acts as chelating agent. This results in the production of TiO_2 nanocrystals. The mixture then after sonication is placed in an autoclave at 120°C for 1–12 h. The powder obtained is then washed with water and ethanol and is annealed at 400°C for 2 h. Flower-like HNSs (**Figure 9**) are formed in this process [29].

By increasing the duration of hydrothermal synthesis, the nanoparticles have attained more flower-like mesoporous morphology due to increased time provided for etching. These structures have proved to be better photocatalytic agents as compared to nanocrystals of TiO_2 as they can provide maximum enhanced surface area, and due to their mesoporosity, maximum dye can be loaded on them. Hence, these structures can be used with perspective of various solar cells and photocatalysis for efficient light-driven reactions.

Yang et al. prepared hierarchical Titania structures by hydrothermal synthesis. Titanium sulfate $(Ti(SO_4)_2)$ and urea $(CO(NH_2)_2)$ were used as precursor materials. Ethylene diaminetetra acetic acid (EDTA) disodium salt was added in them as the chelating agent for TiO_2 formation. $Ti(SO_4)_2$ (3 mmol), urea (24 mmol) and EDTA (3 mmol) were mixed and NH_4F (9 mmol) was added in the mixture for attaching [$Ti(H_2O)(edta)$] with F^{-1} ions. The reaction mixture was dissolved into 60 ml of deionized water for formation of H_2TiO_3 . After stirring for 3 h, the reaction was complete and white powder was obtained, which was then moved in Teflon-lined autoclave at 180°C for 10 h for its complete crystallization. The powder formed was washed with DI water and ethanol to maintain pH at neutral and annealed to recrystallize. Reactions that took place were:

$$O = C (NH_2)_2 + 3H_2O \longrightarrow 2NH_4^+ + 2OH^- + CO_2$$
(3)

$$[Ti(H_2 O)(edta)] \longrightarrow Ti^{4+} + EDTA + H_2 O$$
(4)

$$2\mathrm{Ti}^{4+} + 6\mathrm{H}_2\mathrm{O} \longrightarrow \mathrm{H}_2\mathrm{Ti}_2\mathrm{O}_5\mathrm{H}_2\mathrm{O} + 8\mathrm{H}^+$$
(5)

$$H_2 Ti_2 O_5 H_2 O \longrightarrow 2TiO_2 + 2H_2 O$$
 (6)

Mesoporous nanothorn-like structures are produced as a result of this process [59] shown in **Figure 10**. These structures are employed for gas sensing application of acetone. This hierarchical morphology provides much higher sensitivity and fast response time with minimum recovery speed.

Min et al. prepared hierarchical Titania structures by hydrothermal synthesis. About 1 g of Titanium powder was being dissolved in (0.5 M) 30 ml HF for its oxidation as it is a powerful oxidizing agent. The solution was then mixed with 3 ml NH₃. This solution was moved to Teflon-lined autoclave at 150°C for crystallization for 5 h. The powder obtained was washed via centrifugation and was then dried at 80°C. Nanosheets (**Figure 11**) are being produced as a result of this process [52].

These structures are employed as a photocatalyst material for photodegradation of organic dye. Methylene blue is used as a model dye in this article. Complete photodegradation of organic compound is observed in just 60 min.



Figure 10. FESEM images of hydrothermal synthesis at (a) 5 min, (b) 1 h, (c) 3 h and (d) 5 h [59].



Figure 11. FESEM images of Titania hierarchical nanospheres composed of nanosheet-like structures [52].

2.1.2. Merits

The hydrothermal method has got the following advantages:

- This method is comparatively easy.
- Titania formed via this process can range from nanoparticle- to nanoflower-like structures depending on temperature.
- By increasing the duration and time in hydrothermal reactor, the crystallization of particles can be improved.
- The structures produced are diverse so they can be used in various applications.
- If NaOH or other reducing or oxidizing agents are used, they can be removed easily by washing with deionized water.
- By controlling temperature, one can grow anatase or rutile Titania phase depending on application.
- Hierarchical morphology can be attained.
- A variety of precursors is used for the production of TiO, HNSs.

2.1.3. Demerits

The demerits of this method are listed below:

- Water is used as solvent in this synthesis, so the temperature for crystallization cannot be increased from 100 to 150° C. Otherwise, water will dry out and crystallization may hinder.
- Proper time should be given to materials during synthesis as complete etching should be done for desired morphology.
- Sometimes crystallization times are very prolonged as compared to microwave technique. So it can be termed as a slow process than microwave.

2.1.4. Summary of hydrothermal synthesis

To summarize, hydrothermal treatment of various precursors under control parameters of temperature, pressure and duration gives a variety of morphologies in HNSs of Titania. The

morphology ranges from hierarchical arrangement of nanoparticles to nanorods producing flower-like structures. Increasing temperature increases crystallization of TiO_2 particles, and by increasing duration of hydrothermal synthesis, better etched morphology was obtained. **Table 2** summarizes reported examples of hydrothermal synthesis of HNSs with respect to precursor used for the synthesis and various properties of obtained HNSs together with the application studied. The HNSs obtained from this method varies in size from 20 nm to 4.5 μ m. The surface area of the resultant HNSs ranges from 27 to 170 m²g⁻¹. These structures are exploited in various applications including solar cells, photocatalysis and sensors, etc. and have improved respective performance owing to their unique structural properties.

2.2. Solvothermal synthesis

In this synthesis, the conditions are the same as for a hydrothermal method but non-aqueous solvent is used instead of water. The process takes place in an autoclave and temperature can be increased because of high boiling of certain organic solvents as compared to water. This method results in uniform particle size distribution and high purity products. Also by changing the temperature, morphology of the grown crystals can be varied. In addition to that, different morphologies result due to differences in steric hindrance offered by different functional groups in various organic solvents. **Table 3** shows various routes adopted to synthesize TiO₂ HNSs via solvothermal route.

2.2.1. Examples

Ochanda et al. have presented TiO_2 HNSs by solvothermal synthesis technique. Their method involves mixing of 15 ml of 4 M NaOH solution with 0.5 g TiO₂ fibers. Then, 15 ml ethanol solvent is added to this solution followed by heating in a 50 ml Teflon-lined autoclave at 150°C for 0.5, 1, 6 and 12 h. The resultant white precipitates are then dried in air. Nanoflower-like structures are grown over the nanorod structures with average crystallite size of 4 nm (**Figure 12**) [10].

These structures are then employed for photocatalytic degradation of methylene blue dye. Complete degradation of organic dye has been achieved in 120 min by these structures. Hence, these HNSs can be used for determining photocatalytic behavior and applications like solar cells.

| Reference | Phase | Surface area (m ² c ⁻¹) | Particle size (diameter) | Precursor materials | Morphology | Application |
|------------------------|---------|--|---|-------------------------|--|----------------|
| Ochanda et al. [10] | Anatase | 94.01 | 50–70 nm | TiO ₂ fibers | 3D nanoflowers grown on nanofibers | Photocatalysis |
| Xiang et al. [35] | Anatase | 37 | 2.5–3.0μm (microspheres), 20–40 nm (nanorods) | TiCl ₄ | 3D urchin- like structure composed of nanoneedles | Photocatalysis |

Table 3. Hierarchical TiO₂ nanostructures produced via solvothermal method.



Figure 12. (a) 1 h solvothermal treatment, showing TiO_2 particle nucleation on nanofiber surface. (b) Hierarchical TiO₂ formed after 6 h showing the inception of flower-like structures. (c) After 12 h showing nanoscale flower-like nanostructures, completely covering the nanofiber surface [10].

Xiang et al. have prepared HNSs of Titania by solvothermal synthesis method using toluene. First, TiCl₄ is mixed with distilled water in ice water bath. In another assembly, toluene (30 ml) is mixed with tetrabutyltitanate (TBT). Both solutions are then stirred together for 1 h. The solution is placed in Teflon-lined autoclave for 24 h at 150°C. Micron ranged hierarchical Titania needles are obtained [35] as shown in **Figure 13**. Temperature plays an important role in defining the morphology of the products as HNSs are produced only above 120°C. Sea urchin-like HNSs are formed via 'nucleation–self-assembly–dissolution–recrystallization' growth mechanism without adding any surfactant or template. These structures are then tested for photocatalytic degradation of methylene blue and complete degradation study is completed in 240 min.

2.2.2. Merits

Following are some of the advantages of this technique:

- Better controlled morphologies due to control on temperature and treatment duration.
- Reliable method because of better reproducibility.
- High boiling organic solvents can be used.

2.2.3. Demerits

The method has the following demerits:

- Sometimes solvents are difficult to separate from the materials produced due to high boiling points of the solvents.
- Different solvents will have different effect on growth of target materials.

2.2.4. Summary of solvothermal synthesis

The solvothermal method in addition to the advantages offered by hydrothermal method allows the use of higher temperatures. This is sometimes advantageous in producing better



Figure 13. SEM images (1) nonhierarchical TiO₂ structures grown at 90°C. (a–c) TEM images of 3D hierarchical urchinlike structures having 1D nanoneedles [35].

crystallinity in the products. **Table 3** gives a summary of the reported work on solvothermal synthesis. The prepared HNSs obtained using this method range in size, from a few micrometers to several nanometers. They possess large surface area up to 94 m²g⁻¹. The products have good crystallinity due to high crystallization temperatures offered by possible use of high boiling solvents. Different solvents can provide different chelating effects and hindrance to control morphology of structures. In addition to the type of solvent used, temperature and time control the growth and crystallization of particles during synthesis. These types of HNSs can be used for various photocatalytic applications like solar cells and organic pollutant degradation.

2.3. Microwave synthesis

This is relatively a new technique with many advantages. The key feature of this method is to heat the reaction mixture in less time via electromagnetic radiations. The frequency is kept from 800 to 2450 MHz range. Although it is not much explored for the HNS synthesis, much literature is available on microwave synthesis of nanoparticles [61], nanospheres [62], nanorods [63], nanowires [64] and nanotubes [65] of TiO₂. Dipole molecules rotate in the presence of these radiations and localized "superheating" occurs at ambient pressure. This heat energy provided is used for crystallization of amorphous materials. By this method, reactions can be completed in just a couple of minutes as compared to conventional heating.

Although dedicated microwave lab reactor is the best equipment, modified/non-modified domestic microwave ovens can also be used for the preparation of HNSs. From a few reports found on HNS synthesis, it appears to be an efficient, quick and cost-effective method of HNS synthesis. The key characteristics of prepared samples are given in **Table 4**.

2.3.1. Examples

Javed et al. have prepared 3D-HNSs by microwave irradiation of anatase nanopowder in 10 M NaOH solution at 1 atm without any surfactant. Submicron-sized flower-like HNSs are produced as shown in **Figure 14** [8]. The crystalline phase is anatase with a decrease in surface area as microwave treatment duration increases from 5 to 20 min. The product is applied as photoanode in DSSCs, whereby the use of HNSs has two-fold improved the device efficiency. One reason being the larger light scattering due to morphology of the HNSs.

| Reference | Phase | Surface area (m ² g ⁻¹) | Particle size (diameter) | Crystallite size (nm) | Morphology | Application |
|--------------------------|---------|---|-----------------------------|--------------------------|---|----------------|
| Javed et al. [8] | Anatase | 18 | 500 nm | 5.6 | Nanoflower-like structures | DSSCs |
| Calatayud et al. [38] | Anatase | 113 | 1–2µm | _ | Nanoparticle agglomerates | Photocatalysis |
| Wang el al. [37] | Anatase | 86.90 | 500 nm | 10 | ${\rm TiO}_2$ nanoagglomerates | DSSCs |
| Rahal et al. [66] | Anatase | 47 | 200–300 nm | _ | Flower-shaped nanoparticle agglomerates | Photocatalysis |
| Martínez et al. [67] | Anatase | 73 | 500 nm | 56 | Cauliflower-like hierarchical structures | _ |

Table 4. Hierarchical TiO₂ nanostructures produced via microwave treatment.



Figure 14. TEM images of hierarchical structures produced via microwave irradiation (a) after 5 min and (b) after 20 min [8].

Calatayud et al. prepared hierarchical crystalline TiO_2 via microwaves from amorphous powder using titanium (IV) tetrabutoxide $(\text{Ti}(\text{OBut})_4)$ and anhydrous ethanol as precursor materials. The solution is stirred for 6.5 h for complete hydrolysis and replacement of -butoxide group from -hydroxyl groups. Then, the powder is dried under atmospheric conditions. The powder obtained is washed with water and ethanol and irradiated in microwaves for different time durations. This microwave treatment provides the crystallization temperature and time for conversion of amorphous Titania to crystalline one. Anatase TiO₂ spherical HNSs (**Figure 15**) are produced having size from 1 to 2 μ m [38].

These HNSs are employed for photodegradation of methyl orange (MO), which is completed in 6 h. By increasing microwave irradiation up to 10 min, clear agglomerated structures are produced, but as crystallization time is increased under microwaves, surface area decreases as particle size increases.

Wang et al. have synthesized HNSs by microwave irradiation using $TiCl_4$ (0.5 ml) in ethanol (14 ml) shown in **Figure 16**. After stirring for an hour, the reaction mixture is subjected to microwave irradiation for 10 min at 150°C under pressure of 300 Pa. $TiCl_4$ is hydrolyzed and

Hierarchical Nanostructures of Titanium Dioxide: Synthesis and Applications 19 http://dx.doi.org/10.5772/intechopen.74525



Figure 15. SEM images of TiO_2 spherical structures after microwave treatment: (a and b) after 7 min, (c and d) after 15 min [38].



Figure 16. SEM images of 3D TiO₂ agglomerates [37].

crystallized in microwaves and TiO₂ nanoagglomerates with particle size up to 10 nm are prepared in spherical geometry [37]. The crystallite size is measured to be as small as 10 nm. In the presence of microwave, TiO₂ nanoparticles begin to nucleate and then their growth and aggregation occur during crystallization.

So, microwave heating provides quick crystallization of particles as particles begin to cluster within 3–5 min. Mesoporous structures are produced as a result of this synthesis and they are employed as a photoanode material in DSSCs. A maximum conversion efficiency of 7.64% is reported.

Rahal et al. have prepared TiO_2 hierarchical structures by mixing cetyltrimethyl ammonium bromide (CTAB, 11 mmol) and urea (2.4 g, 40 mmol) in 200 ml H₂O for hydrolysis (**Figure 18**). CTAB is used as a surfactant to control morphology and $(\text{NH}_2)_2$ C=O provides steric hindrance. To this reaction mixture, cyclohexane and 1-pentanol are added after stirring of 30 min. Then, TiF_4 (5.94 g, 48 mmol) is added to the solution and whole liquid media is transferred to Teflon-lined microwave reactor at 800 W. The mixture is irradiated under microwaves for 5 min at 120°C. The product is then washed thoroughly to remove impurities and other compounds and centrifugation is done to take out less dense particles.

Flower-shaped HNSs made of nanoparticle agglomerates (**Figure 17**) are produced with anatase phase [66]. Microwave treatment even for 5 min provides enough time for crystallization of TiO_2 nanoparticles. The prepared structures are utilized in photodegradation of Rhodamine B dye and complete degradation is observed within 1 h.

Martínez et al. [67] have recently reported TiO_2 HNSs prepared by stirring 3 ml of titanium tetra isopropoxide in 50 ml of H_2SO_4 and subsequent microwave treatment in a Teflon vessel at 120°C for 2 h. Anatase Titania is formed as a result of this scheme. Concentration of H_2SO_4 is changed to study the effect on particle size. Cauliflower-shaped HNSs are obtained. The increase in H_2SO_4 concentration increases the particle size.



Figure 17. SEM images (a–d) of TiO_2 hierarchical structures having flower-like shapes after microwave irradiations for 5 min [66].
Hierarchical Nanostructures of Titanium Dioxide: Synthesis and Applications 21 http://dx.doi.org/10.5772/intechopen.74525



Figure 18. Hierarchical structures of TiO_2 (a) H_2SO_4 free- $\text{TiO}_{2'}$ (b) 0.5M- $\text{TiO}_{2'}$ (c) 1M- $\text{TiO}_{2'}$ (d) 1.5M- $\text{TiO}_{2'}$ (e) 2M- $\text{TiO}_{2'}$ (f) 3M- TiO_2 [67].

2.3.2. Merits

- Shorter crystallization time is required.
- Electromagnetic radiations provide much temperature for nucleation and growth during crystallization within less time.
- It is a time-saving process.
- Large material can be synthesized in less time, so a better yield is expected.

2.3.3. Demerits

- The duration of microwaves should be carefully controlled so that optimum crystallization of Titania is done.
- Microwave treatment for longer times and high temperature transform anatase TiO₂ to rutile.

2.3.4. Summary of microwave synthesis

In short, microwave treatment is a quick technique to attain hierarchical morphology in TiO₂ nanostructures. By controlling temperature and exposure duration, HNSs ranging in sizes from micron to nanometers are produced. Localized heating caused by microwaves make this method an energy-efficient one with the possibility of acquiring environment-friendly conditions. The use of NaOH has resulted in submicron-sized HNSs made of radially arranged

nanosheets, whereas by using other precursor materials, simple microwave treatment produces HNSs made of nanoparticle agglomerates. Hence, flower-like hierarchical morphologies are obtained as a result.

2.4. Pulsed laser deposition (PLD)

This technique is well known for its flexibility to grow variety of materials. Nanotree-like structures can be grown via this synthesis route without using any surfactant and prior treatment. Pressure treatment and laser ablation are used for preparation of hierarchical structures by this technique.

It is a top-down approach in which pulsed laser is used to decompose the precursor material and then these materials are deposited on substrates. By controlling the parameters like laser power, temperature, chamber geometry and pressure, one can grow structures of different morphologies from columnar structures to dense forest-like [39] structures. The porosity of structures is increased when grown at high pressure because of fast process. Also the surface area can be controlled by controlling inter columnar spacing and thickness. **Table 5** shows features of structures prepared via dot pattering technique.

2.4.1. Examples

Fonzo et al. have prepared hierarchically organized nanostructured TiO_2 by ablating Titanium foil with KrF excimer laser pulses (h 248 nm, duration 10–15 ns, energy density 4 J/cm²) in dry air (O₂) background with pressure. Thin films of Titania are grown both on silicon and pure titanium substrates. Annealing is done at 400°C for 1 h for crystallization of samples prepared. By changing the pressure of chamber, thickness of the sample is varied from dense columnar structures to tree-like structure [39] (**Figure 19**). This technique can be employed for preparation of HNSs as it provides a stimulating outlook both for photocatalytic and for advanced photovoltaic application, and it also substitutes the time-consuming deposition of different layers and longlasting annealing steps.

Sauvage et al. have prepared hierarchical TiO_2 structures by PLD. Nanoparticles of TiO_2 are grown directly on FTO substrate by ablating Titanium target in the presence of O₂ background. TiO₂ nanostructure attained the symmetry of tree-like structures. Height and thickness of trees increase with respect to deposition time [44]. By increasing pressure from 10 to 40 Pa, the particles formed nanoforest-like structures. The structures formed are shown in **Figure 20**.

| Reference | Phase | Surface area (m² g ⁻¹) | Particle size (diameter) (nm) | Crystallite size (nm) | Morphology | Application |
|---------------------|---------|---------------------------------------|----------------------------------|--------------------------|---|----------------|
| Fonzo et al. [39] | Rutile | 300 | 260 | _ | Nanoforest composed of nanotrees | Photocatalysis |
| Sauvage et al. [44] | Anatase | 86 | 20 | 25 | Nanoforest composed of nanotree-like structures | DSSCs |

Table 5. Hierarchical TiO₂ nanostructures produced via PLD.

Hierarchical Nanostructures of Titanium Dioxide: Synthesis and Applications 23 http://dx.doi.org/10.5772/intechopen.74525



Figure 19. SEM images of different morphologies of TiO₂ at (a) 10 Pa, (b) 20 Pa, (c) 40 Pa [39].



Figure 20. SEM images of nanoforest-like structures prepared at (a) 20 Pa and (b) 40 Pa [44].

This type of assembly hampers electron-hole pair recombination and it facilitates the efficiency if employed in solar cells. This assembly also promotes mass transport of electrons in mesoporous structures. This morphology provided efficient light trapping and high surface area for dye adsorption and efficiency of 5% is obtained. The porosity and surface area can also be optimized for making these structures highly competent for photovoltaic devices.

2.4.2. Merits

- This technique produces better results than anodization.
- The surface area of materials synthesized can be controlled.
- Nanotree-like structures can be formed.
- Large surface area structures can be achieved.
- It is a flexible technique and parameters can be controlled.
- Porosity can be controlled by using high pressure.
- Synthesis can be done without surfactants and chelating agents.
- The photocatalysis is better than anatase powder and TiO₂ produced via anodization [68].

2.4.3. Demerits

- This technique is difficult.
- High pressure is required.
- It is an expensive process to synthesize materials.
- Temperature and pressure relation on particle growth should be clearly known to attain desired morphology.

2.4.4. Summary of PLD

So, by controlling parameters like pressure, temperature and time, nanoforest-type structures were grown via pulsed laser technique. By using intermediate pressure, columnar structures were grown and density of structures decreases by increasing pressure [69]. The particle size was in nanometer ranges. Pulsed laser was used to ablate Titania target on which structures were grown. This technique can be used to synthesize different materials by using different target materials. Hence, the prepared structures can be employed in different applications like dye sensitized solar cells, perovskite solar cells and photodegradation of pollutants.

2.5. Anodization

It is an electrochemical process in which metal sheets are decorated and electrolytic passivation¹ takes place. The thickness of oxide layer is increased in this process. The surface is decorated and finished with more durable and corrosion-resistant surface. The reactions that occur during anodization for oxidation of metals are [70]:

$$2H_2O \rightarrow 4H^+ + O_2 + 4e^- \tag{7}$$

$$Metal + O_2 \rightarrow MO_x \tag{8}$$

And for titanium,

$$\operatorname{Ti} + \operatorname{O}_2 \to \operatorname{TiO}_2$$
 (9)

TiO₂ is formed on titanium surface. The fluoride ion (F^-) present in solution causes dissolution of oxide layers and etching in nanopits starts to prepare nanotubes. Water is the main source of oxidation in anodization. Hydroxyl ions from electrolyte are injected into the body of anodic oxide layer [71]. These anions impede ion transport, which is necessary for movement of metal-ion interface into metal. The anodization also depends on solution diffusion rate and local electric field supplied to a specific area [72]. **Table 6** shows features of structures prepared via dot pattering technique.

¹It is a process of coating of protective coating on substance.

| Reference | Phase | Surface area (m ² g ⁻¹) | Particle size (diameter) (nm) | Crystallite size (nm) | Morphology | Application |
|-------------------|---------|---|----------------------------------|--------------------------|-----------------|-------------------------------------|
| Ali et al. [43] | Anatase | _ | 100 | 40 | Nanotubes | _ |
| Ali et al. [73] | Anatase | _ | 75–90 | _ | Nanotube arrays | Water splitting |
| Zhang et al. [42] | Anatase | - | 200 | - | Nanotubes | Photoelectrocatalytic decomposition |
| Tang et al. [40] | Anatase | 33.4 | 65 | 33.3 | Microspheres | Photocatalysis |
| Smith et al. [72] | Anatase | _ | 120–170 | - | Nanotubes | Photoelectrocatalytic decomposition |

Table 6. Hierarchical TiO₂ nanostructures produced via anodization.

2.5.1. Examples

Ali et al. have prepared hierarchical Titania structures (**Figure 21**) by using Ti foil, ammonium fluoride and ethylene glycol as precursor. DI water has been used in electrolyte preparation. Ti foils are being anodized in ethylene glycol electrolyte containing 0.5 wt% NH_4F and 0.2 wt% DI H_2O for oxidation of titanium. In this process, Ti foil is taken as a working electrode and platinum foil is used as counter electrode. Both electrodes are placed 10 mm apart. Voltage is maintained at 60 V for 24 h using DC power source and Titania nanotubes are prepared. The sample is being annealed at 450°C for 2 h [43]. These structures can provide highly mesoporous structures for various photocatalytic applications.

Ali et al. have prepared hierarchical structures of Titania by anodization technique. Ti foil is used as precursor and glycerol with ammonium fluoride is used as electrolyte. Anodization of Ti foils has been done in glycerol containing 10 wt% H_2O and 0.25 M NH_4F electrolyte solution. The voltage has been set at 30 V against the Pt counter electrode for 4 h. The nanotubes are



Figure 21. (a) SEM images of hierarchical TiO₂ prepared via anodization of TNT in F- residue and (b) cross-sectional view [43].

then dried under a stream of N_2 gas. The sample is annealed at 400°C for 2 h for crystallization of Titania nanotube arrays (TNTAs). The sample obtained is then immersed in 80 mM TiCl₄ for different time intervals and then sintered at 400°C to produce photoelectrodes. Nanorods (**Figure 22**) having flower-like structures are produced after treatment at 120°C with TiCl₄ [73]. These structures are then utilized for water-splitting application. H₂ can also be produced from these structures and can be stored for energy applications.

Zhang et al. prepared hierarchical nanotube-like structures via anodization [42]. The titanium foil is sonicated in ethanol and cold distilled water to remove impurities. After that, N₂ stream is used to dry the foil. Anodization is done using Ti as anode and Pt as cathode material. NH₄F is added in ethylene glycol (EG), which is present in 2 vol% distilled water as electrolyte solution. This electrolyte is used for oxidation of Titanium sheet. Anodization is performed at room temperature in two steps. In step 1, Ti sheet is anodized for 10 min at 50 V and grown nanotubes are removed ultrasonically in DI water. In step 2, the same sheet is anodized under the same condition for 30 min. The powder obtained is cleaned with distilled water under N₂ atmosphere.

Anodized TiO_2 nanotubes are annealed in air at 450°C for 1 h with a heating rate of 5°C/min for crystallization of pure anatase phase as shown in **Figure 23**. These structures are used for photodegradation of organic pollutants. These types of structures show improved photocatalytic activity in degradation of organic dye. The enhanced surface area facilitated the reaction rate.



Figure 22. FESEM images of (a) TNTA, (b) TNTA/TiCl₄ 20 min, (c) TNTA/TiCl₄ 80 min, (d) TNTA/TiCl₄ 120 min [73].



Figure 23. (a) SEM image of top view of porous TiO_2 nanotubes; Top enlarged image shows the diameter and bottom enlarged image shows the side walls [42].

Tang et al. [40] have prepared nanoflakes/nanoparticles hierarchical structures via anodization technique. In this synthesis, electrochemical spark discharge spallation (ESDS) method is applied in an electrolyte of 10 M NaOH in aqueous solution while using as platinum counter electrode. Titanate hierarchical microspherulite structures are produced as a result of this synthesis. The Na⁺ ions are replaced by H⁺ ions by soaking the prepared sample in HCl. The sample is then washed to remove the acidic content and to make pH neutral. The samples obtained are annealed at different temperatures to crystallize them [40].

Dislocations in the sample decrease as the sample is heated above its crystallization temperature. **Table 6** shows some properties of anatase TiO_2 obtained via this synthesis route. The difference in morphology can be seen in SEM image in **Figure 24**. By increasing the time for heat treatment, nanosheets were converted into nanoflakes and nanoparticles due to crystal re-growth with larger energy and with minimal stresses. These structures are employed for photodegradation of organic pollutants.

Smith et al. have prepared hierarchical nanotubular structures via anodization technique [72]. The synthesis follows basic principle of anodization. Titanium foil is etched in the presence of HF, HNO_3 and DI water in volumes of 1:3:50 ml for different time intervals. The etched powder is washed with DI water immediately and is anodized at 60 V for 1 h in presence of NH_4F and ethylene glycol electrolyte. The powder obtained is annealed at 500°C for 2 h. The etching treatment before anodization removed small layers of titanium and provided ripple-like surface. Due to surface roughness, the electric field becomes localized at grains. An initial oxide layer formed during etching is then oxidized during anodization.

The smooth etched layers on foil cause a uniform electric current and porous nanotubes grow in those areas. The prepared hierarchical structures as shown in **Figure 25** showed better results for photoelectrochemical applications. Hierarchical structures provided large surface area for photocatalytic reactions.



Figure 24. (a) H-TMS calcinated at different temperatures: (b) 300°C, (c) 400°C, (d) 500°C, (e) 600°C, and (f) 700°C [40].



Figure 25. SEM image of foil's surface: (a) After 30 s etching (inset shows anodization after 1 h at 60 V) and (b) after 90 s etching [72].

2.5.2. Merits

- The thickness and lengths of the nanotubes produced can be varied by changing voltage time and voltage itself [74].
- High aspect ratio tubes are formed.
- Ease of fabrication.
- The change in anodization conditions does not affect the chemical composition of TiO₂ nanotubes.
- Increasing the electrolyte concentration can cause etching to increase and nanotubes can be formed of long lengths and diameters.
- Structures are highly recommended for DSSCs as high aspect ratio tubes are formed.

2.5.3. Demerits

- Extended warranties of products are not offered in this process.
- Average growth rate can be decreased with increase in anodization time [74].

2.5.4. Summary of anodization

So, hierarchical Titania nanostructures were prepared from anodization technique and nanotube-like structures were prepared. The particle diameter was in nanometer ranges. The diameter and length of nanotubes increase by increasing voltage and voltage time up to optimum level [75]. The prepared powder was used in water-splitting application, which can be used for nuclear thermal and solar thermal plants.

2.6. Photolithography

This is a technique that is used in microfabrication to pattern thin films and bulk materials. Light is being used to transfer pattern onto the light-sensitive photoresist. Photoresist basically is a light-sensitive material, which is used to form pattern coating on the surface. Photoresist is of two types, which are as follows:

- Positive photoresist: The resist is applied over the area on which the underlying material is to be removed.
- Negative photoresist: The resist is applied over the area on which the area other than resist is to be removed.

Then, etching is done to form patterned hierarchical 3D structures. When photopositive resist coating is done over the substrate, then the growth of structure takes place on the same area where we seed/coat the material. The mask contains the exact copy of resist, which we deposit on the substrate and vice versa. **Table 7** shows features of structures prepared via photoli-thography technique.

2.6.1. Examples

Kim et al. have reported HNSs of Titania by photolithography. A negative PR is prepared on 5 mm Ti foil by baking at 120°C. Upon exposure to UV light, PR gets developed. The foil is etched via reactive ion etching. Titanium foil's area that is not covered with the PR is etched out in this process. TiO₂ nanoflowers composed of nanotubes (**Figure 26**) are prepared in this procedure [48].

So, flower-like HNSs are produced via dot patterning technique. The particles are in the micron ranges (diameter). The prepared product is employed in dye-sensitized solar cells and exhibits maximum surface area for dye adsorption. Hence, these show better result for photocatalytic processes.

2.6.2. Merits

- If viscosity of photoresist is controlled, we can achieve well-formed structures.
- Cost-effective process.
- No need of specialized equipment.

| Reference | Phase | Surface area (m ² g ⁻¹) | Particle size (diameter) | Precursor materials | Morphology | Application |
|-----------------|---------|---|-----------------------------|------------------------|-------------------------------------|-------------|
| Kim et al. [48] | Anatase | - | 1.5–2µm | Ti foil | Flower-like structures on nanotubes | DSSCs |

Table 7. Hierarchical TiO₂ nanostructures produced via dot patterning/photolithography.



Figure 26. Hierarchical flower-like structures produced by dot patterning [48].

2.6.3. Demerits

- The nature of solvents, sensitizers and additives should be well studied.
- Sometimes, the step coverage can be poor, i.e., the ability of photoresist to cover the sideedge of the surface steps.

2.6.4. Summary of photolithography

HNSs of Titania are formed via various techniques and different types of structures are formed by these processes. **Table 7** shows the different characteristics of materials obtained by dot patterning. By changing the reaction conditions like time, temperature and pressure and precursor material, different morphological structures are formed, which have different surface area and porosity for applications like dye-sensitized solar cells, photocatalysis, gas sensing and lithium ion batteries.

2.7. Vapor deposition method

As the name suggests, this method involves deposition of vapors of the required material. The material is vaporized from the source and condenses on the substrate. It may or may not involve chemical reactions. Vapors can be deposited on the substrates by two main processes:

- Chemical vapor deposition (CVD)
- Physical vapor deposition (PVD)

Very little work has been done by these techniques to grow TiO_2 HNSs. By these techniques, we can grow hierarchical structures. The film cost, thickness, source material and compositions can be controlled by these processes.

In CVD process, precursors are introduced in the reaction chamber and flow of molecules is regulated by control values. The precursor molecules get deposited over the surface of substrates after chemical reactions take place. Heat energy is provided for chemical reactions to take place. While in PVD, deposition occurs by various routes like evaporation, sputtering and molecular beam epitaxy (MBE). **Table 8** shows different characteristics of HNSs prepared via these processes.

2.7.1. Examples

Flipin et al. [76] grew hierarchical TiO_2 nanotubes by plasma-enhanced chemical vapor deposition technique. Porphyrins and phthalocyanines were used as cost-effective precursor molecules. First of all, seed layer was grown by polycrystalline anatase films for highly dense and homogenous organic nanowires. Physical vacuum deposition was done to grow organic nanowires (ONWs) of phthalocyanine molecules with sublimation temperature of 250°C. As a result, tunable ONWs in the range between 1 and 30 μ m and diameters between 50 and 120 nm were produced. Then, PECVD was done to cap ONWs with TiO₂ shells.

Multistacked nanotrees composed of TiO_2 nanowires were grown as a result of this synthesis as shown in **Figure 27**. These nanotubes were grown as 1D structures provide maximum electron percolation as compared to 0D nanoparticles due to less grain boundaries. These structures were then employed for DSSCs to evaluate their efficiency for current production.

Yoshitake et al. [77] prepared hierarchical TiO_2 structures by CVD method. Titanium tetraisopropoxide (TTIP) was used as a precursor material. About 40 g of water was added to 8 g of TTIP with 2.6 g of dodecyl amine at 273 K. The mixture was stirred with 0.1 M HCl and was kept overnight for aging. The reaction mixture was transferred to autoclave at 373 K for 4 days. The powder obtained was washed with methanol and dry ethyl ether.

| Reference | Phase | Surface area (m ² g ⁻¹) | Particle size (diameter) (nm) | Crystallite size (nm) | Morphology | Application |
|-----------------------|---------|---|----------------------------------|--------------------------------|---|-------------|
| Flipin et al. [76] | Anatase | _ | 50–120 | Below 100 (for all structures) | Nanoforest composed of nanowires | DSSCs |
| Yoshitake et al. [77] | Anatase | 518 | 3.03 | 3.30 | Worm-like spherical agglomerated structures | - |

Table 8. Hierarchical TiO, nanostructures produced via vapor deposition processes.



Figure 27. (a and b) SEM images of multistacked nanoforest [76].



Figure 28. (a) TEM images of structures formed by CVD and (b) worm-like agglomerated 3D TiO₂ structures grown by CVD [77].

CVD of TTIP was done in Pyrex reactor. Pure argon was passed through liquid TTIP at 293 K into the tube where the powder formed by former process was already deposited. After deposition for 24 h, the gas was switched to $N_{2'}$ which passed through water at 293 K. TTIP was decomposed completely for 12 h and finally the powder was treated in dry air at 393 K for 2 h. Spherical agglomerated structures were produced as a result of this synthesis (**Figure 28**).

2.7.2. Merits and demerits of CVD

- There is less wastage of chemicals and substrate.
- If laser is used to heat the precursor material, the deposition becomes selective to the path of laser.
- High temperature is required in case of CVD to initiate chemical reactions. CVD runs at much higher temperature.
- Substances that cannot tolerate high temperatures, which decompose or sublime, cannot be deposited by CVD.

2.7.3. Merits and demerits of PVD

- Processes like sputtering can initiate and undergo PVD, so less use of energy in terms of less usage of heat is required for deposition.
- By process like MBE, we can achieve atomic level growth control.
- Sputtering does not require the use of specific precursor materials as in CVD.
- Cost of the process is very high.
- Vacuum conditions may be required in some depositions.

2.7.4. Summary of vapor deposition processes

These processes can form well-defined structures. Nanocoatings can also be formed as a result of these processes. Temperature, time and target materials need to be well optimized for distinct structure growth. Pressure in the chamber should be controlled in case of physical vapor deposition processes for growth of hierarchical structures.

3. Conclusions and future prospects

In conclusion, this chapter gives an overview of synthesis of HNSs of Titania via different routes. The chemistry and different parameters affecting the properties of HNSs are also briefly discussed. It can be seen that the employed techniques are very powerful in synthesizing TiO, HNSs in the form of agglomerated nanoparticles, nanospheres, nanoflakes or 1D/3D heterostructures. In hydrothermal synthesis, by changing parameters of temperature, concentration of precursors, etching reagents and time, the morphology of TiO, particles can be changed to 3D HNSs. By providing prolonged time for crystallization, the morphology of particles changes. However, in case of solvothermal synthesis, different solvents provide different structures. By using solvents that provide maximum steric hindrance, the morphology of structures can be controlled. Also, solvents with high boiling points can be used. In microwave synthesis, irradiation time, temperature and solvents are key factors in controlling morphology. This method provides short time for crystallization in the presence of radiations and more nucleation sites are formed. In pulsed laser deposition process, nanotree- and nanoforest-like structures are grown from agglomeration of nanoparticles. Pressure plays an important role in controlling the morphology. By increasing voltage in anodization technique, when the energy provided to target material is increased, the diameter and length of structures formed are increased leading to formation of 3D hierarchical-like structures as end products. In photolithography, the structures engraving are much easier and microfabrication can be done by these structures. Vapor deposition processes are new and very little work has been done for TiO, HNSs preparation. These processes can be used to grow very thin films of materials and morphologies can be opted by varying parameters like pressure, temperature, precursors (in case of CVD) and mean free path.

Hence, TiO₂ HNSs with different morphologies can be obtained via different synthetic pathways. These structures can help to achieve maximum scattering with high specific surface area for sunlight entrapment. Hierarchical morphology further helps in better absorption of light and efficient electron-hole pair generation can be achieved. Also, reduced recombination rates are being observed by these structures. These mesoporous structures can help in maximum adsorption of dye molecules. So, these properties shown by TiO₂ hierarchical structures increase the efficiency of phenomena taking place at the interfaces and hence efficient results are seen. These facts make HNSs promising candidates for photovoltaic and photocatalytic applications as can be seen in much of the reported work. These structures can be also employed and exploited in future, for increasing efficiency of various devices like:

- Photoelectrochemical cells (PECs)
- Photovoltaic devices (PVs)
- Organic pollutants degradation
- Water splitting
- Supercapacitors
- Li/Na ion batteries

Hierarchical nanostructures can be mixed with nanoparticles to enhance surface area for photocatalytic reactions. These structures can also be doped, codoped or their hybrid structures can be made to increase efficiency of prepared products.

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References

[1] Javed S, Mujahid M, Islam M, Manzoor U. Morphological effects of reflux condensation on nanocrystalline anatase gel and thin films. Materials Chemistry and Physics. 2012;**132**:509-514. DOI: 10.1016/j.matchemphys.2011.11.062

- [2] Gao L, Cao M, Fu YQ, Zhong Z, Shen Y, Wang M. Hierarchical TiO₂ spheres assisted with graphene for high performance lithium-sulfur battery. Journal of Materials Chemistry A. 2016;4:16454-16461. DOI: 10.1039/c6ta06285g
- [3] Wu W-Q, Lei B-X, Rao H-S, Xu Y-F, Wang Y-F, Su C-Y, Kuang D-B. Hydrothermal fabrication of hierarchically anatase TiO₂ nanowire arrays on FTO glass for dye-sensitized solar cells. Scientific Reports. 2013;3:1352. DOI: 10.1038/srep01352
- [4] Lui G, Liao JY, Duan AS, Zhang ZS, Fowler M, Yu AP. Graphene-wrapped hierarchical TiO₂ nanoflower composites with enhanced photocatalytic performance. Journal of Materials Chemistry A. 2013;1:12255-12262. DOI: 10.1039/c3ta12329d
- [5] Boubault A, Ho K, Hall A, Lambert TN, Ambrosini A. Durability of solar absorber coatings and their cost-effectiveness. Solar Energy Materials & Solar Cells. 2017;166:176-184. DOI: 10.1016/j.solmat.2017.03.010
- [6] Blaabjerg F, Ionel DM, Blaabjerg F, Ionel DM. Renewable energy devices and systems State-of-the-art technology, research and development, challenges and future trends. Electric Power Components & Systems. 2017;43(12)1319-1328. DOI: 10.1080/15325008. 2015.1062819
- [7] Zaleska A. Doped-TiO₂: A review. Recent Patents on Engineering. 2008;2:157-164. DOI: 10.2174/187221208786306289
- [8] Javed S, Akram MA, Mujahid M. Environment friendly template-free microwave synthesis of submicron-sized hierarchical titania nanostructures and their application in photovoltaics. CrystEngComm. 2014;16:10937-10942. DOI: 10.1039/C4CE01826E
- [9] MacWan DP, Dave PN, Chaturvedi S. A review on nano-TiO₂ sol-gel type syntheses and its applications. Journal of Materials Science. 2011;46:3669-3686. DOI: 10.1007/ s10853-011-5378-y
- [10] Paper R, Ochanda FO, Rajukada S, Barnett MR. Controlled synthesis of TiO₂ hierarchical nanofibre structures via electrospinning and solvothermal processes: Photocatalytic activity for degradation of methylene blue. Nanomaterials and Nanotechnology. 2012;2:1-10. DOI: 10.5772/53190
- [11] Li X, Wu G, Liu X, Li W, Li M. Orderly integration of porous TiO₂(B) nanosheets into bunchy hierarchical structure for high-rate and ultralong-lifespan lithium-ion batteries. Nano Energy. 2017;**31**:1-8. DOI: 10.1016/j.nanoen.2016.11.002
- [12] Shen J, Hu W, Li Y, Li L, Lv X, Zhang L. Fabrication of free-standing N-doped carbon/ TiO₂ hierarchical nano fiber films and their application in lithium and sodium storages. 2017;**701**:372-379. DOI: 10.1016/j.jallcom.2017.01.100
- [13] Diebold U. Structure and properties of TiO₂ surfaces: A brief review. Applied Physics A: Materials Science & Processing. 2003;76:681-687. DOI: 10.1007/s00339-002-2004-5
- [14] Bahadur NM, Furusawa T, Sato M, Kurayama F, Suzuki N. Rapid synthesis, characterization and optical properties of TiO₂ coated ZnO nanocomposite particles by a novel microwave irradiation method. Materials Research Bulletin. 2010;45:1383-1388. DOI: 10.1016/j.materresbull.2010.06.048

- [15] Tong YH, Liu YC, Lu SX, Dong L, Chen SJ, Xiao ZY. The optical properties of ZnO nanoparticles capped with polyvinyl butyral. Journal of Sol-Gel Science and Technology. 2004;30:157-161. DOI: 10.1023/B:JSST.0000039500.48283.5a
- [16] Samsudin EM, Goh SN, Wu TY, Ling TT, Hamid SBA, Juan JC. Evaluation on the photocatalytic degradation activity of reactive blue 4 using pure anatase nano-TiO₂. Sains Malaysiana. 2015;44:1011-1019. DOI: 10.17576/jsm-2015-4407-13
- [17] Schnier T, Emara J, Olthof S, Meerholz K. Influence of hybrid perovskite fabrication methods on film formation, electronic structure, and solar cell performance. Journal of Visualized Experiments. 2017:1-8. DOI: 10.3791/55084
- [18] Yang J, Bark C, Kim K, Choi H. Characteristics of the dye-sensitized solar cells using TiO₂ nanotubes treated with TiCl₄. Materials (Basel). 2014;7:3522-3532. DOI: 10.3390/ ma7053522
- [19] Apostolopoulou A, Sygkridou D, Rapsomanikis A. Enhanced performance of mesostructured perovskite solar cells in ambient conditions with a composite TiO₂-In₂O₃ electron transport layer. Solar Energy Materials & Solar Cells. 2017;166:100-107. DOI: 10.1016/j.solmat.2017.03.024
- [20] Hu A, Cheng C, Li X, Jiang J, Ding R, Zhu J, Wu F, Liu J, Huang X. Two novel hierarchical homogeneous nanoarchitectures of TiO₂ nanorods branched and P25-coated TiO₂ nanotube arrays and their photocurrent performances. Nanoscale Research Letters. 2011;6:91. DOI: 10.1186/1556-276X-6-91
- [21] Ren Z, Guo Y, Liu C-H, Gao P-X. Hierarchically nanostructured materials for sustainable environmental applications. Frontiers in Chemistry. 2013;1:18. DOI: 10.3389/ fchem.2013.00018
- [22] Joseph S, Melvin Boby SJ, Theresa Nathan DMG, Sagayaraj P. Investigation on the role of cost effective cathode materials for fabrication of efficient DSSCs with TiNT/TiO₂ nanocomposite photoanodes. Solar Energy Materials & Solar Cells. 2017;165:72-81. DOI: 10.1016/j.solmat.2017.02.038
- [23] Zhu K, Sun Y, Wang R, Shan Z, Liu K. Fast synthesis of uniform mesoporous titania submicrospheres with high tap densities for high-volumetric performance Li-ion batteries. 2017:1-3. DOI: 10.1007/s40843-016-9002-y
- [24] Suprabha T, Roy HG, Thomas J, Praveen Kumar K, Mathew S. Microwave-assisted synthesis of titania nanocubes, nanospheres and nanorods for photocatalytic dye degradation. Nanoscale Research Letters. 2009;4:144-152. DOI: 10.1007/s11671-008-9214-5
- [25] Park J-Y, Lee C, Jung K-W, Jung D. Structure related photocatalytic properties of TiO₂. Bulletin of the Korean Chemical Society. 2009;**30**:402-404
- [26] Luo H, Takata T, Lee Y, Zhao J, Domen K, Yan Y. Photocatalytic activity enhancing for titanium dioxide by co-doping with bromine and chlorine. Chemistry of Materials. 2004;16:846-849. DOI: 10.1021/cm035090w

- [27] Li H, He Y, Liu Z, Jiang B, Huang Y. Rapid synthesis of broadband Ag @ TiO₂ coreshell nanoparticles for solar energy conversion. Solar Energy Materials & Solar Cells. 2017;166:52-60. DOI: 10.1016/j.solmat.2017.03.005
- [28] Ohtani B, Ogawa Y, Nishimoto S. Photocatalytic activity of amorphous-anatase mixture of titanium (IV) oxide particles suspended in aqueous solutions. The Journal of Physical Chemistry B. 1997;5647:3746-3752. DOI: 10.1021/jp962702+
- [29] Zhu T, Li J, Wu Q. Construction of TiO₂ hierarchical nanostructures from nanocrystals and their photocatalytic properties. ACS Applied Materials & Interfaces. 2011;3:3448-3453. DOI: 10.1021/am2006838
- [30] Zhang WP, Xiao XY, Zheng LL, Wan CX. Fabrication of TiO₂/MoS₂ composite photocatalyst and its photocatalytic mechanism for degradation of methyl orange under visible light. Canadian Journal of Chemical Engineering. 2015;93:1594-1602. DOI: 10.1002/ cjce.22245
- [31] Duan Y, Fu N, Liu Q, Fang Y, Zhou X, Zhang J, Lin Y. Sn-doped TiO₂ photoanode for dye-sensitized solar cells. Journal of Physical Chemistry C. 2012;116:8888-8893. DOI: 10.1071/CH11031
- [32] Wang C, Yin L, Zhang L, Qi Y, Lun N, Liu N. Large scale synthesis and gas-sensing properties of anatase TiO₂ three-dimensional hierarchical nanostructures. Langmuir. 2010;26:12841-12848. DOI: 10.1021/la100910u
- [33] Drazic G, Horvat B. Electron microscopy study of TiO₂ hierarchical structures prepared by hydrothermal synthesis. Microscopy and Microanalysis. 2013;19:1584-1585. DOI: 10.1017/S1431927613009914
- [34] Zhao C, Zhang J, Hu Y, Robertson N, Hu PA, Child D, Gibson D, Fu YQ. In-situ microfluidic controlled, low temperature hydrothermal growth of nanoflakes for dye-sensitized solar cells. Scientific Reports. 2015;5:17750. DOI: 10.1038/srep17750
- [35] Xiang L, Zhao X, Yin J, Fan B. Well-organized 3D urchin-like hierarchical TiO₂ microspheres with high photocatalytic activity. Journal of Materials Science. 2012;47:1436-1445. DOI: 10.1007/s10853-011-5924-7
- [36] Yeung KL, Yau ST, Maira AJ, Coronado JM, Soria J, Yue PL. The influence of surface properties on the photocatalytic activity of nanostructured TiO₂. Journal of Catalysis. 2003;**219**:107-116. DOI: 10.1016/S0021-9517(03)00187-8
- [37] Wang X, Tian J, Fei C, Lv L, Wang Y, Cao G. Rapid construction of TiO₂ aggregates using microwave assisted synthesis and its application for dye-sensitized solar cells. RSC Advances. 2015;5:8622-8629. DOI: 10.1039/C4RA11266K
- [38] Calatayud DG, Jardiel T, Peiteado M, Caballero AC, Fernández-Hevia D. Microwaveinduced fast crystallization of amorphous hierarchical anatase microspheres. Nanoscale Research Letters. 2014;9:273. DOI: 10.1186/1556-276X-9-273

- [39] Di Fonzo F, Casari CS, Russo V, Brunella MF, Bassi L, Bottani CE. Hierarchically organized nanostructured TiO₂ for photocatalysis applications. Nanotechnology. 2009;20: 15604. DOI: 10.1088/0957-4484/20/1/015604
- [40] Tang Y, Wee P, Lai Y, Wang X, Gong D, Kanhere PD, Lim TT, Dong Z, Chen Z. Hierarchical TiO₂ nanoflakes and nanoparticles hybrid structure for improved photocatalytic activity. Journal of Physical Chemistry C. 2012;**116**:2772-2780. DOI: 10.1021/jp210479a
- [41] Yuan S, Chen W, Hu S. Fabrication of TiO₂ nanoparticles/surfactant polymer complex film on glassy carbon electrode and its application to sensing trace dopamine. Materials Science and Engineering: C. 2005;25:479-485. DOI: 10.1016/j.msec.2004.12.004
- [42] Zhang Z, Yu Y, Wang P. Hierarchical top-porous/bottom-tubular TiO₂ nanostructures decorated with Pd nanoparticles for efficient photoelectrocatalytic decomposition of synergistic pollutants. ACS Applied Materials & Interfaces. 2012;4:990-996. DOI: 10.1021/am201630s
- [43] Ali G, Yoo SH, Kum JM, Raza HS, Chen D, Cho SO. Formation of hierarchical TiO₂ nanoporous structure from free-standing TiO₂ nanotubes layers. Journal of Nanoparticle Research. 2012;14. DOI: 10.1007/s11051-012-1047-6
- [44] Sauvage F, Di Fonzo F, Li Bassi A, Casari CS, Russo V, Divitini G, Ducati C, Bottani CE, Comte P, Graetzel M. Hierarchical TiO₂ photoanode for dye-sensitized solar cells. Nano Letters. 2010;10:2562-2567. DOI: 10.1021/nl101198b
- [45] Luttrell T, Halpegamage S, Tao J, Kramer A, Sutter E, Batzill M. Why is anatase a better photocatalyst than rutile?—Model studies on epitaxial TiO₂ films. Scientific Reports. 2014;4:4043. DOI: 10.1038/srep04043
- [46] Rahal R, Wankhade A, Cha D, Fihri A, Ould-Chikh S, Patil U, Polshettiwar V. Synthesis of hierarchical anatase TiO₂ nanostructures with tunable morphology and enhanced photocatalytic activity. RSC Advances. 2012;2:7048. DOI: 10.1039/c2ra21104a
- [47] Chu L, Li L, Su J, Tu F, Liu N, Gao Y. A general method for preparing anatase TiO₂ treelike-nanoarrays on various metal wires for fiber dye-sensitized solar cells. Scientific Reports. 2014;4:4420. DOI: 10.1038/srep04420
- [48] Kim W-R, Park H, Choi W-Y. TiO₂ micro-flowers composed of nanotubes and their application to dye-sensitized solar cells. Nanoscale Research Letters. 2014;9:93. DOI: 10.1186/1556-276X-9-93
- [49] Zhu F, Wu D, Li Q, Dong H, Li J, Jiang K, Xu D. Hierarchical TiO₂ microspheres: Synthesis, structural control and their applications in dye-sensitized solar cells. RSC Advances. 2012:11629-11637. DOI: 10.1039/c2ra22043a
- [50] Wang H, Wang B, Yu J, Hu Y, Xia C, Zhang J, Liu R. Significant enhancement of power conversion efficiency for dye sensitized solar cell using 1D/3D network nanostructures as photoanodes. Scientific Reports. 2015;5:9305. DOI: 10.1038/srep09305
- [51] Kim W-R, Park H, Choi W-Y. Conical islands of TiO₂ nanotube arrays in the photoelectrode of dye-sensitized solar cells. Nanoscale Research Letters. 2015;10:63. DOI: 10.1186/ s11671-015-0737-2

- [52] Liu M, Piao L, Wang W. Hierarchical TiO₂ spheres: Facile fabrication and enhanced photocatalysis. Rare Metals. 2011;30:153-156. DOI: 10.1007/s12598-011-0259-8
- [53] Zhuge F, Qiu J, Li X, Gao X, Gan X, Yu W. Toward hierarchical TiO₂ nanotube arrays for efficient dye-sensitized solar cells. Advanced Materials. 2011;23:1330-1334. DOI: 10.1002/ adma.201003902
- [54] Passoni L, Criante L, Fumagalli F, Scotognella F, Lanzani G, Di Fonzo F. Self-assembled hierarchical nanostructures for high-efficiency porous photonic crystals. ACS Nano. 2014;8:12167-12174. DOI: 10.1021/nn5037202
- [55] Liu H, Ma H, Joo J, Yin Y. Contribution of multiple reflections to light utilization efficiency of submicron hollow TiO₂ photocatalyst. 2016;**59**:1017-1026. DOI: 10.1007/ s40843-016-5127-7
- [56] Lin J, Heo Y-U, Nattestad A, Sun Z, Wang L, Kim JH, Dou SX. 3D hierarchical rutile TiO₂ and metal-free organic sensitizer producing dye-sensitized solar cells 8.6% conversion efficiency. Scientific Reports. 2014;4:5769. DOI: 10.1038/srep05769
- [57] Xiang P, Ma W, Xiao T, Jiang L, Tan X, Shu T. Ta-doped hierarchical TiO₂ spheres for dyesensitized solar cells. Journal of Alloys and Compounds. 2016;656:45-50. DOI: 10.1016/j. jallcom.2015.09.203
- [58] Shao F, Sun J, Gao L, Yang S, Luo J. Template-free synthesis of hierarchical TiO₂ structures and their application in dye-sensitized solar cells. ACS Applied Materials & Interfaces. 2011;3:2148-2153. DOI: 10.1021/am200377g
- [59] Yang Y, Hu JX, Liang Y, Zou JP, Xu K, Hu RJ, Zou ZD, Yuan Q, Chen QQ, Lu Y, Yu T, Yuan CL. Anatase TiO₂ hierarchical microspheres consisting of truncated nano-thorns and their structurally enhanced gas sensing performance. Journal of Alloys and Compounds. 2017;694:292-299. DOI: 10.1016/j.jallcom.2016.09.328
- [60] Zheng Z, Huang B, Qin X, Zhang X, Dai Y. Strategic synthesis of hierarchical TiO₂ microspheres with enhanced photocatalytic activity. Chemistry - A European Journal. 2010;16:11266-11270. DOI: 10.1002/chem.201001280
- [61] Wang H, Liu Y, Li M, Huang H, Xu HM, Hong RJ, Shen H. Multifunctional TiO₂ nanowires-modified nanoparticles bilayer film for 3D dye-sensitized solar cells. Optoelectronics and Advanced Materials, Rapid Communications. 2010;4:1166-1169. DOI: 10.1039/ b000000x
- [62] Santhosh N, Govindaraj R, Pandian MS, Ramasamy P. Facile synthesis of mesoporous TiO₂ nanospheres by microwave-assisted hydrothermal method and its applications in dye sensitized solar. Cell. 2017;50003:2-5. DOI: 10.1063/1.4980236
- [63] Jia X, He W, Zhang X, Zhao H. Microwave-assisted synthesis of anatase TiO₂ nanorods with mesopores. Nanotechnology. 2007;18:075602. DOI: 10.1088/0957-4484/18/7/075602
- [64] Chung CC, Chung TW, Yang TCK. Rapid synthesis of titania nanowires by microwaveassisted hydrothermal treatments. Industrial and Engineering Chemistry Research. 2008;47:2301-2307. DOI: 10.1021/ie0713644

- [65] Bregadiolli BA, Fernandes SL, Frederico C, Graeff DO. Easy and fast preparation of TiO₂based nanostructures using microwave assisted hydrothermal synthesis. 2017;20:912-919
- [66] Rahal R, Wankhade A, Cha D, Fihri A, Ould-Chikh S, Patil U. Synthesis of hierarchical anatase TiO₂ nanostructures with tunable morphology and enhanced photocatalytic activity. RSC Advances. 2012:7048-7052. DOI: 10.1039/c2ra21104a
- [67] Perales-Martínez IA, Rodríguez-González V. Towards the hydrothermal growth of hierarchical cauliflower-like TiO₂ anatase structures. Journal of Sol-Gel Science and Technology. 2017;81:741-749. DOI: 10.1007/s10971-016-4241-7
- [68] Brunella MF, Diamanti MV, Pedeferri MP, Di Fonzo F, Casari CS, Bassi AL. Photocatalytic behavior of different titanium dioxide layers. Thin Solid Films. 2007;515:6309-6313. DOI: 10.1016/j.tsf.2006.11.194
- [69] Di Fonzo F, Tonini D, Bassi L, Casari CS, Beghi MG, Bottani CE, Gastaldi D, Vena P, Contro R. Growth regimes in pulsed laser deposition of aluminum oxide films. Applied Physics A: Materials Science & Processing. 2008;93:765-769. DOI: 10.1007/s00339-008-4720-y
- [70] Asmatulu R, Khan S, Anwar M, Rajib. Synthesis of highly ordered titanium dioxide (TiO2) nanotubes: Impact of process parameters. In: 42 Istc. 2010. pp. 35-36. http://www. sampe.org/store/paper.aspx?pid=6406
- [71] Prakasam HE, Shankar K, Paulose M, Varghese OK, Grimes CA. A new benchmark for TiO₂ nanotube array growth by anodization. Society. 2007:7235-7241. DOI: 10.1021/ jp070273h
- [72] Smith YR, Sarma B, Mohanty SK, Misra M. Single-step anodization for synthesis of hierarchical TiO₂ nanotube arrays on foil and wire substrate for enhanced photoelectrochemical water splitting. International Journal of Hydrogen Energy. 2013;38:2062-2069. DOI: 10.1016/j.ijhydene.2012.11.045
- [73] Ali H, Ismai N, Amin MS, Mekewi M. Efficient photoelectrodes from anatase TiO₂ nanotube arrays decorated with particles / rods / 3D microflower rutile crystals for photoelectrochemical water splitting. Journal of Solid State Electrochemistry. 2017;21:1605. DOI: 10.1007/s10008-017-3523-5
- [74] Chernozem RV, Surmeneva MA, Surmenev RA. Influence of anodization time and voltage on the parameters of TiO₂ nanotubes. IOP Conference Series Materials Science Engineering. 2016;116:12025. DOI: 10.1088/1757-899X/116/1/012025
- [75] Alsammarraei AMA, Jaafar HI, Abed KN. The role of anodizing potentials in making TiO₂ nanotubes in (ethylene glycol/NH₄F/water) electrolyte. Applied Scientific Research. 2014;6:115-121
- [76] Nicolas Filippin A, Sanchez-Valencia JR, Idígoras J, Rojas TC, Barranco A, Anta JA, Borras A. Plasma assisted deposition of single and multistacked TiO₂ hierarchical nanotube photoanodes. Nanoscale. 2017;9:8133-8141. DOI: 10.1039/C7NR00923B
- [77] Yoshitake H, Sugihara T, Tatsumi T. Preparation of wormhole-like mesoporous TiO₂ with an extremely large surface area and stabilization of its surface by chemical vapor deposition. Chemistry of Materials. 2002;14:1023-1029. DOI: 10.1021/cm010539b

Novel Two-Dimensional Nanomaterial: High Aspect Ratio Titania Nanoflakes

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Abstract

A novel 2D nanomaterial, high aspect ratio TiO₂ nanoflakes were synthesized by a onestep method. Surface morphology and physical dimensions were characterized using Scanning Electron Microscopy (SEM), Laser Diffraction technology, and Transmission Electron Microscopy (TEM). Micro-sized flakes having a thickness approximately 40 nm were successfully synthesized by spreading a mixture of titanium alkoxide and hydrocarbon on the water surface. Relatively higher specific surface area (2-6 times) and less crystal defects enhanced photocatalytic activities of nanoflakes due to more surface reaction sites. By performing dye degradation under ultraviolet (UV) illumination, titania nanoflakes exhibited the higher photocatalytic efficiency over the commercial photocatalyst, Degussa P25. To the best of our knowledge, this is the first time to continuously synthesize low-dimensional nanomaterials in an efficient and cost effective manner. In practical water purification, traditional separation processes such as sedimentation or filtration could be utilized to easily extract the titania flakes from the treated water. Other applications such as anode material for lithium ion batteries and conducting paste in dye sensitized solar cells (DSSC) were also investigated. The cycling performance of Li-ion battery and energy conversion efficiency of DSSC were significantly improved.

Keywords: low-dimensional nanomaterials, titanium dioxide, nanoflakes, high aspect ratio, one-step synthesis

1. Introduction

Nanoscale functional materials, especially low-dimensional inorganic semiconductor materials have attracted great interest because of their size-dependent optical and electronic properties and potential applications in electronics and photonics. Because nanomaterials offer a high surface-to-volume ratio and short distance from the bulk material to the surface, the

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preparations are vivid [1]. Researchers have been focused on the morphology control, such as synthesis of nanotubes [2], nanowires [3, 4], nanoribbons [5], diskettes [6], nanobelts, nanosaws, nanowalls, nanomultipods, nanorings, nanocages, nanohelixes, nanopropellers, and many others [7–9]. While one-dimensional nanomaterials such as nanowires and nanorods have been extensively studied, 2D nanostructured materials have attracted relatively less attention. However, 2D nanomaterials show strong potential as chemical and biological sensors, nanoelectronic devices, and catalysts with high surface areas and large pore volumes. Many small band gap materials such as ZnO, ZnS, and Bi₂WO₆ with flake-like or plate-like morphologies have been already synthesized successfully [10–12]. For example, Ye et al. synthesized thinner ZnO nanoplates by restricting the crystal growth along (0001) plane with complexation between Zn^{2+} and citrate ions. The 50 nm thick hexagonal nanoplates with uniform 1 µm diameter presented the highest photocatalytic activity over other morphologies including nanorods, microrods, and dumbell-shaped microrods [13]. Liu et al. developed a combustion CVD method to deposit 50 nm to 1 µm thick ZnO flakes on Si substrate for ethanol vapor sensing [14]. Duan et al. developed an integrated autoclaving and pyrolysis process to obtain porous hexagonal ZnO micro-flakes [15]. Amano et al. autoclaved the mixture of bismuth nitrate and sodium tungstate to precipitate thin Bi₂WO₆ crystalline platelets (20–25 nm) with shifted absorption edge to the longer wavelength at 440 nm. The tungstate nanoplates completely oxidize gaseous acetaldehyde under visible light illumination resulting from slow recombination and a long lifetime of generated carriers in the time-resolved infrared absorption spectra [11]. Lanthanum titanate (La,Ti,O,) flakes were prepared by the reaction of titanium sulfate and lanthanum nitrate under the hydrothermal condition [16]. The thin lanthanum titanate flakes demonstrated significantly higher photoactivity to produce water splitting H, from water under UV irradiation over conventional solid-state reaction material due to higher surface area and light absorption. Highly porous CoOOH flakes were prepared by the deposition of layered cobalt acetate hydroxide solution on a nickel foil in 1.0 M KOH solution. The cyclic voltammetry (CV) measurements indicated high rate capacitance with good cycle ability of CoOOH flakes [17]. A novel pigment derived from silica flakes coated with titania from a web coating process were developed in a range of 50–1000 nm thickness [18]. The special color variation effect is achieved by the combination of silica flakes and titania coating resulting in strong light interference and angle-dependent behaviors. Nanosheets with a spacing of 0.6 nm were precipitated on a glass substrate from a SiO₂-TiO₂ gel solution under vibration in a 90°C hot water bath [19]. The good hydrophilicity and antifogging capability without any light exposure for 2000 h received from the hydrated nanosheets with unique physicochemical properties such as roughness and surface chemistry. Although the above materials possess unique properties on optical, gas sensing, electrochemical, and cleaning applications, the relatively expensive precursors or processes hinder practical applications.

Titanium dioxide is a versatile and low cost material for many industrial applications; many scientific works have been focused on particle size control down to the order of tens of nanometers. Nanostructured titanium dioxide were continuously developed in the field of environmental purification, solar energy conversion, pigment, optics, gas sensing, and energy storage [20–22]. However, using TiO₂ nanoparticles for water treatment is limited because of the difficulty of separation from purified water. Besides isotropic nanoparticles, anisotropic nanostructures including nanotubes, nanowires, nanorods, nanofibers, and nanosheets have been successfully synthesized [3, 23–26].

2. High aspect ratio titania nanoflakes

2.1. Syntheses of 2D titania nanomaterials

The most common shape of the fine titanium dioxide particles is spherical in many syntheses and applications. Thin films or fibers have been fabricated by being supported on a substrate or in the interstices in some three-dimension network [27, 28]. Sasaki fabricated thin titania flakes through exfoliation of a layered titanate precursor [25]. Although the specific surface area of the flakes is about 110 m²/g, the photocatalytic activity is still less than commercial product, Degussa P25 ($49 \text{ m}^2/\text{g}$). The freeze-dried nanosheets were also adopted as the anode material in a liquid electrolyte lithium ion battery [29]. The promising electrochemical performance of titania nanosheets were exploring in the charge-discharge characterizations as discharging with smaller slope and lower average voltage than titanium dioxide and lithium titanate. Li et al. in 2007 synthesized Brookite phase titania nanoplates by using titanium trichloride (TiCl₃) precursor through hydrothermal processes [30]. Under the same surface area of loaded $TiO_{,,}$ the brookite nanoplates exhibit the highest efficiency in the beaching of methyl orange solution under UV irradiation. The lamellar titania were synthesized within the lamellar micelle of non-ionic surfactant in cyclohexane [31]. The resembling nanostructures consisted of 40 nm titania flakes with flat, homogenous surface and low defects. Wu et al. utilized the micro-arc oxidation process associated with alkali treatment at pure titanium substrate to develop titania flakes [32]. However, most synthesis methods for these types of particles require multiple, complicated procedures and are typically nonconductive to be scaled up manufacturing as yields are typically milligram or less quantities of material. Examples include template, chemical vapor deposition, hydrothermal, electrochemical anodization, etc. [33–36].

2.2. One-step synthesis of titania nanoflakes

Anatase powders with sizes ranging from 5 to 165 nm were employed various synthesis methods. Regardless of fabrication processes, the optimum particle size range of 25–40 nm within all photocatalytic experiments processes were suggested by Almquist and Biswas [37]. The optimum photocatalysis is a function of competing mechanisms such as light absorption and scattering efficiency of the particles, as well as electron–hole pair combination and interfacial charge transfer. Therefore, we believe a one-step synthesis for titania nanomaterials with at least 1D close to the optimum size of photocatalyst will be a revolution of the titania photocatalyst fabrication. The one-step synthesis is spreading an oil phase consisting of titanium tetraisopropoxide and a low surface tension hydrocarbon at the surface of water to produce micrometer sized titania flakes having a thickness around 40 nm [38, 39]. Moreover, the thickness of nanoflakes could be tuned by changing the volume ratio of titania precursor and hydrocarbon. For instance, 40 nm titania flakes were successfully synthesized using a ratio of

1:8 of titania tetraisopropoxide to hydrocarbon. The reactions of forming TiO_2 in this research could be represented as follows:

$$Ti(OC_{3}H_{7})_{4} + 4H_{2}O \rightarrow Ti(OH) + 4C_{3}H_{7}OH...(hydrolysis)$$
(1)

$$Ti(OH)_{4} \rightarrow TiO_{2} + 2H_{2}O...(condensation)$$
 (2)

The resulting slurry was washed with Nanopure water and isoproponal thoroughly to remove impurities. Dried and well dispersed particles were collected by the supercritical fluid drying process [40]. The following heat treatment for phase transformation was conducted at 400°C. This synthesis has high potential to manufacture gram to kilogram quantities of nanomaterials. Scanning electron microscopy (SEM), laser diffraction analysis, X-ray diffraction (XRD), transmission electron microscopy (TEM), and physisorption techniques were used to further characterize these titania nanoflakes.

2.3. Characterization of titania nanoflakes

The surface morphology of synthesized titania nanoflakes was investigated using SEM images. The images revealed the major diameter was within the order of 10–20 μ m and the thickness was approximately 40 nm (Figure 1). Agglomerations or aggregations were not observed under SEM review when comparing the received samples with and without calcination. Moreover, the thickness of calcined flakes did not changed by the heat treatment. Both the uncalcined and calcined flakes were transparent under the SEM. The surface morphology of titania nanoflakes were similar to exfoliated nanosheets and micro-arc oxidized flakes on titanium substrate (Figure 2) [25, 32]. Light scattering technology such as laser diffraction were also used to quantified the particle size distributions of synthesized and calcined flakes. Theoretically, laser diffraction analysis alone is not designed for characterizing size distribution of anisotropic particles. To have a better understanding of the particle morphology, conjunction with electron microscopic method is necessary. Comparable data of major dimension were obtained by two methods. The statistics data of particle size distribution by volume were shown in Table 1. The synthesized material has wide size distribution spanning from 1 to 100 μ m with a D₅₀ of 20.8 and 19.0 µm for the synthesized and calcined flakes respectively (Figure 3). Some larger flakes may crack or break during the re-crystallization and dehydration in terms of the volume distributions. The average aspect ratio of the flakes is 1:500 resulting from the calculation which divided mean size by thickness (Table 1). Powder X-Ray Diffraction (XRD) monitored the crystalline structure changes of the titania flakes during the heat treatment (Figure 4). The synthesized flakes show broadening and weak peaks which suggests the mixture of amorphous material with a presence of the anatase phase. Pure anatase phase [JCPDS: 21-1272] which is the most photoactive structure were identified by XRD with the seven diffraction peaks in the heat treated flakes [41–43]. No other common phase such as rutile were observed by XRD. Complete phase conversion of amorphous titania was confirmed by comparing the intensity characteristics peaks between calcined flakes and the commercial pure anatase standard materials. The average crystal grain size can be calculated by the Scherer equation:

$$d = \frac{k\lambda}{B\cos\theta_{\scriptscriptstyle B}} \tag{3}$$

Where d is the calculated grain size, λ is the wavelength of X-ray (Cu K α 1.54 Å), β is the fullwidth at half-maximum intensity, and $\theta_{\rm B}$ is the half of the diffraction peak angle. The grain size was determined to be 4 and 9 nm for synthesized and calcined flakes respectively (**Table 2**). High resolution transmission electron microscopy (HR-TEM) images revealed circular crystalline platelets of about 5–8 nm in diameter (**Figure 5**). The interference lattice fringes with separation distance of 0.35 nm corresponded to the interplanar spacing of the (101) planes for anatase [44]. The concentric diffraction rings in the select area diffraction mode indicated random orientation of individual grains over the both flakes which is consistent with the anatase (101), (004), (200), (105) for circles 1–4 respectively (the insets of **Figure 5**). On closer inspection, synthesized samples contained an amorphous layer can be seen surrounding the smaller circular crystallites (**Figure 5a**). After calcination, calcined samples developed some pores due to local rearrangement and growth of crystal grains (**Figure 5b**). Consequently, polycrystalline fine grains of anatase populated throughout the whole calcined flakes. The nitrogen absorption isotherms in conjunction with the Brunauer-Emmett-Teller (BET) model was used



Figure 1. SEM images of titania nanoflakes: (a) synthesized samples (b) calcined samples (c, d) edge views of A and B respectively. Images were obtained without conducting coating.









Figure 2. Literature SEM images of titania flakes: (a) heated at 700°C (b) edge view [25] (c, d, e) micro-arc oxidation flakes in alkaline solution of 1.25 M, 2.5 M, and 5.0 M respectively [32].

to estimated the specific surface area of synthesized and calcined titania nanoflakes. Higher specific surface area usually leads to higher photoactivity from larger amount of adsorbed organic molecules at surface sites which enhance the reaction rate. However, it is usually simultaneously with higher amounts of crystal defects favoring recombination of charge carriers leading to lower photoactivity. Compared to a commercial photocatalyst, Degussa P25 [45], 2–6 times higher surface area were obtained by titania nanoflakes (**Table 3**). The photocatalytic activity of these flakes was investigated by performing dye degradation experiments under ultraviolet activation.

| Sample | D ₁₀ (μm) | D ₅₀ (μm) | D ₉₀ (μm) | Mean (µm) | Standard deviation (µm) |
|--------------------|----------------------|----------------------|----------------------|-----------|-------------------------|
| Synthesized flakes | 5.2 | 20.8 | 81.6 | 39.1 | 58.9 |
| Calcined flakes | 5.1 | 19.0 | 51.8 | 24.7 | 20.9 |

Table 1. Particle diameter statistics for synthesized and calcined titania flakes under investigation.

Novel Two-Dimensional Nanomaterial: High Aspect Ratio Titania Nanoflakes 47 http://dx.doi.org/10.5772/intechopen.73116





2.4. Applications of titania nanoflakes

2.4.1. Photocatalysis of titania nanoflakes

Using TiO₂ nanoparticles for water treatment is limited in practical application since it is very difficult to remove these ultrafine particles due to very small mass. Therefore, the conventional separation methods such as centrifuging, filtration, and sedimentation are difficult and expensive to implement. In addition, the efficiency of photodegradation by using nanoparticles is not very high because of the poor accessibility of the organic pollutants to catalyst surface caused by the agglomeration of particles [46]. Synthesizing larger flake-like titania with nanosized thickness will alleviate this problem. These titania flakes can be easily separated from the treated water by simply filtration or sedimentation. Because the flakes are nano thin, superior photocatalytic properties are retained due to high surface to volume ratios and short diffusion paths, which are favorable for the migration of electrons and holes. This reduces the



Figure 4. XRD patterns of synthesized and calcined titania nanoflakes.

| Sample | $\theta_{\rm B}$ (degree) | d (nm) |
|--------------------|---------------------------|--------|
| Synthesized flakes | 25.91 | 4.1 |
| Calcined flakes | 25.35 | 8.7 |

Table 2. Grain size calculation by the Scherer equation for both nanoflakes.

probability of the recombination of photogenerated electrons and holes. At the same time, the common agglomeration problem caused by nanoparticles can also be mitigated and therefore maintain the advantages of micro and nanostructure. The photocatalytic efficiency of titania nanoflakes were investigated by UV-visible spectroscopy and degradation of methylene blue under UV irradiation. The typical light absorption of the semiconductor materials such as titania showed the sharp decrease in the diffuse reflectance in the UV region (**Figure 6**). Calcined sample demonstrated a blue shift of the onset of reflectance. In semiconductor physics, the general relation between the absorption coefficient and the band gap energy is given by

$$(\alpha h\nu)^m = h\nu - E_{g} \tag{4}$$

Where m is an index depending on the nature of the electron transitions, α is the absorption coefficient, h is the Planck constant, v is the frequency of electromagnetic radiation, and E is band gap energy of the semiconductor. The optical absorption energy of both nanoflakes were determined via extrapolation of $(\alpha hv)^2$ versus hv plot (**Figure 6b**). The quantum confinement effect of higher crystallinity after calcinations and thin flaky morphology could result in an increase in band gap from 3.25 to 3.33 eV, i.e. a blue shift [47]. **Figure 6** compares the photocatalytic activity of P25, synthesized and calcined titania nanoflakes by removing the



Figure 5. HR-TEM images of titania nanoflakes (the SAD pattern as inset) (a) synthesized samples (b) calcined samples the diffraction rings are indexed as (1) 101 (2) 004 (3) 200 (4) 105 for anatase.

| Sample | Specific surface area (m²/g) | Specific pore volume (cm³/g) |
|------------------------|------------------------------|------------------------------|
| Synthesized nanoflakes | 323 | - |
| Calcined nanoflakes | 110 | 0.342 |

Table 3. Physisorption measurements of P25, synthesized and calcined titania nanoflakes.

methylene blue form water under UV light illumination. For comparison, Degussa P25 was used as a reference material. Among all tested samples, calcined flakes exhibited the highest photocatalytic efficiency on the dye degradation. A first order rate reaction was observed which suggested dye concentration is the limiting factor (Figure 7). In contrast, significant enhancement was observed when agitation was added to the system by continuously introducing air bubbles (Figure 7b). A pseudo first order reaction was obtained by adding turbulence resulted in much higher efficiency especially for the flake systems. The oxygen depletion during the photocatalysis process could be one possible explanation of these differences. The flake samples have much higher surface area than P25 and consisted of very small nanocrystallites which imply a large amount of defects (grain boundaries) from the results of XRD and TEM. Fast recombination of photoassisted electron and hole pairs preferentially occurs at these local defect sites and dominates the reaction. Without supplying oxygen to the system, the photocatalytic performance is therefore not proportional to surface area. However, dissolved oxygen may form superoxide radicals as the electron acceptor when applying oxygen to the system [48]. More importantly, eliminating excited conduction band electron would help to suppress the rate limiting step, fast recombination, and result in higher efficiency.

2.4.2. Other applications: Li-ion battery and DSSC

Anatase titanium dioxide is a promising negative electrode material for Li-ion batteries. However, the low intrinsic electrical conductivity and poor cycling performance have limited its application. Among all anatase titania samples, the calcined titania flakes performed higher rate capability, larger reversible capacity, and longer cycling stability [49]. The better



Figure 6. (a) Diffuse reflectance spectra and (b) the dependence of $(\alpha h\nu)^2$ on the photon energy for synthesized and calcined titania flakes.



Figure 7. Photocatalytic decomposition of methylene blue by using synthesized and calcined flakes (a) without bubbling treatment (b) with bubbling treatment.

charge/discharge and rate capabilities resulted from the higher specific surface area of the flakes which leads to faster transportation between Li-ion and electron within the matrix of titania lattice (**Figure 8a**). Besides, the porous morphology of the calcined flakes provided extra space for the volume change during cycling and therefore significantly improved the cycling performance (**Figure 8b**).

Using the same deposition method to assemble the DSSC, integrally and closely bonded films resulted from better particle dispersion of titania flakes (**Figure 9**). In contrast, discontinuity of P25 nanoparticle layers were observed after the evaporation and sintering processes [50]. Improved energy conversion efficiency of DSSC could be attributed to two features of titania flakes: (1) Stronger adsorption of visible dyes from high specific surface area (2) Micron scale in two dimensions lead to stronger light scattering of visible light spectrum. The important IV characteristics of DSSC such as short-circuit current density (I_{sc}) and open-circuit voltage (V_{oc}) were found to be related to the thickness of the TiO₂ photoelectrodes. According to the calculations, calcined titania flakes demonstrated 5 times higher efficiency over the P25 photoelectrodes under the same thickness basis (7.4% vs. 1.2%) (**Figure 10**).



Figure 8. (a) Rate capability and (b) specific discharge capacity comparison of CF-TiO₂ (calcined nanoflakes) and TiO₂ nanoparticles.

Novel Two-Dimensional Nanomaterial: High Aspect Ratio Titania Nanoflakes 51 http://dx.doi.org/10.5772/intechopen.73116



Figure 9. SEM micrographs of sintered photoelectrodes made from (a) P25 nanoparticles (b) calcined titania nanoflakes.



Figure 10. I-V characteristics of DSSCs made from P25 and calcined flakes of similar thickness under AM 1.5 simulated sunlight irradiation.

3. Conclusions

In summary, a high-aspect-ratio titania nanoflakes has been synthesized by the one-step modified surface hydrolysis. Compared to other methods for making low-dimensional nanomaterials, this spreading film process could continuously produce nanoflakes with a cost effective manner. These titania flakes could be easily separated from the treated water by simply sedimentation or filtration and therefore is very suitable for water purification application.

The major summary of applications were listed as follows: (1) Over 99% of methylene blue solution (50 μ M) was degraded by the high aspect ratio calcined titania nanoflakes under UVA irradiation within 2 h, whereas not completely decomposition of dye solutions was achieved

using P25 nanoparticles as photocatalysts under the same process condition. (2) Calcined nanoflakes exhibit larger reversible charge/discharge capacity, better rate capability and excellent cycling stability. (3) 7.4% of photon energy conversion efficiency of calcined flakes based DSSC which was 5 times improvement compared to P25 based cell was accomplished.

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References

- [1] Rothenberger G, Moser J, Gratzel M, Serpone N, Sharma DK. Charge carrier trapping and recombination dynamics in small semiconductor particles. Journal of the American Chemical Society. 1985;107:8054-8059
- [2] Iijima S. Helical microtubules of graphitic carbon. Nature. 1991;354:56-58
- [3] Morales AM, Lieber CM. A laser ablation method for the synthesis of crystalline semiconductor nanowires. Science. 1998;**279**:208-211
- [4] Pan ZW, Dai ZR, Wang ZL. Nanobelts of semiconducting oxides. Science. 2001;291: 1947-1949
- [5] Kudo A, Hijii S. H₂ or O₂ evolution from aqueous solutions on layered oxide photocatalysts consisting of Bi³⁺ with 6s² configuration and d⁰ transition metal ions. Chemistry Letters. 1999;28:1103
- [6] Dai ZR, Pan ZW, Wang ZL. Growth and structure evolution of novel tin oxide diskettes. Journal of the American Chemical Society. 2002;**124**:8673-8680
- [7] Wang ZL. Zinc oxide nanostructures: Growth, properties and applications. Journal of Physics. Condensed Matter. 2004;16:R829-R858
- [8] Ye CH, Fang XS, Hao YF, Teng XM, Zhang LD. Zinc oxide nanostructures: Morphology derivation and evolution. The Journal of Physical Chemistry. B. 2005;**109**:19758-19765

- [9] Shen GZ, Bando Y, Liu BD, Golberg D, Lee C. Characterization and field-emission properties of vertically aligned ZnO nanonails and nanopencils fabricated by a modified thermal-evaporation process. Advanced Functional Materials. 2006;**16**:410-416
- [10] Jang ES, Won JH, Hwang SJ, Choy JH. Fine tuning of the face orientation of ZnO crystals to optimize their photocatalytic activity. Advanced Materials. 2006;**18**:3309-3312
- [11] Amano F, Nogami K, Abe R, Ohtani B. Preparation and characterization of bismuth tungstate polycrystalline flake-ball particles for photocatalytic reactions. The Journal of Physical Chemistry C. 2008;112:9320-9326
- [12] Jang JS, Yu CJ, Choi SH, Ji SM, Kim ES, Lee JS. Topotactic synthesis of mesoporous ZnS and ZnO nanoplates and their photocatalytic activity. Journal of Catalysis. 2008;254:144-155
- [13] Ye C, Bando Y, Shen G, Golberg D. Thickness-dependent photocatalytic performance of ZnO nanoplatelets. The Journal of Physical Chemistry. B. 2006;110:15146-15151
- [14] Ying L, Jian D, Peter JH, Meilin L. Synthesis and gas sensing properties of ZnO single crystal flakes. Journal of Materials Chemistry. 2005;15:2316-2320
- [15] Jinxia D, Xintang H, Hao W, Qiang Z, Fenglou S, Xiang H. Synthesis of porous ZnO micro-flakes via an integrated autoclave and pyrolysis process. Materials Chemistry and Physics. 2007;106:181-186
- [16] Haibo S, Tianyou P, Ping C, Huabing Y, Chunhua Y. Hydrothermal synthesis of flaky crystallized La₂Ti₂O₇ for producing hydrogen from photocatalytic water splitting. Catalysis Letters. 2007;**113**:54-58
- [17] Eiji H, Shinobu F, Iraru H, Masaki I, Haoshen Z. Synthesis of the CoOOH fine nanoflake film with the high rate capacitance property. Journal of Power Sources. 2006;**158**:779-783
- [18] Pfaff G. Special effect pigments based on silica flakes. Inorganic Materials. 2003;39:123-126
- [19] Atsunori M, Tatsuo M, Toshihiro K, Kiyoharu T, Tsutomu M, Masahiro T. Formation and characterization of titania nanosheet-precipitated coatings via sol–gel process with hot water treatment under vibration. Chemistry of Materials. 2005;17:749-757
- [20] Bayykin DV, Friedrich JM, Walsh FC. Protonated titanates and TiO₂ nanostructured materials: Synthesis, properties, and applications. Advanced Materials. 2006;18:2807-2824
- [21] Peng X, Chen A. Large-scale synthesis and characterization of TiO₂-based nanostructures on Ti substrates. Advanced Functional Materials. 2006;18:1355-1362
- [22] Liu S, Chen A. Coadsorption of horseradish peroxidase with thionine on TiO₂ nanotubes for biosensing. Langmuir. 2005;21:8409-8413
- [23] Richter C, Wu Z, Panaitescu E, Wiley RJ, Menton L. Ultra-high-aspect-ratio titania nanotubes. Advanced Materials. 2007;19:946-948
- [24] Wu JM, Zhang TW, Zeng YW, Hayakawa S, Tsuru K, Osaka A. Large-scale preparation of ordered titania nanorods with enhanced photocatalytic activity. Langmuir. 2005;21:6995-7002

- [25] Sasaki T, Nakano S, Yamauchi S, Watanabe M. Fabrication of titanium dioxide thin flakes and their porous aggregate. Chemistry of Materials. 1997;9:602-608
- [26] Moriguchi I, Maeda H, Teraoka Y, Kagawa S. Preparation of a TiO₂ nanoparticulate film using a two-dimensional sol-gel process. Chemistry of Materials. 1997;9:1050-1057
- [27] Klein LC. Sol-Gel Technology for Thin Films, Fibers, Performs, Electronics and Specialty Shapes. Park Ridge, NJ: Noyes Publication; 1988
- [28] Anpo M, Aikawa N, Kubokawa Y, Che M, Louis C, Giamello E. Photoluminescence and photocatalytic activity of highly dispersed titanium oxide anchored onto porous Vycor glass. The Journal of Physical Chemistry. 1985;89:5017-5021
- [29] Norihito K, Yasuhiko T, Hiroshi H, Junji A, Junji A. Synthesis, characterization, and electrochemical properties of a thin flake titania fabricated from exfoliated nanosheets. Journal of Physics and Chemistry of Solids. 2008;69:1447-1449
- [30] Li JG, Ishigaki T, Sun X. Anatase, brookite, and rutile nanocrystals via redox reactions under mild hydrothermal conditions: Phase-selective synthesis and physicochemical properties. The Journal of Physical Chemistry C. 2007;111:4969-4976
- [31] Petr K, Hana L, Olga S, Lenka M, Tomas C. Lamellar micelles-mediated synthesis of nanoscale thick sheets of titania. Materials Letters. 2007;61:2931-2934
- [32] Shu-Yuan W, Wen-Chi L, Keh-Chang C, Ju-Liang H. Study on the preparation of nanoflaky anatase titania layer and their photovoltaic application. Current Applied Physics. 2010;10:S180-S183
- [33] Changdeuck B, Hyunjun Y, Sihyeong K, Kyungeun L, Jiyoung K, Myung MS, Hyunjung S. Template-directed synthesis of oxide nanotubes: Fabrication, characterization, and applications. Chemistry of Materials. 2008;20:756-767
- [34] Bessergenev VG, Pereira RJF, Mateus MC, Khmelinskii IV, Vasconcelos DA, Nicula R, Burkel E, Botelho do Rego AM, Saprykin AI. Study of physical and photocatalytic properties of titanium dioxide thin films prepared from complex precursors by chemical vapour deposition. Thin Solid Films. 2006;503:29-39
- [35] Yupeng G, Nam-Hee L, Hyo-Jin O, Cho-Rong Y, Kyeong-Soon P, Hee-Gyoun L, Kyung-Sub L, Sun-Jae K. Structure-tunable synthesis of titanate nanotube thin films via a simple hydrothermal process. Nanotechnology. 2007;18:295608
- [36] Varghese K, Gong D, Paulose M, Grimes CA, Dickey EC. Crystallization and hightemperature structural stability of titanium oxide nanotube arrays. Journal of Materials Research. 2003;18:156-165
- [37] Almquist CB, Biswas P. Role of synthesis method and particle size of nanostructured TiO, on its photoactivity. Journal of Catalysis. 2002;**212**:145-156
- [38] Yang-Yao L. Photocatalytic activity and dye-sensitized solar cell performance of high aspect ratio titanium dioxide nanoflakes [Ph.D. dissertation]. Gainesville: University of Florida; November, 2010

- [39] Scott B, El-Shall H, Yang-Yao L. A one-step approach to the synthesis of high aspect ratio titania nanoflakes. Global Challenges. 2017;1:1700060
- [40] Tedeschi S, Stevens N, Cepeda C, Lee YY, Powers K, Ranade M, El-Shall H. Novel supercritical fluid processing techniques for the production of an aerosol. Powder Technology. 2009;191:188-193
- [41] Fox AM, Dulay MT. Heterogeneous photocatalysis. Chemical Reviews. 1993;93:341-357
- [42] Hoffmann MR, Martin ST, Choi W, Bahnemann DW. Environmental applications of semiconductor photocatalysis. Chemical Reviews. 1995;95:69-96
- [43] Hagfeldt A, Gratzel M. Light-induced redox reactions in nanocrystalline systems. Chemical Reviews. 1995;95:49-68
- [44] Wang YQ, Hu GQ, Duan XF, Sun HL, Xue QK. Microstructure and formation mechanism of titanium dioxide nanotubes. Chemical Physics Letters. 2002;365:427-431
- [45] Liu AR, Wang SM, Zhao YR, Zheng Z. Low-temperature preparation of nanocrystalline TiO₂ photocatalyst with a very large specific surface area. Materials Chemistry and Physics. 2006;99:131-134
- [46] Takahashi R, Sato S, Sodesawa T, Arai K, Yabuki M. Effect of diffusion in catalytic dehydration of alcohol over silica–alumina with continuous macropores. Journal of Catalysis. 2005;229:24-29
- [47] Sasaki T, Watanabe M. Semiconductor nanosheet crystallites of quasi-TiO₂ and their optical properties. The Journal of Physical Chemistry. B. 1997;101:10159-10161
- [48] Houas A, Lachheb H, Ksibi M, Elaloui E, Guillard C, Herrmann JM. Photocatalytic degradation pathway of methylene blue in water. Applied Catalysis B: Environmental. 2001;31:145-157
- [49] Ming-Che Y, Yang-Yao L, Bo X, Kevin P, Ying Shirley M. TiO₂ flakes as anode materials for Li-ion-batteries. Journal of Power Sources. 2012;207:166-172
- [50] Yang-Yao L, El-Shall H. Ultra-high aspect ratio titania nanoflakes for dye-sensitized solar cells. Applied Surface Science. 2017;426:1263-1270
Mesoporous TiO₂ Thin Films: State of the Art

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Abstract

Mesoporous TiO₂ thin films (MTTFs), thanks to their particularly high surface area, controlled porosity, high flexibility in composition, and surface design, are promising candidates in different application fields such as sensors, self-cleaning coatings, lithium-ion batteries (LIBs), photocatalysis, and new-generation solar cells. This chapter is focused on the synthetic and post-synthesis aspects that can affect the TiO₂ mesoporous structure and consequently the MTTF properties. In particular, after a brief summary of TiO₂ properties, all experimental conditions to prepare MTTFs are reviewed as well as the main characterization techniques employed to study their physicochemical and photocatalytic properties. An overview of the main applications of MTTFs is also proposed, mainly focused on the use of MTTFs in sensors and LIBs.

Keywords: mesoporous TiO, thin films, X-ray diffraction, anatase, rutile and brookite

1. Introduction

Crystalline mesoporous metal oxide materials are potential candidates for a number of applications, such as battery electrodes [1], fuel cells [2, 3], optoelectronic devices [4], photovoltaic devices [5], and photocatalysis [6], due to their variable oxidation states and unusual magnetic, electronic, and optical properties compared to silicates. In particular, titania-based mesoporous materials have been extensively investigated since titania is transparent in the visible region, nontoxically biocompatible, and photocorrosion-free and can be fabricated by relatively cheap methods. For these numerous properties, titania is employed for various applications in diverse scientific fields, ranging from self-cleaning coatings [7], lithium-ion batteries (LIBs) [8], photocatalysis [9], new-generation solar cells [10], and membrane [11]

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to antibacterial applications [12]. However, to design efficient systems and devices for the above-cited uses, stable materials with a well-defined crystalline structure, highly controlled crystallite size and shape, as well as high available surface area and accessible pore networks able to ensure contact with catalytic substrates, polymers, or nanospecies are required [13]. Although the early mesoporous materials were produced in the form of powders, some applications, such as membranes, low-dielectric-constant interlayers, optical sensors, and optoelectronic devices, require ultralow-k dielectrics and low-refractive-index materials with a good mechanical stability and of hydrophobic nature. These requirements led to the preparation of mesoporous thin films [14–16]. After a brief description of the different TiO_2 polymorphs and properties, the present chapter will therefore be dedicated to mesoporous TiO_2 thin films (MTTFs), reviewing the different preparation methods reported throughout the literature, the main characterization techniques employed to study the structure and the morphology of the prepared thin films, and finally the description of their most successful applications.

2. Intrinsic properties of TiO,

Titanium belongs to the IVA group of elements and, as many other metals, is able to form a wide range of oxides. Titanium(IV) dioxide (titania) exists in three common crystalline phases: rutile, which is the thermodynamically stable phase, and the metastable phases anatase and brookite. Anatase and rutile have more extensive applications because they are more stable than brookite (**Figure 1**). In all three forms, titanium (Ti^{4+}) atoms are coordinated to six oxygen (O^{2-}) atoms, forming " TiO_{6} " octahedra. Anatase and rutile have a tetragonal



Figure 1. Crystal structures of TiO₂: (a) anatase, (b) rutile, and (c) brookite (adapted from Ref. [17]) (Table 1).

| Property | | TiO ₂ | |
|---|----------------------|-----------------------|----------------------------|
| Molecular weight (g mol ⁻¹) | | 79.88 | |
| Melting point (°C) | | 1825 | |
| Boiling point (°C) | | 2500-3000 | |
| Property | Anatase | Rutile | Brookite |
| Refractive index [18] | 2.52 | 2.72 | 2.63 |
| Dielectric constant | 31 | 114 | |
| Crystal structure [19, 20] | Tetragonal | Tetragonal | Orthorhombic |
| Space group | I4 ₁ /amd | P4 ₂ / mnm | Pbca |
| Lattice constant (Å) | a = b = 3784 | a = b = 4593 | a = 9184 b = 5447 c = 5145 |
| | c = 9515 | c = 2959 | |
| Molecule/cell | 4 | 2 | 8 |
| Volume (Å ³) | 136.25 | 62.07 | 257.38 |
| Density (g cm ³) | 3.79 | 4.13 | 3.99 |

Table 1. Compared intrinsic properties of main TiO₂ polymorphs.

geometry, differently from brookite, which has an orthorhombic geometry. In rutile, the "TiO₆" octahedron is slightly distorted, while anatase consists of strongly distorted octahedral units. In the rutile structure, each octahedron is surrounded by ten close octahedrons; instead, in the anatase polymorph, each octahedron is in contact with eight neighbors. Interatomic distances also differ between the polymorphs. For anatase, with respect to rutile, the Ti-Ti distances are lengthier and, instead, the Ti-O distances are shorter. These differences in lattice structures cause different mass densities and electronic band structures between the two forms of TiO₂. Due to its intrinsic properties, the anatase phase is the most interesting one for applications.

Titania is an n-type semiconductor since, like other metal transition oxides, the oxygen vacancies represent the predominant defect type in TiO_2 . Indeed, every crystal has various structural defects; for example, point defects, which are empty sites (vacancies), where constituent atoms are missing within the structure and interstitial atoms occupy the space between the regular atomic sites. The point defects contribute to the electrical conductivity in two ways: they can provide ionization, and they can also move in response to an electric field producing an ionic current. An oxygen vacancy is formed by the transfer of an oxygen atom on a normal site to the gaseous state. These oxygen vacancies act as electron donors, so the material contains an excess of electrons resulting in an increase of the electrical conductivity.

 TiO_2 exhibits photocatalytic oxidation (PCO) and photoinduced superhydrophilicity (PSH) when it is illuminated with UV light, making TiO_2 a good candidate for photocatalyst materials and self-cleaning surfaces in air.

The PCO property is activated by absorption of UV photons of energy greater than TiO_2 bandgap energy. For anatase phase this energy is 3.2 eV; therefore, UV light ($\lambda \le 387$ nm) is required, while rutile phase has energy of 3.0 eV ($\lambda = 400$ nm). The absorption of a photon excites an electron to the conduction band (e_{CB} –) generating a positive hole in the valence band (h_{VB} +), so that photoexcitation produces electron-hole pairs.

$$\text{TiO}_2 + hv \rightarrow h_{VB}^+ + e_{CB}^-$$

The charge carriers can migrate to the catalyst surface and initiate redox reactions with adsorbates. The redox potential for hole in VB is +2.53 V, which is sufficiently oxidizing to overcome the binding energy of electron in OH⁻ to form a hydroxyl radical from water. The hydroxyl radical can subsequently oxidize organic species with mineralization producing mineral salts, $CO_{2'}$ and H_2O . Similarly, an electron in CB (E= -0.52 V) is sufficiently reductive to react with O_2 to form O2⁻⁻ (superoxide radical anion), which can react with H⁺ to produce hydroperoxide radical contributing to the degradation of organic molecules (**Figure 2**) [21]. The main drawback in the use of titania as photocatalyst is its high electron-hole recombination rate, but several methods to improve photocatalytic activity by promoting separation of the electron-hole pair have been developed, such as doping and heterojunction coupling.

The PSH property consists in the alteration of the TiO_2 wettability under UV irradiation and in the formation of a highly hydrophilic surface state. One possible explanation of the PSH property is that electrons reduce Ti(IV) cation sites in Ti(III) and holes oxidize O^{2-} anions to molecular oxygen. The expulsion of O_2 molecules creates surface vacancies on which water



Figure 2. Schematic mechanism of TiO₂ photoactivation (adapted from Ref. [22]).

can adsorb as OH groups, giving to the TiO_2 surface its superhydrophilic character. Indeed, when illuminated, titania surface exhibits amphiphilicity caused by the creation of alternating hydrophilic/hydrophobic domains. It was found that in the absence of UV illumination, the water contact angle for TiO_2 was *ca.* 72° (hydrophobic), while UV illumination turned it close to 1° (superhydrophilic) [23]. These photoinduced phenomena coupled with the PCO properties of TiO₂ are at the basis of the self-cleaning properties of TiO₂-covered glasses and walls.

3. Preparation of MTTFs

3.1. Synthetic aspects

 TiO_2 nanomaterials can be classified according to their shape and dimension: 0D nanomaterials refer to nearly spherical nanoparticles (quantum dots); 1D refers to nanowires, nanobelts, and nanorods; and 2D materials correspond to thin films, while 3D is used to indicate porous nanostructures.

Mesoporous thin films have very peculiar features, particularly high surface area, controlled porosity, high flexibility in composition, and surface design [24]. For practical applications, mesoporous thin films must possess a number of general features: (i) they must be continuous and free of crack; (ii) crystalline walls are highly desirable in order to process into functional materials; and (iii) pores must be accessible, preferably from the film surface [25]. As a matter of fact, unlike powder, the internal space of a mesoporous thin film may not be accessible unless there are pores opening at the surfaces [26].

Mesoporous materials can form various pore structures including hexagonal (*p*6mm), cubic (*Ia3d, Im3m,* and *Pm3m*), and disorganized structures (**Figure 3**). Although the hexagonal structure is the most encountered one due to its easy synthetic procedure, this structure has a drawback in terms of pore accessibility when obtained as thin films, since the interfacial energy between the substrate surface and the film materials often lead to the pores laying parallel to the substrate surface [25]. For this reason, recent development of synthesis protocols of mesoporous titania thin films has been achieved to access to cubic structures or to hexagonal structures with aligned vertical pores.



Figure 3. A representation of the structures found in mesoporous materials: (a) hexagonal, (b) cubic (*Ia3d*), (c) cubic (*Im3m*), and (d) cubic (*Pm3m*) (from Ref. 25).

The first mesoporous thin films, which have been the object of extensive studies, were essentially silica-based and structure-directing agents, such as surfactants, were used for their synthesis. The formation mechanism of these materials involves the self-assembly of the templates in supramolecular structures, such as micelles, with the inorganic species associated to their hydrophilic portions. Simultaneously, the inorganic precursor undergoes hydrolysis and condensation reactions [25].

In general, the synthesis of mesoporous materials of transition metal oxides is more difficult than that of silica. A reason may be found in the fact that the hydrolysis and condensation reactions of transition metal ions are much faster (often hard to control due to the excessive rate) with respect to silicon-based precursors. Consequently, the inorganic precursor is prevented to effectively associate with the templates during condensation, and often mesoscopic disorder is obtained in the resulting material [27]. This high reactivity of transition metal and to its ability to exhibit several coordination states, so that the coordination expansion occurs spontaneously upon reaction with water or other nucleophilic reagents [28]. In order to minimize this problem, the precursor solution of Ti is often strongly acidic enough to suppress the hydrolysis and condensation reactions, so that the film material forms a liquid crystal-like state [29].

The synthetic approach adopted for mesoporous titania thin films (MTTFs) is often a combination between the sol-gel chemistry of an inorganic precursor and the self-assembly process of an organic template (evaporation-induced self-assembly (EISA)). The sol-gel process is a synthesis route which involves the preparation of a "sol" and the subsequent gelation upon the solvent removal. A "sol" consists of a liquid with colloidal particles which are not dissolved, but do not agglomerate or sediment. A gel consists of a three-dimensional continuous network, which includes a liquid phase. Sol-gel syntheses can use either a metal-organic precursor or an inorganic precursor. In both cases, a dilute, usually an acidic solution of precursor and an amphiphilic organic template, is introduced in a volatile solvent containing a specific amount of water. The solution is spin- or dip-coated onto virtually any type of substrate. Upon evaporation of the organic solvent, the system self-organizes to form a periodic inorganic-organic composite. As a matter of fact, surfactants can spontaneously self-assemble in micelles when their concentration in a given solvent is higher than the critical micellar concentration (CMC). At higher concentration, micelles can assemble in liquid crystalline arrays. A thermal posttreatment is often used to proceed to the cross-linking of the inorganic framework together with the removal of the organic template, leading, in turn, to the formation of the mesoporous thin film. The two more often encountered pore structures are either a cubic lattice displaying three-dimensionally interconnected pores or channel-like pores arranged in a hexagonal array [30]. Adjustment of the pore architecture of mesoporous materials strongly affects their properties, such as adsorption affinity toward guest molecules and photocatalytic properties of materials [16].

3.2. The TiO, precursor candidates

Two classes of precursor for the preparation of mesoporous thin films can be used: (i) inorganic precursors and (ii) metal-organic precursors. Inorganic precursors are salts that produce in water-solvated cations. The charge transfer from the bonding orbitals of water molecules to empty the orbitals of transition metals makes the water molecules more acidic. Different water complexes can form depending on the magnitude of this electron transfer. A condensation may take place via olation in which a hydroxyl bridge is formed between two metal centers. Olation occurs by a nucleophilic substitution (S_N) where the hydroxyl group is the nucleophile and water is the leaving group; however, oxolation can also occur in which an oxo bridge is formed between two metal centers. Oxolation proceeds through two consecutive steps: the first step is a nucleophilic addition between hydroxy precursors, and the second step is water elimination [28].

Metal-organic precursors are usually metal alkoxides which are more reactive due to the presence of highly electronegative OR groups that stabilize the metal center in the highest oxidation state and render it more susceptible to nucleophilic attack. Hydrolysis and condensations occur by nucleophilic substitution involving a nucleophilic addition followed by a proton transfer and removal of protonated species (via olation or oxolation mechanisms).

In order to prepare MTTFs, titanium chloride (TiCl₄), titanium alkoxides (mostly used tetraisopropoxide or tetraethoxide), and tetrabutyl titanate (TBT) are often used as titanium sources. Handling titanium chloride requires careful attention since it reacts violently with water and high humidity atmosphere in fast exothermic hydrolysis reactions. In this case, alcoholysis or hydrolysis processes release protons that acidify the solution, a necessary step to promote polymerization. Titanium alkoxides are highly reactive and highly hygroscopic precursors requiring to be handled within a moisture-free environment. To induce the polymerization of the inorganic framework, in the case of titanium alkoxides, addition of strong acid such as HCl required, or in alternative, the use of specific chelating agents. HCl is, however, the preferred choice for the production of MTTFs since its high volatility does not impede the efficiency of the evaporation-assisted deposition [13].

3.3. The templating agents

A variety of templates, such as alkyl phosphate anionic surfactants [31], quaternary ammonium cationic templates [32, 33], primary amines [34, 35], and poly(ethylene oxide)-based surfactants [29, 36], have been used to manipulate the pore structures of titania. Nonetheless, to direct and control the morphology of the inorganic framework for the preparation of mesoporous thin films, block copolymers seem to be the more frequently chosen templating agents since their self-assembly properties are driven by evaporation. However, the choice and combination between the Ti source and the templating agent are the crucial steps for the successful preparation of highly organized mesoporous TiO_2 thin films [37]. Hard- and softtemplating syntheses are the two most widely used methods to prepare these porous materials. A comprehensive description of both routes is given in the excellent book chapter written by Bonelli et al. [38], to which interested readers are referred.

The mostly employed soft-template-assisted route takes advantage of the self-assembly properties of organic ionic surfactants or neutral polymeric surfactants allowing to access to a diversity of supramolecular structures ranging from spherical micelles to hexagonal rods and lamellar liquid crystals. The formation of these supramolecular assemblies is governed by non-covalent weak interactions in particular hydrogen bonding, van der Waals forces, and electrostatic interactions. These assemblies are in situ used as soft templates allowing the tuning of the pore size and organization within the resulting porous materials. PEO (polyethylene oxide)-based templates have been extensively used in soft-template synthesis of mesoporous thin films. A study by Stucky [36] suggested that non-hydrolytic reactions take place in their low-water-content systems, allowing the oxide network to be built in a more controlled way. The proposed mechanism suggested that, once the metal center is trapped by the PEO or PPO fragments, nucleophilic reactions occur between the cationic immobilized species, leading to the formation of oligomers attached to the polymer chains. These oligomers are anchoring points for the growing inorganic phase [39].

PEO containing block copolymers are often chosen as the preferred templates since they can easily be produced in variable lengths, allowing in turn to generate differently shaped templates. Furthermore, PEO blocks are highly hydrophilic and favorably interact with Ti-oxo hydrophilic species in solution stabilizing upon drying the inorganic/organic interface at the shell of the formed micelles [39]. Indeed, the relative size of the hydrophilic and hydrophobic domains is in great part responsible for the symmetry of the pore array. After mixing with surfactant followed by casting into thin films, this mixture turns into a liquid crystal-like state, which, in due course, self-assembles into mesostructures on aging under controlled temperature and humidity conditions [27].

The choice of the surfactant is also an influence on the type of mesostructure obtained. It was reported that while Brij 58 $-(EO)_{20}-C_{16}H_{33}$ - leads to an *Im3m* mesoporous structure, the Brij 56, characterized by a smaller hydrophilic domain, leads to hexagonally packed cylindrical micelles with a p6mm symmetry [29].

In a recent study, Lee et al. [27] investigated the influence of the surfactant concentration and reported that a concentration equal to 9% wt for Brij 58 led to an *Im3m* mesoporous structure. Ozin et al. [40, 41] indicated that mesoporous titania thin film having anatase walls can be prepared using triblock copolymers as template materials. According to these reports, the templating agent is also able to affect the crystallinity of the MTTF. Indeed, Innocenzi et al. [42] investigated the above aspect by a correlative analysis of a MTTF and a dense sol-gel titania film (without the block copolymer), prepared under the same conditions; they found that in mesoporous titania thin film (with surfactant) the crystallization to anatase is favored and occurs at lower temperatures.

3.4. Depositions techniques

Two main deposition techniques have been widely used to prepare MTTFs, namely, spincoating or dip-coating.

Spin-coating is a simple process for a rapid deposition of thin films onto flat substrates. The substrate to be covered is held by some rotatable fixture (often using vacuum to clamp the substrate into place), and the coating solution is spread onto the surface; the action of spinning causes the liquid to spin radially outward by the centrifugal force until the thin film is formed. The initial volume of the fluid distributed onto the rotating substrate and the delivery rate have both a minor effect onto the final film thickness. On the other hand, the resulting viscosity

of the fluid to be deposited and the chosen ultimate rotation velocity are both parameters that mainly control the resulting thickness of the film. High angular speed produces thinner film. At a constant speed, the film thickness initially rapidly decreases, but this decrease slows at longer times. Typical coating thickness values are often below 1 μ when spin-coating is used.

Dip-coating is a technique based on the deposition of a wet liquid film by withdrawal of a substrate from a liquid coating medium. This process is very simple, flexible, and economically advantageous. Nevertheless, it is necessary to make provisions for cleanliness in order to obtain a high-quality deposition. Dip-coating is one of the few techniques that allow a simultaneous double-sided coating which may be regarded as an advantage especially in production of optical filters. Typically, film thickness obtained with dip-coating ranges from a few nanometers to 200 nm for oxide coatings. The thickness of the liquid film depends mainly on two factors: (i) the viscosity of the solution and (ii) the speed rate used during the substrate withdrawn from the solution.

In dip-coating, mesoscale ordering is achieved almost instantly after the covered substrate is withdrawn from the solution. Even if the self-assembled structure may form by spincoating, the degree of ordering cannot be as high as in the case of dip-coating. This is probably due to the faster solvent evaporation occurring during spin-coating leading to a more viscous film deposit, which, in turn, makes the rearrangement of the titania and surfactant species in solution that is too sluggish to achieve a high degree of ordering in a short period of time [26].

3.5. Aging conditions

Several parameters such as temperature, aging period, and relative humidity have to be taken into account during the aging phase. Indeed, they all have important effects onto the final mesoporous structure in titania-based system. The evaporation process during the aging period after the spin- or dip-coating deposition plays a critical role not only for the formation of ordered porosity but also to direct the symmetry displayed by the pore arrays [21]. During the last decade, many research groups have reported the effects of the aging conditions onto the mesostructure of titania thin films, and they confirmed that high humidity conditions are a requisite to access highly ordered mesostructure in titania thin films [29, 43, 44].

During the aging phase, the titania species and the surfactant molecules are in a liquid crystallike state, and the mesoscopic ordering is achieved through the rearrangement of these species. The moisture inside the as-synthesized film materials plays a dual role. Kinetically, it is a lubricant to facilitate the rearrangement, and, thermodynamically, it is a structural ingredient to form the mesostructures. According to Lee et al. [27], it is important to keep the moisture of the as-synthesized film at a certain level (70%) until the full ordering is achieved. However, it has been observed that too prolonged treatments at humidity rates higher than 70% can be detrimental to the meso-ordering due to excessive water swelling [45]. Ozin et al. [15] have reported that a high humidity level (*ca.* 60%) during aging favors a cubic structure, while a lower humidity level (40%) favors the hexagonal structure. According to various studies, the aging time should not be longer than 72 h, because films may transform to other unidentified structures of lower order [26, 27]. The aging temperature plays also an important role and is often chosen equal to 18° C, as reported in several studies [25, 27]. However, using ethanolic solutions of TiCl₄ and F127 as surfactants, the mesostructure could be tuned from cubic to hexagonal by aging at 18C or 35° C, respectively [27].

In contrast to most studies, Oveisi et al. [16] recently reported that highly ordered mesostructures can be reached when the condensation reaction of metal alkoxides is occurring after the formation of the liquid crystal thin-film covering (after complete evaporation of solvents). This hypothesis was confirmed by working under non-usual aging conditions: lower temperature (-20°C) and lower humidity (20% RH).

3.6. Thermal posttreatment

After the aging phase, titania thin films are calcinated at high temperature. In this step, a sequence of transformations takes place: evaporation of the remaining solvent and acid (T < 200°C) which activates consolidation of the framework (this step is accompanied by an uniaxial shrinkage of the mesostructure along the z axis); template pyrolysis (T= 250–300°C), which generates the porosity; and crystallite nucleation and growth on walls (T > 300°C) [9].

Typically with mesoporous TiO_2 , the thermal posttreatment effectuated to convert the amorphous titania walls into crystalline walls usually results in the partial or total collapse of the mesoporous network [46, 47]. To circumvent such a drawback, several post-synthesis treatments have been developed mainly devoted to increase the thermal stability of the mesoporous TiO_2 . In particular, Cassiers et al. [48] reported that the posttreatment of an uncalcinated mesoporous titania powder with ammonia resulted in the formation of mesoporous crystalline titania with thermal stability up to 600°C. Sanchez and coworkers [49] claimed that the mesoporous anatase network could be retained with a porosity of 35% above 650°C by applying a specific post-synthesis delayed rapid crystallization (DRC) treatment. Another study demonstrates that the thermal stability of these crystalline films can be enhanced, up to 850°C, by posttreatment of the film in supercritical carbon dioxide (sc-CO₂) with the presence of a small amount of precursor, such as tetramethoxysilane (TMOS) [50].

The thermal posttreatment has to be therefore carefully done and monitored especially if a specific TiO_2 polymorph is sought. Most of the reported literature data available are dedicated to the preferential formation of anatase vs. the rutile polymorph. Although through the literature a large inhomogeneity in temperature range over the control of a selected polymorph is present and reflects the influence of secondary important factors such as the Ti precursor, the template, the deposition technique, and the experiment conditions used to form the TiO_2 mesoporous material [51], most of the reports agree in the temperature range of 350–450°C to promote the exclusive crystallization of the anatase polymorph, while at higher temperature, the rutile phase transformation initiate [42, 52].

3.7. Alignment of the pores

As previously mentioned, the pores of the thin films must be accessible. Indeed, many potential applications of mesoporous thin films are relying on the accessibility of the pores from the surface. Owe to interfacial orientation preferences between the substrate and the material, the 2D hexagonal mesoporous thin films present their pore channels parallel to the surface [25]. For this reason, many research groups have struggled to synthesize cubic mesoporous thin films, which present, regardless of the orientation, pore openings from their surfaces owe to their intrinsic geometry [44, 49–53]. Often, the solution resides in the optimization of the composition of the precursor solution performed by varying the ratios between quantity of surfactant and inorganic precursor [25, 54, 55]. In this context, Koganti et al. [56] showed that a modification of the substrate surface with a Pluronic block copolymer could lower the surface energy and induce the channels to tilt away from the substrate plane. Other groups have varied the aging temperature to form cubic structures [57]. Lee et al. [26] reported the preparation of MTTFs with vertical pores using TiCl₄ as source of titanium, F127 as surfactant, and by applying a specific heat treatment to direct the formation of the 3D network in a cubic phase. Zhou et al. [7] formed MTTFs with vertical pores, by calcination of the film at 450°C, so that the 3D hexagonal mesostructure was transformed to a grid-like mesostructure with quasi-perpendicular porosity through sintering-diffusion and pore merging along the c-axis. Richman et al. [30] used another approach: they synthesized mesoporous films through nanometer-scale epitaxy. They prepared a titania thin film with cubic symmetry and used it as a patterned substrate to direct a hexagonal top silica mesostructured with vertically oriented pore channels. Finally, Yamauchi et al. applied a very strong magnetic field (10T) in mesoporous silica films to align the channels, but the alignment was not homogeneously perfect, and such method remains rather impractical for large areas [58].

4. MTTF characterizations

Beyond the synthesis of MTTFs, it is necessary to deeply characterize their structure, in particular the type of pore arrays, the film thicknesses, the porosity (pore volume, pore size distribution, interconnectivity, and specific surface area), the surface topography, the chemical composition, and the crystallinity grade. The most commonly used characterization techniques for MTTFs are microscopies such as SEM, TEM, or AFM; spectroscopic techniques such as UV-Visible spectroscopy or ellipsometry (E), Fourier transform infrared spectroscopy (FTIR), and Raman spectroscopy; X-ray absorption techniques like XANES and EXAFS; and powder or small-angle X-ray diffraction (XRD).

Spectroscopic ellipsometry (E) is an optical measurement technique based on the change in polarization occurring at many wavelengths. Ellipsometry is often highly sensitive to the properties of 1 nm to 10 μ thick films. The spectral response provides information about the sample properties, such as film thickness, surface conditions such as surface roughness (or the presence of surface contaminants), film thickness uniformity, anisotropy, and some important physical properties, such as refractive index [59]. Fourier transform infrared spectroscopy (FTIR) is a fast, contactless, and nondestructive technique used to control the complete removal of the template and the presence of organic groups. Raman spectroscopy is a useful technique used to determine titania crystalline phase by analyzing the Ti-O-Ti vibrations in the 200–600 cm⁻¹ region. XANES and EXAFS had been used to accurately probe and characterize the Ti(IV) environment in solution and within the final material.

Electron microscopies SEM and TEM are local techniques and should be used as complementary techniques to diffraction. Scanning electron microscopy (SEM) is perhaps the most widely employed thin film and coating characterization instrument. It shows the surface pore arrangement giving information on the MTTF surface morphology. Atomic force microscopy (AFM) provides imaging topography of the sample surface, so it is a local but a very useful technique. The use of a very sharp probe that is scanned across the thin-film surface allows to produce very high-resolution topographic images at the sub-nanometer scale. Many different imaging modes are available in AFM, such as contact mode imaging which works in the repulsive regime because the probe remains in contact with the sample at all times, noncontact mode which works in the attractive regime because the probe is very close to the sample surface without touching it, and tapping mode which works in both the regimes. Tapping mode AFM is the most used mode in the case of titania thin films, whereby a sharp tip (typically, a silicon or silicon nitride crystal) is oscillated above the surface of a sample. Specifically, tapping mode overcomes major problems associated with friction, adhesion, electrostatic forces, and other tip-sample-related issues (**Figure 4**).

X-ray diffraction in Bragg-Brentano geometry is a noncontact and nondestructive technique that provides information about crystallinity, phase, crystallite size, and orientation. Comparison of the obtained XRD profile in the medium and wide-angle region (from $2\theta = 10 \text{ to } 80^\circ$) with reference patterns allows to determine the crystalline phase of the MTTFs as well as possible preferential orientational order through the increase in intensity of specific reflection peaks. The XRD patterns of the three main crystalline phases of TiO₂ are reported in **Figure 5**.

The analysis of XRD patterns must be carefully performed to correctly identify the crystalline phase of the MTTFs, especially when polymorphic forms are present within the film. This task is also often complicated by the presence of the wide halo of the amorphous substrate onto which the MTTF films have been deposited and/or the superposition of the reflection peaks relative to the eventual semicrystalline nature of the substrate used (e.g., when the TiO₂ thin film is deposited on ITO). In **Figure 6** an XRD pattern of a dense anatase TiO₂ thin film deposited on a glass substrate is reported [60], clearly showing the broadening of the background level due to the halo generated by the amorphous support.



Figure 4. (a) Top surface and (b) cross-sectional FESEM micrographs of the 3D hexagonal MTTF [7] and (c) AFM image of MTTF surface [27].



Figure 5. XRD patterns of (a) TiO_2 anatase (JCPDS card no. 21-1272), (b) TiO_2 rutile (JCPDS card no. 21-1276), and (c) TiO_2 brookite (JCPDS card no. 29-1360).

While there are no difficulties in discriminating between the anatase and the rutile phases since the first two reflection peaks are well separated ($2\theta = 25.28^{\circ}$ for d₁₀₁ of anatase vs. $2\theta = 27.44^{\circ}$ for d₁₁₀ of rutile), spotting the difference between anatase and brookite might be more tricky. Only, the reflection peaks at $2\theta = 30.81^{\circ}$ relative to the d₁₂₁ of the brookite phase or at $2\theta = 62.57^{\circ}$ relative to d₂₀₄ of the anatase phase can help in making such a difference and/or recognize the presence of both the polymorphic forms in an XRD pattern [61].

A small-angle diffraction pattern, instead, could reveal the eventual presence of an ordered array of mesopores within the MTTFs, allowing the determination of its geometry, i.e., cubic lamellar or hexagonal [44, 62], as shown in **Figure 7**.



Figure 6. XRD patterns of a dense TiO_2 thin film prepared by sol-gel and dip-coating techniques on a glass substrate (from Ref. 60).



Figure 7. Small-angle XRD patterns of TiO_2 thin films, as-synthesized (bottom) and calcined (top) films for (a) lamellar, (b) hexagonal, and (c) cubic titania mesostructures (figures adapted from Ref. 62).

4.1. Evaluation of the photocatalyst activity

The activity of a photocatalytic titania mesoporous thin film can vary considerably depending on many factors, such as crystallinity, surface-to-volume ratio, pore accessibility, film thickness, and roughness. The photocatalytic activity of MTTFs can be determined evaluating the decomposition of stearic acid (SA), used as probe, under UV illumination (λ = 256 nm). This fatty acid is usually chosen for its high stability under UV illumination in the absence of suitable photocatalyst film. Furthermore, a thin layer of stearic acid can easily be deposited through dip- or spin-coating onto the film from a methanol or chloroform solution. SA provides a reasonably good model compound for solid films since it undergoes oxidative mineralization and this process can be monitored as a function of time [63]:



Figure 8. Disappearance of the stearic acid IR bands (C–H stretches at 2912 and 2847 cm⁻¹) on the surface of a titania thin film after irradiation with UV light (λ = 256 nm) [64].

$$C_{17}H_{35}COOH + 26O_2 + hv \rightarrow 18CO_2 + 18H_2O_2$$

SA decomposition can be demonstrated, for example, by FTIR spectroscopy through the monitoring of the asymmetric C-H stretching mode of the CH_3 group at 2958 cm⁻¹ and the asymmetric and symmetric C-H stretching modes of the CH_2 group at 2923 and 2853 cm⁻¹, respectively (**Figure 8**) [64].

The photocatalyst activity of titania can also be evaluated via photocatalytic oxidation of methylene blue (MB) under UV illumination. MB is often used as model for recalcitrant azodye pollutant, and, being a highly colored organic molecule, its photodecomposition can easily be detected in situ through spectrophotometric methods [65].

5. Applications of MTTFs

Mesoporous TiO₂ thin films have attracted researchers among various fields of applications spanning from sensors, self-cleaning coatings, lithium-ion batteries (LIBs), photocatalysis, and new-generation solar cells. For interested readers, three comprehensive reviews, on the photocatalytic applications of mesoporous TiO₂-based materials [38], on the use of TiO₂-ordered materials for solar radiation applications [66], and on the self-cleaning applications of TiO₂ [67], have recently been published. The present section will therefore only cover the applications of mesoporous TiO₂ in sensor and LIB applications.

5.1. Sensors

A good sensor requires high sensitivity, fast response, and good selectivity. Furthermore, low-cost materials and easy fabrication processes are important advantages for practical uses. Mesoporous titania thin films are excellent candidates for sensing applications because of the enhancement of the sensing signal due to the increased surface. Nevertheless, the MTTF sensitivity is also affected by the pore size and the carrier's diffusion length. The sensing mechanism includes three steps: initially, TiO, surface binds the analyte molecules; subsequently, a specific chemical or biochemical reaction takes place at the interface and gives rise to a chemical signal, converted, in the third step, into an electronic signal in turn amplified and detected. TiO_2 sensors can detect several gases, including either oxidative gas (O_2, NO_2) or reductive gas (H_2, CO, NH_3) . The working principle of these sensors relies on the changes of the electronic resistance, due to the interaction of TiO₂ with the surrounding environment. The vacancies on TiO₂ surface play an important role, since oxygen is adsorbed on these surface vacancies when the film is exposed to air forming anionic oxygen. When a gas molecule is in contact with a gas sensor based on MTTFs, first this molecule is physisorbed on TiO₂ surface through van der Waals forces and dipole interactions; immediately after, the gas molecule is chemisorbed via a strong chemical bond formed between the gas and the surface atoms of TiO₂. In this step, a charge transfer induced by the redox reaction between titania and the gas molecule occurs [68]. When a reducing gas (e.g., CO) is detected by a chemical sensor, the following reaction takes place:

$$CO + O^- \rightarrow CO_2 + e^-$$

In this case, CO molecules react with adsorbed oxygen ions on the mesoporous film surface, which results, in turn, in an overall decrease of the electrical resistance of the metal oxide thin films. On the contrary, if a chemical sensor is exposed to an oxidation gas (e.g., NO₂), the following oxidizing reaction may take place:

$$NO_2 + e^- \rightarrow NO_2^-$$

In this example, NO_2 molecules cause a depletion of electrons from the TiO_2 surface, which results in an increase of electrical resistance. The conductivity change can be easily transferred into resistance signal, which is the best-known sensor output signal.

Titania nanostructured materials are good candidates also for biosensing, because TiO_2 is able to form coordination bonds with the amine and the carboxylic groups of biomolecules, such as enzymes, while maintaining the enzyme's biocatalytic activity. Furthermore, TiO_2 is characterized by high stability and biocompatibility. A biosensor is an analytical device, which converts a biological response into readable or quantified signal. Biosensors can be applied to analyze a variety of samples including body fluids, food samples, and cell cultures [68]. The biosensing mechanism is based on a biochemical reaction. Typically in (bio-)electrochemistry, a measurable current (amperometric), a measurable potential, or a charge accumulation (potentiometric) will be generated upon the alteration of the conductive properties of a medium between electrodes when the sensing takes place.

Titania mesoporous thin films have been also used as sensors for *Escherichia coli*, an enterohemorrhagic bacterium whose infections have a low incidence rate but can have severe and sometimes fatal health consequences and thus represent some of the most serious diseases due to the contamination of water and food [69]. Titania films treated with APTES ((3-aminopropyl) triethoxysilane) and GA (glutaraldehyde) were functionalized with specific antibodies anti-*Escherichia coli* antibodies. In this case, FTIR spectroscopy has been used as an optical transduction method: the spectroscopic signals originated from the various functional groups related to proteins, lipid, and carbohydrates can be used for the identification and structural characterization of different pathogens and subspecies.

5.2. Lithium-ion batteries (LIBs)

Lithium-ion batteries (LIBs) are rechargeable batteries widely used in laptop, mobile phones, and electric vehicles. These batteries are characterized by high-energy density, low maintenance, little self-discharge, and no memory effect, which means that it is not necessary to completely discharge them before charging. In a conventional LIB cell, lithium metal oxide (e.g., $LiCoO_2$) is used as cathode, while graphite is used as preferred anode. The two electrodes are separated by a porous membrane and soaked in a nonaqueous liquid electrolyte. During insertion (or intercalation), ions move into the electrode. During the reverse process, extraction (or de-intercalation), ions move back out. Upon charging, the lithium ions move from the cathode to enter the anode, while in the discharging phase, the reverse phenomenon takes place. A variety of metal oxides, in particular TiO_2 , have been investigated as potential electrode materials for LIBs. Compared with the currently commercialized graphite anode, these metal oxide materials have demonstrated various advantages, such as very high capacity,

widespread availability, good stability, and environmental benignity. Generally, the reversible reaction between Li and TiO_2 can be expressed by the following equation:

$$xLi^{+} + TiO_2 + xe^{-} \rightarrow Li_x TiO_2 (0 < x < 1)$$

where x is the mole fraction of Li in TiO_2 . This redox reaction typically takes place at around 1.7 V vs. Li⁺/Li. Lithium ions reversibly insert/extract into/from the interstitial vacancies of the TiO₂ framework, with a specific percentage depending on the TiO₂ crystalline form and morphology. Specifically, anatase is probably the most electrochemically active form of TiO₂ for this purpose [8]. Moreover, it has been demonstrated that anatase exposing (001) facets exhibits efficient Li⁺ ion diffusion along this direction (c-axis) facilitating a fast lithium insertion/extraction [70].

 TiO_2 presents many advantages in its usage as anode material for LIBS, such as the low-volume expansion upon lithiation (<4%), good stability, and lack of lithium plating. However, TiO_2 is also characterized by some limitations, including a limited Li⁺ ion diffusion, low capacity, and low electrical conductivity [71]. A possibility to overcome these drawbacks is represented by the nanostructuration of TiO_2 , which provides a higher specific surface area and shorter diffusion pathways for electrons and Li⁺ ions, compared to the corresponding bulk materials [72]. In this context, vertically oriented TiO_2 nanotubes have been exploited as anode materials for LIBs by many groups [73–75]. However, the preparation of nanostructured TiO_2 in the form of mesoporous thin films could offer some advantages, such as higher specific surface area and thinner walls than a TiO_2 nanotube array [76]. For example, Ortiz et al. prepared mesoporous titania thin films on titanium substrates, with a hexagonally ordered porous structure, and they tested these samples as anode materials for LIBs, reporting an improved electrochemical performance, without the necessity of additives to enhance the transport properties of the electrode [77]. The enhanced electrochemical activity was ascribed to the higher area and volumetric capacity of these films due to the presence of the 3D-ordered mesostructure.

6. Conclusions and perspectives

Undeniable great progresses have been made in recent years in the design and synthesis of mesoporous TiO_2 thin films featuring novel and well-designed structures and morphologies as well as to further explore and enhance their applications. Nevertheless, challenges are remaining in developing cheap, low toxic, and reproducible synthetic approaches for achieving an easy and precise control over the pore size, wall thickness, surface area, morphology, and crystallinity.

For optoelectronic applications, the main concern resides into the deposition of organized MTTFs onto semiconductive electrodes such as ITO or FTO keeping a homogenous disposition of the pores on the whole device electrode, and although some preliminary attempts have been made [52, 78], it remains a challenging issue owned to the wettability difference between ITO and Si wafers. Moreover, while small-sized devices have been tested, on large scale, difficulties are encountered to maintain such uniform orientation of the pores, especially in

the case of vertically aligned pore arrays, the most suited geometry for efficient optoelectronic devices. For these reasons, scientists are investigating also the possibility of depositing nanotubes of TiO_2 from anodization of sputtered titanium onto different substrates. The best results have been so far obtained for depositions performed onto quartz. However, in the case of semiconductive substrates, several problems are arising, the most important one being the easy loss of contact between the formed TiO_2 nanotubes and the semiconductive layer, which will definitely require further and intense research activities to circumvent such a drawback.

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References

- [1] Liu P, Lee SH, Tracy CW, Yan Y, Turner JA. Preparation and lithium insertion properties of mesoporous vanadium oxide. Advanced Materials. 2002;14(1):27-30. DOI: 10.1002/ 1521-4095(20020104)14:1<27::AID-ADMA27>3.0.CO;2-6
- [2] Mamak M, Coombs N, Ozin G. Mesoporous yttria–zirconia and metal–yttria–zirconia solid solutions for fuel cells. Advanced Materials. 2000;12(3):198-202. DOI: 10.1002/ (SICI)1521-4095(200002)12:3<198::AID-ADMA198>3.0.CO;2-2
- [3] Mamak M, Coombs N, Ozin G. Self-assembling solid oxide fuel cell materials: Mesoporous yttria-zirconia and metal-yttria-zirconia solid solutions. Journal of the American Chemical Society. 2000;122(37):8932-8939. DOI: 10.1021/ja0013677
- [4] Frindell KL, Bartl MH, Popitsch A, Stucky GD. Sensitized luminescence of trivalent europium by three-dimensionally arranged anatase nanocrystals in mesostructured titania thin films. Angewandte Chemie International Edition. 2002;41(6):959-962. DOI: 10.1002/1521-3773(20020315)41:6<959::AID-ANIE959>3.0.CO;2-M
- [5] Grätzel M. Mesoporous oxide junctions and nanostructured solar cells. Current Opinion in Colloid & Interface Science. 1999;4:314-321. DOI: org/10.1016/S1359-0294(99)90013-4
- [6] Takahara Y, Kondo JN, Takata T, Lu D, Domen K. Mesoporous tantalum oxide. 1. Characterization and photocatalytic activity for the overall water decomposition. Chemistry of .Materials. 2001;13(4):1194-1199. DOI: 10.1021/cm000572i

- [7] Zhou H, Wang C, Feng Z, Li S, Xu B. Formation of grid-like mesoporous titania film via structural transformation and its surface superhydrophilicity conversion. Surface & Coatings Technology. 2012;207:34-41. DOI: org/10.1016/j.surfcoat.2012.04.067
- [8] Wu HB, Chen JS, Hing HH, Lou XW. Nanostructured metal oxide-based materials as advanced anodes for lithium-ion batteries. Nanoscale. 2012;4:2526-2542. DOI: 10.1039/ C2NR11966H
- [9] Ochiai T, Fujishima A. Photoelectrochemical properties of TiO₂ photocatalyst and its applications for environmental purification. Journal of Photochemistry and Photobiology C: Photochemistry Reviews. 2012;13(4):247-262. DOI: org/10.1016/j.jphotochemrev.2012.07.001
- [10] Grätzel M. Recent advances in sensitized mesoscopic solar cells. Accounts in Chemical Research. 2009;42(11):1788-1798. DOI: 10.1021/ar900141y
- [11] Choi H, Stathatos E, Dionysiou DD. Photocatalytic TiO₂ films and membranes for the development of efficient wastewater treatment and reuse systems. Desalination. 2007; 202(1-3):199-206. DOI: org/10.1016/j.desal.2005.12.055
- [12] Zhang L, Bai H, Liu L, Sun DD. Dimension induced intrinsic physio-electrical effects of nanostructured TiO₂ on its antibacterial properties. Chemical Engineering Journal. 2018;**334**:1309-1315. DOI: org/10.1016/j.cej.2017.11.075
- [13] Soler-Illia GJAA, Angelomé PC, Fuertes MC, Grosso D, Boissière C. Critical aspects in the production of periodically ordered mesoporous titania thin films. Nanoscale. 2012; 4:2549-2566. DOI: 10.1039/C2NR11817C
- [14] Aksay IA, Trau M, Manne S, Honma I, Yao N, Zhou L, Fenter P, Eisenberger PM, Gruner SM. Biomimetic pathways for assembling inorganic thin films. Science. 1996;273(5277): 892-898. DOI: 10.1126/science.273.5277.892
- [15] Yang H, Kuperman A, Coombs N, Mamiche-Afara S, Ozin GA. Synthesis of oriented films of mesoporous silica on mica. Nature. 1996;379:703-705. DOI: 10.1038/379703a0
- [16] Oveisi H, Suzuki N, Nemoto Y, Srinivasu P, Beitollahi A, Yamauchi Y. Critical effect of aging condition on mesostructural ordering in mesoporous titania thin film. Thin Solid Films, 2010,518(23),6714-6719. DOI: org/10.1016/j.tsf.2010.05.112
- [17] Moellmann J, Ehrlich S, Tonner R, Grimme S. A DFT-D study of structural and energetic properties of TiO₂ modifications. Journal of Physics Condensed Matter. 2012;24(42)-424206). DOI: 10.1088/0953-8984/24/42/424206
- [18] Li J-G, Ishiaki T, Sun X. Anatase, brookite, and rutile nanocrystals via redox reactions under mild hydrothermal conditions: Phase-selective synthesis and physicochemical properties. Journal of Physical Chemistry C. 2007;111(13):4969-4976. DOI: 10.1021/jp0673258
- [19] Cromer DT, Herrington K. The structures of anatase and rutile. Journal of the American Chemical Society. 1955;77(18):4708-4709. DOI: 10.1021/ja01623a004
- [20] Baur WH. Atomabstände und bindungswinkel im Brookit, TiO₂. Acta Crystallographica. 1961;14:214. DOI: 10.1107/S0365110X61000747

- [21] Turchi CS, Ollis DF. Photocatalytic degradation of organic water contaminants: Mechanisms involving hydroxyl radical attack. Journal of Catalysis. 1990;122(1):178-192. DOI: org/10.1016/0021-9517(90)90269-P
- [22] Sze Tung W, Daoud WA. Self-cleaning fibers via nanotechnology: A virtual reality. Journal of Materials Chemistry. 2011;21:7858-7869. DOI: 10.1039/C0JM03856C
- [23] Fujishima A, Rao TN, Tryk DA. Titanium dioxide photocatalysis. Journal of photochemistry and photobiology C: Photochemistry Reviews. 2000;1(1):1-21. DOI: org/10.1016/ S1389-5567(00)00002-2
- [24] Innocenzi P, Malfatti L. Mesoporous thin films: Properties and applications. Chemical Society Reviews. 2013;42:4198-4216. DOI: 10.1039/C3CS35377J
- [25] Lee UH, Kim MH, Kwon YU Mesoporous thin films with accessible pores from surfaces. Bulletin of the Korean Chemical Society. 2006;27(6):808-816. DOI: org/10.5012/ bkcs.2006.27.6.808
- [26] Koh CW, Lee UH, Song JK, Lee HR, Kim MH, Suh M, Kwon YU. Mesoporous titania thin film with highly ordered and fully accessible vertical pores and crystalline walls. Chemistry: An Asian Journal. 2008;3:862-867. DOI: 10.1002/asia.200700331
- [27] Lee HU, Lee H, Wen S, Mho S, Kwon YU. Mesoporous titania thin films with pseudocubic structure: Synthetic studies and applications to nanomembranes and nanotemplates. Microporous and mesoporous materials. 2006;88(1-3):48-55. DOI: org/10.1016/j. micromeso.2005.08.017
- [28] Brinker CJ, Scherer GW. Sol-Gel Science. The Physics and Chemistry of Sol-Gel Processing. Academic Press INC; 1990. p. 908. ISBN-13: 978-0-12-134970-7. ISBN-10: 0-12-34970-5
- [29] Crepaldi EL, Soler-Illia G, Grosso D, Cagnol F, Ribot F, Sanchez C. Controlled formation of highly organized mesoporous titania thin films: From mesostructured hybrids to mesoporous nanoanatase TiO₂. Journal of the American Chemical Society. 2003;**125**(32):9770-9986. DOI: 10.1021/ja030070g
- [30] Richman EK, Brezesinski T, Tolbert SH. Vertically oriented hexagonal mesoporous films formed through nanometre-scale epitaxy. Nature Materials. 2008;7:712-717. DOI: 10.1038/ nmat2257
- [31] Antonelli DM, Ying JY. Synthesis of hexagonally packed mesoporous TiO₂ by a modified sol–gel method. Angewandte Chemie International Edition in English. 1995;34(18):2014-2017. DOI: 10.1002/anie.199520141
- [32] Stone VF, Davis RJ. Synthesis, characterization, and photocatalytic activity of titania and niobia mesoporous molecular sieves. Chemistry of Materials. 1998;10(5):1468-1474. DOI: 10.1021/cm980050r
- [33] Yuan Z-Y, Vantomme A, Leonard A, Su B-L. Surfactant-assisted synthesis of unprecedented hierarchical meso-macrostructured zirconia. Chemical Communications. 2003;0:1558-1559. DOI: 10.1039/B303272H

- [34] Suh Y, Lee J, Rhee H. Synthesis of thermally stable tetragonal Zirconia with large surface area and its catalytic activity in the skeletal isomerization of 1-butene. Catalysis Letters. 2003;**90**(1-2):103-109. DOI: org/10.1023/A:1025884714465
- [35] Tian ZR, Tong W, Wang J, Duan N, Krishnan VV, Suib SL. Manganese oxide mesoporous structures: Mixed-valent semiconducting catalysts. Science. 1997;276(5314):926-930. DOI: 10.1126/science.276.5314.926
- [36] Yang P, Zhao D, Margolese DL, Chmelka BF, Stucky GD. Generalized syntheses of largepore mesoporous metal oxides with semicrystalline frameworks. Nature. 1998;396: 152-155. DOI: 10.1038/24132
- [37] Wang J, Wu J, Li H. A review of mesoporous TiO₂ thin films. Material Matters. 2012; 7(2):2-6
- [38] Bonelli B, Esposito S, Freyria FS. In: Janus M, editor. Mesoporous Titania: Synthesis, Properties and Comparison with Non-Porous Titania, Titanium Dioxide. InTech; 2017. DOI: 10.5772/intechopen.68884
- [39] Soler-Illia GJAA, Sanchez C. Interactions between poly(ethylene oxide)-based surfactants and transition metal alkoxides: Their role in the templated construction of mesostructured hybrid organic–inorganic composites. New Journal of Chemistry. 2000;24:493-499. DOI: 10.1039/B002518F
- [40] Choi SY, Mamak M, Coombs N, Chopra N, Ozin GA. Thermally stable two-dimensional hexagonal mesoporous nanocrystalline anatase, meso-nc-TiO₂: Bulk and crack-free thin film morphologies. Advanced Functional Materials. 2004;14(4):335-344. DOI: 10.1002/ adfm.200305039
- [41] Choi SY, Mamak M, Speakman S, Chopra N, Ozin GA. Evolution of nanocrystallinity in periodic mesoporous anatase thin films. Small. 2005;1(2):226-232. DOI: 10.1002/smll. 200400038
- [42] Innocenzi P, Malfatti L, Kidchob T, Enzo S, Della Ventura G, Schade U, Marcelli A. Correlative analysis of the crystallization of sol-gel dense and mesoporous anatase titania films. Journal of Physical Chemstry C. 2010;114(51):22385-22391. DOI: 10.1021/ jp1042766
- [43] Soler-Illia GJAA, Innocenzi P. Mesoporous hybrid thin films: The physics and chemistry beneath. Chemistry: A European Journal. 2006;12(17):4478-4494. DOI: 10.1002/ chem.200500801
- [44] Pan JH, Lee WI. Selective control of cubic and hexagonal mesophases for titania and silica thin films with spin-coating. New Journal of Chemistry. 2005;29:841-846. DOI: 10.1039/B417310D
- [45] Henderson MJ, Gibaud A, Bardeau JF, White JW. An X-ray reflectivity study of evaporation-induced self-assembled titania-based films. Journal of Materials Chemistry. 2006;16:2478-2484. DOI: 10.1039/B601677D
- [46] Sayari A, Liu P. Non-silica periodic mesostructured materials: Recent progress. Microporous Materials. 1997;12:149-177. DOI: org/10.1016/S0927-6513(97)00059-X

- [47] Schüth F. Non-siliceous mesostructured and mesoporous materials. Chemistry of Materials. 2001;13(10):3184-3195. DOI: 10.1021/cm011030j
- [48] Cassiers K, Linssen T, Meynen V, Van Der Voort P, Cool P, Vansant EF. A new strategy towards ultra stable mesoporous titania with nanosized anatase walls. Chemical Communications. 2003:1178-1179. DOI: 10.1039/B302116E
- [49] Grosso D, Soler-Illia GJAA, Crepaldi EL, Cagnol F, Sinturel C, Bourgeois A, Brunet-Bruneau A, Amenitsch H, Albouy PA, Sanchez C. Highly porous TiO₂ anatase optical thin films with cubic mesostructure stabilized at 700°C. Chemistry of Materials. 2003; 15(24):4562-4570. DOI: 10.1021/cm031060h
- [50] Wang K, Morris MA, Holmes JD. Preparation of mesoporous titania thin films with remarkably high thermal stability. Chemistry of Materials. 2005;17(6):1269-1271. DOI: 10.1021/cm047912a
- [51] Girish Kumar S, Koteswara Rao KSR. Polymorphic phase transition among the titania crystal structures using a solution-based approach: from precursor chemistry to nucleation process. Nanoscale. 2014;6:11574-11632. DOI: 10.1039/C4NR01657B
- [52] Uchida H, Patel MN, May A, Gupta G, Stevenson KJ, Johnston KP. Highly-ordered mesoporous titania thin films prepared via surfactant assembly on conductive indium–tinoxide/glass substrate and its optical properties. Thin Solid films. 2010;518(12):3169-3176. DOI: org/10.1016/j.tsf.2009.08.050
- [53] Wang XC, Yu JC, Yip HY, Wu L, Wong PK, Lai SY. A mesoporous Pt/TiO₂ nanoarchitecture with catalytic and photocatalytic functions. Chemistry: A European Journal. 2005; 11:2997-3004. DOI: 10.1002/chem.200401248
- [54] Hwang YK, Lee KC, Kwon YU. Nanoparticle routes to mesoporous titania thin films. Chemical Communications. 2001;0:1738-1739. DOI: 10.1039/B104699N
- [55] Angelome PC, Aldabe-Bilmes S, Calvo ME, Crepaldi EL, Grosso D, Sanchez C, Soler-Illia GJAA. Hybrid non-silica mesoporous thin films New Journal of Chemistry. 2005;29: 59-63. DOI:10.1039/B415324C
- [56] Koganti VR, Dunphy D, Gowrishankar V, McGehee MD, Li XF, Wang J, Rankin SE. Generalized coating route to silica and titania films with orthogonally tilted cylindrical nanopore arrays. Nano Letters. 2006;6(11):2567-2570. DOI: 10.1021/nl061992v
- [57] Hayward RC, Alberius PCA, Kramer EJ, Chmelka BF. Thin films of bicontinuous cubic mesostructured silica templated by a nonionic surfactant. Langmuir. 2004;20(14):5998-6004. DOI: 10.1021/la030442z
- [58] Yamauchi Y, Sawada M, Sugiyama A, Osaka T, Sakka Y, Kuroda K. Magnetically induced orientation of mesochannels in 2D-hexagonal mesoporous silica films. Journal of Materials Chemistry. 2006;16:3693-3700. DOI: 10.1039/B608780A
- [59] Bass JD, Grosso D, Boissière C, Sanchez C. Pyrolysis, crystallization, and sintering of mesostructured titania thin films assessed by in situ thermal ellipsometry. Journal of the American Chemical Society. 2008;130(25):7882-7897. DOI: 10.1021/ja078140x

- [60] Fan Q, McQuillin B, Ray AK, Turner ML, Seddon AB. High density non-porous anatase titania thin films for device applications. Journal of Physics D: Applied Physics. 2000;33:2683-2686. DOI: 10.1088/0022-3727/33/21/303
- [61] Di Paola A, Bellardita M, Palmisano L. Brookite, the least known TiO₂ photocatalyst. Catalysts. 2013;3(1):36-73. DOI: 10.3390/catal3010036
- [62] Alberius PC, Frindell KL, Hayward RC, Kramer EJ, Stucky GD, Chmelka BF. General predictive syntheses of cubic, hexagonal and lamellar silica and titania mesostructured thin films. Chemistry of Materials. 2002;14:3284-3294. DOI: 10.1021/cm011209u
- [63] Mills A, Wang J. Simultaneous monitoring of the destruction of stearic acid and generation of carbon dioxide by self-cleaning semiconductor photocatalytic films. Journal of Photochemistry and Photobiology A: Chemistry. 2006;182(2):181-186. DOI: org/10.1016/j. jphotochem.2006.02.010
- [64] Wang K, Yao B, Morris MA, Holmes JD. Supercritical Fluid Processing of Thermally Stable Mesoporous Titania Thin Films with Enhanced Photocatalytic Activity. Chemistry of Materials. 2005;17(19):4825-4831. DOI: 10.1021/cm0508571
- [65] Mastropietro TF, Meringolo C, Poerio T, Scarpelli F, Godbert N, Di Profio G, Fontananova E. Multistimuli activation of TiO2/α-alumina membranes for degradation of methylene blue. Industrial and Engineering Chemistry Research. 2017;56(39):11049-11057. DOI: 10.1021/acs.iecr.7b02778
- [66] Machado AEH, Borges KA, Silva TA, Santos LM, Borges MF, Machado WA, Caixeta BP, França MD, Oliveira SM, Trovó AG, Patrocínio AOT. Applications of mesoporous ordered semiconductor materials — case study of TiO₂, Ms. Bello SR. editor, Solar Radiation Applications, INTECH; 2015, DOI: 10.5772/59602
- [67] BanerjeeS, DionysiouDD, PillaiSC. Self-cleaning applications of TiO₂ by photo-induced hydrophilicity and photocatalysis. Applied Catalysis B: Environmental. 2015;176: 396-428. DOI: org/10.1016/j.apcatb.2015.03.058
- [68] Bai J, Zhou B. Titanium dioxide nanomaterials for sensor applications. Chemical Reviews. 2014;114(19):10131-10176. DOI: 10.1021/cr400625j
- [69] Mura S, Greppi G, Marongiu ML, Roggero PP, Ravindranath SP, Mauer LJ, Schibeci N, Perria F, Piccinini M, Innocenzi P, Irudayaraj J. FTIR nanobiosensors for *Escherichia coli* detection. Beilstein Journal of Nanotechnology. 2012;3:485-492. DOI: 10.3762/bjnano.3.55
- [70] Chen JC, Tan YL, Li CM, Cheah YL, Luan D, Madhavi S, Chiang Boey FY, Archer LA, Lou XW. Constructing hierarchical spheres from large ultrathin anatase TiO₂ nanosheets with nearly 100% exposed (001) facets for fast reversible lithium storage. Journal of the American Chemical Society. 2010;**132**(17):6124-6130. DOI: 10.1021/ja100102y
- [71] Liu Y, Yang Y. Recent progress of TiO₂-based anodes for Li ion batteries. Journal of Nanomaterials. 2016, Article ID 8123652, 15 pages. DOI: 10.1155/2016/8123652
- [72] Zhang Y, Tang Y, Li W, Chen X. Nanostructured TiO₂ based anode materials for highperformance rechargeable lithium-ion batteries. Chemistry of Nanomaterials for Energy, biology and more. 2016;2(8):764-775. DOI: 10.1002/cnma.201600093

- [73] Fang H-T, Liu M, Wang D-W, Sun T, Guan D-S, Li F, Zhou J, Sham T-K, Cheng H-M. Comparison of the rate capability of nanostructured amorphous and anatase TiO₂ for lithium insertion using anodic TiO₂ nanotube arrays. Nanotechnology. 2009;**20**(22):225701-225708. DOI: 10.1088/0957-4484/20/22/225701
- [74] Ortiz GF, Hanzu I, Djenizian T, Lavela P, Tirado JL, Knauth P. Alternative Li-ion battery electrode based on self-organized titania nanotubes. Chemistry of Materials. 2009; 21(1):63-67. DOI: 10.1021/cm801670u
- [75] Wang K, Wei M, Morris MA, Zhou H, Holmes JD. Mesoporous titania nanotubes: Their preparation and application as electrode materials for rechargeable lithium batteries. Advanced Materials. 2007;19(19):3016-3020. DOI: 10.1002/adma.200602189
- [76] Su X, Wu QL, Zhan X, Wu J, Wei S, Guo Z. Advanced titania nanostructures and composites for lithium ion battery. Journal of Materials Science. 2012;47(6):2519-2534. DOI: 10.1007/s10853-011-5974-x
- [77] Ortiz GF, Berenguer-Murcia A, Cabello M, Cazorla-Amorós D, Tirado JL. Ordered mesoporous titanium oxide for thin film microbatteries with enhanced lithium storage. Electrochimica Acta. 2015;166:293-301. DOI: 10.1016/j.electacta.2015.03.034
- [78] Jang K-S, Song M-G, Cho S-H, Kim J-D. Using the effects of pH and moisture to synthesize highly organized mesoporous titania thin films. Chemical Communications. 2004;13:1514-1515. DOI: 10.1039/B404409F

Pure and Nanocomposite Thin Films Based on TiO₂ Prepared by Sol-Gel Process: Characterization and Applications

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Abstract

Titanium dioxide (TiO_2) thin films have innumerable applications, and the preparation of nanocomposites based on TiO₂ favors the coupling of different structures that can lead to additional or enhanced properties. The aim of this chapter is to show the preparation and characterization of TiO₂ thin films and some nanocomposites based on anatase-TiO₂, prepared by sol-gel process using the dip-coating technique. TiO₂ thin films were prepared by sol-gel process onto borosilicate glass, steel, magnet, and silicon substrates from alcoholic starting solutions containing titanium isopropoxide, isopropyl alcohol, and acids to the control of the velocity of gelation. The doped thin films, such as SiO₂/TiO₂, Ag/TiO₂, and Nb/TiO₂, were prepared adding the dopants in a form of salts or alkoxides in starting solution. The morphological, structural, and textural characterization of the films was made using X-ray diffraction (XRD), high resolution transmission electron microscopy with energy-dispersive spectrometer (EDS) detector, atomic force microscopy/nanoindentation, and UV-Vis spectroscopy. Photoelectrical, mechanical, biological, optical, and surface properties were evaluated.

Keywords: TiO₂ thin films, Ag/TiO₂, Nb/TiO₂, SiO₂/TiO₂

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1. Introduction

Titanium dioxide (TiO_2) is a multifunctional, semiconductor and polymorphic material, which is commercialized in rutile or anatase phases, both in tetragonal crystal structures. TiO_2 is used in industry since 1918 as pigment in paints, paper, plastic, drugs, cosmetics, etc. In the last years, with the beginning of nanotechnology, powder and films of titanium dioxide have been widely studied due to its new properties obtained by decreasing the particles size. The wide range of application is due to its electronic and structural properties, such as high transmittance in the visible, high refractive index (n = 2.6), high photocatalytic activity, and chemical stability. These properties make TiO_2 an excellent material for use in photocatalysis, antimicrobial surfaces, selfcleaning and hydrophobic surfaces, photovoltaic cells, gas sensor, photochromic devices, etc. [1].

Titanium is the second transition metal on the periodic table and has $Ar-3d^24s^2$ distribution. It was discovered in 1791 by the mineralogist William Gregor, in the region of Cornwall, United Kingdom, in the mineral ilmenite (FeTiO₃). In 1795, it was isolated by the German chemist Heinrich Klaproth in the form of TiO₂ rutile phase. Titanium dioxide can be found in three different crystalline phases: anatase, brookite, and rutile. By thermal treatment, it is possible to convert the anatase and brookite phases in rutile, which is thermodynamically stable at high temperatures. The anatase phase is more reactive, mainly in nanometric dimension, and is frequently used in photocatalytic applications.

As semiconductor, TiO_2 can be studied in terms of the energy band theory, whose bandgap energy (3.2–3.6 eV) can be supplied by photons with energy in the near ultraviolet range and whose separation between valence and conduction bands is intrinsically linked with its optical and electronic properties. These bandgap values depend on the particle size, phase, and used dopant, making possible the modulation of these values. In the case of thin films, which traditionally are formed by TiO₂ nanoparticles, the thickness also contributes to the modulation of the bandgap values. Several studies are made aiming the best quality of the films and the decrease in the bandgap energy by introduction of dopants in the TiO₂ structures to improve the photocatalytic propriety in the visible region of the light [1, 2].

The introduction of dopants in the TiO_2 thin film structure such as SiO_2 , Ag, and Nb, among others, changes its properties expanding the range of possible applications. The methods of preparation also influence significantly its morphology, structure, and texture, modifying its properties. Several methods can be used to obtain thin films such as chemical vapor deposition, sputtering, spray pyrolysis, and sol-gel process. The sol-gel process [3] allows the preparation of thin films with high purity, thermal and mechanical resistance, chemical durability and the control of morphology, composition, thickness, and porosity. Thin film depositions using the sol-gel process can be realized by dip-coating, spin-coating, or spray-coating techniques. These techniques are economically feasible and can be applied to substrates with large surfaces and different forms.

1.1. Sol-gel process

The sol-gel process [3] that leads to the formation of TiO_2 films is based on mechanisms of hydrolysis and polycondensation of titanium alkoxides mixed with alcohol and catalytic agents. There are various kinds of Ti alkoxides such as titanium isopropoxide (Ti(O'Pr)_4) and

titanium ethoxide $(Ti_4(OEt)_{16})$, among others, that need to be used preferentially with their correspondent alcohol. The precursor solution, also called sol, is a colloidal suspension of Ti surrounded by ligands, with physical-chemical properties adequate to the formation of a film. After a deposition, which can be by dip-coating, spin-coating, and spray-coating processes, the film is formed by a wet gel that became a dry gel after drying process. The hydrolysis of the alkoxide group to form Ti–OH occurs due to nucleophilic substitution of O–R groups (alkyl group) by hydroxyl groups (–OH) and the condensation of the group Ti–OH, to produce Ti–O–Ti and by-products (H₂O and ROH), leading to formation of the gel, according to the equation below:

$$Ti(OR)_{n} + nH_{2}O \rightarrow Ti(OH)_{n} + nROH$$
(1)

$$\operatorname{Ti}(OH)_{n} \to \operatorname{Ti}(O_{n/2}) + n/2 \operatorname{H}_{2}O$$
(2)

$$TiOR + TiOH \rightarrow TiO_2 + ROH$$
 (3)

This mechanism is relatively complex because the reactions occur simultaneously during the process of deposition. In this proposed mechanism, the alkoxide precursor passes by the sequences, oligomer, polymer, and colloid, and it finishes as an amorphous porous solid structure. Thermal treatments are used for the preparation of nanocrystalline thin films. With the use of doping salts in the precursor solutions, the mechanism becomes more complex due to the introduction of other metals in the gel network.

The dip-coating technique [4] consists into dip a substrate in the sol and removes it at constant speed (**Figure 1**), resulting in an M–O–M oxide network that forms a wet gel film. The network structure, the morphology, and the thickness of the film depend on the contributions of the reactions of hydrolysis and condensation that must occur in approximately the same velocity of substrate withdrawal. Otherwise, the solution may run down the substrate. These properties may be controlled varying the experimental conditions: type of organic binder, the molecular structure of the precursor, water/alkoxide ratio, type of catalyst and solvent,



Figure 1. (a) Dip-coating equipment and (b) substrate withdrawal of the solution for film formation.

withdrawal speed, and solution viscosity. After the deposition, the gel film is formed by a solid structure impregnated with the solvent, and a drying process can be used to convert the wet gel in a dry porous film. Denser film can be tailored by different temperatures of thermal treatment, leading to films with different specific surface areas and porosities.

The advantage of the dip-coating process is the ease of deposition in substrates of any size and shape, facilitating the industrial process.

2. TiO₂ thin films

2.1. Experimental

TiO, thin films were prepared by sol-gel process [2, 5] using titanium isopropoxide (Aldrich, 98%) as the precursor of titania mixed with isopropyl alcohol and hydrochloric acid in stoichiometric amounts. The precursor solution was kept under agitation at room temperature for 1 h and rested until the viscosity reaches the best value condition, between 2 and 5 cP. The films were prepared using solutions with 2 < pH < 4 and atmosphere relative humidity <40%, since they are opaque and not adherent for other pH and relative humidity values. The films were deposited onto clean substrates (borosilicate glass, steel, silicon, and magnets) at room conditions (25°C, relative air humidity lower than 30%), using a dip-coating equipment with withdrawal speed between 0.2 and 1.5 mm/s. The substrates were washed with standard cleaning method before dipping. After each dip-coating process, the wet films were dried in air for 30 min and thermally treated at temperatures between 100 and 500°C for a range of time (between 10 and 60 min) to convert them into porous or densified oxide films. Depending on the thermal treatment temperature, the films can be amorphous or nanocrystalline. Some samples were submitted at UV-C light (lamp Girardi RSE20B, 254 nm-15 W) to crystallize without increasing the temperature. Crystalline structures were investigated by an X-ray diffraction (incidence angle of 5°) using a diffractometer Rigaku (Geigerflex model 3034). The samples were analyzed by atomic force microscopy (AFM) in an Asylum Research, model MFP-3D-SA, to observe the topography and possible coating defects, such as cracks and peeling. Morphological characterization was evaluated by transmission electron microscopy (FEI TECNAI G2 20 at acceleration tension of 200 kV). Electron diffraction was also used to determine the structure of the crystalline phases. The films were pulled from glass substrates and mounted onto 200 mesh copper grids coated with holey carbon films for examination. The morphology and composition were evaluated by a scanning electron microscope (SEM) FEI Quanta 200 FEG with an energy-dispersive spectrometer (EDS). The transparency and thickness of the films deposited on glasses were verified by the optical transmission spectra measured with an ultraviolet and visible spectrometer (U3010, Hitachi).

2.2. Results

The TiO₂ films obtained by sol-gel process using the dip-coating technique are transparent, homogeneous, adherent, durable, and free of micro-cracks. **Figure 2a** shows thin films removed



Figure 2. (a) TiO_2 thin films removed from a glass substrate and (b) thickness and refractive index of TiO_2 thin films in function of thermal treatment temperature.

from a glass substrate. The thickness of the films deposited in glass and dried in air can range from 40 to 800 nm for each coating, depending on the withdrawal speed and viscosity. After heating, the film thickness decreases due to the densification process, reaching values between 20 and 300 nm each coating. When the number of coating increased, the thickness can reach 800 nm after calcination without cracks.

After drying, the films are porous when treated at low temperatures, and the density increases as a function of heating temperature and time. The porosity of the films leads to a variation in the refraction index that can change from 1.9 to 2.3 ($\lambda = 550$ nm) for porosities between 20 and 5%, respectively. **Figure 2b** shows an example of the variation of thickness and refractive index in the function of thermal treatment temperature of TiO₂ film. When the TiO₂ films are deposited in substrates that cannot be thermally treated, such as polymers and cotton, the densification and crystallization can be made by UV light treatment. **Figure 3** shows images of TiO₂ films heated at 100 and 400°C for 10 min.

The film formed after drying at room temperature is amorphous and contains organic contaminants in the network. With increasing in temperature of thermal treatment, the film structure changes to anatase phase around ~300°C and to rutile phase above ~600°C.

According to the literature, the values of the phase transition of TiO_2 can change in some degrees also depending on the type and time of drying, used dopant, and particle size, among others factors. **Figure 4** shows typical diffractograms of TiO_2 films deposited in glass substrate in two temperatures, generating an amorphous material at 100°C and a nanocrystalline material at 400°C. **Figure 5** shows SEM and TEM images of the film and the respective electron diffraction that confirm its anatase phase.



Figure 3. Atomic force microscopy of TiO, films heated at (a) 100°C and (b) 400°C.

 TiO_2 thin films are used in the confection of optical devices (linear and nonlinear) due to the transparency throughout the visible spectrum, high linear and nonlinear refractive index that change in function of the wavelength, and dielectric properties. Their nonlinearity can make possible operations such as logic, all-optical switching, and wavelength conversion. Their high linear index of refraction can improve optical confinement as waveguide. The optical and electric properties of the thin films made by sol-gel process can be modulated according to the desired application. **Figure 6** shows transmittance curves of TiO₂ thin films deposited on glass substrates as a function of the number of layers. Each layer measures approximately 60 nm.

By these spectra it is possible to calculate the bandgap of the films using, for example, the Tauc method. The value measured in this case was 3.4 eV, meaning that the photocatalytic activity occurs at a wavelength in the UV region. Several studies are made aiming to reduce



Figure 4. XRD patterns of TiO₂ thin films heated at (a) 100°C and (b) 400°C.

the bandgap of the TiO_2 anatase phase to the visible region to make it a competitive energy source with application in photocatalysis, solar cells, and artificial photosynthesis.

 TiO_2 films are also used in the preparation of hydrophobic and self-cleaning surfaces in several substrates. **Figure 7** shows water drops over the film surface and over the glass substrate surface. The contact angle can be change varying the film porosity and the number of layers, for example.

The TiO_2 self-cleaning surfaces have the ability to remove greasy dirt and bacteria from their surfaces due to their photocatalytic property, which promotes the breakdown of fat molecules or destroys the membranes of bacteria. The self-cleaning property is frequently connected to hydrophobic surfaces, because the dusts can be removed by the rolling of the water droplets in the surface.



Figure 5. TiO₂ thin film images: (a) SEM image of the film over a glass substrate, (b) and (c) TEM images of the film, and (d) electron diffraction of the film.



Figure 6. UV–Vis spectra of the films deposited on (a) both sides of a glass substrate and heated at 100°C: (a) glass, (b) one layer, (c) two layers, (d) three layers, (e) four layers, (f) five layers; (b) one side of the glass substrate and heated at 400°C: (a) one layer, (b) two layers, (c) three layers, and (d) five layers.



Figure 7. TiO₂ thin film deposited on (a) the film surface and on (b) the glass surface.

3. SiO_2/TiO_2 thin films

When Si alkoxide is mixed with Ti alkoxide to the preparation of precursors of TiO_2/SiO_2 thin films for utilization of the sol-gel process, the nanocomposites produced can combine or enhance the properties of the well-known pure oxides: TiO_2 and SiO_2 [6]. These nanomaterials can offer enhanced photocatalytic activities, persistent superhydrophilicity, modulated refractive index, enhanced resistance to corrosion, and superior mechanical properties such as larger mechanical resistance and hardness. The deposition of TiO_2/SiO_2 thin films in different substrates such as glasses, metals, ceramics, and polymers enables the application of these films in many purposes such as self-cleaning surfaces, antireflection surfaces, anticorrosion protection, wear resistance protection, fungicide and bactericide surfaces, water and air treatment devices, planar waveguides, nonlinear optical devices, etc. The most important fact is that two or more of these applications can be combined in TiO_2/SiO_2 multifunctional surfaces [7, 8].

In this work, the preparation of TiO_2/SiO_2 nanocomposite thin films was made using titanium isopropoxide (Aldrich, purity >98%), isopropyl alcohol and hydrochloric acid, to prepare the TiO_2 precursor solution and tetraethyl orthosilicate (Aldrich, purity >98%), isopropyl alcohol,

hydrochloric acid, and distilled water to prepare the SiO₂ precursor solution. The pH of both solutions was maintained in 3. SiO₂ precursor solution was refluxed for 24 h at 60°C. Both the prepared solutions were aged for 24 h before the mixture. Then, TiO_2/SiO_2 precursor solutions



Figure 8. 3D topographies of the five-layer $xTiO_2/(100-x)SiO_2$ films: (a) $TiO_{2'}$ (b) $Si_{20}Ti_{80'}$ (c) $Si_{40}Ti_{60'}$ (d) $Si_{60}Ti_{40'}$ (e) $Si_{80}Ti_{20'}$ and (f) SiO_2 .



Figure 9. Optical properties modulation of the $xTiO_2/(100-x)SiO_2$ films: (a) transmittance and (b) refractive index in the function of wavelength.

with different $xTiO_2/(100-x)SiO_2$ molar ratios (x = 0, 20, 40, 60, 80, and 100%) were prepared and stirred for 1 h. The final viscosity of the solutions was maintained in approximately 2.2 cP. The films were deposited on properly clean glass substrates with a constant withdraw speed of 1.0 mm/s at 25°C and relative air humidity about 30%. The drying process occurred at 80°C in air for 10 min. This stage (deposition and drying) was repeated five times for thickness control. Finally, the samples were thermally treated at 500°C for 1 h.

The TiO₂ thin films were formed by anatase phase, and the SiO₂ thin films were amorphous according to XRD patterns and Raman spectroscopy results. The TiO₂/SiO₂ thin films are formed by the anatase phase dispersed in a vitreous matrix. The anatase phase is fundamental for the desired applications due to their optical and photocatalytic property. The microstructure, morphology, and texture of the $xTiO_2/(100-x)SiO_2$ thin films change substantially due to the mixture of the titanium and silicon oxide, as seen in AFM images of **Figure 8**.

With the addition of SiO₂, the titania nanoparticles remain dispersed in the vitreous matrix, and because of that, TiO₂ and SiO₂ pure films have higher root-mean-square (RMS) roughness (2.2 and 6.0 nm, respectively) than TiO₂/SiO₂ films (between 0.2 and 1.2 nm). The surface smoothing, after the mixture of TiO₂ and SiO₂, resulted in an enhanced hardness that changes to 4.5 GPa for both pure films and to approximately 7.4 GPa for all nanocomposite thin films. These properties are essential for outdoor applications, special windows, glasses of cars, and other vehicles, among others, since the film surfaces can be subjected to intense mechanical wear of air particles. Moreover, TiO₂/SiO₂ nanocomposite thin films present a persistent superhydrophilicity, which is required for application on self-cleaning surfaces and water/air treatment, promoting a better washing of the contaminants in the surface, which can be obtained with the rain precipitation. These nanocomposites increase the adsorption of pollutants by the surface.

The optical properties of the $xTiO_2/(100-x)SiO_2$ films are modulated by Ti/Si rate variation, as seen in **Figure 9**.

The possibility to modulate the transmittance and refractive index (n) of the $xTiO_2/(100-x)$ SiO₂ thin films is essential in applications as antireflection surfaces, filters, and planar waveguides, since this wide variation of n (from 1.45 to 2.18 in visible light) permits the

construction of different structural models of devices. The variation in the refraction index in function of incident light wavelength of 2.0–2.8 (**Figure 9b**) is also very important to the construction of nonlinear optic devices [9].

4. Ag/TiO₂ thin films

 TiO_2 exhibits a high energy bandgap (3.2–3.8 eV) which corresponds to UV irradiation with a wavelength smaller than 388 nm. To overcome this limitation, several studies have been performed showing the modification of TiO_2 with metal and nonmetal species aiming to extend the light absorption to the visible range and simultaneously increasing the recombination time of the electron-hole pairs formed. In particular, nanocomposite thin films of silver and titania have been of considerable interest since silver nanoparticles can act as electron traps, contributing to electron-hole separation and creating a local electric field capable of facilitating the electron excitation and consequently their photocatalytic properties. The improvement in the photocatalytic properties leads to surfaces with better bactericide, hydrophobicity, and self-cleaning characteristics [10].

Ag/TiO₂ coatings were prepared from alcoholic solution containing titanium isopropoxide and silver nitrate dissolved in a mixture of isopropyl alcohol in several atomic ratios. Acid conditions (pH = 4) were reached after acetic acid addition. This precursor solution was stirred at room temperature during 1 h and submitted to UV-C irradiation (254 nm) treatment in air for 100 min. This procedure has been used to produce metallic Ag from Ag⁺ ions. The films were deposited onto clean substrates as borosilicate, silicon, 316 L stainless steel, and magnets (NdFeB) with withdrawal speed of 8 mm s⁻¹. After deposition, the coatings with one to five layers were dried in air for 20 min and were thermally treated for 1 h between 100 and 400°C [5, 11].

Figure 10 shows the characteristic diffractogram of Ag/TiO₂ thin films with five layers deposited on glass and heated at 400°C.

According to XRD patterns, the coatings heated at 400°C show indexed peak characteristic of crystalline metallic Ag and anatase phase (PDF #1-562). The diffractogram of the film heated at 100°C was characteristic of a noncrystalline material, as expected. The substrates of 316 L stainless steel and magnets showed similar XRD patterns. SEM images of Ag/TiO₂ heated at 400°C deposited on different substrates are shown in **Figure 11**.

The structure of the used substrates has induced the formation of nano- and microstructures of metallic silver with different sizes and morphologies supported on the TiO_2 thin film surfaces. This formation occurs due to thermal treatment that induces the diffusion of the metal nanoparticles to the film surface. In the borosilicate substrate (**Figure 11a**), the formation of spherical Ag nanoparticles with a bimodal particle size distribution is observed. When substrates of 316 L stainless steel and magnets (NdFeB) were used, Ag dendrite micro- and nanostructures were formed (**Figure 11b** and **c**). A trimodal size distribution is observed for the particles present on the surface of the Ag/TiO₂ film deposited on silicon (**Figure 11d**). Particularly in this film, the Ag particles show dimensions of 5–150 nm.



Figure 10. XRD patterns of Ag/TiO₂ thin films with five layers heated at 100°C and 400°C and deposited on (a) borosilicate and (b) silicon substrates (400°C).

Energy-dispersive spectra (EDS) shown in **Figure 12** has confirmed the elemental composition of the Ag/TiO_2 films treated at 400°C deposited on 316 L stainless steel. In this film's circular, micrometric and submicrometric structures also are observed besides the dendrites mentioned above. Brightness regions on the micrograph are constituted only by Ag, while the other regions are formed by TiO_2 matrix in the anatase phase, according to the XRD results. The analyses for the other substrates were similar.



Figure 11. SEM images of Ag/TiO₂ heated at 400°C and deposited on (a) borosilicate, (b) magnet, (c) 316 L stainless steel, and (d) silicon substrates.


Figure 12. SEM-EDS of Ag/TiO₂ thin film heated at 400°C and deposited on 316 L stainless steel and EDS spectra from different regions in the surface.



Figure 13. AFM images of (a and b) 316 L stainless steel and (c and d) Ag/TiO₂ thin film deposited on 316 L stainless steel and heated at 400° C (one layer).



Figure 14. (a) Ag/TiO₂ thin film transmittance in the function of wavelength: (a) glass, (b) one layer, (c) two layers, (d) three layers, and (e) four layers. (b) Absorption spectra of (a) TiO₂; (b) Ag/TiO₂, Ag:Ti = 1:6; and (c) Ag/TiO₂, Ag:Ti = 1:100.

Figure 13 shows AFM images of Ag/TiO_2 thin films with one layer deposited on 316 L stainless steel substrate. The surface roughness of the 316 L stainless steel, whose texture is shown in **Figure 13a** and **b**, is ~40 nm, a much higher value compared to the roughness value of the borosilicate substrate, which is about 0.20 nm. It is observed that the Ag/TiO₂ films deposited on the steel substrates reduce their roughness as a function of the number of layers deposited. With four layers, the roughness value decreases to 7 nm. In addition, the Ag/TiO₂ films are formed by silver nanoparticles dispersed on the surface of the TiO₂ matrix with sizes between 20 and 50 nm.

The introduction of silver in the TiO_2 structure changes their optic properties as can be seen in **Figure 14a**, represented by the variation of transmittance in the function of wavelength. The bandgap decreases, depending on the amount of silver in the crystalline structure (Tauc method), until values of 1.75 eV depend on the concentration of silver, according to the literature [9].

Figure 14b shows the absorption spectra of pure and doped TiO_2 , emphasizing the photonic property of the Ag/TiO₂ thin films, with absorption peaks between 490 and 520 nm that changed with the variation of the molar ratio (Ag:Ti). These photonic surfaces provide new possibilities to increase the efficiency of solar energy conversion by confinement of the light, improve bandgap effects, and enhance optical transmission as well as nonlinear optical switching in surface polaritonic structures.

Other utilizations of Ag/TiO_2 thin films are in hydrophilic/hydrophobic surfaces and in bactericide and fungicide devices [5], since the silver increases the TiO_2 efficiency.

5. Nb/TiO, thin films

Traditionally, the niobium is used mainly in the confection of metallic alloys for several industrial applications [12]. However, the use of niobium to produce ceramic materials is increasing in the last few years with several applications into catalysis, supercapacitor, and battery components, among others. The incorporation of the niobium in other material structures, causing substitutional defects, has been studied to improve several material properties, such as TiO_2 . Examples of applications of Nb-doped TiO_2 are its use as photocatalyst, dye-sensitized solar cells, gas sensors, magnetic properties, and transparent conductive oxide (TCO) for several electronic devices.

Several methods are being used to synthesize and deposit Nb-doped TiO₂ thin films in different types of substrates. However, the most used deposition methods are chemical vapor deposition (CVD), sputtering, and sol-gel process. In the sol-gel synthesis of Nb-doped TiO₂, the use of mainly two niobium precursors, niobium ethoxide [Nb(OCH₂CH₃)₅], and niobium pentachloride (NbCl₅) that are very expensive is reported in the literature [13]. In this work, Nb/TiO₂ coatings were prepared from alcoholic solution containing titanium isopropoxide and ammonium-(bisaquo oxobisoxalato) niobate-trihydrate (produced by CBMM, Brazil) dissolved in a mixture of isopropyl alcohol. Acid conditions (pH = 4) were reached after acetic acid addition. The precursor solution was stirred at room temperature during 1 hour and deposited by dipcoating process in clean glass substrates with withdrawal speed between 0.8 and 3.7 mm s⁻¹. After deposition, the coatings with one to five layers were dried in air for 20 min and were thermally treated for 1 h between 100 and 500°C.

The Nb-TiO₂ thin films obtained are transparent, adherent, free of micro-cracks, and with visual appearance more homogeneous than the other deposited thin films. The niobium increases the mechanical resistance of the surface.

A theoretical study using density functional theory (DFT) showed that the insertion of niobium in the titanium dioxide matrix, causing the substitution of Ti⁴⁺ cations for Nb⁵⁺ cations, changes its lattice parameters, cell volume, and bandgap [14]. Therefore, the structures of the materials calcined at 500°C were found to be crystalline in the anatase phase (PDF #1-562). The thin films doped with 0.5, 1, and 3% molar ratio Nb:Ti showed a displacement of the 101 and 200 peaks to lower angles, evidencing the substitution of the niobium inside the crystal structure, as shown in **Figure 15**.



Figure 15. XRD patterns of TiO, thin films with different niobium concentrations, calcined at 500°C.



Figure 16. 3D micrographs of (a) 2% Nb-doped TiO, and (b) pure TiO,, calcined at 500°C.



Figure 17. UV-Vis spectra of several TiO_2 and Nb/TiO_2 thin films with different calcination temperatures and numbers of layers.

The increase of niobium content in the thin film promoted a considerable variation in the lattice parameters, whose d_{101} changed to 3.49 for pure TiO₂ and to 3.55 for 3% Nb/TiO₂. The crystallite size decreased from 11 to 7 nm, which agreed with the DFT results previously reported. AFM 3D micrographs (**Figure 16a** and **b**) show that the TiO_2 has larger particle size and RMS roughness of 2.2 ± 0.1 nm, while the 2% Nb/TiO₂ film presents a RMS roughness of 0.6 ± 0.2 nm and smaller nanoparticles. All Nb/TiO₂ thin films presented different profiles than TiO₂ thin films, with smaller nanoparticles and RMS roughness and, therefore, more homogeneity, adherence, and visual quality.

UV-Vis spectra seen in **Figure 17** show that also it is possible to modulate the transmittance of the thin films as a function of the wavelength to obtain optical filters. All studied films showed similar bandgap values obtained by the Tauc method, between 3.6 and 3.4 eV. The insertion of niobium on the TiO_2 structure led to a denser film with higher refractive index and high mechanical resistance.

6. Conclusion

The sol-gel deposition parameters such as the density of the precursor solution, concentration of oxides, viscosity, withdrawal velocity, number of dips, and drying temperature influence the characteristics of the films such as thickness, porosity, refractive index, particle size, particle shape, and oxidation degree. Someway, all dopants used improved the quality and the range of application of the TiO_2 films. The addition of SiO_2 in the TiO_2 films changes their mechanical, optical, and surface properties. The addition of Ag increases its photocatalytic activity, improving fungicide and bactericide properties of the films. The hydrophobicity/hydrophilicity change capacity was improved too. The doping with Nb improves the mechanical resistance of the films. All these properties can be applied in the confection of best photocatalytic surfaces to be used in the production of solar energy, self-cleaning surface, and optical and nonlinear optical devices.

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References

- Khataee A, Mansoori GA. Nanostructured Titanium Dioxide Materials. World Scientific; 2012
- [2] Viana MM, Mohallem TDS, Nascimento GLT, Mohallem NDS. Nanocrystalline titanium oxide thin films prepared by sol-gel process. Brazilian Journal of Physics. 2006;36:1081-1083
- [3] Brinker CJ, Scherrer GW. Sol-Gel Science. San Diego: Academic Press; 1990
- [4] Mohallem NDS. BaTiO₃ thin films prepared by dip-coating process. MRS Proceedings. 1994;341:379
- [5] Silva AFR, Mohallem NDS, Viana MM. TiO₂ and silver/titanium dioxide thin films with self-cleaning properties. Advanced Materials Letters. 2017;8:444
- [6] Mohallem NDS, Aegerter MA. Multilayer SiO₂ and TiO₂ coatings on glasses by the solgel process. Journal of Non-Crystalline Solids. 1988;100(1-3):526-530
- [7] Glaubitt W, Lobmann P. Antireflective coatings prepared by sol–gel processing: Principles and applications. Journal of the European Ceramic Society. 2012;**32**(11):2995-2999
- [8] Jesus MAML, da Silva JT, Timò G, Paiva PP, Dantas MS, Ferreira AM. Superhydrophilic self-cleaning surfaces based on TiO₂ and TiO₂/SiO₂ composite films for photovoltaic module cover glass. Applied Adhesion Science. 2015;3(1):1-9
- [9] Hari M, Joseph SA, Mathew S, Radhakrishnan P, Nampoori VPN. Band-gap tuning and nonlinear optical characterization of Ag:TiO₂ nanocomposites. Journal of Applied Physics. 2012;**112**:074307
- [10] Viana MM, Mohallem NDS, Miquita DR, Balzuweit K, Silva-Pinto E. Preparation of amorphous and crystalline Ag/TiO₂ nanocomposite thin films. Applied Surface Science. 2013;265:130
- [11] Yadav S, Jaiswar G. Review on undoped/doped TiO₂ nanomaterial; synthesis and photocatalytic and antimicrobial activity. Journal of the Chinese Chemical Society. 2017;64:103-116
- [12] Wen M, Wen C, Hodgson P, Li Y. Fabrication of Ti–Nb–Ag alloy via powder metallurgy for biomedical applications. Materials & Design (1980-2015). 2014;56:629-634
- [13] Bakhshayesh AM, Bakhshayesh N. Improved short-circuit current density of dye-sensitized solar cells aided by Sr, Nb co-doped TiO₂ spherical particles derived from sol-gel route. Journal of Sol-Gel Science and Technology. 2016;77:228-239
- [14] Kamisaka H, Hitosugi T, Suenaga T, Hasegawa T, Yamashita K. Density functional theory based first-principle calculation of Nb-doped anatase TiO₂ and its interactions with oxygen vacancies and interstitial oxygen. The Journal of Chemical Physics. 2009;131. https://doi.org/10.1063/1.3157283

Novel TiO₂ Photocatalyst Using Nonaqueous Solvent-Controlled Sol-Gel Route

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Additional information is available at the end of the chapter

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Abstract

Synthesis of metal oxide nanoparticles with tailored properties is of great interest because of their potential in environmental, sensor, biomedical and energy applications. Specifically, TiO_2 gets special attention because of its high stability, biocompatibility, tunable band gap and surface properties. Aqueous sol-gel routes for the synthesis of TiO_2 nanoparticles are well established but suffer from little control over morphology and reproducibility. Nonaqueous solvent controlled sol-gel routes are good alternative to aqueous routes for the synthesis of highly crystalline TiO_2 nanoparticles with high purity and controlled doping of large size metallic ions. Present chapter describes the successful doping of large sized Zr and Na metal ions at Ti site and their influence on photo catalytic activity of TiO_2 . The higher photo catalytic activity (even better than commercially available Degussa P25) of metal doped TiO_2 nanopawder is attributed to large surface area and reduced electron-hole recombination rate.

Keywords: $TiO_{2'}$ metal-doped $TiO_{2'}$ nanoparticle, nonaqueous, solvent controlled, sol-gel, photocatalytic activity

1. Introduction

Metal oxide nanoparticles (MONPs) are well-known for their outstanding role especially for environmental, sensor, biomedical and energy applications [1–10]. Among MONPs, TiO_2 nanoparticles are least toxic [11] and therefore synthesis of nanostructured TiO_2 with tailored properties has been most extensively investigated in recent years. TiO₂ occurs in three different phases [12], anatase, rutile and brookite with rutile as most stable phase and anatase as most desirable phase. TiO₂ is associated with outstanding properties including high stability,

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exceptional biocompatibility, corrosion resistance, high photosensitivity and reactivity, as well as cost-effective and easy synthesis [13–16]. Semiconducting nature of anatase TiO₂ (Band gap of 3.2 eV) [17] allows it to degrade toxic organic compounds into simple hydrocarbons such as CO_2 and H_2O under UV irradiation. Under UV irradiation of energy greater than or equal to energy gap of TiO₂, electrons and holes are produced in valence band and conduction band, respectively. These electrons and holes result in formation of oxygen active species (OH^{*}, H_2O_2 , O_2^{-} , IO_2) at surface of TiO₂, which reacts with toxic organic compounds and decompose them. Thus, TiO₂ is well known photocatalyst largely utilized for water reclamation, air purification, soil remediation, surface wettability adjustment, bacteria killing, solar cells, sensors, self-cleaning and anti-reflective surfaces [18–25].

A large number of synthesis methods have been employed for designing of TiO₂ nanoparticles with controlled shape, size, good yield and high dispersibility (less agglomeration). The shape and size of nanoparticles greatly affect the photocatalytic performance of the photocatalyst [26, 27]. Highly pure metal oxides can be prepared by conventional solid state route [28], but high processing temperature requirement limits its frequent use for synthesis. The biological synthesis method [11, 29] leads to formation of cost-effective, mono-dispersed nanoparticles but reproducibility needs improvement. To overcome all these difficulties during nanoparticles synthesis, alternative well-known liquid phase synthesis methods such as sol-gel [30, 31], hydrothermal [32, 33], microemulsion [34, 35], reverse microemulsion [36], sonochemical [37, 38] and microwave [39, 40] are employed. Among these synthesis methods, the sol-gel synthesis route gets special attention because of following reasons:

- 1. Homogeneity of starting precursor at molecular scale.
- 2. Low processing temperature.
- 3. Cost-effective.
- 4. Easy doping.

Sol-gel route can also yield multifold nanostructures such as nanoparticle, nanorods, nanotubes, aerogels and zeolites at a single platform. In addition, good yield and reproducibility are the key features of sol-gel route.

The present chapter will highlight the features of nonaqueous solvent controlled sol-gel route for the synthesis of pure and metal doped TiO_2 nanoparticles. Effects of metal doping and synthesis strategy on structural and surface properties are correlated with photocatalytic activity of pure and metal doped TiO₂ photocatalyst.

2. Synthesis

2.1. General overview

The sol-gel route [41, 42] involves the mixing of metal precursor into either water or organic solvent followed by formation of 3-dimensional network resulting in viscous gel, which in

general results in amorphous powder after drying process. The process of mixing is known as hydrolysis, while formation of 3-dimensional network is called as condensation. These two processes are further controlled by many parameters including nature of metal precursor, ratio of precursor to solvent, nature of solvent, capping agents (surfactants), pH and temperature. **Figure 1** summarizes the various types of sol-gel routes.

Aqueous sol-gel route [41], as its name suggests, uses water as solvent to dissolve metal precursor and to complete hydrolysis process. The hydrolysis process is extremely fast due to high reactivity of water with precursors and therefore, generally there is little control over morphology and reproducibility. Nonaqueous sol-gel routes offer a good alternative to get rid of these difficulties [43, 44]. An organic solvent (alcohols, ketones, aldehydes or ethers) is used to complete the hydrolysis process instead of water. Besides, the oxygen required for metal-oxide formation is supplied by organic solvent in nonaqueous sol-gel route, whereas water plays the role of oxygen donor in aqueous sol-gel synthesis. However, inclusion or exclusion of some surfactant (consisting of hydrophilic and hydrophobic groups) in reaction solution further classifies the nonaqueous sol-gel route into surfactant assisted and solvent controlled (surfactant free) routes respectively. The main advantage of surfactant assisted nonaqueous sol-gel route is that the surfactant acts as capping agent and results in highly mono-dispersed nanoparticles. In addition a good control over particle size, morphology with outstanding reproducibility is direct consequence of surfactant-assisted nonaqueous sol-gel route. Moreover, the surface properties of nanoparticles can be easily tailored by exchanging surfactants with other functional groups. However this method is also prone to certain limitations like impurities in nanoparticles and toxic effects due to surfactants. These limitations impose restrictions on the surface sensitive applications (photocatalytic, biomedical and sensing) of nanoparticles.

2.2. Solvent controlled nonaqueous sol-gel route

A good alternative to surfactant assisted nonaqueous sol-gel route [45, 46] is solvent controlled nonaqueous sol-gel route. The solvent in itself plays role of oxygen donor necessary for oxide formation and stabilizing agent to control shape, size and morphology of nanoparticles. This modified sol-gel route also facilitates highly pure nanoparticles completely free



Figure 1. Various types of sol-gel synthesis routes.

from toxic surfactants but suffers from tendency to agglomerate. However toxic effect of halides cannot be neglected when metal oxide nanoparticles are prepared by reacting metal halides with organic solvents. In order to avoid halide impurities from metal oxide nanoparticles it is wise to use metal alkoxides, acetates or acetylacetonates as metal precursor. In the following subsections, synthesis of pristine and metal doped TiO₂ nanoparticles using halide free, nonaqueous, solvent controlled sol-gel route [2, 10] is described.

2.2.1. Synthesis of pristine TiO,

Titanium tetra iso-propoxide (TTIP) was used as Titanium precursor and methoxyethanol as organic solvent. 20 ml TTIP is added to 40 ml methoxyethanol and mixed using magnetic stirrer. The pH of solution is adjusted to value 3 using 1 M HNO₃, which also catalyzes the hydrolysis process. The mixing is continued until viscous gel is formed, which is then dried under IR lamp and pulverized to obtain amorphous powder. The pure anatase TiO₂ nanopowder is formed after calcining the amorphous powder at 450°C for 1 hour. The chemical reactions occurring during hydrolysis and condensation in the synthesis are listed below.

Ti $[OR]_4 + 4 HOR' \rightarrow Ti [OH]_4 + ROR' (Hydrolysis)$

Ti $[OH]_4 \rightarrow TiO_2 + 2H_2O$ (Condensation)

2.2.2. Synthesis of metal doped TiO₂

What is the motivation for metal doping in TiO_2 ? As explained earlier, TiO_2 is wide band gap semiconductor and requires UV irradiation for its operation as a photo catalyst. The contribution of UV light in the solar radiation is less than 5%. Therefore, it is required to tune the band gap of TiO_2 to visible range so that no extra source of radiation energy (other than solar light) is required. Also, pristine TiO_2 suffers from higher recombination rate of charge carriers (electron and hole) resulting in less photocatalytic efficiency. Metals [10, 47–52] and nonmetals [53–58] are well known for their ability to reduce the band gap of TiO_2 by generating energy states between valence band and conduction band. These energy states serve as charge carrier trapping center and therefore reduce the electron hole recombination rate. The reduction in electron hole recombination rate results in remarkable improvement in photocatalytic performance. In addition, noble metals (Ag, Au and Pt), transition metals [59–61] and nonmetals doping in TiO_2 reduces the band gap of TiO_2 to visible range doped TiO_2 nanoparticles are found to have small size as compared to pristine TiO_2 , which improves the surface area and consequently boosts up the photocatalytic performance. However, favorable change in properties of TiO_2 by doping is largely affected by synthesis methods.

In current chapter, synthesis and photocatalytic properties of TiO_2 nanoparticles doped with one transition metal, Zirconium (Zr) and one other alkali metal, sodium (Na) are discussed. Both these metals have higher ionic radii (~0.79 Å for Zr and ~1.02 Å for Na) as compared to titanium (~0.68 Å for Ti). Large ionic radii and low valence ionic metallic dopant in host Ti4+ always results in strain in the crystal structure that favors the formation of oxygen vacancies [62]. These oxygen vacancies are prone to trap electrons and suppress grain growth resulting

in reduced charge recombination rate and small crystallite size respectively. There are many reports which claimed contradictory reports on photocatalytic activity of TiO₂ after doping of same dopant under different synthesis routes. Bessekhouad et al. [63] compared the photo catalytic efficiency of Na doped TiO₂ nanopowder prepared via two methods: sol-gel route and impregnation technology. They found that photo catalytic efficiency of nanopowder prepared by impregnation technology is higher than nanopowder prepared by aqueous sol-gel route. In addition, Na doping in TiO₂ matrix via aqueous sol-gel route decreases the photocatalytic efficiency due to migration of Na at TiO₂ surface instead of entering in the lattice. On the other hand, Yang et al. [64] showed higher photocatalytic activity of Na doped TiO₂ nanopowder prepared via solvothermal method. XRD analysis by Yang et al. [64], Xie et al. [65] as well as Bessekhouad et al. [63] could not confirm the doping of large sized Na into TiO₂ lattice and therefore hinted at the tendency of large sized Na + ions to migrate to TiO₂ surface. Therefore, it is required to study the effect of synthesis method on doping mechanism and photocatalytic activity of large sized metal dopants in TiO₂ matrix.

In [2, 10] Zr and Na has been doped in TiO_2 matrix individually by solvent controlled nonaqueous sol-gel route. Easily dissolvable zirconium oxy-nitrate and sodium nitrate are used as precursor of Zr and Na respectively. To achieve nominal dopants concentration, calculated amount of precursor is added to solvent prior to addition of Ti precursor. After complete dissolution of dopant precursor, Ti precursor is added to reaction solution and similar steps are followed as in preparation of doped TiO₂ nanopowder.

3. Characterization of pristine and metal doped TiO₂

3.1. Phase and structural characterization

X-ray diffraction (XRD) is an important tool used to determine the phase purity of sample, crystal structure, lattice parameter, average crystallite size and quantitative phase analysis. Generally, as prepared TiO_2 by sol-gel route is amorphous and therefore requires different heat treatment to form crystalline phases. Low (300–500°C), moderate (500–700°C) and high (more than 700°C) calcination temperature results in pure anatase phase, mixture of anatase and rutile, and pure rutile phase respectively [66]. The anatase to rutile (A-R) phase transformation is largely affected by type and amount of metal doping. Choi et al. [67] studied effect of single metal ion doping on A-R phase transformation temperature in TiO_2 prepared by sol-gel route. They observed that many metals such as Pt, Cr, V, Fe, La doping in TiO_2 lowers the A-R transformation temperature, whereas Ru metal shows opposite behavior. Xie et al. [65] and Singh et al. [2] also reported increased A-R transformation temperature in Na doped TiO_2 nanopowder. The presence of rutile structure in anatase phase affects the photocatalytic activity of metal doped TiO_2 .

Figure 2(A) and **Figure 2(B)** shows the XRD pattern of Zr doped TiO_2 and Na doped TiO_2 with pristine TiO_2 respectively. Very fine powders of TiO_2 based photocatalysts prepared by nonaqueous solvent controlled sol-gel route [2, 10] are used to perform XRD using Cu K α radiation (0.154 nm). Clearly, pure anatase phase of TiO_2 is formed for pristine as well as in Zr and Na doped TiO₂ nanopowder and matches with JCPDS card number 841286. In general, there are two types of doping (i) substitutional, and (ii) interstitial. Which one of these two



Figure 2. The XRD patterns of Zr (A) and Na (B) doped TiO₂ nano-powder calcined at 450°C for 1 hr.: (a & e) pristine TiO₂; (b) Ti_{0.95}Zr_{0.05}O₂; (c) Ti_{0.90}Zr_{0.10}O₂; (d) Ti_{0.85}Zr_{0.15}O₂; (f) Ti_{0.96}Na_{0.04}O₂; (g) Ti_{0.92}Na_{0.08}O₂ and (h) Ti_{0.90}Na_{0.10}O₂. Figure (A) reprinted with permission from Reference [10]. Copyright 2017, Elsevier.

types of doping is favored, depends on size of guest ion as compared to host ion and volume size of interstitial position in the host lattice. Substitutional doping is preferred in case where size of guest ion is comparable or slightly larger than lattice ion, whereas if size of guest ion is much smaller than lattice ion then it occupies interstitial position of host lattice.

XRD peaks of crystal planes of Zr doped TiO₂ (**Figure 2(A)**) shows red shift in 20 values, which confirms the substitutional doping of Zr^{4+} at Ti⁴⁺ site [10]. The substitutional doping of Zr in TiO₂ results in an increase in cell parameter and cell volume as reported by Yu et al. [68] and Wang et al. [69] Thus, incorporation of large sized Zr results in lattice strain and hence leads to formation of oxygen vacancies and suppresses the grain growth. Similar behavior is observed for Na doped TiO₂ nanopowder (**Figure 2(B)**) [2]. However formation of oxygen vacancies in Na doped TiO₂ can occur not only due to strain induced by Na doping but also due to lower valence state of Na⁺¹ ion. It should be noted that there are contradictory literature reports regarding doping of Na in TiO₂. Xie et al. [65] who used aqueous sol-gel synthesis, reported that large size Na cannot substitute Ti and therefore migrates to TiO₂ surface forming Na-O bonds as there is no peak shift is observed in XRD patterns. Thus it appears that substitutional doping of Na at Ti in TiO₂, as indicated by the XRD peak shifts in **Figure 2(B)**, is facilitated by nonaqueous solvent controlled sol-gel route, which was used by Singh et al. [10].

The crystallite size of pristine and doped TiO_2 nanopowder are calculated by well-known Debye Scherrer formula and tabulated in **Table 1**. In both, Zr doped TiO_2 and Na doped $\text{TiO}_{2'}$ the crystallite size reduces for certain dopant concentration and hence increases the surface area of nanoparticles. Additionally, A-R phase transformation temperature is increased due to doping Zr⁴⁺ and Na⁺¹ in TiO₂ matrix [10, 65, 68, 69].

3.2. Microstructural characterization

XRD gives structural information like lattice constant and crystalline phases averaged over bulk of the material. TEM on the other hand is able to give microstructural information on

| Sample | TiO ₂ | $Ti_{0.95}Zr_{0.05}O_2$ | Ti _{0.9} Zr _{0.1} O ₂ | Ti _{0.96} Na _{0.04} O ₂ | $Ti_{0.92}Na_{0.08}O_2$ | Ti _{0.9} Na _{0.1} O ₂ |
|-----------------------|------------------|-------------------------|--|--|-------------------------|--|
| Particle size (nm) | 19.0 | 14.0 | 11.0 | 11.0 | 10.5 | 11.0 |

Table 1. Particle size (calculated by Debye Scherrer formula) of pristine and metal doped TiO, nanoparticles.

a nano meter length scale. In addition, grain boundaries, dislocations and structural defects could be easily identified by TEM. In this technique, a well-focused electron beam impinges on an ultrathin specimen in a high vacuum column, with the help of electromagnetic lenses. The impinged electron beam interacts with specimen and gets transmitted. A controlled and sophisticated system of electromagnetic lenses is used to focus the transmitted electron beam on a fluorescent screen. Selected area electron diffraction, diffraction contrast imaging, high resolution imaging and energy dispersive X-ray spectroscopy are some of the most commonly used TEM techniques for the characterization of materials.

Figure 3 shows the bright field TEM images, selective area electron diffraction (SAED) patterns and HRTEM images of pristine and metal doped TiO_2 nanopowder prepared by nonaqueous solvent controlled sol-gel route. Clearly, the particle size reduces with metal doping in comparison to pristine TiO_2 , which is in agreement with XRD results. The SAED ring pattern and HRTEM images confirm the crystalline nature of pristine as well as metal doped TiO_2 nanoparticles. The SAED diffraction rings could be indexed as (101), (004) and (200) lattice planes of pristine anatase TiO_2 . The increase in lattice spacing with Zr and Na doping indicates large metal ion substitution at Ti site in agreement with XRD results.



Figure 3. TEM images (a, b and c with insets shows respective selective area electron diffraction pattern) and HRTEM images (d, e and f). Figure (b&e) reprinted with permission from Ref. [10]. Copyright 2017, Elsevier.



Figure 4. (A) Principle of photoluminescence spectroscopy. (B) PL spectra of pristine and Na doped TiO, nanopowder.

3.3. Photoluminescence study

Photoluminescence (PL) spectroscopy is a versatile and powerful optical method to investigate the energy levels in materials. The material is irradiated with light photons of energy greater than or equal to band gap energy of material. This results in the excitation of electrons from valence band to the excited states (**Figure 4(A)**) of material. These electrons relax to conduction band by losing excess energy via nonradiative process. When these electrons return to their valence band, the energy is released in the form of photons and the process is known as photoluminescence. The energy of emitted photons is determined by the difference in atomic energy levels, while the intensity of emitted light gives us information regarding recombination of electrons and holes.

The energy and intensity of emitted light in PL spectra of particular material is highly affected by doping. **Figure 4(B)** shows the PL spectra of pristine and Na doped TiO₂ nanopowder at excitation wavelength 390 nm. The shape of PL signal remains same while intensity reduces with increase in doping concentration of Na in TiO₂ matrix. This is attributed to the fact that Na doping in TiO₂ matrix results in formation of oxygen vacancies resulting in energy states lying between valence band and conduction band that trap the electrons form conduction band and thereby reduce electron-hole recombination [68]. However, the PL signal intensity increases for Ti_{0.9}Na_{0.1}O₂ sample. This is attributed to fact that excessive formation of oxygen vacancies might act as recombination centers [70].

4. Photocatalytic activity

The photocatalytic activity of prepared photo catalyst can be measured by many different test methods [71], which have been accepted at national and international standards. We have used German standard DIN 52980¹¹ for the determination of photocatalytic activity. This standard

method is based on the degradation of organic dye methylene blue (MB) by photo catalyst under UV irradiation. The degradation results are further confirmed by measuring total organic carbon (TOC) of initial dye aqueous solution and degraded dye aqueous solution by TOC analyzer.

4.1. Degradation experiment

The photocatalytic activity of pristine and metal doped TiO, is evaluated by degrading aqueous solution of MB dye under ultraviolet (UV) irradiation. In order to compare photocatalytic activity of photo catalyst prepared by nonaqueous solvent controlled sol-gel route with commercial photo catalyst, the photocatalytic activity of well-known commercially available Degussa P25 TiO, is also evaluated. The initial concentration of MB aqueous solution is 5 mg/L. About 100 ml of MB dye aqueous solution (pH 5) is taken in 100 ml borosil glass beaker and 60 mg of photo catalyst is added in the solution. The beaker is kept on magnetic stirrer for uniform suspension of photo catalyst in the solution throughout the experiment. The reaction mixture is irradiated by UV light of peak wavelength at 365 nm and the intensity of UV light at the surface of reaction mixture is 10 mW/cm². The distance between reaction mixture and UV light source is 20 cm resulting in light intensity of 8×10^4 lux over reaction mixture. In order to complete adsorption-desorption equilibrium between photo catalyst and dye, the reaction mixture is stirred for 20 minutes in completely dark chamber. After achieving adsorption-desorption equilibrium, the reaction mixture is irradiated with UV light and a small amount of solution is withdrawn at regular time intervals. The withdrawn sample is centrifuged to separate out nanoparticles from the solution and absorbance of supernatant measured using UV-Visible spectrometer. The photocatalytic degradation percentage of dye for different time intervals is plotted for several photo catalysts and without catalyst (WC).

The degradation percentage of dye is calculated using Eq. 1. The rate constant (k) for the photocatalytic degradation of dye is determined from pseudo first order law using Eq. 2.

Degradation % =
$$\left(\left(C_0 - C_t \right) / C_0 \right) \times 100$$
 (1)

$$\ln\left(C_{0}/C_{t}\right) = kt \tag{2}$$

where C_0 is dye concentration before UV irradiation and C_t is dye concentration after t time of UV irradiation.

In order to further confirm the degradation results, TOC of irradiated and nonirradiated dye aqueous solution is measured and TOC removal rate percentage is calculated using Eq. 3.

$$TOC \% = \left((TOC_0 - TOC_t) / TOC_0 \right) \times 100$$
(3)

where TOC_0 and TOC_t are the TOC values of dye solution before and after time 't' of UV irradiation respectively.

4.2. Degradation results and mechanism

The photocatalytic activity of prepared Na doped TiO₂ photo catalyst can be compared from **Figure 5**. Clearly, the degradation percentage of MB dye is highest for Ti_{0.92}Na_{0.08}O₂, even superior to commercially available Degussa P25 catalyst. The k values for degradation of MB dye by WC, P25, pristine TiO₂ and Ti_{0.92}Na_{0.08}O₂ are 0.86×10^{-3} , 30.52×10^{-3} , 3.02×10^{-3} and 43.24×10^{-3} min⁻¹, respectively. TOC results are in accordance as well. This enhancement in photocatalytic activity of TiO₂ with Na doping is attributed to its smaller crystallite size and reduced rate of electron-hole recombination. Similarly, Ti_{0.9}Zr_{0.1}O₂ shows enhanced photocatalytic activity [10] for which, in addition to reduction in crystallite size and electron-hole recombination, band gap was also reduced due to Zr doping.

The photocatalytic degradation of dye at the surface of TiO_2 is well explained in the existing literature [56, 72]. The reactions occurring at the surface of semiconductor TiO_2 under UV irradiation are depicted in the Eqs. 4–8. The electrons are excited to conduction band while holes are formed in conduction band after absorption of photons having energy greater than or equal to energy gap of semiconductor. In case of pristine TiO_2 , most of these electrons recombine with holes; few of them react with adsorbed oxygen forming reactive oxygen active specie (ROS) O_2^{-} . Similarly holes in the valence band reacts with water molecules and form ROS OH* radicals. These ROS actually reacts with dye molecules and degrade them into simple hydrocarbons H₂O and CO₂.

$$TiO_{2} + hv = e^{-} + h^{+}$$
(4)

$$e^{-} + O_2 = O_2^{-}$$
 (5)

$$H_{2}O + h^{+} = OH^{*} + H^{+}$$
 (6)

$$O_2^- + 2H^+ + e^- = 2 OH^*$$
 (7)

$$AB + OH^* = Degradation products$$
 (8)



N

Figure 5. Photocatalytic degradation (A) and mineralization (B) of MB dye under 60 minute of UV irradiation.



Figure 6. Effect of metal doping on degradation mechanism of pristine TiO₂.

In pristine TiO_2 the higher recombination rate of electron-hole results in fewer number of ROS radicals and hence less photocatalytic activity. In addition, large energy gap and small surface area also limit the degradation efficiency. Metal doping in TiO_2 results in large surface area, band gap tuning toward visible range and reduced electron-hole recombination rate. This most general proposed mechanism for degradation of dye at surface of metal doped TiO_2 is depicted in **Figure 6**.

5. Conclusion

In this chapter the importance of recently reported nonaqueous solvent controlled sol-gel route for the synthesis of metal doped TiO_2 with improved photocatalytic properties discussed. Pristine as well as Zr and Na doped TiO_2 nanoparticles have been prepared by this modified sol-gel route and their photocatalytic activity evaluated. Successful doping of these large metal ions in TiO_2 lattice using this synthesis route was confirmed by shifts in XRD peak positions and increase in d spacing observed from HRTEM images.

The photocatalytic activity of metal doped TiO_2 nanopowder is found to be much higher than pristine TiO_2 , and even superior to commercially available Degussa P25 TiO_2 photo catalyst. This is attributed to large surface area due to small grain size and reduced electron hole

recombination due to formation of oxygen vacancies in metal doped TiO_2 . The reduction in electron-hole recombination increases the availability of electrons and holes which reacts with adsorbed oxygen and water molecules forming large number of reactive oxygen active species leading to enhanced photocatalytic activity.

In past years, only few MONPs have been prepared by this nonaqueous, solvent controlled, sol-gel route. This method has great potential to synthesize functional nanoparticles of desired composition, size and surface properties essential for different applications.

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Conflict of interest

There are no conflicts of interest to declare.

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References

- [1] Tang SCN, Lo IMC. Magnetic nanoparticles: Essential factors for sustainable environmental applications. Water Research. 2013;**47**:2613-2632. DOI: 10.1016/j.watres.2013.02.039
- [2] Singh I, Birajdar B. Synthesis, characterization and photocatalytic activity of mesoporous Na-doped TiO₂ nano-powder prepared via a solvent-controlled non-aqueous solgel route. RSC Advances. 2017;7:54053-54062. DOI: 10.1039/c7ra10108b
- [3] Ngomsik AF, Bee A, Draye M, Cote G, Cabuil V. Magnetic nano- and microparticles for metal removal and environmental applications: A review. Comptes Rendus Chimie. 2005; 8:963-970. DOI: 10.1016/j.crci.2005.01.001
- [4] Karlsson HL, Cronholm P, Gustafsson J, Moeller L. Copper oxide nanoparticles are highly toxic: A comparison between metal oxide nanoparticles and carbon nanotubes. Chemical Research in Toxicology. 2008;21:1726-1732. DOI: 10.1021/tx800064j

- [5] Rahman MM, Khan SB, Jamal A, Faisal M, Aisiri AM. Iron oxide nanoparticles. InTech Open; 2011. p. 43-66. DOI: 10.5772/27698
- [6] Mir IA, Singh I, Birajdar B, Rawat K. A facile platform for photocatalytic reduction of methylene blue dye by CdSe-TiO₂ nanoparticles. Water Conservation Science and Engineering. 2017;2:43-50. DOI: 10.1007/s41101-017-0023-5
- [7] Franke ME, Koplin TJ, Simon U. Metal and metal oxide nanoparticles in chemiresistors: Does the nanoscale matter? Small. 2006;**2**:36-50. DOI: 10.1002/smll.200500261
- [8] Simon-Deckers A. Size-, composition- and shape-dependent toxicological impact of metal oxide nanoparticles and carbon nanotubes towards bacteria. Environmental Science and Technology. 2009;43:8423-8429. DOI: 10.1021/es9016975
- [9] Sarkar S, Guibal E, Quignard F, SenGupta AK. Polymer-supported metals and metal oxide nanoparticles: Synthesis, characterization, and applications. Journal of Nanoparticle Research. 2012;14:1-24. DOI: 10.1007/s11051-011-0715-2
- [10] Singh I, Kumar R, Birajdar BI. Zirconium doped TiO₂ nano-powder via halide free non-aqueous solvent controlled sol-gel route. Journal of Environmental Chemical Engineering. 2017;5:2955-2963. DOI: https://doi.org/10.1016/j.jece.2017.05.046
- [11] Seabra A, Durán N. Nanotoxicology of metal oxide nanoparticles. Metals (Basel). 2015;
 5:934-975. DOI: 10.3390/met5020934
- [12] Reyes-Coronado D, Rodr??guez-Gattorno G, Espinosa-Pesqueira ME, Cab C, De Coss R, Oskam G. Phase-pure TiO₂ nanoparticles: Anatase, brookite and rutile. Nanotechnology. 2008;19:145605-145614. DOI: 10.1088/0957-4484/19/14/145605
- [13] Pillai SC, Periyat P, George R, McCormack DE, Seery MK, Hayden H, Colreavy J, Corr D, Hinder SJ. Synthesis of high-temperature stable anatase TiO₂ photocatalyst. Journal of Physical Chemistry C. 2007;**111**:1605-1611. DOI: 10.1021/jp065933h
- [14] Karpagavalli R, Zhou A, Chellamuthu P, Nguyen K. Corrosion beheaviour and biocompatibility of nanostructured TiO₂ film on Ti6Al4V. Journal of Biomedical Materials Research Part A. 2007;83:97-103. DOI: 10.1002/jbm.a
- [15] Tachikawa T, Fujitsuka M, Majima T. Mechanistic insight into the TiO₂ photocatalytic reactions: Design of new photocatalysts. Journal of Physical Chemistry C. 2007;**111**:5259-5275. DOI: 10.1021/jp069005u
- [16] Zhu YF, Zhang L, Gao C, Cao LL. The synthesis of nanosized TiO\$_2\$ powder using a sol-gel method with TiCl\$_4\$ as a precursor. Journal of Materials Science. 2000;35:4049-4054. DOI: 10.1023/A:1004882120249
- [17] Scanlon DO, Dunnill CW, Buckeridge J, Shevlin SA, Logsdail AJ, Woodley SM, Catlow CRA, Powell MJ, Palgrave RG, Parkin IP, Watson GW, Keal TW, Sherwood P, Walsh A, Sokol AA. Band alignment of rutile and anatase TiO₂. Nature Materials. 2013;**12**:798-801. DOI: 10.1038/nmat3697
- [18] Ryu J, Choi W. Substrate-specific photocatalytic activities of TiO and multiactivity test for water treatment application substrate-specific photocatalytic activities of TiO 2 and

multiactivity test for water treatment application. Environmental Science & Technology. 2008;**42**:294-300. DOI: 10.1021/es071470x

- [19] Obee TN, Brown RT. TiO₂ photocatalysis for indoor air applications: Effects of humidity and trace contaminant levels on the oxidation rates of formaldehyde, toluene, and 1,3-butadiene. Environmental Science & Technology. 1995;29:1223-1231. DOI: 10.1021/ es00005a013
- [20] Wang TC, Lu N, Li J, Wu Y. Plasma-TiO₂ catalytic method for high-efficiency remediation of p-nitrophenol contaminated soil in pulsed discharge. Environmental Science & Technology. 2011;45:9301-9307. DOI: 10.1021/es2014314
- [21] Lai Y, Huang J, Cui Z, Ge M, Zhang KQ, Chen Z, Chi L. Recent advances in TiO₂-based nanostructured surfaces with controllable wettability and adhesion. Small. 2016;12:2203-2224. DOI: 10.1002/smll.201501837
- [22] Wei C, Lin WY, Zainal Z, Williams NE, Zhu K, Kruzlc AP, Smith RL, Rajeshwar K. Bactericidal activity of TiO₂ photocatalyst in aqueous media: Toward a solar-assisted water disinfection system. Environmental Science & Technology. 1994;28:934-938. DOI: 10.1021/es00054a027
- [23] Park N-G, van de Lagemaat J, Frank AJ. Comparison of dye-sensitized rutile- and anatase-based TiO₂ solar cells. The Journal of Physical Chemistry. B. 2000;104:8989-8994. DOI: 10.1021/jp9943651
- [24] Kirner U, Schierbaum KD, Göpel W, Leibold B, Nicoloso N, Weppner W, Fischer D, Chu WF. Low and high temperature TiO₂ oxygen sensors. Sensors and Actuators B: Chemical. 1990;1:103-107. DOI: 10.1016/0925-4005(90)80181-X
- [25] Zhang X, Fujishima A, Jin M, Emeline AV, Murakami T. Double-layered TiO₂-SiO₂ nanostructured films with self-cleaning and antireflective properties. The Journal of Physical Chemistry. B. 2006;110:25142-25148. DOI: 10.1021/jp064442u
- [26] Wu N, Wang J, Tafen DN, Wang H, Zheng J-G, Lewis JP, Liu X, Leonard SS, Manivannan A. Shape-enhanced photocatalytic activity of single-crystalline anatase TiO₂ (101) nanobelts. Journal of the American Chemical Society. 2010;132:6679-6685. DOI: 10.1021/ja909456f
- [27] Mclaren A, Valdes-Solis T, Li G, Tsang SC. Shape and size effects of ZnO nanocrystals on photocatalytic activity. Journal of the American Chemical Society. 2009;131:12540-12541
- [28] Sun Z-P, Liu L, Zhang L, Jia D-Z. Rapid synthesis of ZnO nano-rods by one-step, roomtemperature, solid-state reaction and their gas-sensing properties. Nanotechnology. 2006;17:2266-2270. DOI: 10.1088/0957-4484/17/9/032
- [29] Durán N, Seabra AB. Metallic oxide nanoparticles: State of the art in biogenic syntheses and their mechanisms. Applied Microbiology and Biotechnology. 2012;95:275-288. DOI: 10.1007/s00253-012-4118-9
- [30] Wang CC, Ying JY. Sol-gel synthesis and hydrothermal processing of anatase and rutile titania nanocrystals. Chemistry of Materials. 1999;11:3113-3120. DOI: 10.1021/cm990180f

- [31] Niederberger M. Nonaqueous sol gel routes to metal oxide nanoparticles. Accounts of Chemical Research. 2007;40:793-800. DOI: 10.1021/ar600035e
- [32] Titirici MM, Antonietti M, Thomas A. A generalized synthesis of metal oxide hollow spheres using a hydrothermal approach. Chemistry of Materials. 2006;18:3808-3812. DOI: 10.1021/cm052768u
- [33] Adschiri T, Hakuta Y, Sue K, Arai K. Hydrothermal synthesis of metal oxide nanoparticles at supercritical conditions. Journal of Nanoparticle Research. 2001;3:227-235. DOI: 10.1023/A:1017541705569
- [34] Santra S, Tapec R, Theodoropoulou N, Dobson J, Hebard A, Tan W. Synthesis and characterization of silica-coated iron oxide nanoparticles in microemulsion: The effect of nonionic surfactants. Langmuir. 2001;17:2900-2906. DOI: 10.1021/la0008636
- [35] Hingorani S, Pillai V, Kumar P, Multani MS, Shah DO. Microemulsion mediated synthesis of zinc-oxide nanoparticles for varistor studies. Materials Research Bulletin. 1993; 28:1303-1310. DOI: 10.1016/0025-5408(93)90178-G
- [36] Zarur A, Ying J. Reverse microemulsion synthesis of nanostructured complex oxides for catalytic combustion. Nature. 2000;403:65-67. DOI: 10.1038/47450
- [37] Vijaya Kumar R, Diamant Y, Gedanken A. Sonochemical synthesis and characterization of nanometer-size transition metal oxides from metal acetates. Chemistry of Materials. 2000;12:2301-2305. DOI: 10.1021/cm000166z
- [38] Guo J, Zhu S, Chen Z, Li Y, Yu Z, Liu Q, Li J, Feng C, Zhang D. Sonochemical synthesis of TiO₂ nanoparticles on graphene for use as photocatalyst. Ultrasonics Sonochemistry. 2011;18:1082-1090. DOI: 10.1016/j.ultsonch.2011.03.021
- [39] Mirzaei A, Neri G. Microwave-assisted synthesis of metal oxide nanostructures for gas sensing application: A review. Sensors and Actuators B: Chemical. 2016;237:749-775. DOI: 10.1016/j.snb.2016.06.114
- [40] Bilecka I, Djerdj I, Niederberger M. One-minute synthesis of crystalline binary and ternary metal oxide nanoparticles. Chemical Communications. 2008;7:886-888. DOI: 10.1039/B717334B
- [41] Brinker CJ, Scherer GW. Sol-Gel_Science_The_physics_and_chemistry_of_sol-gel_processing_-_Brinker_1990.pdfl; 1990. 462. DOI:10.1016/S0254-0584(02)00315-2
- [42] Kulkarni SK. Nanotechnology: Principles and Practices. 3rd ed. Chem: Springer; 2007. 103 p. DOI: 10.1007/978-3-642-227-6
- [43] Niederberger M, Pinna N. Metal oxide nanoparticles in organic solvents: Synthesis formation, assembly and application. London: Springer; 2009. DOI: 10.1007/978-1-84882-671-7
- [44] Niederberger M, Garnweitner G, Pinna N, Neri G. Non-aqueous routes to crystalline metal oxide nanoparticles: Formation mechanisms and applications. Progress in Solid State Chemistry. 2005;33:59-70. DOI: 10.1016/j.progsolidstchem.2005.11.032

- [45] Niederberger M, Garnweitner G, Ba J, Polleux J, Pinna N. Nonaqueous synthesis, assembly and formation mechanisms of metal oxide nanocrystals. International Journal of Nanotechnology. 2007;4:263-281. DOI: 10.1504/IJNT.2007.013473
- [46] Garnweitner G, Niederberger M. Nonaqueous and surfactant-free synthesis routes to metal oxide nanoparticles. Journal of the American Ceramic Society. 2006;89:1801-1808. DOI: 10.1111/j.1551-2916.2006.01005.x
- [47] Wu P, Xie R, Imlay K, Shang JK. Visible-light-induced bactericidal activity of titanium dioxide codoped with nitrogen and silver. Environmental Science & Technology. 2010;44:6992-6997. DOI: 10.1021/es101343c
- [48] Traversa E, Di Vona ML, Nunziante P, Licoccia S, Sasaki T, Koshizaki N. Sol-gel preparation and characterization of Ag-TiO₂ nanocomposite thin films. Journal of Sol-Gel Science and Technology. 2000;19:733-736. DOI: 10.1023/A:1008787412057
- [49] Cao X, Liu C, Hu Y, Yang W, Chen J. Synthesis of N/Fe comodified TiO₂ loaded on bentonite for enhanced photocatalytic activity under UV-Vis light. Journal of Nanomaterials. 2016;2016:1-11. DOI: 10.115/2016/8182190
- [50] Wu X, Yin S, Dong Q, Guo C, Kimura T, Matsushita J, Sato T. Photocatalytic properties of Nd and C codoped TiO₂ with the whole range of visible light absorption. Journal of Physical Chemistry C. 2013;117:8345-8352. DOI: 10.1021/jp402063n
- [51] Zhang H, Chen G. potent antibacterial activities of Ag/TiO₂ nanocomposite powders synthesized by a one-pot sol-gel method. Environmental Science & Technology. 2009; 43:2905-2910. DOI: 10.1021/es803450f
- [52] Zhao G, Kozuka H, Yoko T. Sol-gel preparation and photoelectrochemical properties of TiO₂ films containing Au and Ag metal particles. Thin Solid Films. 1996;277:147-154. DOI: 10.1016/0040-6090(95)08006-6
- [53] Eslami A, Amini MM, Yazdanbakhsh AR, Safari A, Asadi A. N, S co-doped TiO₂ nanoparticles and nanosheets in simulated solar light for photocatalytic degradation of nonsteroidal anti-inflammatory drugs in water: A comparative study. Journal of Chemical Technology and Biotechnology. 2016;91:2693-2704. DOI: 10.1002/jctb.4877
- [54] Liu JW, Han R, Wang HT, Zhao Y, Lu WJ, Wu HY, Yu TF, Zhang YX. Degradation of PCP-Na with La-B co-doped TiO₂ series synthesized by the sol-gel hydrothermal method under visible and solar light irradiation. Journal of Molecular Catalysis A: Chemical. 2011;**344**:145-152. DOI: 10.1016/j.molcata.2011.04.022
- [55] Lu N, Quan X, Li J, Chen S, Yu H, Chen G. Fabrication of boron-doped TiO₂ nanotube array electrode and investigation of its photoelectrochemical capability. Journal of Physical Chemistry C. 2007;**111**:11836-11842. DOI: 10.1021/jp071359d
- [56] Kumar SG, Devi LG. Review on modified TiO₂ photocatalysis under UV/visible light: Selected results and related mechanisms on interfacial charge carrier transfer dynamics. The Journal of Physical Chemistry. A. 2011;115:13211-13241. DOI: 10.1021/ jp204364a

- [57] Yu J, Zhou M, Cheng B, Zhao X. Preparation, characterization and photocatalytic activity of in situ N,S-codoped TiO₂ powders. Journal of Molecular Catalysis A: Chemical. 2006;**246**:176-184. DOI: 10.1016/j.molcata.2005.10.034
- [58] Cho IS, Lee CH, Feng Y, Logar M, Rao PM, Cai L, Kim DR, Sinclair R, Zheng X. Codoping titanium dioxide nanowires with tungsten and carbon for enhanced photoelectrochemical performance. Nature Communications. 2013;4:1723. DOI: 10.1038/ncomms2729
- [59] Obuya EA, Joshi PC, Gray TA, Keane TC, Jr WEJ. Application of Pt-TiO₂ nanofibers in photosensitized degradation of rhodamine B. International Journal of Chemistry. 2014;6:1-16. DOI: 10.5539/ijc.v6n1p1
- [60] Haick H, Paz Y. Long-range effects of noble metals on the photocatalytic properties of titanium dioxide. The Journal of Physical Chemistry. B. 2003;107:2319-2326. DOI: 10.1021/jp026940i
- [61] Epifani M, Giannini C, Tapfer L, Vasanelli L. Sol gel synthesis and characterization of Ag and Au nanoparticles. Journal of the American Ceramic Society. 2000;83:2385-2393. DOI: 10.1111/j.1151-2916.2000.tb01566.x
- [62] Pan X, Yang M-Q, Fu X, Zhang N, Xu Y-J. Defective TiO₂ with oxygen vacancies: Synthesis, properties and photocatalytic applications. Nanoscale. 2013;5:3601. DOI: 10.1039/ c3nr00476g
- [63] Bessekhouad Y, Robert D, Weber JV, Chaoui N. Effect of alkaline-doped TiO₂ on photocatalytic efficiency. Journal of Photochemistry and Photobiology A: Chemistry. 2004; 167:49-57. DOI: 10.1016/j.jphotochem.2003.12.001
- [64] Yang G, Yan Z, Xiao T, Yang B. Lowerature synthesis of alkalis doped TiO₂ photocatalysts and their photocatalytic performance for degradation of methyl orange. Journal of Alloys and Compounds. 2013;580:15-22. DOI: 10.1016/j.jallcom.2013.05.074
- [65] Xie H, Li N, Liu B, Yang J, Zhao X. Role of sodium ion on TiO₂ photocatalyst: Influencing crystallographic properties or serving as the recombination center of charge carriers? Journal of Physical Chemistry C. 2016;**120**:10390-10399. DOI: 10.1021/acs.jpcc.6b01730
- [66] Zhang J, Xu Q, Feng Z, Li M, Li C. Importance of the relationship between surface phases and photocatalytic activity of TiO₂. Angewandte Chemie, International Edition. 2008; 47:1766-1769. DOI: 10.1002/anie.200704788
- [67] Hoffmann MR. Effects of single metal-ion doping on the visible-light photoreactivity of TiO₂ effects of single metal-ion doping on the visible-light photoreactivity of TiO₂. Journal of Physical Chemistry C. 2010;**114**:783-792. DOI: 10.1021/jp908088x
- [68] Yu JC, Lin J, Kwok RWM. Ti1-xZrxO2 solid solutions for the photocatalytic degradation of acetone in air. The Journal of Physical Chemistry. B. 1998;102:5094-5098. DOI: 10.1021/ jp980332e
- [69] Wang J, Yu Y, Li S, Guo L, Wang E, Cao Y. Doping behavior of Zr4+ ions in Zr4+-doped TiO₂ nanoparticles. Journal of Physical Chemistry C. 2013;117:27120-27126. DOI: 10.1021/ jp407662d

- [70] Bellardita M, Addamo M, Di Paola A, Palmisano L. Photocatalytic behaviour of metalloaded TiO₂ aqueous dispersions and films. Chemical Physics. 2007;**339**:94-103. DOI: 10.1016/j.chemphys.2007.06.003
- [71] Macías-Sánchez J, Hinojosa-Reyes L, Guzmán-Mar JL, Peralta-Hernández JM, Hernández-Ramírez A. Performance of the photo-Fenton process in the degradation of a model azo dye mixture. Photochemical & Photobiological Sciences. 2011;10:332-337. DOI: 10.1039/ C0PP00158A
- [72] Linsebigler AL, Linsebigler AL, Yates JT Jr, Lu G, Lu G, Yates JT. Photocatalysis on TiO₂ surfaces: Principles, mechanisms, and selected results. Chemical Reviews. 1995;95: 735-758. DOI: 10.1021/cr00035a013

Factor Affecting Geometry of TiO₂ Nanotube Arrays (TNAs) in Aqueous and Organic Electrolyte

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Additional information is available at the end of the chapter

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Abstract

TiO₂ nanotube arrays (TNA) have attracted scientific interest due to the combination of functional material properties with controllable nanostructure. Superior properties of TNA, including vectorial pathway of e^- transport, minimized e^- recombination, and high specific surface area render them as the most promising candidate for environment remediation, energy conversion and biocompatibility applications. The superior properties and efficacy of the TNA in various applications influenced by structural characteristics such as pore size, length and wall thickness. Therefore in this chapter the effect of various electrochemical parameters such as applied voltage, anodization time, electrolyte composition on the formation of controlled dimension of TNA in aqueous and organic electrolytes are reviewed.

Keywords: TiO₂ nanotube arrays (TNA), anodization, electrochemical parameters, aqueous electrolyte, organic electrolytes

1. Introduction

Within the last decade, nanoscale and nanostructured metal oxide materials have strongly influenced numerous fields in science and technology. Among the various nanostructured oxide materials, TiO₂ nanotube arrays (TNA) have received special attention due to its enhanced properties, cost-effective fabrication and higher surface-to-volume ratio [1]. TNA offers unique properties and a high functionality for various applications such as photocatalysis [2, 3], solar cell [4–6], biomedical [7, 8], and sensors [9, 10]. Their performance in various applications significantly determined by geometry, shape, and morphology of nanostructures [11]. In this concern, a

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defined arrangement and a vertical and homogeneous alignment over the entire substrate surface, based on the self-organized anodic oxidation is pursued. Electrochemical anodization is widely used because of its controllable, reproducible results and simplicity of the process. The feasibility to tune the size and shape of nanotubular arrays to the desired dimensions and meeting the demands of specific applications by means of controlled anodic oxidation of the metal substrate have widen the application of TNA. Furthermore, it is a cost-effective method and the tubes prepared via this method have good adherent strength.

2. Factor affecting geometry and composition of TNA

The anodic growth of self-organized tubular structure is well known as the equilibrium reaction between electrochemical oxidation at the metal/electrolyte interface and chemical dissolution at the oxide/electrolyte interface [12, 13]. The structural characteristics of the nano-tube arrays can be controlled through various synthesis parameters, including applied potential [14–16], anodization time [14, 17, 18], electrolyte type and chemical composition [12, 13, 19]. Therefore, this section provides a comprehensive review on the influence of aforementioned parameters on the formation of TNA.

2.1. TNA synthesis using aqueous electrolytes

Gong and co-workers [20] first obtained self-organized, highly-uniform TNA by anodizing Ti in aqueous electrolyte containing 0.5 wt% HF under applied potential of 10–20 V. The pore size increased with increasing applied potential while the nanotube length was dependent on the anodization time. Titanium undergoes electrochemical oxidation process as follow: Ti + 2H₂O \rightarrow TiO₂ + 4H⁺ (Reaction 1) and chemical dissolution process: TiO₂ + 6HF \rightarrow [TiF₆]²⁻ +2H₂O + 2H⁺ (Reaction 2) to form nantubular structure. However, the length of nanotubes was limited to a maximum of ~500 nm, due to the restriction imposed by high chemical dissolution of formed oxide by strong acidity of HF aqueous electrolyte, *c.a.*, pH < 2 [14, 21]. The chemical dissolution (Reaction 2). The model proposed by Macak and co-workers suggest that F⁻ and H⁺ are attracted toward the pore bottom during anodization (**Figure 1a**), followed by establishment of pH profile as in (**Figure 1b**). The variation in pH profile triggers different degree of dissolution rate along the tube inner surface (**Figure 1c**).

This work directly leads to the use of buffer solution as electrolyte to control pH and increase the length of nanotube produced. Reaction 2 permits the dissolution reaction and become the core foundation of field-assisted dissolution model. Since then, many authors have adapted the dissolution process into their research framework such that field-assisted dissolution model is gradually established for TNA anodization [22–24].

Large number of F^- and H^+ ions in HF aqueous electrolyte dominates high chemical dissolution and thus hinders the equilibrium growth of the nanotube arrays [12]. Beranek et al. [25] found that the incorporation of low concentration of HF aqueous electrolyte with acetic acid



Figure 1. (a) Schematic diagram to illustrate the presence of NH_4^+ and F^- that creates a local acidification, (b) pH profile within the nanotube, (c) rate of dissolution of the tube.

 (H_2SO_4) addition could reduce the chemical dissolution, and thus allows the formation of porous TiO₂ with improved structural morphologies. This basis was later used to obtain TNA with well-defined tubular structure over applied potential range of 10–25 V [14]. The nanotube length and pore diameter increased linearly with increasing applied potential. In summary, the structural morphologies of anodic growth oxides can be controlled by the acidity of electrolyte [26].

Macak et al. [12] investigated the influence of the electrolyte acidity on the growth of nanotube arrays using HF, potassium fluoride (KF) and sodium fluoride (NaF) as F⁻ sources. TNA with ~280 nm long and ~40 nm pore diameter were formed in strong acidity (pH < 1) HF aqueous electrolyte after 2 h of anodization at 10 V. The increase in the pH value of electrolyte to 1.3 and 2.8 by using KF and NaF instead of HF resulted in the formation of TNA with the nanotube length of ~320 and 590 nm, respectively. TNA with a maximum length of 1.5 μ m were achieved at 25 V. Moreover, the nanotube length is proportional to the anodization time, and thus resulted in the formation of nanotube arrays with length of ~800 nm, ~1.8 μ m and ~2.3 μ m after exposure for 20, 60 and 90 h in electrolyte with pH of 3.8. It is interesting to note that the acidity of electrolyte plays an essential role for the growth of long nanotube arrays instead of

the anodization time. The increase of pH value from 3.8 to 4.5 resulted in significant increase in the nanotube length from ~800 nm to ~4.4 μ m after anodization at 10 V for 20 h.

The significance of the pH value of an electrolyte on the growth of TNA was proven by Bauer et al. [27]. Self-organized TNA was successfully formed in 1 M H_3PO_4 containing 0.3 wt% HF over applied potential range from 1 V to 25 V. Weak acidity of H_3PO_4 governs the local acidification during pore growth, and thus allowed the control of nanotube geometry over wide range of applied potential [12]. In 2007, Allam and Grimes [28] demonstrated an alternative method to fabricate TNA using hydrochloride (HCl) instead of fluoride-containing electrolyte. The anodization in 3 M HCl aqueous electrolyte at 20 V for 20 min allowed the formation of TNA with the nanotube length of ~600 nm. However, high chemical dissolution of aqueous electrolytes still remains as significant restriction in achieving long nanotubes with smooth walls. This limitation of forming long TNA in aqueous electrolyte has extended the use organic electrolyte to reduce the chemical dissolution process.

2.2. TNA synthesis using organic electrolytes

An organic electrolyte is known as efficient solvent in anodic fabrication of highly-ordered selforganized porous alumina (Al₂O₃) at high applied potential, *c.a.*, 100 V [29, 30]. The incorporation of organic component from the electrolyte into anodic oxide film is known to lower the relative permittivity of oxide and increase its dielectric breakdown potential [18], thereby allowing the anodic growth of oxide film under wide range of applied potential [13, 31].

2.2.1. Dimethyl sulfoxide (DMSO)

Ruan et al. [19] demonstrated the anodic growth of TNA in fluorinated dimethyl sulfoxide (DMSO) and ethanol (EtOH) mixture. Well-aligned TNA with 2.3 μ m in length were formed by anodization in 1:1 DMSO and EtOH mixture containing 4 wt% HF at 20 V for 70 h. DMSO is a dipolar aprotic solvent. Unlike protic solvents, aprotic solvents do not have a hydrogen atom directly bonded to an electronegative atom, such as oxygen or nitrogen. DMSO has a very weak ability to donate protons (hydrogen bond donation) and it is more basic than water, implying that DMSO has a protophilic nature [21]. DMSO accepts the hydrogen proton from HF and thus allows the formation of long nanotubes by the reduction of the chemical dissolution. However, the donation of oxygen in organic electrolyte is more difficult than aqueous electrolyte, and thus limited the nanotube length even after long anodization time. Discrete nanotube arrays obtained in 1:1 DMSO and EtOH mixture exhibited fourfold higher photocurrent density as compared to that formed in aqueous electrolyte [20]. This reveals the potential of organic electrolyte for the formation of long TNA for superior photoelectrochemical properties. The nanotube length was later increased up to 93 μ m by anodization in DMSO containing 2 wt% HF at 60 V for 70 h refer to Figure 2a-d [13, 15].

To enhance the oxidation rate in organic electrolyte, water usually serves as a source of O^{2-} and hydroxyl ion; OH^{-} [13, 15]. Several authors reported that small amount of water addition could improve the adhesion between the nanotube and underlying oxide barrier layer. This facilitates the growth of long nanotubes [32, 33]. Large amount of water addition however

Factor Affecting Geometry of TiO₂ Nanotube Arrays (TNAs) in Aqueous and Organic Electrolyte 121 http://dx.doi.org/10.5772/intechopen.74193



Figure 2. (a) Cross-sectional, (b) magnified-cross sectional, (c) surface and (d) pore bottom morphologies of TNA grown in DMSO containing 2 wt% HF at 60 V for 70 h [19].

decreased the viscosity of electrolyte [3, 34], leading to high chemical dissolution by the higher diffusion rate of reactant ions [35]. The minimum amount of water less than 5 wt% limits the chemical dissolution and thus allows the nanotube to grow deeply into the metal without significant loss at the pore mouth. Besides, thinner barrier layer in such condition allows greater ionic conduction and faster movement of the metal/oxide interface into the metal, thus producing long TNA [13, 32].

The significance of anodization parameters, including applied potential, F^- concentration, water content and anodization time on the structural characteristics of TNA were extensively investigated by Yoriya et al. [33] and the finding are presented in **Figure 3a-e**. Higher applied potentials provide a greater driving force for both electronic and ionic conduction and thus allow the growth of long nanotube arrays. A maximum length of TNA of 101 μ m was achieved by anodic growth in DMSO containing 2 wt% HF at 60 V for 70 h.

Figure 3b reveals that 2 wt% HF concentration allowed the formation of longest nanotube at both 40 and 60 V. HF concentration higher than 2% greatly increases the chemical dissolution, and thus reduces nanotube length. Furthermore, chemical dissolution is relatively lower than electrochemical oxidation in DMSO electrolyte containing less than 2 wt% HF, resulting in the formation of short nanotubes. The addition of H₂O facilitates the extraction of O^{2–} and OH[–]



Figure 3. Variation of TiO_2 nanotube array length as a function of (a) applied voltage for a 70 h anodization using DMSO containing 2% HF with and without a pre-anodization step to template the surface, (b) HF concentration in DMSO for 40 and 60 V 70 h anodization, (c) variation of nanotube length obtained from a 2.0% HF-DMSO containing different deionized water concentrations (40 V, 40 h), and (d) duration for a 40 V anodization in 2.0% HF-DMSO electrolytes with 0, 3, and 5% deionized water content [33].

from electrolyte to form oxide, contributing to the formation of long nanotube with thick walls. However, high H₂O amount (> 2 wt%) dominates chemical dissolution and thus reduces the nanotube length (**Figure 3c**). **Figure 3d** shows that nanotube length increased up to 70 h and then decreased continuously. The shorter nanotube length after 70 h is caused by slow diffusion of F^- , due to the accumulation of reaction products at the tube bottom, as well as significant loss at atop of nanotube by high chemical dissolution [5, 13].

2.2.2. Amide – Formamide (FA) and N-methylformamide (NMF)

Formamide (FA) and *N*-methylformamide (NMF) have been used as electrolyte for fabricating long nanotubes with high growth rate [15]. FA and NMF are both protophilic like DMSO, meaning that their acidity nature is weaker than water [21]. The dielectric constant of FA and NMF are 111 and 182.4, respectively, which are much higher than water; ~78.39. Higher dielectric constant of electrolyte induces more charges on the oxide layer and thus improves

the extraction of Ti⁴⁺ ions, and facilitates the dissolution of HF for it to be chemically available at the oxide/electrolyte interface [13]. Paulose et al. [15] fabricated TNA of ~69 μ m long in FA electrolyte containing 0.27 M NH₄F at 35 V for 48 h. It is noticeable that the growth rate increased to ~24.3 nm min⁻¹, which is relatively higher than that formed in DMSO [19] or aqueous electrolyte [36]. Shankar et al. [13] further investigated the influence of applied potential at 20–30 V, and NH₄F concentration in the range of 0.11– 0.37 M. The nanotube length and pore size increase with increasing applied potential and concentration of NH₄F, achieving a maximum length of ~78 μ m in FA containing 0.37 M NH₄F. Besides, the incorporation of high polarity electrolyte, NMF into FA also accelerates the chemical dissolution and thus results in nanotubes with larger pore size.

2.2.3. Glycerol

The diffusion of ionic species in electrolyte greatly affects the growth of TNA by local acidification at the pore bottom [12]. Macak and colleagues [34] investigated the influence of electrolyte viscosity on the formation of TNA by anodization in various types of electrolyte; 1 M ammonium sulfate [(NH₄)₂SO₄] containing 0.5 wt% NH₄F, 1:1 glycerol and H₂O mixture containing 0.5 wt% NH₄F, and glycerol containing 0.5 wt% NH₄F. The viscosities of these electrolytes were ~0.001, ~0.004 and ~1.5 Pa.s, respectively. The anodization in (NH₄)₂SO₄ electrolyte allowed the formation of TNA with length of ~2 µm while the anodization in glycerol electrolyte resulted in nanotube arrays with ~1.3 µm in length. However, the incorporation of large amount of water leads to the presence of ripples at the nanotube walls, resulting from high chemical dissolution in electrolyte. The nanotube length formed in glycerol-based electrolyte increases almost linearly with increasing anodization time, and achieved ~6.1 µm after anodization at 20 V for 18 h.

The viscosity of electrolyte can be also affected by anodization temperature [34, 37]. The viscosity of glycerol containing 0.5 wt% NH₄F decreases from 12 Pa.s to 1.5 and 0.3 Pa.s by increasing temperature from 0°C to 20 and 40°C, respectively. Low viscosity facilitates the diffusion of reactants at the pore tip, resulting in long nanotube with large pore. As mentioned earlier, the incorporation of organic species from organic electrolyte into the oxide film during anodization allows the growth of nanotube arrays under a wide range of applied potential. Alivov et al. [31] investigated the formation behavior of TNA in a broad range of applied potential of 5–350 V and F⁻ concentration of 0.1–0.7 wt%. TNA were formed in glycerol under applied potential of 10–240 V, and the applied potential is disproportional to F⁻ concentration.

2.2.4. Ethylene glycol (EG)

The anodization in high viscosity (μ_v) electrolyte of about 945 cP at 25°C resulted in relatively shorter nanotube length as compared to that formed in aqueous electrolyte. Hence, the potential of low viscosity polyol solvent, such as ethylene glycol (EG, $\mu_v = 16$ cP at 25°C) for the formation of TNA was investigated by [34]. TNA with ~1.6 µm in length were obtained by anodization in EG containing 0.5 wt% NH₄F at 12 V for 3 h. The significant increase in the nanotube length in EG-based electrolyte could be attributed to lower diffusion resistance in electrolyte with lower viscosity [21]. The potential of EG as efficient electrolyte was later confirmed by [32]. The anodization in EG containing 0.25 wt% NH₄F at 60 V allowed the rapid formation of nanotube arrays with the growth rate up to 131.4 nm min⁻¹. The resulting nanotube arrays exhibited length of 134 μ m and pore size of 25 nm after 17 h of anodization. The nanotube length was further increased to 220 μ m by anodization in EG containing 0.3 wt% NH₄F and 2 wt% H₂O [13], implying the significant role of H₂O addition on the growth of long nanotube arrays.

The influences of anodization parameters, including H_2O content, NH_4F concentration, applied potential and anodization time on the growth of TNA in EG-based electrolytes were systematically investigated by Prakasam et al. [35]. The increase in the H_2O content and NH_4F concentration stimulate electrochemical oxidation at the metal/oxide interface and chemical dissolution at the oxide/electrolyte interface, resulting in longer nanotube length up to 220 µm by anodization in EG containing 2 wt% H_2O and 0.3 wt% NH_4F . Further increase of water content and NH_4F concentration leads to disequilibrium reaction between electrochemical oxidation and chemical dissolution and thus resulted in shorter nanotube in the range of 54–136 µm (**Table 1**).

In the presence of optimum H_2O content, O^{2-} and/or OH^- are injected into the body of the oxide layer, and affect the structure efficiently to impede the ionic transport at barrier layer [38]. This greatly accelerates the inward movement of the metal/oxide interface into the metal surface and thus resulting in long nanotubes with thick walls. Higher content of H_2O largely increases the number of extracted oxygen and/or hydroxyl ions per unit area of the oxide layer, leading to higher chemical dissolution. The increase in the F^- concentration provides higher chemical dissolution at the oxide/electrolyte interface, thereby allowing higher number of ion migrate across thin barrier layer. This resulted in the formation of long nanotube with thin walls. However, high chemical dissolution in electrolyte containing high F^- concentration induces a significant loss from the pore mouth and thus formed short nanotubes.

The anodic growth of TNA in used electrolyte significantly increased the nanotube length. Lower electrical conductivity of used electrolyte hinders ionic migration across barrier layer, thereby reducing loss at the pore tip by high chemical dissolution. Inner and outer diameters and nanotube length were found to increase with increasing applied potential from 20 V to 60 V (**Table 2**). Further increase of applied potential to 65 V resulted in further increase in inner and outer diameters but decreased the nanotube length. This implies a significant loss at the pore tip by high chemical dissolution under applied potential higher than 60 V. The anodization time is

| | | 0.1 wt% HN4F | 0.3 wt% HN4F | 0.5 wt% HN4F |
|-------------|-------|--------------|--------------|--------------|
| 1 % Val H-O | Fresh | 54 | 67 | 47 |
| 1 % V01 H2U | Used | 70 | 156 | 115 |
| 2.0/ WalthO | Fresh | 85 | 165 | 106 |
| 2 % V01 H2U | Used | 105 | 220 | 45 |
| 2 % Val H-O | Fresh | - | 136 | 85 |
| 5 % V01 H2U | Used | - | 100 | 66 |

Table 1. Summary of nanotube length (in μ m) obtained by varying the concentration of H₂O of 1–3 wt%, and NH4F of 0.1–0.5 wt% in EG with respect to fresh and once-used solution [35].

| Voltage | Inner diameter | Outer diameter | Length |
|---------|----------------|----------------|--------|
| (V) | (nm) | (nm) | (mm) |
| 20 | 45 | 65 | 5 |
| 40 | 70 | 115 | 30 |
| 50 | 90 | 140 | 45 |
| 60 | 105 | 155 | 165 |
| 65 | 135 | 185 | 105 |

Table 2. Summary of nanotube inner diameter, outer diameter and length obtained by anodization in fresh-EG containing 2 and 0.3 wt% NH_4F at different applied potential for 17 h [35].

also an important available. The nanotube length increased with increasing anodization time, and achieved a maximum of 360 μ m at 96 h. The growth rate was found as 241.7 nm min⁻¹ at 4 h. It decreased exponentially and reached a minimum of 62.5 nm min⁻¹ at 96 h. Paulose and co-workers [15] later achieved the formation of ultra-long TNA with 1000 μ m in length by anodization in EG containing 3.5 wt% H₂O and 0.6 wt% NH₄F at 60 V for 216 h.

2.2.5. Polyol – Diethylene glycol (DEG), triethylene glycol (TEG), polyethylene glycol (PEG)

The investigation of organic electrolyte was extended to several types of polyol solvents, for example diethylene glycol (DEG), triethylene glycol (TEG) and polyethylene glycol (PEG) in comparison to EG [39]. Large amount of oxy and hydroxyl groups in TEG and PEG allows higher self-association via intra- and intermolecular hydrogen bonds, and consequently forms anatase crystallite by bridging the oxygen atom and hydroxyl groups in TiO₂. However, their high viscosity and molecular weight retard the growth of nanotubes, and thus does not satisfy the requirement of practical applications. In 2010, Sreekantan et al. [3] demonstrated extremely fast-formation of TNA with approximately \sim 15 µm in length by anodization in EG containing excessive-fluoride 0.5 wt% NH₄F and 1 wt% H₂O. The nanotubes were formed with high growth rate up to 308.3 nm min⁻¹. However, high chemical dissolution in EG containing excessive-fluoride limits the anodization time at 1 h. Recently, the addition of alkali species appears as alternative approach to improve the balance between electrochemical oxidation and chemical dissolution. The incorporation of sodium carbonate (NaCO₃) into EG allowed the rapid growth of TNA with the growth rate up to 1 μ m min⁻¹ [40]. It is noteworthy that the anodic growth of TNA in EG is only method that induces the carbon species into the nanotube through the pyrogenation of ethylene (C_2H_2) in EG [41], thereby enabling visible-light absorption [42] without urther processing [43, 44].

3. Conclusion

TNA is by far among the most investigated functional metal oxide. The possibility of growing porous anodic nanostructure, particularly self-organized and highly-ordered TNA through anodization has further enlarged the research interest on this TNA due to specific advantages, such as large surface area, relatively long electron diffusion length and biocompatibility. In this

chapter, the formation of TNA and various parameters, which affects the tube formation and properties of TNA were discussed. The tube length, thickness, and diameter were varied according to the pH, electrolytes, anodization potential, and time. Today, TNA are used as solar cell, self-cleaning coating, orthopedic and dental implants, and also an effective drug delivery carrier for the cancer therapy.

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Conflict of interest

There is no conflict of interest in this chapter.

Author details

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References

- Zhao J, Wang X, Li L. Electrochemical fabrication of well-ordered titania nanotubes in H₃PO₄/HF electrolytes. Electronics Letters. 2005;41:771-772. DOI: 10.1049/el:20051328
- [2] Saharudin KA, Sreekantan S, Lai CW. Fabrication and photocatalysis of nanotubular C-doped TiO₂ arrays: Impact of annealing atmosphere on the degradation efficiency of methyl orange. Materials Science in Semiconductor Processing. 2014;20:1-6. DOI: 10.1016/j. mssp2013.12.019

- [3] Sreekantan S, Saharudin KA, Lockman Z, Tzu TW. Fast-rate formation of TiO₂ nanotube arrays in an organic bath and their applications in photocatalysis. Nanotechnology. 2010; 21:365603. DOI: 10.1088/0957-4484/21/36/365603
- [4] Park H, Kim W-R, Jeong H-T, Lee J-J, Kim H-G, Choi W-Y. Fabrication of dye-sensitized solar cells by transplanting highly ordered TiO₂ nanotube arrays. Solar Energy Materials and Solar Cells. 2011;95:184-189. DOI: 10.1016/j.solmat.2010.02.017
- [5] Roy P, Berger S, Schmuki. TiO₂ nanotubes: Synthesis and applications. Angewandte Chemie. 2011;50:2904-2939. DOI: 10.1002/anie.201001374
- [6] Alivov Y, Fan ZY. Dye-sensitized solar cells using TiO₂ nanoparticles transformed from nanotube arrays. Journal of Materials Science. 2010;45:2902-2906. DOI: 10.1007/s10853-010-4281-2
- [7] Saharudin KA, Sreekantan S, Abd Aziz S, Hazan R, Lai CW, Mydin R. Surface modification and bioactivity of anodic Ti₆Al₄V alloy. Journal of Nanoscience and Nanotechnology. 2013;13:1696-1705. DOI: 10.1166/jnn.2013.7115
- [8] Lin Z, Lee G-H, Liu C-M, Lee I-S. Controls in wettability of TiOx films for biomedical applications. Surface and Coatings Technology. 2010;205:S391-S3S7. DOI: 10.1016/j. surfcoat.2010.08.052
- [9] Mun K-S, Alvarez SD, Choi W-Y, Sailor MJ. A stable, label-free optical interferometric biosensor based on TiO₂ nanotube arrays. ACS Nano. 2010;4:2070-2076. DOI: 10.1021/ nn901312f
- [10] Kwon Y, Kim H, Lee S, Chin I-J, Seong T-Y, Lee WI, et al. Enhanced ethanol sensing properties of TiO₂ nanotube sensors. Sensors and Actuators B: Chemical. 2012;173:441-446. DOI: 10.1016/j.snb.2012.07.062
- [11] Peighambardoust N-S, Nasirpouri F. Manipulating morphology, pore geometry and ordering degree of TiO₂ nanotube arrays by anodic oxidation. Surface and Coatings Technology. 2013;235:727-734. DOI: 10.1016/j.surfcoat.2013.08.058
- [12] Macak JM, Tsuchiya H, Schmuki P. High-aspect-ratio TiO₂ nanotubes by anodization of titanium. Angewandte Chemie. 2005;44:2100-2102. DOI: 10.1002/anie.200462459
- [13] Shankar K, Mor GK, Prakasam HE, Yoriya S, Paulose M, Varghese OK, et al. Highlyordered TiO₂ nanotube arrays up to 220 μm in length: Use in water photoelectrolysis and dye-sensitized solar cells. Nanotechnology. 2007;18:065707. DOI: 10.1088/0957-4484/18/6/ 065707
- [14] Cai QY, Paulose M, Varghese OK, Grimes CA. The effect of electrolyte composition on the fabrication of self-organized titanium oxide nanotube arrays by anodic oxidation. Journal of Materials Research. 2005;20:230-236. DOI: 10.1557/JMR.2005.0020
- [15] Paulose M, Prakasam HE, Varghese OK, Peng L, Popat KC, Mor GK, et al. TiO₂ nanotube arrays of 1000 μm length by anodization of titanium foil: Phenol red diffusion. The Journal of Physical Chemistry C. 2007;**111**:14992-14997. DOI: 10.1021/jp075258r

- [16] Lockman Z, Ismail S, Sreekantan S, Schmidt-Mende L, MacManus-Driscoll JL. The rapid growth of 3 µm long titania nanotubes by anodization of titanium in a neutral electrochemical bath. Nanotechnology. 2010;21. DOI: 10.1088/0957-4484/21/5/055601
- [17] Wan J, Yan X, Ding J, Wang M, Hu K. Self-organized highly ordered TiO₂ nanotubes in organic aqueous system. Materials Characterization. 2009;60:1534-1540. DOI: 10.1016/j. matchar.2009.09.002
- [18] Antony RP, Mathews T, Dash S, Tyagi AK, Raj B. X-ray photoelectron spectroscopic studies of anodically synthesized self aligned TiO₂ nanotube arrays and the effect of electrochemical parameters on tube morphology. Materials Chemistry and Physics. 2012; 132:957-966. DOI: 10.1016/j.matchemphys.2011.12.041
- [19] Ruan C, Paulose M, Varghese OK, Mor GK, Grimes CA. Fabrication of highly ordered TiO₂ nanotube arrays using an organic electrolyte. The Journal of Physical Chemistry B. 2005;109:15754-15759. DOI: 10.1021/jp052736u
- [20] Gong D, Grimes CA, Varghese OK, Hu WC, Singh RS, Chen Z, et al. Titanium oxide nanotube arrays prepared by anodic oxidation. Journal of Materials Research. 2001;16: 3331-3334. DOI: 10.1557/JMR.2001.0457
- [21] Mohamed AER, Rohani S. Modified TiO₂ nanotube arrays (TNTAs): Progressive strategies towards visible light responsive photoanode, a review. Energy & Environmental Science. 2011;4:1065-1086. DOI: 10.1039/C0EE00488J
- [22] Taveira LV, Macák JM, Tsuchiya H, Dick LFP, Schmuki P. Initiation and growth of selforganized TiO₂ nanotubes Anodically formed in NH₄F/(NH₄)₂SO₄ electrolytes. Journal of the Electrochemical Society. 2005;**152**:B405. DOI: 10.1149/1.2008980
- [23] Yasuda K, Schmuki P. Control of morphology and composition of self-organized zirconium titanate nanotubes formed in (NH₄)₂SO₄/NH₄F electrolytes. Electrochimica Acta. 2007;52:4053-4061. DOI: 10.1016/j.electacta.2006.11.023
- [24] Ghicov A, Schmuki P. Self-ordering electrochemistry: A review on growth and functionality of TiO₂ nanotubes and other self-aligned MOx structures. Chemical Communications. 2009:2791-2808. DOI: 10.1039/B822726H
- [25] Beranek R, Hildebrand H, Schmuki P. Self-organized porous titanium oxide prepared in H₂SO₄/HF electrolytes. Electrochemical and Solid-State Letters. 2003;6:B12. DOI: 10.1149/ 1.1545192
- [26] Sreekantan S, Hazan R, Lockman Z. Photoactivity of anatase–rutile TiO₂ nanotubes formed by anodization method. Thin Solid Films. 2009;518:16-21. DOI: 10.1016/j.tsf.2009.06.002
- [27] Bauer S, Kleber S, Schmuki P. TiO₂ nanotubes: Tailoring the geometry in H₃PO₄/HF electrolytes. Electrochemistry Communications. 2006;8:1321-1325. DOI: 10.1016/j.elecom.2006. 05.030
- [28] Allam NK, Grimes CA. Formation of vertically oriented TiO₂ nanotube arrays using a fluoride free HCl aqueous electrolyte. The Journal of Physical Chemistry C. 2007;111: 13028-13032. DOI: 10.1021/jp073924i
- [29] Morita M, Shibata T, Yoshimoto N, Ishikawa M. Anodic behavior of aluminum in organic solutions with different electrolytic salts for lithium ion batteries. Electrochimica Acta. 2002;47:2787-2793. DOI: 10.1016/S0013-4686(02)00164-0
- [30] Ono S, Saito M, Asoh H. Self-ordering of anodic porous alumina formed in organic acid electrolytes. Electrochimica Acta. 2005;51:827-833. DOI: 10.1016/j.electacta.2005.05.058
- [31] Alivov Y, Pandikunta M, Nikishin S, Fan ZY. The anodization voltage influence on the properties of TiO₂ nanotubes grown by electrochemical oxidation. Nanotechnology. 2009; 20:225602. DOI: 10.1088/0957-4484/20/22/225602
- [32] Paulose M, Shankar K, Yoriya S, Prakasam HE, Varghese OK, Mor GK, et al. Anodic growth of highly ordered TiO₂ nanotube arrays to 134 μm in length. Journal of Physical Chemistry B. 2006;**110**:16179-16184. DOI: 10.1021/jp064020k
- [33] Yoriya S, Paulose M, Varghese OK, Mor GK, Grimes CA. Fabrication of vertically oriented TiO2 nanotube arrays using dimethyl sulfoxide electrolytes. The Journal of Physical Chemistry C. 2007;111:13770-13776. DOI: 10.1021/jp074655z
- [34] Macak JM, Schmuki P. Anodic growth of self-organized anodic TiO₂ nanotubes in viscous electrolytes. Electrochimica Acta. 2006;52:1258-1264. DOI: 10.1016/j.electacta.2006.07.021
- [35] Prakasam HE, Shankar K, Paulose M, Varghese OK, Grimes CA. A new benchmark for TiO₂ nanotube array growth by anodization. The Journal of Physical Chemistry C. 2007; 111:7235-7241. DOI: 10.1021/jp070273h
- [36] Cai Q, Yang L, Yu Y. Investigations on the self-organized growth of TiO₂ nanotube arrays by anodic oxidization. Thin Solid Films. 2006;515:1802-1806. DOI: 10.1016/j.tsf.2006. 06.040
- [37] Lee K, Kim D, Schmuki P. Highly self-ordered nanochannel TiO₂ structures by anodization in a hot glycerol electrolyte. Chemical Communications. 2011;47:5789-5791. DOI: 10.1039/C1CC11160D
- [38] Li Y-M, Young L. Non-thickness-limited growth of anodic oxide films on tantalum. Journal of the Electrochemical Society. 2001;148:B337-BB42. DOI: 10.1149/1.1386387
- [39] Allam NK, Grimes CA. Room temperature one-step polyol synthesis of anatase TiO₂ nanotube arrays: Photoelectrochemical properties. Langmuir : The ACS Journal of Surfaces and Colloids. 2009;25:7234-7240. DOI: 10.1021/la9012747
- [40] Wang D, Liu L, Zhang F, Tao K, Pippel E, Domen K. Spontaneous phase and morphology transformations of anodized titania nanotubes induced by water at room temperature. Nano Letters. 2011;11:3649-3655. DOI: 10.1021/nl2015262

- [41] An G, Ma W, Sun Z, Liu Z, Han B, Miao S, et al. Preparation of titania/carbon nanotube composites using supercritical ethanol and their photocatalytic activity for phenol degradation under visible light irradiation. Carbon. 2007;45:1795-1801. DOI: 10.1016/j.carbon.2007.04.034
- [42] Mohapatra S, Misra M, Mahajan V, Raja K. A novel method for the synthesis of titania nanotubes using sonoelectrochemical method and its application for photoelectrochemical splitting of water. Journal of Catalysis. 2007;**246**:362-369. DOI: 10.1016/j.jcat.2006.12.020
- [43] Park JH, Kim S, Bard AJ. Novel carbon-doped TiO₂ nanotube arrays with high aspect ratios for efficient solar water splitting. Nano Letters. 2006;6:24-28. DOI: 10.1021/nl051807y
- [44] Raja KS, Gandhi T, Misra M. Effect of water content of ethylene glycol as electrolyte for synthesis of ordered titania nanotubes. Electrochemistry Communications. 2007;9:1069-1076. DOI: 10.1016/j.elecom.2006.12.024

Recent Advances in TiO₂ Nanotube-Based Materials for Photocatalytic Applications Designed by Anodic Oxidation

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Additional information is available at the end of the chapter

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Abstract

This book chapter reports some spectacular and interesting 1D nanostructures of $TiO_{2'}$ which are grown by the anodic oxidation. Under suitable conditions, conventional onestep anodic oxidation is available to grow TiO_2 nanotube arrays (TNAs) and TiO_2 nanowires/nanotubes; meanwhile, two-step anodic oxidation allows fabricating some novel TNAs with spectacular morphologies such as highly ordered TNAs, bamboo-type TNAs, and lotus root-shaped TNAs. The formation mechanisms of these nanostructures during the anodic oxidation processes are elusive via studying effects of several key parameters such as oxidizing voltage, processing time, and electrolytes. In addition, the photocatalytic activity of the TNA-based nanomaterials is characterized by the degradation of pharmaceutical model, methylene blue, or the photoelectrochemical effect.

Keywords: TiO_2 nanotube arrays, anodic oxidation, formation mechanism, photocatalysts, PEC

1. Introduction

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Titanium dioxide (TiO₂) is the most widely used one for applications in photocatalysis, dyesensitized solar cells, and biomedical devices owing to some outstanding properties [1–8]. The fascinating properties like strong oxidizing abilities, chemical stability, nontoxicity, ease of preparation, favorable band-edge positions, water insolubility, multifaceted electronic properties, and super hydrophilicity. TiO₂ has three metastable phases of rutile, brookite, and anatase, in which rutile ($E_g = 3.0 \text{ eV}$) and anatase ($E_g = 3.2 \text{ eV}$) are the most commonly synthesized

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and used phases for applications. Rutile is the most stable phase for bulk $TiO_{2'}$ while it is anatase phase for nanoscale size crystallite TiO_2 due to surface energy effect [9]. Anatase can transfer into rutile by annealing temperatures in range of 500–700°C. Compared to rutile phase of $TiO_{2'}$ anatase generally possesses better photocatalytic activity owing to its wider bandgap (~3.2 eV), lower electron–hole recombination rate, and higher charge carrier mobility.

For many applications of TiO_{ν} it is crucial to maximize the specific surface area to enhance catalytic reactions and achieve a maximum overall efficiency. Therefore, nanoparticulated forms of TiO, are widely used [1]. Though providing high surface area, the charge carrier transport of nanoparticulated forms is limited due to the structural disorders. Instead, 1D TiO, nanostructures such as TiO, nanotube arrays (TNAs) and TiO, nanowires on nanotube arrays (NTWs/TNAs) are of great interests because of the higher control of the chemical or physical behavior. By diminishing dimensions to the nanoscale, TNAs and TNWs/TNAs not only provide large surface-to-volume ratio and unidirectional electrical channel but also may change the electronic properties owing to quantum size effects' strong contribution of surface reconstruction or surface curvature. Complex hybrid nanostructures such as TNWs/ TNAs [10], brush-type nanostructure [11], and bamboo-type TiO, nanotube [12] have been fabricated successfully by anodic oxidation, which have a great potential to simultaneously provide high surface area, good charge transport, and usually have better performance than simple nanostructures. It is worthy to mention that the form of nanostructured TiO₂ film on Ti substrate offers a great advantage that it is able to retrieve after usage in photocatalytic applications. TiO₂ nanotubes were readily fabricated by template-assisted processes, hydrothermal method, and electrochemical anodic oxidation [1, 3, 6, 13]. Among these methods, TNAs prepared by electrochemical anodization are simple, cost-effective, recyclable, suitable for rapid production, and notable to yield uniform TNAs with vertical alignment and diverse morphology [1, 6, 10, 14, 15].

This book chapter provides some of the spectacular and surprising 1D nanostructures of TiO₂ prepared by anodic oxidation method for photocatalytic applications. The first section will focus exclusively on the growths of self-organized TNAs and TNWs/TNAs using conventional one-step anodic oxidation as well as their photocatalytic performances. The second section will review some novel modified TNA structures fabricated by two-step anodic oxidation, including highly ordered TNAs, the modified TNAs, and their photoelectrochemical water splitting performance.

2. One-dimensional nanostructured $\mathrm{TiO}_{\rm 2}$ grown by one-step anodic oxidation

2.1. TiO, nanotube arrays (TNAs): formation mechanism and photocatalytic activity

In 1999, Zwilling and coworkers reported the first self-organized anodic oxides on titanium in chromic acid electrolytes containing hydrofluoric acid [16]. In this work, an organized nano-tube layer with thickness up to approximately 500 nm was grown on a Ti sheet at low voltage.

However, the tube structure was not highly organized, and the tubes showed considerable sidewall inhomogeneity [16]. Moreover, the thickness of TNA layer did not increase with anodizing time, and the limited thickness was ascribed to an oxide growth/chemical dissolution equilibrium (steady state).

Figure 1 illustrates the setup of an anodic anodization process in our experiments that is also a typical process in the literature. Titanium foils (99.9% purity, 0.5 mm thickness) are used as the substrate for growing 1D nanostructures of TiO_2 . Prior to anodization, Ti foil was ultrasonically cleaned in acetone, methanol, and deionized water (each solvent 10 min) and then dried by a purging N₂ gas. The TNA film area on Ti foil is 1 × 1.5 cm. The anodization is carried out at room temperature using a two-electrode system with the Ti foil as an anode and a stainless steel foil (SS304 or platinum plate for researches) as a cathode. The electrolytes consisted of 0.5 wt% NH₄F in solution of ethylene glycol and water (99:1 in wt.%). The applied voltage of 30–60 V and anodizing time of 0.5–6 hrs are usually used.

2.1.1. Formation mechanism of TiO₂ nanotubes

TNA growth is driven by two simultaneously occurring reactions in the anodization process: (1) the electric field-driven anodic oxidation of Ti to form TiO_2 and (2) the electric field-assisted chemical dissolution of the TiO_2 layer [8, 14]. The reactions are given below:

Anodic reaction:
$$Ti + 2H_2O - 4e = TiO_2 + 4H^+$$
 (1)

Cathodic reaction:
$$4H^+ + 4e = 2H_2$$
 (2)

Chemical etching (dissolution) reaction: $TiO_2 + 6F^- + 4NH_4^+ = TiF_6^{2-} + 2H_2O$ (3)



Figure 1. A schematic of an electrochemical anodization process.

In the anodic oxidation process, the current density (j) changes with anodizing time (t). **Figure 2(a)** illustrates the current transient curve recorded during the anodization of titanium foil. Initially, the current density rapidly decreases, then slightly increases, and finally remains a constant [1]. According to the variations of current density with reaction time, three stages of the TNA growth process were defined as shown in **Figure 2(a)**. In the early stages (I), the current density rapidly decreases because of the formation of the non-conductive thin oxide layer (see also **Figure 2(b)**). Next, there is a slight increase in the current density owing to the local growth of pits. Finally, the current density remains a constant due to reaching the balance between field-assisted anodic oxidation and chemical-/ field-assisted dissolution current, and the initial pits will grow and develop into nanotube arrays. Notably, the diameter and length of the nanotubes gradually increase when the dissolution rate of the wall of the nanopores is slower than that of the growth rate of nanopores. And, the diameter and length of NTs no longer change when the growth rate is equal to the dissolution rate [17].

2.1.2. An application of TiO_2 nanotubes in photoelectrocatalytic degradation of model environmental pharmaceuticals

A selected optimal TiO_2 nanotube was prepared at 30 V for 16 h in ethylene glycol solution containing 0.20 mol L⁻¹ NH₄F and 0.50 mol L⁻¹ HAc. **Figure 3(a)** shows structure-morphology of the TNAs through the FESEM and HRTEM images. Clearly, perfect NTAs are obtained with average inner diameter approximately 70 nm length of about 7.5 µm. TNAs have anatase phase which is confirmed by the selected area electron diffraction pattern recorded from the circled area. In addition, the lattice fringes spacing of 0.352 nm corresponds to {101} planes of anatase TiO₂. To evaluate the photocatalytic activity of the TNA photoanodes, the authors



Figure 2. (a) Typical current–time (j-t) characteristics after applied voltage in the absence (---) and presence (—) of fluoride ions in the electrolyte. Either compact oxide (fluoride free) or porous/tubular metal oxide formation (containing fluoride) formed by different morphological stages (I–III). The growth process of TiO₂ nanotube arrays (TNAs): (b) non-conductive thin oxide layer forming, (c) local growth of the pits, and (d) growth of the semicircle pores and developed nanotube arrays. (e) a typical TNA prepared by using an electrolyte consisting of ethylene glycol and water (99:1 in wt%) with 0.5 wt% NH₄F, at 30 V for 30 mins.

Recent Advances in TiO₂ Nanotube-Based Materials for Photocatalytic Applications Designed... 135 http://dx.doi.org/10.5772/intechopen.77063



Figure 3. TiO_2 nanotubes prepared at 30 V for 16 h in ethylene glycol solution containing 0.50 Mol L⁻¹ HAc and 0.20 Mol L⁻¹ NH₄F: (a) FESEM image and a HRTEM image of nanotube wall (inset), (b) degradation of acyclovir under different processes including electrolysis (EC), photocatalysis (PC), and photoelectrocatalysis (PEC) using the TiO₂ nanotube photoanode [17].

performed experiments using a model compound of pharmaceutical, acyclovir (20 mg L⁻¹), in a three-electrode thin layer photoelectrochemical reactor with a reaction volume of 100 μ L under UVA irradiation [17]. An aqueous solution containing 0.2 mol –¹ NaNO₃ and 20 mgL⁻¹ acyclovir was injected into the reactor under different constant speeds to adjust the reaction time. An applied potential of +1 V constant and illumination of 10 mWcm⁻² from UV-LED array were used for the PEC experiment. Photocatalysis (PC) and electrolysis (EC) degradation experiments were conducted under identical experimental conditions as photoelectrocatalysis (PEC) experiments, except the electrochemical system was disconnected and the light switched off, respectively [17].

Figure 3(b) presents the degradation of acyclovir under EC, PC, and PEC processes using the TNA photoanode. There was no measurable change in acyclovir concentration within residence time up to 370 s for the EC process. The degradation efficiencies of acyclovir in the PC process were 62.0 and 69.0% at residence times of 180 and 370 s, respectively. In comparison, the PEC degradation efficiencies increased remarkably to 83.0% at 180 s and 96.2% at 370 s. The significantly faster degradation of acyclovir for PEC process than those of PC and EC is attributed to two reasons: First, under an appropriate applied potential bias to the photoanode, it is enable to remove the photogenerated electrons and prolong the lifetime of photoholes for direct photohole reactions, and the oxidation power of the photoholes (3.1 V) is greater than that of photogenerated radicals such 'OH (2.8 V) [17]. Second, the light adsorption capability and charge transfer is enhanced owing to the tubular structure of the TNA photoanode. Thus, the separation of photogenerated electrons and holes assisted by the application of a potential bias is accelerated, which in turn enhances the concentration of photoholes and promotes effectively the degradation of acyclovir.

2.2. TiO, nanowires on nanotube arrays (TNWs/TNAs)

2.2.1. Fabrication of TiO, films and other experimental details

 TiO_2 films with morphology of TNWs/TNAs were grown on Ti foils by anodic oxidation. The electrolyte consists of ethylene glycol and water (99:1 in wt%) and 0.5 wt% NH₄F. First, the anodizing voltage was varied from 20 to 80 V at a fixed processing time of 1 h. Then, the anodizing time varied from 30 to 120 min at a fixed voltage of 40 V. After fabrication of the TNWs/TNAs, thermal annealing was performed in the air at 450°C for 2 h, at a heating rate of 2°C/min.

2.2.2. Effect of anodization voltage

Figure 4 shows the surface morphology of the TiO_2 films prepared at different anodizing voltages from 20 to 80 V, in a 0.5 wt% NH_4F solution, and at a constant anodizing time of 1 h. At 20 V, it exhibits highly ordered TNAs with a tube inner wall diameter of 40 nm and a wall thickness of 20 nm. Meanwhile, as increasing the voltage to 40 V, TNWs with a wire width ~50 nm appears on the top of TNAs which has tube diameters of 60 nm in diameter and ~10 nm in wall thickness. When the voltage increases to 60 V, TNWs with a width of ~20 nm fully covered on the TNAs with a tube diameter of 80 nm and a wall thickness of ~10 nm. Strikingly, TNW-free TNAs with a tube diameter of ~110 nm are obtained at a high voltage of 80 V [10].

2.2.3. Effect of anodization time

In order to explore the formation mechanism of TNWs/TNAs, we observe the morphology evolution of TiO₂ film as a function of anodizing time from 30 to 120 min at a fixed anodizing voltage of 40 V (Figure 5). At 30 min, a highly ordered TNA structure is obtained, and it has a tube length of 12.2 µm, diameter of 60 nm, and wall thickness of 18 nm. The steady-state growth rate of the TNA length at up to 30 min is ~0.4 µm/min. As further increasing the anodizing time to 35, 38, and 40 min, the surface morphology near the top of the TNA exhibits a gradual change. Indeed, the wall thickness decreases from 18 nm at 30 min to 12 nm at 35 min near the top of the TNAs due to the increased electrochemical etching with anodizing time. Noticeably, the wall thickness of the 35-min TNAs almost remains the same value of ~18 nm in the middle section of nanotubes (see the inset), implying that enhanced electrochemical etching occurs near the top of the nanotube mouths, with respect to the middle section. It is a transitional stage at 38 and 40 min, where the wall thicknesses are even thinner and especially the tubes start disintegrating. After 45 min, TNAs near the top surface are broken up, along with thinning of wall thickness down to ~10 nm. At 60 min, TNWs with a width of ~50 nm is covered on surface. The nanowires fell down on the top of the TNAs as its length is over $\sim 2 \,\mu$ m. At longer anodizing time of 90 and 120 min, TNWs are completely covered on the top of TNAs. Due to chemical etching, the width of TNWs decreased from 50 nm (at 60 min) down to ~30 nm (at 90 min) and then to ~20 nm (at 120 min). Moreover, as the time increase from 90 to 120 min, the nanowire structure emerges upon further etching, while the length of the TNAs is slightly increased from 11 μ m (90 min) to 12 μ m (120 min) [10].

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Figure 4. Anodizing voltage dependence of surface morphology for the TiO_2 films prepared by anodic oxidation at a constant anodizing time of 1 h [10].



Figure 5. Anodizing time dependence of surface morphology of the TiO_2 films prepared by anodic oxidation under at a constant anodizing voltage of 40 V [10].

The formation of TNWs/TNAs is governed by two key factors of (1) the strength of the electric field and (2) the processing time. In fact, **Figure 6(a)** summarizes the required conditions for forming TNWs/TNAs as functions of anodizing voltage and processing time in a fixed electrolyte solution. For example, TNWs/TNAs are obtained for 120 min at 30 V; meanwhile, it takes only 30 min for anodizing voltage of 50–60 V. The influence of the electric field strength on the formation of TNWs/TNAs is elucidated by considering the ion migration under electric field in the electrolyte. In principle, the flux of ions in the presence of electric field can be expressed as [10]

$$J_i = -D_i \frac{\partial c_i}{\partial x} - u_i c_i E \tag{4}$$

where J_i is the flux of species *i* of concentration c_i in direction *x*, D_i is the diffusion coefficient, $\partial c/\partial x$ is the concentration gradient, u_i is the mobility of species *i*, and *E* is the electric field strength. Evidently, since ion migration in the electric field is considerable to the ion diffusion process under a concentration gradient, the field strength significantly drives the ion transport in the electrolyte. According to Eq. 4, higher field strength leads to higher ion flux in the electrolyte. Consequently, under a high field strength (or high voltage), the TNW/ TNA structure is formed in a shorter time. Notably, the growth of TNWs with characteristic of longer processing times for lower voltages is only found in the anodizing voltage range of 30–60 V. To get a deeper insight into the role of electric field strength in the formation of TNWs onto TNAs, the voltage dependence of the pore diameter and wall thickness of TNA's top section before the emergence of nanowires is investigated, and the results are shown in **Figure 6(b)**. For the cases with no TNW formation, for example, at ≤ 20 or ≥ 80 V, the tube diameter and wall thickness are obtained from TNAs prepared at anodizing time of 30 min. As can be seen in **Figure 6(b)**, the pore diameter of the TNA's mouth increases from 30 to 110 nm with increasing the voltage from 10 to 80 V, agreeing with the reported results [18]. Meanwhile, the wall thickness of the TNA's mouths decreases from 20 to 8 nm when the applied voltage is increased from 10 to 80 V. The TNW/TNA film is only found when the tube wall thickness is in range of 10–15 nm. As shown in Figure 6(a) and (b), the dissolution rate would be too low to break up TiO₂ tube wall when the applied voltage is sufficiently low and thus only TNA structure is found. By contrary, if the anodizing voltage is too high, which



Figure 6. (a) Conditions of required anodizing voltage and processing time (shaded zone) for forming TNWs/TNAs. (b) The pore diameter and wall thickness of TNA's top section prior to the emergence of nanowires, as a function of voltage.

leads to high dissolution rate to completely remove the top section of TiO_2 nanotubes, and consequently TNW-free TNAs with a thin wall thickness of ~8 nm are observed.

2.2.4. Formation mechanism of TNWs/TNAs

At some proper conditions of anodic oxidation, TNW's cover on TNAs can be fabricated. J. H. Lim et al. proposed the "bamboo-splitting" model for the TNW formation mechanism [19]. In addition, the formation TNWs can also be clearly explained "strings of through holes" model by M.Y. Hsu et al., as illustrated in **Figure 7** [10]. It follows four stages. First, the ordered TNAs are formed as processing the anodization, accompanying with field-enhanced chemical drilling by a high H⁺ concentration at the pore bottom of nanotubes, in conjunction with a protective environment maintained along the pore walls by the highly viscous EG solution. At this stage, field-enhanced further dissolution in the tube bottom is still occurring during anodization process (**Figure 7(a)**). Second, the migration of F⁻ ions toward the electric field to the bottom of anode is inhibited by the highly viscous solution, which results in the much higher F⁻ concentration at the tube than at the tube bottom. Notably, in the electrolyte with water content, the chemical dissolution reaction of TNAs is further enhanced by hydrogen ions (reaction (3) above). Consequently, the tube mouth part is thinner than the lower sections, as shown in **Figure 7(a)**. The inner tube is found to be nonuniform and rough (**Figure 7(b)** inset), and thus when the tube mouth is thin enough



Figure 7. Schematic diagrams and corresponding SEM images of four stages in the TNW/TNA formation mechanism: (a) thinning the tube wall thickness with high roughness near the TNA's mouths, (b) forming strings through holes in the top section of TNAs, (c) splitting into nanowires, and (d) collapsing and further thinning of nanowires [10].

(< 10 nm), it can be etched through under high dissolution reaction with high concentration of F⁻ ions (**Figure 7(b**)). By increasing processing time, strings of through holes are formed on the tube wall, and they would initiate and propagate downward from the top to bottom of TNAs (or along the F⁻ migration direction), while the holes near the top expand and connect to split into nanowires (**Figure 7(c**)) as the anodizing time increases. With further increasing anodizing time, the nanowires exhibit smooth at the edges and narrower wire width due to the sufficient chemical etching. When the wire length is too long (i.e., over ~5 µm), the nanowires would collapse onto TNAs, as illustrated in **Figure 7d**. Briefly, the proposed formation mechanism of TNWs/TNAs by one-step anodic oxidation follows four stages: (a) thinning the tube wall thickness with high roughness near the TNA's mouths, (b) forming strings through holes in the top section of the TNAs, (c) splitting into nanowires, and (d) collapsing and further thinning of nanowires [10].

2.2.5. Photocatalytic performance

The photocatalytic performance of TNW/TNA nanostructure in comparison with other morphologies of TNAs and TiO₂ nanoparticles is presented in this part. The TiO₂ P25 nanoparticle films were fabricated by the doctor-blade method. For making a reliable comparison, the film thickness of TiO₂ nanoparticles was controlled to be comparable to that of TNW/TNA films (~11 μ m) by controlling the height of the blade above the Ti substrate and/or the concentration of TiO₂ paste. The effect of various TiO₂ morphologies on the photocatalytic degradation of methylene blue (MB) was examined under the 360 nm wavelength irradiation of an 8 W HeCd lamp. To make a reliable comparison, diameters of nanotubes (40–100 nm)



Figure 8. Photocatalytic degradation of methylene blue of various TNAs, TNWs/TNAs, and TiO₂ nanoparticle films, C/C₀ vs. reaction time under UV light irradiation (8 W, 360 nm wavelength) [10].

and film thickness (~11 µm) are kept almost the same between TNAs and TNWs/TNAs by adjusting processing conditions. **Figure 8** shows the photocatalytic activity of TNAs and TNW/TNA films and TiO₂, C_t/C_0 as a function of UV irradiation time, in a MB solution with $C_0 = 2.5 \times 10^{-5}$ M. We used the pseudo first-order kinetics as described by the Langmuir-Hinshelwood model [20]. Thus, the photodegradation rate of MB could be expressed by the following Eqs. (5) and (6):

$$C_t = C_o e^{-kt} \tag{5}$$

$$\ln C_t / C_o = -kt \tag{6}$$

where *k* is the reaction rate constant, *t* is the irradiation time, and C_0 and C_t are the initial concentration and the reaction concentration of MB. The reaction rate constants (k) were calculated from the experimental data using a linear regression. For TNAs with various tube diameters at a fixed tube thickness, the *k* values were 9.80×10^{-2} , 8.48×10^{-2} , 6.73×10^{-2} , and 5.49×10^{-2} h⁻¹ for tube diameter of 40, 60, 80, and 100 nm, respectively. Clearly, a smaller tube diameter results in a higher reaction rate [10]. In comparison, at the same tube diameter of 60 nm, the k value of 20 nmTNWs/60 nmTNAs was 48% higher than that of pure TNAs (12.54×10^{-2} vs. 8.40×10^{-2} h⁻¹). Similarly, at a fixed tube diameter of 40 nm, the rate constant k for 20 nm TNWs/40 nm TNAs enhanced approximately 33% over the pure TNA one (13.05×10^{-2} vs. $\times 9.8 \times 10^{-2}$ h⁻¹) [10]. It is found that the photocatalytic activity of TNWs/TNAs enhanced remarkably (up to 33–48%) over the corresponding pure TNAs.

Table 1 summarizes the calculated dye adsorption and the *k* values of various TiO₂ films. For TNAs, a smaller tube diameter yields a higher dye adsorption because of its larger surface area, which results in enhanced photocatalytic efficiency. The difference in surface area of TNAs comes from different densities of nanotube. As the anodizing voltage increases, tube density decreases with increasing tube diameter to result in a decrease of dye adsorption and photocatalytic efficiency. The dye adsorption of TNWs/TNAs is significantly higher than that of the corresponding TNA film because the former that offers larger surface area than the latter. Indeed, the congregation of the bundled nanowires connected to the nanotube mouths induces surface area enhancement over the TNAs. It is also found from Table 1 that the change percentages of the reaction rate constants for both TNAs and TNWs/TNAs are higher than those of dye adsorption. This indicates that besides the predominant factor of surface area, the 1D nanostructures of TNAs and TNWs/TNAs offer the promotion of charge transport and reduced recombination rate. Though having smaller surface area than TiO₂ nanoparticles, both the faster transport and slower recombination of 1D structures and the providing additional surface area from TNWs, the photocatalytic performance of TNWs/ TNAs has achieved a very high efficiency ($k = 13.05 \times 10^{-2} h^{-1}$) that is very close to the k value of TiO₂ nanoparticles $(13.05 \times 10^{-2} h^{-1})$ [10]. It is worthy to mention that the immobilized film forms (i.e., TNAs and TNWs/TNAs on Ti plates) are more practical than TiO₂ powdery form. The photocatalytic performance of TNWs/TNAs may be further improved by optimizing the width and density of TNWs covering on TNAs.

| TiO ₂ film | Dye adsorption (×10 ⁻⁸ mol/cm ²) | Change (%) relative to nanoparticles | Reaction rate constants (k (×10 ⁻² h ⁻¹)) | Change (%) relative to nanoparticles |
|--------------------------------|--|---|--|--------------------------------------|
| 100 nm TNAs | 1.22 | 29% | 5.49 | 38% |
| 80 nm TNAs | 1.65 | 39% | 6.73 | 47% |
| 60 nm TNAs | 2.33 | 55% | 8.48 | 59% |
| 40 nm TNAs | 2.72 | 64% | 9.80 | 68% |
| 60 nm TNAs/20 nm TNWs | 3.21 | 76% | 12.54 | 87% |
| 40 nm TNAs/20 nm TNWs | 3.58 | 85% | 13.05 | 91% |
| TiO ₂ nanoparticles | 4.22 | 100% | 14.38 | 100% |

Table 1. Dye adsorption, reaction rate constants (k), and change percentage of various TiO₂ films.

3. Highly ordered TNAs and modified TNAs designed by two-step anodic oxidation

Using one-step anodization, the produced TNAs usually present disparity in tube lengths and relatively rough surfaces. It has been recently demonstrated that a two-step anodization is possible for preparation of highly ordered and uniform TNAs [14, 15] or unique hierarchical top layer/TNAs with significantly better performances in dye-sensitized solar cells [21] and in photoelectrochemical (PEC) water splitting [6]. A typical process of two-step anodization includes (1) the one-step anodization for growth TiO₂ nanotubes, (2) subsequent removal of the as-grown TNAs by ultrasonication, and (3) the two-step anodization to grow TiO₂ NTs from the same substrate [14, 15].

3.1. Highly ordered TNAs

The SEM images of the highly ordered nanotubes, bamboo-type nanotubes, and lotus rootshaped nanostructure of TiO₂ are shown in **Figure 9**. These nanostructures are prepared by two-step anodization method, in which electrolyte contained ethylene glycol ($C_2H_6O_2$), 0.25% (in mass) NH₄F and 1% (in volume) H₂O. Noticeably, prior to performing the anodization, the electrolyte was aged under a voltage of 60 V for 60 h. In the first step, a Ti foil was anodized at 60 V for 24 h to grow a layer of TiO₂ nanotubes, and then the layer was removed ultrasonically in deionized water. **Figure 9(a)** and **(c)** shows the top view and side view of the TNAs prepared under an anodizing voltage of 60 V in the two-step anodization, which is much more uniform in alignment and length than the TNAs fabricated by the corresponding one-step anodization [15]. **Figure 9b** presents the imprint pattern left on the Ti surface after peeling off from the Ti foil ultrasonically. Clearly, each nanotube is surrounded by six nearest neighbors, and each nanotube has six protrusions with hexagonal pattern at the fringe of its top end, suggesting that the nanotubes in the two-step anodization directly developed from the imprint pattern left on the Ti surface. It is found that the aging the electrolyte is necessary for improving the quality of the imprint patterns or avoiding the initial random patterns of TNAs. The ordered imprints play the role of template for the nanotube growth. Owing to the regular distribution across the surface of the pretreated Ti foil at the very beginning, the uniformity and orderliness of the nanotube arrays were developed during the two-step anodization [15]. Intriguingly, a thin porous film is covered on the top of the nanotube layer as taking a closer look at **Figure 9a**. It is well known that the length of a nanotube does not increase when the rate of oxidation at the Ti/oxide interface at the bottom equals the rate of dissolution at the oxide/electrolyte interface at the top. Hence, the porous film on the top of the TNA plays a role as the protecting layer from dissolution, and consequently the preparation of long nanotubes is possible.

The side walls of the TNAs have obvious thickness variation, which often refers to ripples, as shown in **Figure 9d**. So far, the ripples are formed due to the periodic oscillations of the current in anodization [12]. Indeed, the bamboo-shaped nanotube, a nanostructure with more drastic ripples along the side walls, has been successfully fabricated by using anodic oxidation with ac voltage [12, 15]. **Figure 9e** shows bamboo-shaped tubes which were synthesized in EG electrolytes containing 0.3 wt % NH₄F and 5 vol % H₂O under different anodization sequences of 60 V for 2 min and 10 V for 2 min. The inset illustrates the anodization sequence for the formation of bamboo-type TNAs. The anodic oxidation growth of bamboo-type TiO₂ nanotubes is illustrated by the schematic in **Figure 9e**, where ridge formation between the second section and third section of nanotubes is at the third high-voltage step [12]. The formation mechanism is that the low-voltage step reduces pH and ion diffusion gradient inside TiO₂ nanotubes and induces formation of bamboo ridges on outer tube walls when a second high-voltage step is conducted [12]. Length and ridge spacing of bamboo-type nanotubes can be easily tuned by adjusting electrolyte composition and time of high-voltage step [12].

Figure 9(g) and **(h)** presents the morphology of a lotus root-shaped nanostructure, which was obtained using anodizing voltage of 30 V in the second step and 60 V in the first step. The nanostructure exhibits two levels, and it resembles as a lotus root in shape. The first level consists of cells with size of approximately $0.2 \mu m$, as highlighted by a hexagon in the inset of **Figure 9g** [15]. The second-level structure is constituted by the pores with smaller diameters inside the cells (one of them highlighted by a circle in the inset of **Figure 9g**). Noticeably, the nanopores all evolved in the interior of the cells or such nanopores did not extend across any neighboring cells. By comparing the size and shape, it is found that the first-level structure corresponds to the imprints of Ti surface after the removal of the nanotube layer in the one-step anodization. In addition, this lotus root-shaped nanostructure was only obtained when the second-step voltage was low enough [15]. When the second-step voltage is lower than the first-step voltage, for example, 30 vs. 60 V, the generated nanotubes in the second-step anodization will be thinner than those generated in the first-step anodization. Therefore, several nanotubes simultaneously developed inside one imprint to result in the lotus root-shaped nanostructure, as shown in **Figure 9(g)** and **(h)** [15].



Figure 9. Nanotube array generated in the two-step anodization under a 60 V voltage: (a) top view and (b) the exposed Ti surface after the removal of the nanotube layer. Side view of the TiO_2 nanotubes generated in the two-step anodization: (c) the side view of the nanotubes and (d) zoom-in view of the nanotubes with the ripple features [15]. (c) the bamboo-shaped tubes were synthesized in EG electrolytes containing 0.3 wt % NH₄F and 5 vol % H₂O under different anodization sequences of 60 V for 2 min and 10 V for 2 min. (inset) Anodization sequence for the formation of bamboo-type TiO_2 nanotube arrays. Schematic showing growth of bamboo-type TiO_2 nanotubes via anodic oxidation: Ridge formation between the second section and third section of nanotubes at the third high-voltage step [12]. (f) the bamboo-shaped tubes generated under another square-waved anodizing voltage (the 30 V voltage lasted 90 s and the 60 V voltage still lasted 10 s). (g) and (h) Lotus root-shaped nanostructure obtained under a 30 V anodizing voltage in the two-step anodization: (a) top view and (b) side view [15].

3.2. Modified TNAs designed by two-step anodic oxidation

Figure 10(a) presents the two-step anodization process and morphological characteristics under three different voltage regimes of the one-step anodization. Fascinating hierarchical top layer/TNAs has been successfully fabricated by using two-step anodization with controlled anodizing voltages [6]. The electrolytes consisted of 0.5 wt% NH₄F in EG solution with 2 vol% water. The one-step anodization was conducted at anodizing voltages of 60, 80, or 100 V for 60 min to grow TNAs on Ti sheet, and then the as-grown TNAs were ultrasonically removed in DI water. The Ti sheet surface has a regular hexagonally packed round concave morphology (see **Figure 10a**). Next, the second-step anodization was performed using the same Ti sheet at various potentials of 20–100 V and tunable processing time to control the thickness of TNAs. Finally, samples were cleaned with DI water, dried with nitrogen gas, and annealed at 450°C for 1 h in the air.

The hierarchical top layer/TNAs are an outcome of the competition between the electric fielddriven anodic oxidation [reaction (1) above, $v_{electro}$] of Ti to form TiO₂ and the electric fieldassisted chemical dissolution of the TiO₂ layer [reaction (3) above, v_{dis}] [8, 14]. The anodic oxidation reaction occurs as Ti⁴⁺ ejection and deposition on the surface in the form of TiO₂, while the TiF₆²⁻ etching reaction occurs from the top to bottom of the as-grown TiO₂. The anodic oxidation rate is very fast and dominated over the NH₄F etching rate, resulting in a thin oxide layer in the early stage [14, 15]. In the late stage, the deposition rate of TiO₂ at the entrance of the nanotubes slows down, while field-induced random dissolution of the surface becomes more significant or dominant to form pore-like structures, which further develop into TNA structures [8, 14]. At certain relative rates between TiO₂ deposition and



Figure 10. (a) Two-step anodization synthesis of the hierarchical TiO_2 nanotubes. (b–f) Plan-view and cross-sectional scanning electron microscopy (SEM) images of the hierarchical TiO_2 nanotubes prepared at a fixed one-step voltage of 60 V and various two-step voltages from 20 to 100 V. (g) the TNAs prepared at 100 V for the first step and 80 V for the second step [6].

dissolution, a layer of interconnected nanopores can be constructed on the top of TiO_2 , as shown in **Figure 10** [6]. The highly ordered hexagonal imprints after ultrasonication plays as a template for the subsequent growth of TNAs with a hierarchical porous top layer [15].

Figure 10(b)–(f) shows SEM images of the modified TNAs prepared at a fixed voltage of 60 V for the one-step anodization and at different voltages from 20 to 100 V for the two-step anodization. Figure 10(g) is the TNAs prepared at 100 V for the first step and 80 V for the second step. When the density of applied electric field increases, $v_{electro}$ increases, whereas v_{dis} decreases due to Coulomb force on the TiF₆²⁻ anion. Thus, the unique nanoring/nanotube hierarchical nanostructures is formed at the low two-step voltages of 20 and 40 V because of the relatively high v_{did} relatively little accumulation/deposition of Ti(OH)₄ occurred at the openings of the nanotubes where the nanotubes met the bulk electrolyte (Figure 10(b)-(c)). As the anodization voltage increases further, the accumulation/deposition of $Ti(OH)_4$ at the entrance of the nanotubes increases to form nanopore and nanohole top structures, with the diameters of the openings decreasing with increasing voltages. Furthermore, at high anodization voltages, an increase in v_{dectro} favors the formation of a thicker oxide layer owing to the preferred growth at the bottom of the concavity generated in the one-step anodization where the electrical resistance is the lowest. Consequently, the diameters of the bottom tubes of TNAs increase with increasing voltages (Figure 10(d)-(f)) [6]. To investigate the effect of the voltage in the one-step anodization step, a comparison between Figure 10e (S-60-80) and 10 g (S-100-80) can be made. Clearly, S-60-80 exhibits a nanopore/TNA structure, whereas S-100-80 presents a nanohole-nanocave/TNA structure, which consists of holes with a pore size of ~50 nm and concaves with closed bottoms. The formation of a thick oxide barrier layer in the one-step anodization step at the high voltage (i.e., 100 V) should be attributed to the formation of S-100-80 morphology. The insets in Figure 10 confirm that all samples had a uniform length of TNAs in the range of $1.3-1.5 \,\mu m$ for minimizing the effect of tube length disparity on PEC performance.

The photocurrent densities of different samples were determined by linear sweep photovoltammetry measurements using a three-electrode electrochemical system in a 1 M KOH electrolyte under AM 1.5 G (100 mW/cm²) illumination. Three major conclusions can be drawn from the results in Figure 11(a). (1) The photocurrent densities of all samples prepared by two-step anodization are consistently higher than the ones prepared by the conventional one-step method under the same conditions. This implies that the hierarchical TiO₂ nanostructures favor better PEC performances. Indeed, the one-step prepared TNAs only obtained a photocurrent density of 0.345 mAcm⁻² at 0.23 V vs. Ag/AgCl or 1.23 V vs. RHE, which is the potential often chosen as a metric to evaluate the performance of photoanodes as it corresponds to the water oxidation potential. Among all samples, S-60-80 achieved the highest photocurrent density of 1.59 mAcm⁻² at the same potential [6]. (2) The photocurrent densities (I) of different nanostructured TNAs presented a general order of Inanopore/ $_{\text{TNA}} > I_{\text{nanoring/TNA}} > I_{\text{nanohole-nanocave/TNA}}$. The photocurrent density of the nanohole-nanocave/TNA sample (i.e., S-100-80) possesses a low value of 0.480 mAcm⁻² that should be due to the closed nanocave structures on its surface, and thus it effectively blocks the light absorption and solution infiltration. Moreover, the nanopore/TNA samples (i.e., S-60-60, S-60-80, and S-60-100) exhibited higher photocurrent densities than the nanoring/TNA samples (i.e., S-60-20 and Recent Advances in TiO₂ Nanotube-Based Materials for Photocatalytic Applications Designed... 147 http://dx.doi.org/10.5772/intechopen.77063



Figure 11. Photoelectrochemical properties of hierarchical TiO_2 nanotube electrodes: (a) linear-sweep voltammograms collected with a scan rate of 5 mVs⁻¹ In the dark and under illumination and (b) amperometric *I*–*t* curves at an applied potential of 1.23 V vs. RHE under illumination with 60 s light on/off cycles [6].

S-60-40) because the formers have better degree of crystallinity and higher optical absorption (to be discussed in the later section). (3) Among all of the nanopore/TNA samples, S-60-80 achieved the highest photocurrent density, which attributed to its better optical absorption and its uniform morphology for reducing structural defects that serve as photoelectron/hole recombination centers (**Figure 10e**) and thus favor high PEC performance.

A photocatalyst material with a better optical absorption and higher crystallinity will subsequently result in a better PEC performance. *P. Wang* et al. found that all two-step hierarchical TNA samples exhibited better UV–Vis absorption than one-step TNA sample because of their unique hierarchical nanostructures and improved morphological uniformity [6]. A better surface morphological uniformity should result in enhanced optical absorption because the material has better periodicity of the photonic crystals formed by the top porous layers. It is found that the crystallite size of TNAs increases with increasing anodizing voltages [22]. Therefore, a high anodizing voltage favors the formation of bigger crystal nucleus and thus results in a better crystallinity and less defects to obtain the better PEC performance, which agreed well with the aforementioned results [6]. In addition, the photoelectrode stability of the hierarchical TNAs was assessed via amperometric (I – t) measurements, performing at a fixed electrode potential of 1.23 V vs. RHE under alternating light on and light off with a cycle of 60 s. As can be seen in **Figure 11(b)**, fast photoresponses were recorded for all samples, and this photocurrent pattern was highly reproducible for many on/off cycles [6].

4. Conclusions

It is demonstrated that various spectacular and interesting 1D nanostructures of TiO_2 have been grown and designed by anodic oxidation. TiO_2 nanotube arrays and TiO_2 nanowires/ nanotubes are generally obtained by conventional one-step anodic oxidation with suitable conditions. The effects of anodizing voltage, processing time, and electrolytes on the morphologies of anodic oxidation TiO_2 nanomaterials are reported. Meanwhile, two-step anodic oxidation allows growing some spectacular TiO_2 nanostructures such as highly ordered TNAs, bamboo-type TNAs, and lotus root-shaped TNAs. In addition, the formation mechanisms and photocatalytic activities of some TNA-based nanomaterials prepared by anodic oxidation are presented and discussed.

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References

- Roy P, Berger S, Schmuki P. TiO₂ nanotubes: Synthesis and applications. Angewandte Chemie International Edition. 2011;50:2904-2939. DOI: 10.1002/anie.201001374
- [2] Mohamed AER, Rohani S. Modified TiO₂ nanotube arrays (TNTAs): Progressive strategies towards visible light responsive photoanode—A review. Energy & Environmental Science. 2011;4:1065. DOI: 10.1039/c0ee00488j
- [3] Lai CW, Juan JC, Ko WB, Bee S, Hamid SBA. An overview: Recent development of titanium oxide nanotubes as photocatalyst for dye degradation. International Journal of Photoenergy. 2014;2014:524135. DOI: 10.1155/2014/524135
- [4] Yin ZF, Wu L, Yang HG, Su YH. Recent progress in biomedical applications of titanium dioxide. Physical Chemistry Chemical Physics. 2013;15:4844-4858. DOI: 10.1039/ c3cp43938k
- [5] Kubacka A, Fernández-García M, Colón G. Advanced nanoarchitectures for solar photocatalytic applications. Chemical Reviews. 2012;**112**:1555-1614. DOI: 10.1021/cr100454n

- [6] Zhang Z, Wang P. Optimization of photoelectrochemical water splitting performance on hierarchical TiO₂ nanotube arrays. Energy & Environmental Science. 2012;5:6506. DOI: 10.1039/c2ee03461a
- [7] Hoffmann MR, Martin ST, Choi W, Bahnemann DW. Environmental applications of semiconductor photocatalysis. Chemical Reviews. 1995;95:69-96
- [8] Yan J, Zhou F. TiO₂ nanotubes: Structure optimization for solar cells. Journal of Materials Chemistry. 2011;21:9406. DOI: 10.1039/c1jm10274e
- [9] Reyes-Coronado D, Rodriguez-Gattorno D, Espinosa-Pesqueira ME, Cabb C, De Cross R, Oskam G. Phase-pure TiO₂ nanoparticles: Anatase, brookite and rutile. Nanotechnology. 2008;**19**:145605. DOI: 10.1088/0957-4484/19/14/145605
- [10] Hsu M-Y, Hsu H-L, Leu J. TiO₂ nanowires on anodic TiO₂ nanotube arrays (TNWs/TNAs): Formation mechanism and photocatalytic performance. Journal of the Electrochemical Society. 2012;159:H722-H727
- [11] Turkevych I, Pihosh Y, Hara K, Wang Z-S, Kondo M. Hierarchically organized micro/ nano-structures of TiO₂. Japanese Journal of Applied Physics. 2009;48:06FE02. DOI: 10.1143/JJAP.48.06FE02
- [12] Luan X, Guan D, Wang Y. Facile synthesis and morphology control of bamboo-type TiO₂ Nanotube arrays for high-efficiency dye-sensitized solar cells. The Journal of Physical Chemistry C 2012;**116**:14257–14263. DOI: 10.1021/jp305280q
- [13] Ge MZ, Cao C-Y, Huang J-Y, Li S-H, Zhang S-N, Deng S, Li Q-S, Zhang K-Q, Lai YK. Synthesis, modification, and photo/photoelectrocatalytic degradation applications of TiO₂ nanotube arrays: A review. Nanotechnology Reviews. 2016;5:75-112. DOI: 10.1515/ ntrev-2015-0049
- [14] Wang D, Yu B, Wang C, Zhou F, Liu W. A novel protocol toward perfect alignment of anodized TiO₂ nanotubes. Advanced Materials. 2009;21:1964-1967. DOI: 10.1002/ adma.200801996
- [15] Li S, Zhang G, Guo D, Yu L, Zhang W. Anodization fabrication of highly ordered TiO₂ nanotubes. Journal of Physical Chemistry C. 2009;**113**:12759-12765. DOI: 10.1021/ jp903037f
- [16] Zwilling V, Darque-Ceretti E, Boutry-Forveille A, David D, Perrin MY, Aucouturier M. Structure and physicochemistry of anodic oxide films on titanium and TA6V alloy. Surface and Interface Analysis. 1999;27:629
- [17] Nie X, Chen J, Li G, Shi H, Zhao H, Wong PK, An T. Synthesis and characterization of TiO₂ nanotube photoanode and its application in photoelectrocatalytic degradation of model environmental pharmaceuticals. Journal of Chemical Technology and Biotechnology. 2013;88:1488-1497. DOI: 10.1002/jctb.3992
- [18] Pichat P, Disdier J, Hoang-Van C, Mas D, Goutailler G, Gaysse C. Purification/deodorization of indoor air and gaseous effluents by TiO₂ photocatalysis. Catalysis Today. 2000;63:363-369

- [19] Lim JH, Choi J. Titanium oxide nanowires originating from anodically grown nanotubes: The bamboo-splitting model. Small. 2007;**3**:1504-1507. DOI: 10.1002/smll.200700114
- [20] Sharma SD, Saini KK, Kant C, Sharma CP, Jain SC. Photodegradation of dye pollutant under UV light by nano-catalyst doped titania thin films. Applied Catalysis B: Environmental. 2008;84:233-240. DOI: 10.1016/j.apcatb.2008.04.017
- [21] Ye M, Xin X, Lin C, Lin Z. High efficiency dye-sensitized solar cells based on hierarchically. Nano Letters. 2011;11:3214-3220. DOI: 10.1021/nl2014845
- [22] Allam NK, Grimes CA. Room temperature one-step polyol synthesis of anatase TiO₂ nanotube arrays: Photoelectrochemical properties. Langmuir. 2009;25:7234-7240. DOI: 10.1021/la9012747

Synthetic Methods for Titanium Dioxide Nanoparticles: A Review

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Abstract

Titanium dioxide (TiO_2) semiconductor nanoparticles are one kind of important and promising photocatalysts in photocatalysis because of their unique optical and electronic properties. Their properties, which are determined by the preparation method, are very crucial in photocatalysis. In this chapter, an overview was carried out on the different methods that are used or have been used to prepare titanium dioxide nanoparticles. There are various methods that can be used to synthesize TiO_2 and the most commonly used methods include sol-gel process, chemical vapor deposition (CVD) and hydrothermal method among others. This review will focus on selected preparation methods of titanium dioxide photocatalyst.

Keywords: titanium dioxide, synthetic methods, photocatalyst, semiconductor

1. Introduction

Titanium dioxide photocatalyst is a well-known and well researched photocatalyst due to its interesting properties which include stability, non-toxicity, biocompatibility, optical and electrical properties. It exists mainly in three different forms namely anatase, rutile and brookite and their structures are shown in **Figure 1** [1]. Upon heating, both anatase and brookite convert to rutile which is more stable at all temperatures and pressures below 60 kbar, according to thermodynamic calculations [2]. **Table 1** shows some of the structural and physical properties of the anatase and rutile phase of titanium dioxide [3].

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Figure 1. Different forms titanium dioxide [1].

The recent development of nanotechnology has proved that nanomaterials such as nano-sized titanium dioxide photocatalysts can have high activity in the photodegradation of a wide range of organic and inorganic contaminants in water. It is believed that photocatalysis will soon be recognized as one of the most effective means of dealing with various kinds of wastewater since organic pollutants can be completely degraded to harmless matter under normal conditions of temperature and pressure.

It is capable of degrading pollutants such as herbicides, carboxylic acids and alcohols completely to carbon dioxide, water and simple minerals [4]. For it to be very effective, it should have certain properties such as suitable particle size, shape, crystallinity and a good ratio of anatase to rutile. This is the reason why most researchers have been trying to use different methods to get particles with suitable characteristics for environmental remediation or for other applications of interest. Several studies have proved that TiO₂ nanostructures, in particular, titanium dioxide nanotubes (TNTs) have their performance improved in photovoltaics [5]

| Property | Anatase | Rutile |
|------------------------------|------------------------------|------------------------------|
| Molecular weight (g/mol) | 79.88 | 79.88 |
| Melting point (°C) | 1825 | 1825 |
| Boiling point (°C) | 2500-3000 | 2500-3000 |
| Specific gravity | 3.9 | 4.0 |
| Light absorption (nm) | $\lambda \le 385 \text{ nm}$ | $\lambda \le 415 \text{ nm}$ |
| Mohr's hardness | 5.5 | 6.5 to 7 |
| Refractive index | 2.55 | 2.75 |
| Dielectric constant | 31 | 114 |
| Crystal structure | Tetragonal | Tetragonal |
| Lattice constants (Å) | a = 3.784 | a = 4.5936 |
| | c = 9.515 | c = 2.9587 |
| Density (g/cm ³) | 3.79 | 4.13 |
| Ti–O bond length (Å) | 1.937 (4) | 1.949 (4) |
| | 1.965 (2) | 1.980 (2) |

Table 1. Properties of the anatase and rutile phase of titanium dioxide [3].

and photocatalysis [6] compared to nanoparticulate forms of titanium oxide. Recently, bundles and arrays of TNTs with different qualities have been synthesized by a variety of different techniques such as template-assisted, sol-gel, hydrothermal, electro-anodization, chemical vapor deposition and physical vapor deposition [7].

There are other various techniques for preparing titanium dioxide (TiO_2) nanoparticles and these include reverse micelles, the sol-gel process, the metal organic chemical vapor deposition (MOCVD) [8], gas phase (aerosol) synthesis [9], wet-chemical synthesis by precipitation of hydroxides from salts, microemulsion-mediated methods [10] and electrochemical synthesis. These methods can be divided into five general groups namely sol-gel, deposition methods, sonochemical and microwave-assisted methods, hydro/solvothermal methods and oxidation methods.

2. Synthetic methods

2.1. Deposition methods

In these methods, materials in the vapor state are condensed to form a solid phase material. The process is normally carried out in a vacuum chamber and if a chemical reaction takes place, it is called chemical vapor deposition (CVD) and physical vapor deposition (PVD) if no reaction occurs. Examples of CVD include electrostatic spray hydrolysis, diffusion flame pyrolysis, thermal plasma pyrolysis, ultrasonic spray pyrolysis, laser-induced pyrolysis and

ultrasonic-assisted hydrolysis. TiO_2 films with grain size less than 30 nm and TiO_2 nanoparticles with sizes less than 10 nm were synthesized by pyrolysis of titanium tetraisopropoxide (TTIP) in a helium/oxygen atmosphere [11]. Thermal plasma synthesis [12] and spray pyrolysis [13] have been used in some studies but they are complex, capital and energy-intensive and the properties of the powder are not easy to control.

2.1.1. Electrophoretic deposition

This is the most favored method due to several reasons, which include effectiveness in the fabrication of coatings and films from suspensions [14], a short period of time is required for deposition, the ability to deposit a film on a non-uniform surface, it is cost effective, it is easy to control the thickness of the films, ability to utilize suspensions of low solids loadings, homogeneity of resultant coatings, simple apparatus requirements, binder-free process and it is possible to prepare homogeneous coated layers or deposited films [15, 16].

The process involves the movement of charged particles in a suspension medium followed by deposition on a substrate under an applied DC voltage [17, 18] as shown in **Figure 2**. When the voltage is applied to the electrodes, an electric field is created that interacts with the surface charge of the nanoparticles, producing a force that makes the particle move toward the electrode of the opposite charge and their accumulation on this electrode leads to the formation of a homogeneous layer.

Different thickness of the films can be achieved by changing the deposition parameters such as voltage, deposition time, solvent type, zeta potential particle and loading in the suspension [17]. Some researchers have used different combinations in titanium dioxide thin film



Figure 2. Schematic setup of the electrophoretic deposition cell [16].

deposition for different applications such as biomedical applications [19], ceramic coatings [20] and dye-sensitized solar cells [21-23]. Nyongesa and Aduda used electrophoretic deposition technique to deposit titanium dioxide thin films on conducting glass substrates for application in water purification [16]. In the study, they found out that ethanol was a better solvent to use compared to toluene, propanol or water, which they believed was due to its high dielectric constant (ϵ) of 24.3. Water is not a suitable suspension medium due to water electrolysis which takes place during the deposition and this can cause gas bubbles to accumulate at the electrode surfaces, which is detrimental to the electrophoretically deposited coating. The best parameters for good adherence of the nanoparticles were: pH value of 3, solid loading of 4.0 wt% and a voltage of 20 V [16]. In a similar study by Nguu et al. [24], to achieve a uniform film of 5 µm, the best voltage and time were 35 V and 90 s, respectively, and they discovered that extended deposition times (>90.0 s) resulted in formation of agglomeration [24]. In another study by Dhiflaoui et al., it was found that the coatings deposited at 20 V for 4 min were the most homogeneous [25]. They also discovered that transformation of anatase to rutile depends on the electric current in the electrochemical cell. When the voltage is increased, the modulus of elasticity and hardness of the films also increase.

2.1.2. Spray pyrolysis

This is a deposition technique that enabled production of a variety of products in the form of fine dispersive porous or dense powders or films. The first reactors for nanoparticles by flame synthesis (FS) started in the 1940s, to produce fumed silica. In 1971, G.D. Ulrich reported the first principles of the FS method. Silica and titanium dioxide were the first materials to be produced by flame synthesis and patented [26] but with time TiO₂ became the largest material produced by flame aerosol reactors [9]. The number of researchers using FS has increased in the last years.

Generally, this method can be divided into two groups that are spray pyrolysis synthesis (SPS), which results in powders and spray pyrolysis deposition (SPD), which results in thin films. The method involves the passing of precursor's flux across a direct flame. It can proceed either by supplemental burners that are mounted near the spray nozzle, or by additional feeding of the nozzle by oxidant that could be air or pure oxygen and the combustibles. If an organic solvent is used, it can serve as a flame fuel as well. A nozzle or a nebulizer can be used but the use of a nozzle implies that the diameter of the spray droplets depends on the diameter of the nozzle outlet tip, the surface tension of the respective precursor solution, its viscosity and the pressure difference before and after the spraying [27]. Kozhukharov and Tchaoushev [28] recommended the production of ultrafine dispersive powders by swift rise of the temperature inside the chamber. In this process, the already formed solid particles undergo further splitting, due to mechanical tensions and or phase transitions occurring [28].

Adhesion to the substrate is important for the quality of the deposited film which means SPD could be performed either directly by hot spray, or by cold spray on preliminary heated substrate. Several parameters of the pyrolysis process, such as the size of the spray droplets, chemical composition of the obtained products, their crystal phases and density can be controlled. Selection and precursor preparation is a challenging task when multi-component materials are to be produced. The precursor should be fed into the reactor at low pulsation

rates as sprays are sensitive to oscillations in the liquid fuel supply which can affect nanoparticle growth conditions. When the flow rate of the precursor is increased, the particle diameter also increases but decreases when the dispersion gas flow rate is increased as a result of rapid mixing reactants and oxidizers [29].

Some important advantages of this technique include the possibility to produce uniform and dense films which have desirable crystallinity by multiple repetitions of spraying and or annealing cycles and the ability to fabricate entire multilayer devices by subsequent deposition of different functional layers, in the same chamber [27]. In spray pyrolysis methods, nanoparticles and thin films are produced in a one-step process and there is no need for further purification or excessive drying procedures, which could have a negative impact on the total thermal budget and cost of production of titanium dioxide nanoparticles [30]. Besides the above mentioned advantages, there are some limitations of this method and these include the need to control temperature and the difficulty in obtaining low temperature allotropic forms of the respective products hence in a large scale production, there is a need for cooling systems, and precise temperature control.

With a lot effort being put in trying to develop the technique, a new spray pyrolysis setup has been designed to overcome limitations of previous systems such as reproducibility, temperature control, gas flow rate and solution rate accuracy. The new system is almost fully computerized. A schematic representation of the spray pyrolysis system is shown in **Figure 3**.

2.2. Oxidation methods

These methods involve the oxidation of titanium metal using oxidants or anodization. Anodization of titanium sheet under a voltage between 10 and 20 V in 0.5% hydrogen fluoride



Figure 3. Schematic representation of spray pyrolysis system: (a) vertical chambers; (b) horizontal chambers and (c) chambers for film deposition [27].

leads to the formation of aligned TiO₂ nanotubes whose diameter is controlled by varying the applied voltage [31]. In another study, crystallized TiO₂ nanotubes were obtained when anodized titanium plate was heat treated at 500°C for 6 h in an oxygen environment [32]. Direct oxidation of the titanium metal with hydrogen peroxide has also been found to lead to the formation of TiO₂ nanorods. The TiO₂ can be obtained by placing a cleaned Ti metal plate in a 50 mL solution of 30 wt% H₂O₂ at 353 K for 72 h [33]. Formation of crystalline TiO₂ occurs via mechanism of dissolution precipitation and this phase can be controlled by addition of NaX (X = F⁻, Cl⁻, SO₄²⁻) inorganic salts. Addition of Na₂SO₄ and NaF results in the formation of anatase phase and when rutile phase is needed, NaCl can be added during dissolution precipitation [34].

Acetone, pure oxygen and a mixture of oxygen and argon can be used as sources of oxygen for oxidation of titanium metal. Acetone is a good source of oxygen and when used at high temperatures, it results in nanorods which are well aligned and highly dense. Use of pure oxygen or a mixture of oxygen and argon results in crystal grain films and morphology of the nanoparticles can be controlled by the diffusion competition of oxygen and titanium [8].

2.3. Sonochemical and microwave-assisted methods

The sonochemical method has been applied to produce highly photoactive TiO_2 nanoparticles by the hydrolysis of titanium tetraisopropoxide (TTIP) in pure water or in an ethanol/water mixture under ultrasonic radiation [35]. Sonochemistry arises from *acoustic cavitation* which is the formation, growth and collapse of bubbles within a liquid medium. Heat (~5000 K) and high pressures (~1000 atm) are produced by cavitational collapse [31].

In microwave-assisted methods, there is a use of microwaves which are electromagnetic waves with frequencies which range from 0.3 to 300 GHz and with wavelengths between 1 mm and 1 m. According to Zhu and Chen [36], microwave heating involves two main mechanisms namely dipolar polarization and ionic conduction. Any materials that contain mobile electric charges such as polar molecules or conducting ions are generally heat by microwaves. In the microwave, heat is generated by rotation, friction and collision of molecules as polar molecules try to orientate with the rapidly changing alternating electric field. If ions are present in solution, they will move through the solution and constantly changing directions based on the orientation of the electric field resulting in local temperature rise due to friction and collision [37].

Microwave heating is as an alternative heat source for rapid heating with shorter reaction time and higher reaction rate, selectivity and yield as compared to the conventional heating methods [36]. There are two types of microwave heating: pulsed microwave heating and continuous microwave heating. Jacob et al. in 1995 proposed two models of the mechanism for microwaveinduced reaction rate enhancements. The first mechanism assumes that, although the reaction time is heavily shortened for a microwave-induced reaction, the kinetics or mechanism of the chemical reaction is not altered implying that the enhancement of the reaction rate is due to the thermal heating effect [38]. The second proposed mechanism makes an assumption that there are "nonthermal microwave effects" in addition to the thermal effects hence the effects of microwave irradiation in chemical reactions are due to both thermal effects and nonthermal effects [39]. The nonthermal effects are due to direct interaction of microwaves with certain molecules in the reaction medium. Microwave radiations can also be applied to produce various TiO, nanomaterials [40]. In industrial processing, this method has an advantage of rapid heat transfer and selective heating. This technique provides uniform distribution of energy within the sample, better reproducibility and excellent control of experimental parameters. The colloidal TiO, nanoparticles can be prepared in a short period of time (within 5–60 min) compared to several hours needed for the conventional methods of forced hydrolysis at high temperatures (~195°C) [41]. TiO, nanotubes which are open-ended and multi-walled with diameters of 8-12 nm and lengths between 200 and 1000 nm were also prepared using this method [33]. TiO, nanoparticles in the anatase phase were prepared by Baldassari et al. [42] using microwave-assisted hydrolysis of titanium tetrachloride (TiCl₄) in a dilute acidic aqueous medium. They found out that the product almost completely crystallized in a short reaction time of 30 min under microwavehydrothermal conditions. The acid that they used was to obtain a pure anatase phase was H₂SO₄ since the sulfate prevented the crystallization of brookite. In another study, they also prepared TiO₂ nanoparticles in the rutile phase from TiCl₄ by a microwave-hydrothermal process at different temperatures between 100 and 160°C for 5–120 min [42]. The morphology and size of the resulting nanoparticles can be varied by changing the time of reaction, microwave power and reactant concentration.

2.4. Hydro/solvothermal methods

These are two processes, solvothermal and hydrothermal which are almost similar. The hydrothermal method is a process of crystallizing a substance at a high temperature and high vapor pressure using an aqueous solution of the material [43]. It is commonly depicted as crystal synthesis or crystal growth from substances which are insoluble in customary temperature (100°C) and pressure (<1 atm). The process is carried out in autoclaves under controlled temperature and pressure. It allows the use of temperatures above the boiling point of water/ organic solution. Hydrothermal synthesis is characterized as a concoction response occurring in a dissolvable at temperatures over the dissolvable breaking point and at pressures above bar. Compared to hydrothermal method, the solvothermal method uses a non-aqueous solvent, has better control of the properties of TiO, and the temperature can be increased much higher meaning high boiling point solvents can be used. The hydrothermal strategy exploits that by expanding temperature and pressure the essential properties of water and consequently its capacities as a solvent changes. Important characteristics such as the ionic product density, thermal conductivity, viscosity, heat capacity and the dielectric constant are all highly pressure and temperature dependent and by tuning the synthesis parameters, specific solvent properties can be obtained. Feng et al. [44] produced TiO, nanorods by treating titanium tetrachloride solution saturated with sodium chloride at 160°C for 2 h. Kim et al. [45] used the solvothermal method to prepare TiO, of good quality without the use of surfactants.

The first report of the hydrothermal growth of crystals was by a German geologist Karl Emil in 1845 [46]. The hydrothermal method can be used to synthesize a single crystal of the material depending on the solubility of the material in the solvent. Single crystal growth is done in a high pressure vessel called an autoclave. These are hermitically sealed steel vessels that can withstand high temperatures and pressure for long durations. Also, the vessel must be chemically inert and must not take part in the hydrothermal process. A number of substances such as oxides [47], tungstate [48], molybdates [49], carbonates [50] and silicates [51] can be

synthesized. The different approaches in the hydrothermal technique can be broadly classified as temperature-difference technique, temperature-reduction technique and metastablephase technique [52]. Temperature-difference technique is a method in which the autoclave is heated to two temperature zones. The solute dissolves in the hotter zone (lower part) and the saturated solution moves from the lower part to the upper part (at a relatively lower temperature) due to the difference in temperature. The cooler solution in the upper portion descends to the lower part resulting in a counter flow. Eventually, the solution in the upper part becomes supersaturated due to the reduction in temperature and the material starts to crystallize. Temperature-reduction technique is a method in which instead of having the two temperature zones, the autoclave is slowly cooled down with the saturated solution inside it. However, this technique has the disadvantage of difficulty in controlling the growth process. Metastable-phase technique is a method based on the difference in solubility between the crystal growth phase and that serving as the starting material. The solution consists of compounds that are thermodynamically unstable under the growth conditions. The solubility of the compounds that are in the metastable phase is more than that of its stable phase. The compounds crystallize due to the decomposition of the metastable phase.

The advantages of the hydrothermal method are that it is an easy method to obtain nanotube morphology, variation in the synthesis method can be implemented to enhance the properties of TiO₂ nanotubes, and it is a feasible method for different applications. However, the disadvantages include long synthesis duration, the need for a highly concentrated NaOH solution (contaminating the TiO, nanotubes with NaOH) and precisely controlling the diameter of the nanotubes [53]. Furthermore, hydrothermal methods are disadvantaged by the high cost of equipment and the inability to monitor crystals in the process of their growth. Hydrothermal synthesis cannot be affected at both temperatures and pressures below the critical point for a specific solvent above which differences between liquid and vapor disappear, and can only take place under supercritical conditions. The hydrothermal method is affected by alkaline concentration, temperature and reaction time. Temperature is important for promoting growth of crystals and nucleation of nanoparticles. Generally, as temperature increases, the yield, length and degree of crystallinity of nanotubes also increase and with the optimal temperature between 100 and 200°C. As hydrothermal time increases, yield also increases, but prolonged hydrothermal time results in morphological changes of nanoparticles, for example, nanotubes to nanofibers [54].

Solvothermal method allows shape, control of size, distribution and crystallinity of TiO_2 nanoparticles better than the hydrothermal method. These can be achieved by controlling the following parameters; solvent, addition of surfactants, titanium precursors, reaction temperature and reaction time [55]. Use of organic solvents in the solvothermal method results in a product that is free from foreign anions since organic solvents exhibit low relative permittivity as well as being free from ionic species.

2.5. Sol-gel methods

Sol-gel process is a wet-chemical technique that is mostly used in the field of materials science and ceramic engineering. It can be defined as the conversion of a precursor solution to an inorganic solid through polymerization reactions induced by water. Hydrolysis forms a sol which is basically a dispersion of colloidal particles in a liquid, and condensation leads in the formation of a gel. Compared to the methods discussed above, the sol-gel process is very promising for synthesis and preparation of inorganic and organic-inorganic hybrid nanomaterials because it allows the use of low processing temperatures (<100°C) and molecular level composition homogeneity [56]. Particle size and shape and are easy to control using the sol-gel method.

The sol-gel process produces fine, spherical powders of uniform size and has been widely used to synthesize TiO₂ materials and normally proceeds via an acid-catalyzed step of titanium (IV) alkoxides [57]. One of the most attractive features of the sol-gel process is the possibility to shape the resulting material into desired forms such as fiber, film and monodispersed powder. Several steps and conditions are applied in a sol-gel process to control the final morphology as suggested by Mehrotra and Singh [58] in **Figure 4**.

Typical precursors are metal oxides and metal chlorides. A metal alkoxide consists of an M—O—R linkage where M is the metal, O is oxygen and R is an alkyl group. The polarization that takes place in the M—O bond makes it susceptible to nucleophilic attack. In the presence of water, the alkoxide undergoes a nucleophilic substitution reaction in which the alkoxy groups (OR) are replaced by the hydroxyl groups from water and this process is called hydrolysis. The metal hydroxide groups will link and generate a hydrated metal-oxide network which eventually forms small nuclei and this process is called condensation.

The chemistry, hydrolysis and poly condensation reactions are very convenient to obtain both polymeric and particulate titanium sols:

$$\text{TiOR} + \text{mH}_2 \text{O} \rightarrow \text{Ti}(\text{OR})_{4-n}(\text{OH})_n + n\text{ROH}$$
(1)

$$Ti-OH + OR-Ti \rightarrow Ti-O-Ti + ROH$$
(2)

$$Ti-OH+OH-Ti \rightarrow Ti-O-Ti+H_2O$$
 (3)

Polycondensation turns monomers into oligomers and, lastly, polymers. As long as the number of alkoxide groups, is greater than 2, complex random branching may occur finally leading to fractal structures.

Metal alkoxides used for the sol-gel process are generally very reactive and thus there is need for controlling the reactivity in order to obtain sols and gels with desirable properties by using modifiers or addition of chelating ligands such as β -diketones, carboxylic acids or other complex ligands [56]. These modifiers react with alkoxides giving rise to new molecular precursors that can be used in sol-gel processing to provide better control of the hydrolysiscondensation process. These new precursors reduce reactivity and functionality, prevent condensation and lead to formation of species that are smaller. Livage et al. in 1988 investigated the use of acetylacetone to improve the sol-gel processing of metal alkoxides [59].

Modification by modifiers reduces the number of M—OR bonds available for hydrolysis and thus hydrolytic susceptibility. If β -diketones are used, they decrease the nuclearity resulting in small particles since these ligands are surface capping reagents and polymerization lockers. Carboxylate ligands such as acetic acid mostly act as bridging chelating ligands.

Synthetic Methods for Titanium Dioxide Nanoparticles: A Review 161 http://dx.doi.org/10.5772/intechopen.75425



Figure 4. Different sol-gel process steps to control the final morphology of the product [58].

There are several advantages of the sol-gel process and these include [60]: (i) use of low temperatures during preparation, (ii) easy and effective control of particle size, shape and properties, (iii) better homogeneity from raw materials, (iv) better purity from the starting materials and it is possible to design the material structure and property through the proper selection of the precursor.

2.5.1. Sol-gel process parameters affecting properties of TiO,

There are various parameters that influence the size and properties of the TiO_2 particles produced via the sol-gel process. To get TiO_2 particles with desirable properties, the parameters that influence hydrolysis and condensation reactions of the sol-gel process should be controlled. It has been established that some parameters are more important than others. The parameters include pH, nature and concentration of the catalyst, water/precursor molar ratio, reaction temperature, precursor concentration, type of solvent and type of precursor [61, 62].

2.5.1.1. Precursor concentration

Particle size increases with increasing precursor concentration due to enhanced coagulation and sintering resulting from the large concentration of TiO_2 nuclei generated at high TTIP precursor concentrations [63]. Increase in precursor concentration increases the crystallinity of the anatase, and enhances transformation from anatase to rutile [64].

2.5.1.2. Water content

The amount of water is a crucial parameter in controlling the hydrolysis reaction. Xiaobo [31] reported that the development of Ti–O–Ti chains through alkoxylation is favored when the content of water is low, with low hydrolysis rates and excess titanium alkoxide in the

reaction mixture. The amount of water should not be too low otherwise the hydrolysis of the alkoxides with water will be incomplete and condensation occurs between the monomers of $(OH)_x Ti(OR)_{4-x}$ [65]. Other researchers reported that the ratio of water to the alkoxide required for particle formation should be greater than 2.5 as deduced from the equation R= $[H_2O]/[TEOT] > 2.5$ [66]. The largest R value reported was 7 which gave particles with average size of 300 nm. If the amount of water is increased, a stronger nucleophilic reaction between water and alkoxide molecules occurs resulting in more alkoxyl groups being substituted by OH groups of water. The monomers obtained then interact with each other to form a three-dimensional network structure. When R is over a critical value, the hydrolysis is more complete and more alkoxides convert to the corresponding metal hydrates, M(OH)z which then react with each other to form particle-like polymers [65]. The formation of Ti(OH)₄ is favored by high hydrolysis rates caused by large amounts of water.

According to a study by Yu and Wang [65], the molar ratio of $H_2O/alkoxides$ (Rw) used in the sol-gel process strongly affect the characteristics of the resultant oxides as shown in **Figure 5(a)**. They suggested that the reaction mechanisms for sol-gel conversion depend on Rw used and they came up with three different mechanisms as shown in **Figure 5(b)**. All mechanisms could occur at the same time but there would be a dominant one [65]. Case I: When Rw is less than four (Rw < 4), the hydrolysis between alkoxides and water is incomplete hence condensation reaction occurs between the monomers. Case II: When Rw is increased to between two and four ($2 < Rw \le 4$), stronger nucleophilic reaction between water and alkoxide molecules monomers occurs and a three-dimensional network is formed. Case III: When Rw used is over the critical value the hydrolysis will be complete. The alkoxides will convert to the corresponding metal hydrates. The monomers will react with each other to form particle-like polymers.

2.5.1.3. pH

The pH of the sol-gel system for the preparation of uniform nanoparticles of anatase titania from condensed TiO_2 gel is a key factor for controlling the final particle size and shape of the product [67]. The grain size of the TiO_2 particles generally increases with increase in pH of the sol [68]. When the hydrogen ion concentration is high, the particles grow rapidly to form large grains because the hydrogen ions interfere in the reaction and decrease the nucleation rate. The new nucleus has enough time to grow and aggregate into large TiO_2 particles [69]. Matijevic et al. [70] reported the synthesis of TiO_2 spherical particles of a narrow size by aging a highly acidic solution of titanium tetrachloride at elevated temperatures for 6–47 h. The amount of acid (pH) determines not only the size of the nanoparticles but also the stability of the sol [71].

2.5.1.4. Temperature

The sol-gel temperature is a critical parameter in controlling the properties of the resulting TiO_2 nanoparticles. Vorkapic and Matsoukas [71] studied the effect of the hydrolysis temperature on particle size where they varied the temperature between 0 and 50°C and they found out that low hydrolysis temperatures favored formation of larger particles. When the temperature was increased, the size decreased and reached a minimum in the range 25–50°C. High

Synthetic Methods for Titanium Dioxide Nanoparticles: A Review 163 http://dx.doi.org/10.5772/intechopen.75425



Figure 5. Sol-gel processes with different water contents [65].

temperatures increase the thermal energy of the colloid, decreases viscosity and the dielectric constant of the solvent, thus lowering the electrostatic barrier against aggregation resulting in larger particles [72].

2.5.1.5. Precursor type

Vorkapic and Matsoukas investigated the effect of different alkoxides on the size of the TiO_2 nanoparticles and they found out that at 25°C, the final size decreases with increase in the

length of the alkoxy group [71]. Their results showed that particle size decreased in the order ethoxide > propoxide > isopropoxide > butoxide, corresponding to the order of decreasing reactivity of the alkoxide hence the lower hydrolysis rate.

2.5.1.6. Solvent type and concentration

In general, after nucleation, the particles grow by molecular addition or aggregation and this particle growth is affected by the kinds of solvents used because particle interaction potential is different in each solvent. The increase in the amount and molecular weight of the alcohol was found to increase the size of the particles and the smallest size was obtained when no alcohol was used [71]. This is due to the fact that an increase in both concentration and molecular weight leads to a decrease in the dielectric constant of the solvent resulting in decreased stability and enhanced rate of re-aggregation and larger particle size. The formation of TiO_2 from thermal hydrolysis of titanium tetrachloride in water/n-propanol mixtures was investigated by Park et al. [73]. The study showed that when powders were redispersed in various solvents the degree of aggregation increased in the order: methanol > ethanol > propanol suggesting that colloidal destabilization was the primary mechanism by which these alcohols influenced particle size.

In another study by Xu et al. [74], the photocatalytic activity of unsupported TiO_2 gradually increased with increase in the chain of the solvent used in preparation due to the increase in the content of anatase and a decrease in particle size. They found out that when the solvent was changed from methanol to 2-pentanol, the content of anatase increased from 68 to 91% with a decrease in particle size from 11.6 to 10.5 nm. The increase in alcohol concentration in the sol-gel reaction mixture can slow down the hydrolysis rate and the resulting sol would possess a high content of amorphous TiO₂.

2.6. Template-based methods

Template-assisted synthesis is an easy, cost effective and highly versatile approach to fabricate nanostructures. Whenever microporous or nanoporous materials are utilized as templates, one-dimensional (1D) nanostructures can be integrated by saving a material of decision inside the format's nano-channels. Template-based synthesis is a method in which a nanoporous material is used as the mold and the desired nanotube material is coated on the walls of the mold. There are two approaches for template-based synthesis which are the negative and positive template. The template is then dissolved to get the nanotubes or nanorods. If the material of interest is coated on the inner walls, then it is a negative template-based synthesis. If the material is coated on the outer walls of the template then is a positive template-based synthesis. In the negative template synthesis, if the pores of the mold are entirely filled, then nanorods can be synthesized. The most commonly used template for negative template synthesis is anodic aluminum oxide. Yuan et al. showed the synthesis of TiO, nanotubes and nanorods using anodic aluminum oxide as a template [75]. The walls of the template were coated using the hydrolysis method. The anodic aluminum oxide was used as the membrane between deionized water and the Ti(OC₄H₉)₄ solution in C₄H₉OH during hydrolysis. The thickness of the nanotubes walls were controlled by varying the concentration of $Ti(OC_4H_9)_4$. Jiang et al. reported the synthesis of TiO, nanotubes by immersing anodic aluminum oxide
in an aqueous ammonium hexafluorotitanate solution [76]. Michailowski et al. showed the synthesis of TiO_2 nanotubes via a thermal decomposition process of Ti(Oi-Pr)_4 using anodic aluminum oxide as a template [77]. Correspondingly, Liang et al. revealed the synthesis of TiO_2 nanotubes through atomic layer deposition [78]. Anodic aluminum oxide was utilized as the template, and TiCl_4 was used as the precursor for the atomic layer deposition of TiO_2 .

The atomic layer deposition approach is a highly conformal coating process, and the thickness can be controlled very precisely. Therefore, in this method, the thickness of the walls of the nanotube can be controlled very precisely. The entire undesired TiO, deposited layer on the top surface of the template is eliminated by mechanical polishing. Hoyer showed the synthesis of TiO, nanotubes using positive template [77]. In this approach, TiO, was deposited on poly(methyl methacrylate) nanorods arrays by the electrochemical deposition procedure. The nanorods were selectively etched to form TiO₂ nanotubes. The nanorods were, however, fabricated using an anodic aluminum oxide template. Likewise, TiO, nanotubes were synthesized using electrospun poly(L-lactide) fibers as a positive template [79]. Jung et al. confirmed the synthesis of double wall TiO, nanotubes which were fabricated by condensing Ti(Oi-Pr), precursors onto both surfaces of the self-assembled organogel tubes [80]. In comparison to negative templatebased synthesis, the positive-based template has a better control on the smoothness of the inner and outer wall. The advantage of this template-based synthesis is that the dimensions of the nanotubes can be controlled by controlling the pore dimensions of the template. The disadvantages of this technique are that the fabrication process is relatively more complicated, and the nanotube morphology can be destroyed during fabrication steps such as mechanical polishing.

Nanoporous media typically used as templates for 1D nanostructure fabrication include track-etch membranes, which are commonly made from polymers including poly(carbonate), poly(ethylene terephthalate) or poly(imide) [81, 82] and anodized aluminum oxide (AAO), which can be purchased commercially or fabricated using a well-known anodization process [81–84]. In addition to nanoporous materials, templates can also be fabricated using lithographic techniques. The use of AAO templates is especially attractive because of its simple, low cost and highly controllable fabrication method. Vertically orientated CrO_2 nanorods arrays were obtained through atmospheric-pressure CVD assisted by AAO templates and were etched to form nanotubes. Such ordered nanorods within an AAO template may be significantly applied in ultrahigh-density perpendicular magnetic recording devices.

2.7. Electrochemical anodization

Electro-anodization is an electrolytic process used to grow the oxide layer on the surface of the metal. When anodizing, the metal to be treated forms an anode electrode of an electric circuit. Anodization alters the microscopic texture of the surface and the crystal structure of the metal close to the surface.

Metal anodization has been greatly used in industry as a surface treatment technique to render materials with resistance against uncontrolled oxidation, abrasion and corrosion. Anodizing increases corrosion resistance of oxide film over a metallic surface and wears resistance, and also improves adhesion for paint primers and glues than bare metal [85]. Although this technique has been developed for a long time, it was until 1990s that researchers discovered that

highly ordered nanoporous structures can be achieved by varying anodization conditions including electrolyte composition and concentration, temperature, as well as anodization voltage [86]. The dense and uniform layer of anodized oxide inhibits ionic conductivity, thus they can be regarded as barrier oxides to effectively protect the metal from further corrosion. On top of that, the anodized oxide film can improve the surface properties of metal, such as wearing, galling and dielectric layer.

Among all metals that can be anodized, aluminum and titanium can be anodized into nanoporous structures with well controlled depth, diameter and pitch. The working metal is set as anode to oxidize during the electrochemical process and cathode can be any electronic conductor mainly platinum, which would not react in the anodizing bath. The electrolyte is chosen according to its higher growing rate of the oxide compared to its dissolution rate or by the insolubility with the anodized metal. As the reaction progresses the metal at positive terminal withdraws electrons, by so doing allowing the ions on the metal surface to react with water in the electrolyte to form a dense oxide layer. Later the electrons return back to the electrolyte where they react with hydrogen ions to form hydrogen gas. When metals are exposed to sufficient anodic voltage supply in an electrochemical configuration, an oxidation reaction takes place ($M \rightarrow M^{n+} + ne^{-}$). Depending mainly on the electrolyte and the anodization parameters, there are essentially three possibilities for reactions to occur:

- **1.** The Mⁿ⁺ ions are solvatized in the electrolyte, that is, the metal is continuously dissolved and corrosion, or electropolishing of the metal is observed.
- **2.** The Mⁿ⁺ ions form react with O²⁻ provided by H₂O in the electrolyte and form a compact oxide layer (MO), if MO is not stable in the electrolyte.
- **3.** After some time during anodization process, completion between solvatization and oxide formation is established, which results to porous oxide layer.

Many properties of these transition metal anodic oxides become more and more important when the possibilities on a micro or nano scale are explored. Anodic oxide films, with the inherent nanoporous structure, exhibit high surface area, and short solid-state diffusion path for catalysis, electrochemical devices and energy applications. The other advantage of the anodic oxide micro/nano structures is that, the fabrications are achieved by chemical or electrochemical processes that are relatively simple and cost effective. The morphologies of anodic oxides include powders, rods, wires and tubes. Materials ranging from Al, Ti, Zr, W to Ta have all been investigated to form self-assembly nanotubes structures [87]. Among these transition metals oxide nanotubes, anodic titanium oxide (ATO) and anodic aluminum oxide (AAO) are among the most widely studied for their functional properties.

2.7.1. Mechanism of growth of the TiO, nanotubes

This section reviews the growth mechanism of titanium dioxide nanotubes (TNTs) by electrochemical anodization technique in fluoride-containing electrolyte solution. The formation of TNTs in acidic electrolyte conditions containing fluoride ions are generally agreed to form in the field assisted oxidation and dissolution of formed titanium oxide surface. This process involves two vital steps that occur simultaneously, the formation of titanium oxide and dissolution of the oxide. The process can be explained by the following reactions:

$$Ti + 2H_2O \rightarrow TiO_2 + 4e^- + 4H^+ Oxidation$$
 (4)

$$TiO_2 + 6F^- + 6H^+ \rightarrow [TiF_6]^{2-} + 2H_2 O Dissolution$$
(5)

This process usually takes place in a two electrode setup, where titanium film serves as anode and platinum as cathode. The anode Ti is immersed into electrolyte solution, ionic species such as OH⁻ and F⁻ are adsorbed on the surface. The growth of anodic oxide layer depends on the field-aided transport of mobile ions through the oxide. Depending on the speed of the ionic species (Ti⁴⁺ and O²⁻), the growth of the new oxide proceeds at the interface between the metal and oxide or at the interface between oxide and electrolyte (compact anodic oxide layers may grow at either interfaces, but under most conditions oxide grows at the metal-oxide interface). The growth of an anodic oxide layer is determined by the field-aided transport of mobile ions through the oxide.

The presence of fluorides in the electrolyte strongly affects the anodization process, as fluorides form water soluble $[TiF_6]^{2-}$ species. On one hand, complexation occurs with Ti^{4+} ions that are ejected at the oxide-electrolyte interface [after migration through the oxide film; Eq. (6)]:

$$\mathrm{Ti}^{4+} + 6\mathrm{F}^{-} \rightarrow [\mathrm{TiF}_{6}]^{2-} \tag{6}$$

And on the other hand by chemical attack of the formed TiO_2 Eq. (5).

Depending on the fluoride concentration, three very different electrochemical characteristics can be obtained [87]. If the fluoride content is very low ($\leq 0.05 \text{ wt\%}$), a characteristic as in the fluoride ion-free case is observed; that is, after anodizing the material to a voltage above up, a stable compact oxide layer is formed. If the fluoride concentration is high (~1 wt%), no oxide formation can be observed, as all the Ti⁴⁺ formed immediately reacts with the abundant fluoride to form soluble $[\text{TiF}_6]^{2-}$ (the reaction may then be controlled by diffusion of $[\text{TiF}_6]^{2-}$ from the surface, and electro polishing of the sample occurs).

For intermediate fluoride concentrations, a competition between oxide formation and Ti⁴⁺ solvatization takes place and porous oxide or nanotube formation can be observed. A typical I-t curve for conditions that leads to nanotubes formation. The curve shows three stages: in the initial stage of anodization, the curve essentially follows the fluoride-free case and if samples are removed from the electrolyte, a compact oxide layer is present. In stage II, a current increase occurs, and irregular nanoscale pores are initially formed that penetrate the initial compact oxide (the current increases as the reactive area increases). In stage III, the current drops again as a regular nanoporous structure or nanotube layer forms. The penetrated compact oxide (random pore layer and initiation layer) often remains as remnants that are frequently found after anodization on the tube tops [87, 88]. Various efforts have been directed toward removing these layers [89, 90], as they interfere with any transport process into the tubes or hamper the exploitation of tube size effects [91, 92]. After self-organization occurred, the tube growth continues at steady current densities. For extended anodization, the growth may be determined by diffusional effects [93] and thus agitation (and gravity effects) and viscosity may become important. The length of the TNTs is determined by the dynamic equilibrium between the oxide formation and chemical dissolution of the oxide. Water oxidation at the anode results in the formation of oxygen and the hydrogen formation at the cathode as shown in Eq. (7). Meanwhile, a small amount of hydrogen ions from the electrolyte is reduced to form hydrogen bubbles at the cathode shown in Eq. (8). These bubbles can be clearly observed at the cathode during the experiments, while there is no apparent observations of oxygen bubbles flowing up toward the electrolyte surface at the anode electrode. It is possible that there might be only about 2% amount of water volume resulting to no obvious phenomenon.

$$H_2O \rightarrow O_2 + 4H^+ + 4e^-$$
 (7)

$$2H^+ + 2e^- \rightarrow H_2 \tag{8}$$

3. Conclusion

In this review, we summarized some of the progress in the synthesis of titanium dioxide nanoparticles. A lot of effort has been put recently in the synthesis of nanostructured TiO_2 with different properties and applications. The modifications of the nanoparticles brought some new properties resulting in new applications. From the synthetic methods that have been reviewed, it is clear that there is still a potential to come up with nanostructured TiO_2 particles with different properties through the modifications of the existing methods. Although the nanoparticles with new properties might be more efficient, their toxicity should be assessed.

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References

 Byranvand MM, Kharat AN, Fatholahi L, Beiranvan ZMA. Review on synthesis of Nano-TiO₂ via different methods. Journal of Nanostructures. 2013;3:1-9

- [2] Banfield JF, Zhang H. Nanoparticles in the environment. Reviews in Mineralogy and Geochemistry. 2001;44(1):1-58
- [3] Brock T, Groteklaes M, Mischke. European Coatings Handbook. Hannover, Germany: Vincent Verlag; 2000
- [4] Beydoun D, Amal R, Low G. Role of nanoparticles in photocatalysis. Journal of Nanoparticle Research. 1999;1:439
- [5] Adachi M, Murata Y, Okada T, Yoshikawa S. Formation of titania nanotubes and applications for dye-sensitized solar cells. Journal of the Elelectrochemical Society. 2003;150(8): G488-G493
- [6] Halary-Wagner E, Wagner F, Hoffmann P. Titanium Dioxide Thin Film Deposition on Polymer Substrates by Light Induced Chemical Vapour Deposition. Submitted to Euro-CVD 14, Paris, France; 2003
- [7] Macák M. Growth of anodic self-organazed titanium dioxide nanotube layers [Ph.D. thesis]. University Erlangen-Nürnberg-Germany; 2008
- [8] Chen X, Mao SS. Titanium dioxide nanomaterials: Synthesis, properties, modifications, and applications. Chemical Reviews. 2007;107:2891-2959
- [9] Pratsinis SE. History of manufacture of fine particles in high-temperature aerosol reactors. In: Ensor DS, editor. Aerosol Science and Technology: History and Reviews, 1st ed. RTI International, Research Triangle Park: 2011
- [10] Chabra V, Pillai V, Mishra BK, Morrone A, Shah DO. Synthesis, characterization, and properties of microemulsion-mediated nanophase TiO, particles. Langmuir. 1995;11:3307
- [11] Seifried S, Winterer M, Hahn H. Nanocrystalline Titania films and particles by chemical vapor synthesis. Chemical Vapour Deposition. 2000;6(5):239-244
- [12] Oh SM, Ishigaki T. Preparation of pure rutile and anatase TiO₂ nanopowders using RF thermal plasma. Thin Solid Films. 2004;457:186-191
- [13] Gablenz S, Voltske D, Abicht HP, Neumann-Zoralek J. Preparation of fine TiO₂ powders via spray hydrolysis of titanium tetraisopropoxide. Journal of Materials Science Letters. 1998;17(7):537-539
- [14] Boccacini A, Zhitomisrky I. Application of electrophoretic and electrolytic deposition techniques in ceramic processing. Current Opinion in Solid State and Material Science. 2002;6:257-260
- [15] Besra L, Liu M. A review on fundamentals and applications of electrophoretic deposition (EPD). Progress in Materials Science. 2007;52(1):1-61
- [16] Nyongesa F, Aduda B. Electrophoretic deposition of titanium dioxide thin films for photocatalytic water purification systems. Advances in Materials. 2017;6(4):31-37. DOI: 10.11648/j.am.20170604.11
- [17] Narayan MR, Raturi A. Deposition and characterisation of titanium dioxide films formed by electrophoretic deposition. Journal of Materials Engineering Innovation. 2012;**3**(1):17-31

- [18] Cabanas-Polo S, Boccaccini A. Electrophoretic deposition of nanoscale TiO₂: Technology and applications. Journal of the European Ceramic Society. 2015;36:265-283. DOI: 10.1016/ j. jeurceramsoc.2015.05.030
- [19] Ma J, Wang C, Peng KW. Electrophoretic deposition of porous hydroxyapatite scaffold. Biomaterials. 2003;24:3505-3510
- [20] Put S, Biest O, Anne G, Vleugels J. Microstructural engineering of FGMs by electrophoretic deposition. Journal of Material Processing Technology. 2004;143-144:572-577
- [21] Xue Z, Zhang W, Yin X, Cheng Y, Wang L, Liu B. Enhanced conversion efficiency of flexible dye-sensitized solar cells by optimization of the nanoparticle size with an electrophoretic deposition technique. RSC Advances. 2012;2:7074-7080
- [22] Miyasaka T, Kijitori Y. Low-temperature fabrication of dye-sensitized plastic electrodes by electrophoretic preparation of mesoporous TiO₂ layers. Journal of Electrochemical Society. 2004;151(11):A1767-A1773
- [23] Benehkohal N. Innovations in Electrophoretic Deposition of Nanotitania-Based Photoanodes for Use in Dyesensitized Solar Cells [PhD Thesis]. McGill University; 2013
- [24] Nguu J, Nyongesa F, Musembi R, Aduda B. Electrophoretic deposition and characterization of TiO₂/Nb₂O₅ composite thin films for dye sensitized solar cells. Journal of Materials Physics and Chemistry. 2018;6(1):1-8
- [25] Dhiflaoui H, Khlifi K, Cheikhlarbi AB. Effect of deposition parameters on electrophoretically deposited TiO₂. Journal of Material Sciences. 2016;4(3):7-15
- [26] Keskinen H. Synthesis of Nanoparticles and Preparation of Deposits by Liquid Flame Spray [DTech Thesis]. Tampere: Tampere University of Technology; 2007
- [27] Kozhukharov S, Tchaoushev S. Spray pyrolysis equipment for various applications. Journal of Chemical Technology and Metallurgy. 2013;48(1):111-118
- [28] Kozhukharov S, Tchaoushev S. Perspectives for development and industrial application of spray pyrolysis method. Annual Proceeds. "Angel Kanchev" University of Ruse. 2011;50(9):46-50
- [29] Wegner K, Schimmoeller B, Thiebant B, Fernandez C, Rao TN. Pilot plants for industrial nanoparticle production by flame spray pyrolysis. Kona Powder and Particle Journal. 2011;29:251-265
- [30] Taziwa T, Meyer E. Fabrication of TiO₂ Nanoparticles and Thin Films by Ultrasonic Spray Pyrolysis: Design and Optimization. ISBN 978-953-51-3312-4, Print ISBN 978-953-51-3311-7
- [31] Xiaobo C. Titanium dioxide nanomaterials and their energy applications. Chinese Journal of Catalysis. 2009;**30**:839-851
- [32] Varghese OK, Gong DW, Paulose M, Grimes CA, Dickey EC. Crystallization and high temperature structural stability of titanium oxide nanotube arrays. Journal of Materials Research. 2003;18:156

- [33] Kim H, Noh K, Choi C, Khamwannah J, Villwock D, Jin S. Extreme superomniphobicity of multiwalled 8 nnn TiO₂ nanotubes. Langmuir. 2011;27:10191-10196
- [34] Malekshahi Byranvand M, Nemati Kharat A, Fatholahi L, Malekshahi Beiranvand Z. A review on synthesis of nano-TiO₂ via different methods. Journal of Nanostructures. 2013; 3(1):1-9
- [35] Yu JC, Yu JG, Ho W, Zhang LZ. Preparation of highly photocatalytic active nano-sized TiO₂ particles via ultrasonic irradiation. Chemical Communications. 2001:1942-1943. 10.1039/ B105471F
- [36] Zhu Y, Chen F. Microwave-assisted preparation of inorganic nanostructures in liquid phase. Chemical Reviews. 2014;**114**(12):6462-6555
- [37] Collins MJ Jr. Future trends in microwave synthesis. Future Medicinal Chemistry. 2010; 2(2):151-155
- [38] Jacob J, Chia LHL, Boey FYC. Thermal and nonthermal interaction of microwave-radiation with materials. Journal of Materials Science. 1995;30:5321
- [39] de la Hoz A, Díaz-Ortiz Á, Moreno A. Microwaves in organic synthesis. Thermal and non-thermal microwave effects. Chemical Society Reviews. 2005;34:164
- [40] Gressel-Michel E, Chaumont D, Stuerga D. From a microwave flash-synthesized TiO₂ colloidal suspension to TiO₂ thin films. Journal of Colloid and Interface Science. 2005;285: 674-679
- [41] Corradi AB, Bondioli F, Focher B, Ferrari AM, Grippo C, Mariani E, Villa C. Conventional and microwave-hydrothermal synthesis of TiO₂ nanopowders. Journal of the American Ceramic Society. 2005;88(9):2639-2641
- [42] Baldassari S, Komarneni S, Mariani E, Villa C. Rapid microwave-hydrothermal synthesis of anatase form of titanium dioxide. Journal of the American Ceramic Society. 2005;88:3238
- [43] Reis KP, Ramanan A, Whittingham MS. Hydrothermal synthesis of sodium tungstates. Chemistry of Materials. 1990;2:219-221
- [44] Feng XJ, Zhai J, Jiang L. The fabrication and switchable superhydrophobicity of TiO₂ nanorod films. Angewandte Chemie International Edition. 2005;44(32):5115-5118
- [45] Kim CS, Moon BK, Park JH, Choi BC, Seo HJ. Solvothermal synthesis of nanocrystalline TiO₂ in toluene with surfactant. Journal of Crystal Growth. 2003;257:309
- [46] Christensen AN. Hydrothermal preparation of some oxides and some oxide hydroxides at temperatures up to 900°C and pressures up to 80 kb. Materials Research Bulletin. 1971;6:691-697
- [47] Zapf PJ, Hammond RP, Haushalter RC, Zubieta J. Variations on a one-dimensional theme: The hydrothermal syntheses of inorganic/organic composite solids of the iron molybdate family. Chemistry of Materials. 1998;10:1366-1373. DOI: 10.1021/cm9707667

- [48] Zheng W, Liu R, Peng D, Meng G. Hydrothermal synthesis of LaFeO₃ under carbonate containing medium. Materials Letters. 2000;43:19-22
- [49] Song H, Rioux RM, Hoefelmeyer JD, Komor R, Niesz K, Grass M, Yang P, Somorjai GA. Hydrothermal growth of mesoporous SBA-15 silica in the presence of PVP-stabilized Pt nanoparticles: Synthesis, characterization, and catalytic properties. Journal of American Chemical Society. 2006;128:3027-3037. DOI: 10.1021/ja057383r
- [50] Albu SP, Ghicov A, Aldabergenova S, Drechsel P, LeClere D, Thompson GE, Macak JM, Schmuki P. Formation of double-walled TiO₂ nanotubes and nobust anatase membranes communication. Advanced Materials. 2008;20:4135
- [51] Loryuenyong V, Angamnuaysiri K, Sukcharoenpong J, Suwannasri A. Sol-gel template synthesis and photocatalytic behavior of anatase titania nanoparticles. ScienceAsia. 2012;38(3):301-306
- [52] Yu XF, Lu YX, Wlodarski W, Kandasamy S, Kalantar-Zadeh K. Fabrication of nanostructured TiO₂ by anodization: A comparison between electrolytes and substrates. Sensors and Actuators B. 2008;130(1):25-31
- [53] Masuda H, Yamada H, Satoh M, Asoh H, Nakao M, Tamamura T. Highly ordered nanochannel-array architecture in anodic alumina. Applied Physics Letters. 1997;71:2770-2772. DOI: 10.1063/1.120128
- [54] Liu N, Chen X, Zhang J, Schwank JW. A review on TiO₂-based nanotubes synthesized via hydrothermal method: Formation mechanism, structure modification, and photocatalytic applications. Catalysis Today. 2014;225:34-51. DOI: 10.1016/j.cattod.2013.10.090
- [55] Stride JA, Tuong NT. Controlled synthesis of titanium dioxide nanostructures. Solid State Phenomena. 2010;162:261-294. ISSN 1662-9779
- [56] Attar AS, Ghamsari MS, Hajiesmaeilbaigi F, Mirdamadi S, Katagiri K, Baetzold RC. Journal of the American Chemical Society. 1981;103:6116
- [57] Oskam G, Nellore A, Penn RL, Searson PC. The growth kinetics of TiO₂ nanoparticles from titanium (IV) alkoxide at high water/titanium ratio. Journal of Physical Chemistry B. 2003;107:1734. DOI: 10.1021/jp021237f
- [58] Mehrotra RC, Singh A. Recent trends in metal alkoxide chemistry. Progress in Inorganic Chemistry. 1997;46:239-454
- [59] Livage J, Henry M, Sanchez C. Sol-gel chemistry of transition metal oxides. Progress in Solid State Chemistry. 1988;18:259-341
- [60] Ting KT, Yi SL, Yi JC, Hsin CA. Review of photocatalysts prepared by sol-gel method for VOCs removal. International Journal of Molecular Sciences. 2010;11:2336-2361. DOI: 10.3390/ijms11062336
- [61] Ding X, Qi Z, He Y. Effect of hydrolysis water on the preparation of nano-crystalline titania powders via a sol-gel process. Journal of Materials Science Letters. 1995;14(1):21-22. DOI: 10.1007/BF02565273

- [62] Arroyo R, Rodriquez R, Salinas P. Master behaviour for gelation in a sol-gel process under different temperature and pH conditions. Journal of Non-Crystalline Solids. 1993; 163(1):90-96
- [63] Jang HD, Jeong J. The effect of temperature on particle size in gas-phase production of TiO₂. Aerosol Science and Technology. 1995;23:553-560
- [64] Kim CS, Nakaso K, Xia B, Okuyama K, Shimada M. A new observation on the phase transformation of TiO₂ nanoparticles produced by a CVD method. Aerosol Science and Technology. 2005;39:104-112. DOI: 10.1080/027868290906986
- [65] Yu HF, Wang SM. Effects of water content and pH on gel-derived TiO₂-SiO₂. Journal of Non-Crystalline Solids. 2000;261:260-267
- [66] Barringer EA, Bowen HK. Formation, packing and sintering of monodispersed TiO₂ powders. Journal of the American Ceramic Society. 1982;65:199
- [67] Sugimoto T, Okada K, Itoh H. Synthetic of uniform spindle-type titania particles by the gel-sol method. Journal of Colloid & Interface Science. 1997;193:140
- [68] Jahromi HS, Taghdisian H, Afshar S, Tasharrofi S. Effects of pH and polyethylene glycol on surface morphology of TiO₂ thin film. Surface & Coatings Technology. 2009;203: 1991-1996
- [69] Chai LY, Yu YF, Zhang G, Peng B, Wei SW. Effect of surfactant on preparation TiO₂ by pyrohydrolysis. Transaction of Nonferrous Metals Society of China. 2007;17:176-180
- [70] Matijevic E, Budnik M, Meites L. Preparation and mechanism of formation of titanium dioxide hydrosols of narrow size distribution. Journal of Colloid Interface Science. 1997;61(2):302-311
- [71] Vorkapic D, Matsoukas D. Effect of temperature and alcohols in the preparation of titania nanoparticles from alkoxides. Journal of the American Ceramic Society. 1998;81:2815-2820
- [72] Moon YT, Park HK, Kim DK, Kim CH. Preparation of monodisperse ZrO₂ by microwave heating of zirconyl chloride solutions. Journal of the American Ceramic Society. 1995;78:2690-2694
- [73] Park J, Bauer S, Von Der Mark K, Schmuki P. Nanosize and vitality: TiO₂ nanotube diameter directs cell fate. Nano Letters. 2007;7(6):1686-1691
- [74] Xu Y, Zheng W, Liu W. Enhanced photocatalytic activity of supported TiO₂: Dispersing effect of SiO₂. Journal of Photochemistry and Photobiology. 1999;122:57-60. DOI: 10.1016/ S1010-6030(98)00470-5
- [75] Yuan L, Meng S, Zhou Y, Yue ZJ. Controlled synthesis of anatase TiO₂ nanotube and nanowire arrays via AAO template-based hydrolysis. Journal of Materials Chemistry A. 2013;1:2552-2557
- [76] Jiang WF, Ling YH, Hao SJ, Li HY, Bai XD, Cang DQ. In situ template synthesis of TiO₂ nanotube array films. Key Engineering Materials. 2007;336-338:2200-2202

- [77] Michailowski A, AlMawlawi D, Cheng G, Moskovits M. Highly regular anatase nanotubule arrays fabricated in porous anodic templates. Chemical Physics Letters. 2001;349:1-5
- [78] Liang YC, Wang CC, Kei CC, Hsueh YC, Cho WH, Perng TP. Photocatalysis of Ag-loaded TiO₂ nanotube arrays formed by atomic layer deposition. The Journal of Physical Chemistry C. 2011;115:9498-9502
- [79] Hoyer P. Semiconductor nanotube formation by a two-step template process. Advanced Materials. 1996;8:857-859
- [80] Jung H, Kobayashi H, van Bommel KJC, Shinkai S, Shimizu T. Creation of novel helical ribbon and double-layered nanotube TiO₂ structures using an organogel template. Chemistry of Materials. 2002;14(4):1445-1447
- [81] Baker LA, Jin P, Martin CR. Biomaterials and biotechnologies based on nanotube membranes. Critical Reviews in Solid State and Materials Sciences. 2005;30:183-205
- [82] Liang Z, Susha AS, Yu A, Caruso F. Nanotubes prepared by layer-by-layer coating of porous membrane templates. Advanced Materials. 2003;15(21):1849-1853
- [83] Steinhart M, Wehrspohn RB, Gosele U, Wendorff JH. Nanotubes by template wetting: A modular assembly system. Angewandte Chemie International Edition. 2004;43(11): 1334-1344
- [84] Steinhart M, Wendorff JH, Wehrspohn RB. Nanotubes à la carte: Wetting of porous templates. Chemphyschem. 2003;4(11):1171-1176
- [85] Chen CC, Fang D, Luo Z. Fabrication and characterization of highly-ordered valvemetal oxide nanotubes and their derivative nanostructures. Reviews in Nanoscience and Nanotechnology. 2012;(4):229-256
- [86] Beranek R, Hildebrand H, Schmuki P. Self-organized porous titanium oxide prepared in H₂SO₄/HF electrolytes. Electrochemical and Solid-State Letters. 2003;6(3):B12-B14
- [87] Kim D, Schmidt-Stein F, Hahn R, Schmuki P. Gravity assisted growth of self-organized anodic oxide nanotubes on titanium. Electrochemistry Communications. 2008;10:1082-1086
- [88] Song YY, Lynch R, Kim D, Roy P, Schmuki P. TiO₂ nanotubes: Efficient suppression of top etching during anodic growth. Electrochemical and Solid-State Letters. 2009; 12(7):C17-C20
- [89] Albu SP, Schmuki P. TiO₂ nanotubes grown in different organic electrolytes: Two-size self-organization, single vs. double-walled tubes, and giant diameters. Physica Status Solidi (RRL)-Rapid Research Letters. 2010;4(8-9):215-217
- [90] Park KH, Heo SJ, Koak JY, Kim SK, Lee JB, Kim SH, Lim YL. Osseointegration of anodized titanium implants under different current voltages: A rabbit study. Journal of Oral Rehabilitation. 2007;34(3):517-527

- [91] Albu SP, Ghicov A, Macak JM, Hahn R, Schmuki P. Self-organized, free-standing TiO₂ nanotube membrane for flow-through photocatalytic applications. Nano Letters. 2007; 7(5):1286-1289
- [92] Macak JM, Tshchiya H, Ghicov A, Yasuda K, Hahn R, Bauer S, Schmuki P. TiO₂ nanotubes: Self-organized electrochemical formation, properties and applications. Current Opinion in Solid State and Materials Science. 2007;11(1-2):3-18
- [93] Yasuda K, Schmuki P. Control of morphology and composition of self-organized zirconium titanate nanotubes formed in (NH₄)₂SO₄/NH₄F electrolytes. Electrochimica Acta. 2007;52(12):4053-4061

Innovation in the Electrophoretic Deposition of TiO₂ Using Different Stabilizing Agents and Zeta Potential

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Abstract

Surface engineering is gaining increasing relevance in various industrial sectors and in research, and in this sense, zeta potential measurements, being a physicochemical parameter of interface, are key to linking the functionality of a coating with its application environment. In this work, different stabilizing agents with different chemical structure and electrical charge were used to improve the stability of the TiO_2 particles. The influence of the electrophoretic deposition (EPD) parameters (potential and deposition time) and the concentration of chitosan and TiO_2 in suspension were studied to find the best deposition performance on the titanium substrate. The composition and structure of the coatings were evaluated by infrared spectroscopies (FT-IR) and scanning electron microscopy (SEM). It was observed that the TiO_2 particles were dispersed in the chitosan matrix through simultaneous deposition. Corrosion resistance was evaluated by electrochemical polarization curves, indicating a higher corrosion resistance of TiO_2 and TiO_2 -chitosan coatings compared to the pure titanium substrate in a solution of sulfuric acid.

Keywords: electrophoretic deposition, zeta potential, chitosan, TiO,

1. Introduction

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Nowadays, surface engineering is of great scientific and technological relevance focused on the development of new methods to achieve desired surface properties and provide better performance of materials.

The methods of surface modification are used to develop a wide range of functional properties including physical, chemical, biological, electrical, electronic, magnetic, adhesion, mechanical, wear-resistant, and corrosion-resistant properties on the required substrate surfaces.

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The industrial sectors that demand the development and application of the surface modification of materials are the automotive, aerospace, missile, energy, electronics, biomedical, textile, petroleum, petrochemical, chemical, steel, energy, cement, machine tool, and construction industries [1].

There are different methods that allow the coating of a surface, to mention some, such as painting, carburizing, nitriding, sputtering, electrophoretic deposition, spray coatings, electrodeposition, ion implantation, ion plating, thermal oxidation, laser cladding, electroless deposition, chemical vapor deposition, solvent casting, dip coating, and sol-gel coating [2].

Within the variety of coating methods, the electrophoretic deposition (EPD) has several advantages, such as low deposition time, simple and cheap equipment, little restriction of the shape of substrates; deposition is achieved both inside of the cavities and on the outside cavity surfaces, control the film thickness and uniformity, applicability to any powdered solid that forms a stable, a wide range of particle sizes, from micro- to nanometric particles (colloidal suspensions) [3].

Almost all types of substrates, including metal oxides, ceramics, polymers, and composite materials, can be coated by EPD with similar or different materials.

Using EPD, the coating of different substrates has been made with a variety of materials, to mention a few, metals, polymers, ceramics, glasses, carbon nanotubes, nanoparticles, zeolite, hydroxyapatite, silica, alumina, proteins, bacteria, and cells [4–8].

Moreover, considering the functionality and application the films can be used in antioxidant coatings, bioactive coating, cell fuel, tissue engineering, composites, medical implants, scaffolds, microelectronic devices, wear-resistant, sensors, nanoscale assembly, luminescent materials, gas diffusion electrode, biomedical, multilayer composites, bactericide surfaces, piezoelectric motors, photocatalyst and photovoltaics, corrosion protective, and water purification [9–22].

EPD is based on the movement of charged particles suspended in a solution through application of an external electric field (electrophoresis mechanism). This electric field enables the consolidation of particles into films, cast onto any shaped substrate, or into thick and bulk components.

The electrophoretic deposition process is generally described in three stages: the first consists in the application of an electric field between an anode and a cathode, which are submerged in the suspension of the charged particles, which causes the migration of the charged particles toward the opposite charged electrode. Subsequently, the particles begin to accumulate on the surface of the electrode resulting in the formation of a thin and thick film. Finally, a thermal treatment step is carried out to improve the characteristics of electrodeposits [1, 2].

To employ electrophoretic deposition successfully, a basic understanding of the colloidal stability, the deposition kinetics, and the constrained drying and sintering issues of the deposit is necessary.

Although the EPD technique is simple, it is necessary to understand the coupled electrical and physicochemical phenomena of the particles that are initially suspended, and at the end

of the process, are adhered to a surface. For this purpose, it is advisable to analyze the physicochemical environment to which a suspended particle is subjected, either dispersed or in the colloidal phase. One of the best known models for studying the colloidal phase or the stability of suspended particles is the double electrical layer (DEL), which consists of recognizing the distribution of electric charges around a particle surrounded by solvent molecules and counter ions that define its solid–liquid interface [2–4].

The zeta potential (ζ) is an electrochemical parameter that allows estimating the nature of the surface charge of the suspended particles, establishing whether the electrophoretic deposition process is anodic or cathodic and deposition kinetic. For example, if we compare a $\zeta = 100 \text{ mV}$ with a $\zeta = 10 \text{ mV}$, the electrophoretic velocity is expected to be 10 times higher. This effect results in more homogeneous deposits and the thickness will depend on the deposit time.

In this paper, the use of different stabilizing agents such as surfactants and biopolyelectrolytes with different ionic nature and chain length was proposed to improve the stability of the TiO₂ dispersions.

On the other hand, the zeta potential was used as a strategy to predict the performance of the EPD process. The profiles of $\zeta = f$ (pH) and $\zeta = f$ (dose stabilizing agent) were made as a strategic guide to establish the best conditions of the EPD, in order to achieve homogeneous deposits in an efficient way (short times, mass yield, sufficient adhesion, and resistant to corrosion). These TiO₂ coatings have potential uses in biomedical applications, water treatment, and photocatalytic materials.

2. Experimental

2.1. Metallographic preparation of titanium substrates

Titanium sheets were used as a substrate for their high mechanical resistance and corrosion, sectioned in square pieces with dimensions 1×1 cm and 0.1 cm thick for the cathode and 3×3 cm and 0.1 cm for the anode.

2.2. Profiles of $\zeta = f$ (pH) of TiO₂ and different stabilizing agents

The surface charge density, isoelectric point, and stabilizing agents-dosing strategy for the formulation of TiO_2 dispersion were determined with the profiles $\zeta = f(\text{pH})$. The zeta potential measurement was performed using the SZ-100 of Horiba Scientific equipment based on studies by López-Maldonado et al. [23, 24].

2.3. Colloidal titration of TiO₂ dispersions

The profiles of $\zeta = f$ (stabilizing agent dose) were performed to determine the dose of the stabilizing agent and improve the stability of the TiO₂ dispersion. The TiO₂ dispersions were prepared with water and water/ethanol mixtures (90:10 and 50:50) using surfactants of different chemical nature such as CTAB, SDS, Betaine, and Triton X-100 and a cationic

biopolyelectrolyte chitosan (Ch), see **Figure 1**. The nominal concentration of TiO_2 was kept fixed at a value of 0.1% wt, while the concentration of the dispersing agents was varied.

The zeta potential measurements were approximated with the equipment called Stabino Particle Charge Mapping.

The stabilizing agents used in the colloidal titration of the TiO₂ dispersion are shown in **Table 1**.

2.4. EPD process of TiO₂ with stabilizing agents

To assign the function of each electrode in the EPD cell (anode or cathode), it was necessary to measure the zeta potential of the dispersed particles of each formulation, before the experiment (see **Figure 2**). All experiments were performed in a conventional 2-electrode electrophoresis cell, with a capacity of 50 mL. All TiO₂ dispersions were prepared from 40 mL of a TiO₂ 0.1 wt. % (water) dispersion and then 4 mL of each stabilizing agent 1 wt. % was added, achieving a weight ratio of stabilizing agent to TiO₂ of 1:1. For the EPD process, a potential difference of 10 V and an electrodeposition time of 1 h were used. Working electrodes and



Figure 1. Chemical structure of stabilizing agents.

Innovation in the Electrophoretic Deposition of TiO₂ Using Different Stabilizing Agents and Zeta... 181 http://dx.doi.org/10.5772/intechopen.73210

| Dispersion | Stabilizing agent | Type of stabilizer |
|------------------|-------------------|--------------------|
| TiO ₂ | SDS | Anionic |
| | СТАВ | Cationic |
| | Triton X-100 | No ionic |
| | Betaine | Amphoteric |
| | Ch | Biopolyelectrolyte |





Figure 2. Experimental strategy for making TiO₂ coatings by EPD.

titanium counter electrodes were used with an area of 1 and 9 cm², respectively. All TiO_2 electrodeposits were carried out under pressure and at room temperature.

2.5. Physicochemical characterization of TiO₂ coatings

Electrodeposits of TiO₂ obtained on Ti sheets, were characterized by Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, and scanning electron microscopy (SEM). FTIR spectra of samples were recorded using a Nicolet FT-IR spectrometer. The SEM-EDS analysis was performed on SEM (ZEISS EVO-MA15), equipped with an EDS (energy dispersive spectroscopy) BRUKER detector microscope to observe the composition.

3. Results and discussion

3.1. Profiles of $\zeta = f(pH)$ of TiO₂ and different stabilizing agents

The zeta potential is a parameter by electrochemical nature that allows to study and predict the interactions occurring at the molecular level between the colloidal particles TiO_2 and the different stabilizing agents, also it indicates the degree of stability of dispersion in an aqueous medium from the point electrically. The aim is to employ ζ measurements to know and understand the behavior of the type of stabilizing agents in the EPD process performance.

In **Figure 3**, the behavior of the surface charge density of TiO₂ particles and stabilizing agents is shown. TiO₂ has an anionic character, according to the zeta potential = -7.8 mV, which remains constant at pH 4–11. This implies that by electrostatic interactions, the TiO₂ can interact with the stabilizing agents of opposite charge. Chitosan presents its isoelectric point ($\zeta = 0$) at pH = 6.5, at pH lower than the IEP, shows a cationic character and at pH > IEP, the chitosan becomes an insoluble material and precipitates.

The CTAB presents a cationic character at a pH of 3–11 (ζ = 12.0 mV), this is attributed to the functional group of the surfactant that maintains its positive charge in this pH range. Similarly, the SDS presents a constant charge density, ζ = –12.0 mV at pH 3–11, but of anionic character due to the functional group, it has in its structure. As expected, the Triton X-100 showed a nonionic character (ζ = –3.0 mV), according to the zeta potential value very close to zero, throughout the pH range.

Betaine, being an amphiphilic compound, presented an isoelectric point at pH = 3.0 and another at pH = 12.0, corresponding to the two types of functional groups it has in its structure.

It is well known that an excess or lack of ions on the surface of a material such as TiO_2 causes low mobility and therefore, deficiency of fixation on the surface of the metal electrode to be coated. For this reason, a better understanding of the surface properties of a dispersion, such as the profiles $\zeta = f$ (pH), may lead to improved surface performance of the material.

3.2. Colloidal titration of TiO₂ dispersions

Considering the profiles of $\zeta = f$ (pH) of the stabilizing agents and of TiO₂, various formulations can be developed in which the TiO₂ can have a greater stability and a positive or



Figure 3. Profiles of $\zeta = f(pH)$ of TiO₂ and different stabilizing agents.

negative surface charge density. Additionally, this implies that we can perform an anodic or cathodic electrodeposit, depending on the application.

The addition of a stabilizing agent seeks that the zeta potential value of TiO₂ ($\zeta = -7.8$ mV) moves farther from $\zeta = 0$ mV, that is, becomes more negative or very positive. This allows the TiO₂ particles to be more stable and avoid the sedimentation phenomenon.

In this work, only the characteristics of the TiO_2 electrodeposits with chitosan are discussed, however, as mentioned above, there are a series of options to perform the coatings using different stabilizing agents and evaluate their physicochemical properties based on their application.

In **Figure 4**, the profiles of $\zeta = f$ (stabilizing agent dose) of the dispersion of TiO₂ 0.1 wt. % are shown.

The addition of SDS and betaine did not significantly increase the stability of TiO₂ particles, which could be expected since they are negatively charged density compounds and would increase the repulsion forces of TiO₂ particles. The addition of Triton X-100 caused a decrease of $\zeta = -7.8$ mV TiO₂ at $\zeta = -3.0$ mV, at a dose of 11 mg Triton X-100.

On the other hand, the addition of the cationic stabilizing agents, CTAB and Ch, caused an inversion of the surface charge density of the TiO_2 particles with a dose of 4 mg. With the CTAB, a ζ = 9.0 mV was reached, while with Ch, a ζ = 6.0 mV, this difference is attributed to the CTAB having a higher surface charge density.



Figure 4. Profiles of ζ = f (stabilizing agent dose) of the dispersion of TiO₂ 0.1 wt. %.

For the present research, it is desired zeta potential values that guarantee stability to achieve a more homogeneous deposit (in terms of grain size and roughness). This indicates that controlling the doses of dispersing agent in such a way as to obtain values of zeta potential farthest from zero will cause the attraction force between the particles to decrease and, in turn, increase the force of attraction toward one of the poles of the electrophoretic cell. This effect is also reflected in a lower voltage demand in the electrophoretic cell and therefore the elimination of electrolysis reactions at the electrodes.

3.3. EPD process

In **Figure 5**, the effect of the electrodeposition time on the deposited TiO_2 -Ch mass is shown. It is observed that 6 mg are deposited in the first 30 min, in a longer time the amount of deposit shows an exponential behavior (**Figure 6**).

3.4. Evaluation of the Ti/TiO₂-CTAB and Ti/TiO₂-chitosan coating

The SEM images and the corresponding chemical microanalysis of the Ti/TiO_2 coating prepared by electrophoresis are presented in **Figure 7**. In the images of **Figure 7a**, the ceramic type structure of TiO_2 -CTAB is observed, morphologically very different from the plastic type structure obtained by impregnation of the chitosan in the layer shown in **Figure 7b**.

EDX elemental analysis indicates the presence of titanium and oxygen (TiO_2) on the surface of the electrodes. In addition, carbon signals suggest the presence of CTAB and chitosan from the dispersions. **Figure 8** shows the EDX spectra corresponding to Ti/TiO₂-CTAB and Ti/TiO₂-chitosan electrodes obtained by 10 V electrodeposits.



Figure 5. Influence of the electrodeposition time on the coating mass of TiO₂.

Innovation in the Electrophoretic Deposition of TiO₂ Using Different Stabilizing Agents and Zeta... 185 http://dx.doi.org/10.5772/intechopen.73210



Figure 6. Schematic representation of the interface model for the EPO process of TiO₂ using chitosan.



Figure 7. Micrographies of the EPD deposits with the dispersions of (a) TiO₂-CTAB and (b) TiO₂-chitosan.



Figure 8. Spectrum of surface chemical analysis by EDX of the coatings with the dispersions of (a) TiO_2 -CTAB and (b) TiO_2 -Chitosan.

The analysis of the chemical composition of the electrodes showing a higher percentage by weight of carbon by the coating TiO_2 -chitosan, this is attributed to the molecular weight of the chitosan that is above the CTAB.

In **Figure 9**, the FTIR spectra of the TiO_2 -Ch/Ti coating are shown using EPD (time = 5 min, 10 V) and the chitosan, the coating spectrum shows a wide absorption between 3350 and 3270 cm⁻¹ to a combination of ways to stretch the OH and NH bonds in the chitosan and

Innovation in the Electrophoretic Deposition of TiO₂ Using Different Stabilizing Agents and Zeta... 187 http://dx.doi.org/10.5772/intechopen.73210



Figure 9. Micrographies of the EPD deposits with the dispersions of (a) TiO₂-CTAB and (b) TiO₂-chitosan.

hydrogen bonds between the polysaccharide chains. The band at 1650 cm⁻¹ is assigned to the amine group of stretching vibration C=O (amine I) located in the acetylated chitosan units. The band at 1600 cm⁻¹ is the result of the signal corresponding to amine II and the bending vibration NH (amine II). These signals confirm the presence of the chitosan chains with the TiO₂ particles in the Ti substrate.



Figure 10. Polarization curves of the TiO₂-Ch electrodes in 0.5 M sulfuric acid.

In **Figure 10**, it can be seen that all TiO_2 -chitosan coatings show a lower voltage compared to the Ti electrode, which means that TiO_2 -chitosan composite coatings tend to oxidize more easily, because the more negative the difference of the slower the oxidation reaction of the species to the coating, and the faster the reduction reaction of the species to the coating, therefore, higher protective properties are obtained than the Ti electrode (**Figure 6**).

However, the growth of the TiO_2 -chitosan layer appears to displace the overpotentials more negatively. The fact that the chitosan layer does not reduce the corrosion potential may be due to its reaction with the medium, due to the degradation effects of chitosan.

4. Conclusions

The use of the zeta potential measurements allows to determine the pH range in which a stabilizing agent is effective and can interact with the TiO_2 particles to improve its stability. Through the profiles of $\zeta = f$ (stabilizing agent dose), the exact amount that is required to achieve a surface charge density that improves the performance of the electrodeposition process is determined. Additionally, the zeta potential is a guide parameter that allows addressing if the electrophoretic deposition process is cathodic or anodic, using either a surfactant or a biopolyelectrolyte.

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Conflict of interest

The authors state that there is no conflict of interest.

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References

- [1] Hamaker HC. Formation of deposition by electrophoresis. Transactions of the Faraday Society. 1940;**36**:279-283
- [2] Sarkar P, Nicholson PS. Electrophoretic deposition (EPD): Mechanism, kinetics and application to ceramics. Journal of the American Ceramic Society. 1996;**79**:1987-2002
- [3] Gani MSJ. Electrophoretic deposition. A review. Industrial Ceramics. 1994;14:163-174
- [4] Heavens N. Electrophoretic deposition as a processing route for ceramics. In: G.P. Binner, editor. Advanced ceramic processing and technology. Vol. 1. Park Ridge, NJ; Noyes Publications; 1990. pp. 255-283
- [5] Zhitomirsky I, Boccaccini AR. Application of electrophoretic and electrolytic deposition techniques in ceramics processing. Current Opinion in Solid State and Materials Science. 2002;6: 251-260. DOI: https://doi.org/10.1016/S1359-0286(02)00080-3
- [6] Besra L, Liu M. A review on fundamentals and applications of electrophoretic deposition (EPD). Progress in Materials Science. 2007;52:1-61. DOI: https://doi.org/10.1016/j. pmatsci.2006.07.001
- [7] Il C, Ryan MP, Boccaccini AR. Electrophoretic deposition: From traditional ceramics to nanotechnology. Journal of the European Ceramic Society. 2008;28:1353-1367. DOI: https://doi.org/10.1016/j.jeurceramsoc.2007.12.011
- [8] Ferrari B, Moreno R. Electrophoretic deposition of aqueous alumina slips, Journal of the European Ceramic Society. 1997;17:549-556. DOI: https://doi.org/10.1016/S0955-2219(96)00113-6
- [9] Ferrari B, Moreno R. EPD kinetics: A review. Journal of the European Ceramic Society. 2010;**30**:1069-1078. DOI: https://doi.org/10.1016/j.jeurceramsoc.2009.08.022
- [10] Hasegawa K, Kunugi S, Tatsumisago M, Minami T. Preparation of thick films by electrophoretic deposition using modified silica particles derived by sol–gel method. Journal of Sol-Gel Science and Technology. 1999;15:243-249
- [11] Shana W, Zhang Y, Yang W, Ke C, Gao Z, Ye Y, Tang Y. Electrophoretic deposition of nanosized zeolites in non-aqueous medium and its application in fabricating thin zeolite membranes. Microporous and Mesoporous Materials. 2004;69:35-42. DOI: https://doi. org/10.1016/j.micromeso.2004.01.003
- [12] Yum JH, Seo SY, Lee S, Sung YE. Y3Al5O12: Ce0.05 phosphor coating on gallium nitride for white light emitting diodes. Journal of the Electrochemical Society. 2003;150:47-52
- [13] Shane MJ, Talbot JB, Schreiber RG, Ross CL, Sluzky E, Hesse KR. Electrophoretic deposition of phosphors: I conductivity and zeta potential measurements. Journal of Colloid and Interface Science. 1994;165:325-333

- [14] Ochsenkuehn-Petropoulou MT, Altzoumailis AF, Argyropoulou R, Ochsenkuehn KM. Superconducting coatings of MgB2 prepared by electrophoretic deposition. Analytical and Bioanalytical Chemistry. 2004;379:792-795
- [15] Hayashi K, Furuya N. Preparation of gas diffusion electrodes by electrophoretic deposition. Journal of the Electrochemical Society. 2004;151:354-A357
- [16] Dougami N, Takada T. Modification of metal oxide semiconductor gas sensor by electrophoretic deposition. Sensors and Actuators B: Chemical. 2003;93:316-320. DOI: https:// doi.org/10.1016/S0925-4005(03)00219-3
- [17] Limmer SJ. Cao G, Sol–gel electrophoretic deposition for the growth of oxide nanorods. Advanced Materials. 2003;15:427-431
- [18] Put S, Vleugels J, Anné G, Van der Biest O. Functionally graded ceramic and ceramicmetal composites shaped by electrophoretic deposition. Colloids and Surfaces A: Physicochemical and Engineering Aspects. 2003;222:223-232. DOI: https://doi.org/ 10.1016/S0927-7757(03)00227-9
- [19] Fernandez A, Lassaletta G, Jiménez VM, Justo A, González-Elipe AR, Herrmann JM, Tahiri H, Ait-Ichou Y. Preparation and characterization of TiO₂ photocatalysts supported on various rigid supports (glass, quartz and stainless steel). Comparative studies of photocatalytic activity in water purification. Applied Catalysis B: Environmental. 1995;7: 49-63. DOI: https://doi.org/10.1016/0926-3373(95)00026-7
- [20] Patel KD, Fiqi AE, Lee HY, Singh RK, Kim DA, Lee HH, Kim HW. Chitosan-nanobioactive glass electrophoretic coatings with bone regenerative and drug delivering potential. Journal of Materials Chemistry. 2012;22:24945-24956
- [21] Wang C, Huang Y. Facile preparation of fluorescent Ag-clusters-chitosan-hybrid nanocomposites for bio-applications. New Journal of Chemistry. 2014;38:657-662
- [22] Cui C, Liu H, Li Y, Sun J, Wang R, Liu S, Greer AL. Fabrication and biocompatibility of nano-TiO2/titanium alloys biomaterials. Materials Letters. 2005;59:3144-3148
- [23] López-Maldonado EA, Oropeza-Guzman MT, Jurado-Baizaval JL, Ochoa-Terán A. Coagulation–flocculation mechanisms in wastewater treatment plants through zeta potential measurements. Journal of Hazardous Materials. 2014;279:1-10. DOI: 10.1016/j. jhazmat.2014.06.025
- [24] López-Maldonado EA, Ochoa-Terán A, Oropeza-Guzmán MT. A multiparameter colloidal titrations for the determination of cationic polyelectrolytes. Journal of Environmental Protection. 2012;3:1559-1570. DOI: 10.4236/jep.2012.311172

Luminescence from TiO₂ Nanotubes and Related Nanostructures Investigated Using Synchrotron X-Ray Absorption Near-Edge Structure and X-Ray Excited Optical Luminescence

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Additional information is available at the end of the chapter

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Abstract

Understanding the optical property of nanostructured TiO₂ is crucial for their use in a variety of applications such as solar cells, photocatalysis, and light emitting devices. Herein, we introduce the use of synchrotron radiation-based spectroscopic techniques: X-ray absorption near-edge structure (XANES) and X-ray excited optical luminescence (XEOL) in analyzing the luminescence properties of anodized TiO₂ nanotubes (TiO₂ NT) and related materials. A description on the spectroscopic technique is first given, including conventional XANES-XEOL combined analysis and a more recently developed 2D XANES-XEOL probing technique. We then discuss several examples of analyzing the luminescence mechanism of TiO₂ NT using XANES and XEOL technique, which are the phase transformation accompanied luminescence, luminescence from TiO₂ NT hierarchical structure, and metal particle–coated TiO₂ NT.

Keywords: TiO₂ nanotubes, luminescence, X-ray absorption near-edge structure, X-ray excited optical luminescence, Ti L-edge, phase transformation, hierarchical structure, metal nanoparticles

1. Introduction

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The properties and potential applications of TiO_2 nanotubes (TiO_2NT) have been actively researched. Because of their 1D tubular structure, they provide an ideal media for highly directional charge transport, and are explored in many photoelectrochemical applications such as solar cells [1], photocatalysis [2], sensors [3], and battery electrodes [4]. Besides, the high biocompatibility of TiO_2 also makes it an excellent coating for substrate for depositing bioactive species [5].

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In TiO₂, Ti and O form distorted octahedra, and the different octahedra packing leads to various crystal phases, such as anatase, rutile, brookite, and B-phase. Anatase is a low-density metastable phase, and contains catalytically active crystal facets, and a relatively loose structure. Rutile is the most thermodynamically stable phase with the highest density. Brookite is less common, although it has been reported that it is an intermediate phase during phase transformation [6]. B-phase has a highly distorted structure, which commonly occurs during hydrothermal synthesis, and is a good candidate as ion battery electrode [7, 8]. The crystal phases are highly sensitive to temperature, and with increasing temperature, phase transformation occurs. Under mild calcination temperature (200-600°C), TiO₂ NT forms an anatase phase, while higher calcination temperature induces an irreversible phase transformation to rutile [9, 10]. Studies on various TiO_2 nanostructures, such as nanoparticles, nanowires, thin films, suggest that the phase transformation temperature highly depends on the morphology and composition of materials [11–13]. In fact, with well-controlled synthesis, an anatase-rutile composite can provide better catalytic performance than single-phase TiO₂ [14, 15]. TiO₂ nanotubes produced electrochemically from a Ti foil are usually in an amorphous form and transform to anatase phase with calcination temperature below 600°C. Although the exact transformation temperature can be adjusted by nanotube size or introducing dopant, at higher temperature, all anatase TiO₂ eventually transforms to the thermodynamically stable rutile phase.

Synthesis strategies of TiO_2 nanotubes have been developed for more than a decade, and they can now be synthesized with well-controlled diameters, lengths, wall thicknesses, and surface roughness [16, 17]. Hydrothermal, anodization, and template-assisted methods are successful in producing TiO_2 NT. Besides, some complex structures such as tube-in-tube [18], particle-decorated [19], and hierarchical structures [20] have also been reported. Such structures exhibit unusual electronic and optical properties and their potential applications in various fields are still actively explored.

The luminescence properties of TiO_2 are strongly dependent on crystal phases and the quality of the crystallinity. For example, upon X-ray excitation, anatase usually exhibits a visible green emission at around 550 nm, while rutile shows an intense near-IR emission at around 800 nm. Both emissions have energies lower than the bandgap, so they both are of a defect origin. The visible green emission is highly sensitive to surface structure and the presence of impurities, and is affected by modifying the surface condition of TiO_2 [21, 22], while the near IR emission is relatively stable. In addition, a recent work reports that weak bandgap emission has been observed from ultra-small amorphous TiO_2 nanograss structures (unzipped TiO_2 NT) [20]. It is thus crucial to establish a connection between the observed luminescence and the structure of the materials.

The conventional way of detecting luminescence is photoluminescence, PL (often called fluorescence), which uses visible or UV light as an excitation source. In wide bandgap semiconductors such as TiO_2 , valence electrons are excited to the conduction band, and radiative recombination is recorded with a spectrometer. The experiment setup is readily available, and it is a direct probe of the emission from a sample. However, since the electrons are from the entire valence band, it lacks element specificity. In other words, we know at what wavelength the sample is emitting light, but we do not know what is responsible for it. In this chapter, we highlight a characterization technique that probes luminescence of materials with element and site specificity: X-ray absorption near-edge structure (XANES) in combination with X-ray excited optical luminescence (XEOL). It is conducted at synchrotron radiation facility, and utilizes a tunable X-ray to monitor the luminescence from material upon core electron excitation. XANES-XEOL analysis, especially in the soft X-ray range, has proven an effective technique in studying the luminescence mechanism of various light-emitting materials, such as ZnO nanowires [23], and GaN-ZnO solid solution [24].

The content of the chapter is organized as follows: we first give an overview of the methods for producing highly oriented nanotubes by anodization, followed by an introduction of the XANES and XEOL techniques. Then, we use two sets of examples to demonstrate how XANES-XEOL method is applied in analyzing the luminescence mechanism of TiO_2 NT: first is the phase transformation associated luminescence and second is the TiO_2 hierarchical structures and doped structures. Finally, an outlook of this material and the use of synchrotron X-ray spectroscopy are given.

2. Material synthesis and characterization techniques

2.1. Electrochemical anodization

 TiO_2 NT discussed in this chapter is synthesized using electrochemical anodization, which is a well-developed synthetic strategy for producing highly oriented TiO_2 nanotube arrays grown on Ti foils. **Figure 1a** shows a schematic layout of the anodization setup. A piece of Ti foil is used as the anode, and a piece of Pt foil is used as the cathode. The two electrodes are immersed in an ethylene glycol-based electrolyte which contains F^- (from either HF or NH₄F), and a voltage of several tens of volts is applied [17]. After certain duration, TiO_2 NT will form on the Ti foil, with a typical morphology, shown in **Figure 1b**. By controlling the electrolyte composition, voltage, and the duration of the anodization, TiO_2 NT can be produced with controlled diameter, length, and wall thickness. The as-formed TiO_2 NT has an amorphous structure, so post-annealing is often required to produce TiO_2 NT of desired crystal phases.



Figure 1. (a) Experimental setup of anodization and (b) a typical top-view SEM image of as-prepared TiO₂NT.

2.2. X-ray absorption near-edge structure

X-ray absorption near-edge structure (XANES) is a technique that probes the local chemical environment of an element in a compound. It utilizes a tunable X-ray source from synchrotron to excite a core electron of the element of interest and monitor the modulation of the absorption coefficient at the absorption edge. Once the energy of the incoming X-ray is sufficient to induce a core electron transition, there is a sharp increase in the absorption coefficient, which is called an "edge" in the corresponding absorption spectrum. The energy position of the "edge" marks the onset energy where electronic transition occurs. Above the edge, spectrum usually exhibits rich features, which are due to multiple scattering between the outgoing electron and the electrons from surrounding atoms. These features are regarded as the "fingerprint" of the material, since they are highly sensitive to the local geometry and the species of neighboring atoms. In short, the photoelectron propagates away from the absorbing atom, samples the neighboring atoms via backscattering, brings the information back to the absorbing atom, the information appears as spectral features in the XANES. In recent years, XANES has been recognized as a valuable technique and has been used to analyze various novel nanomaterials used in catalysis [25], solar cells [26], batteries [27], and so on. It can provide element specific chemical structure with both surface and bulk sensitivity by selecting different detection modes (i.e. total electron yield (TEY) for measuring a few angstroms to nanometers on the surface, and fluorescence yield (FY) for measuring several hundreds of nanometers (as for TiO_2) with soft X-rays and a few micrometers under the surface. This advantage makes XANES an ideal non-destructive probe for analyzing layered, core-shell, or heterostructures. In addition, it can be combined with in situ facility to study the involvement of chemical species during chemical reaction in catalysis [28] or electrochemical cycling [29]. When using a micro- or nanosized probing beam, XANES can also be conducted with site sensitivity, to achieve chemical structure mapping of soil [30], biofilms [31], or nanocomposite [32].

The rich information in XANES is obtained by excitation of core electrons in the element of interest and at appropriate energy levels. As for TiO₂, XANES collected at three edges are of particular interest. The Ti L_{3,2}-edge is the excitation of Ti 2p electrons ($2p_{3/2}$ for L₃, and $2p_{1/2}$ for L₂) to the previously unoccupied electronic states with d and s characters. The Ti K-edge, which is the excitation of Ti 1s electron, and the O K-edge, which excites the O 1s electron into previously unoccupied p states. Since the conduction band of TiO₂ is mainly composed of hybridized Ti 3d and O 2p states, which makes the Ti L_{3,2}- and the O K-edges ideal for the investigate the structure and bonding, hence chemical reactivity of TiO₂. The Ti K-edge, on the other hand, is also used in identifying Ti-based species, but the spectra analysis strongly focuses on the pre-edge features, which is the 1s to 3d dipole forbidden, quadruple transition [33, 34]. Besides, the Ti K-edge is more often used to study the bonding information by looking at absorption features well-above the edge (i.e. the extended X-ray absorption fine structure) [27, 34]. Herein, we limit our discussion on the Ti L_{3,2}-edge.

Figure 2 shows typical XANES spectra of TiO_2 at the Ti $L_{3,2}$ -edge of anatase and rutile. In a Ti $L_{3,2}$ -edge XANES, there are two sets of peaks, which belong to the L_3 - and L_2 -edge features. In each set, there is a sharp peak at lower energy (a and a') and a broad peak at higher energy (b and b'). Due to crystal field splitting, the conduction band of TiO_2 can actually be interpreted

Luminescence from TiO₂ Nanotubes and Related Nanostructures Investigated Using Synchrotron X-Ray... 195 http://dx.doi.org/10.5772/intechopen.72856



Figure 2. Typical XANES spectra of anatase and rutile TiO_2 at the Ti $L_{3,2}$ -edge.

using a molecular orbital perspective. That is, in the octahedral field, the 3d orbitals are divided into two energy levels, t_{2g} and e_g , and they correspond to the a (a') and b (b') peaks, respectively. The e_g peak exhibits further splitting due to the reduced symmetry of O_h in anatase and rutile. For anatase, it is reduced to a D_{2d} symmetry, and for rutile, a D_{2h} symmetry, and in XANES, the difference is identified by the intensity ratio of the e_g doublet: anatase has a stronger peak b_1 and rutile has a stronger peak b_2 .

The difference in crystal structure is also seen at the Ti L_2 -edge. Due to the lifetime broadening and the background from the L_3 edge, the Ti L_2 -edge does not exhibit features that are as sharp as the ones at the L_3 -edge. However, we can still see that the b' peak maximum shifts, so that the distance between a' and b' is larger in rutile than in anatase.

Based on these features, one could perform a composition analysis on any TiO_2 material, which contains a mixed phase of anatase and rutile using linear combination fit. We illustrate this with examples in the next section.

2.3. X-ray excited optical luminescence (XEOL)

XEOL is an X-ray photon-in, optical photon-out technique. It monitors the luminescence from a material under X-ray excitation. It differs from laboratory photoluminescence by its excitation source. When X-ray is used, electrons at deeper level are excited, leaving core hole, instead of just valence hole behind as in PL. The core hole is then filled with electrons at shallower levels, producing Auger electrons and a hole at an outer shell. The energetic electrons continue to travel in the solid, losing its energy and producing shallower core holes. This cascade process, often called "thermalization", is repeated until the hole is created at the top of valence band and fully thermalized electrons settling in the bottom of the conduction band. Then, the valence holes recombine with electrons at the bottom of the conduction band, producing luminescence via radiative excitonic de-excitation (near bandgap emission) and energy transfer to the impurity and defect states in the band gap (defect emission). **Figure 3** illustrates the process.

Since the energy of core electrons is element specific, XANES allows to track the absorption behavior of an element to provide element-specific local environment, a combined XEOL-XANES technique will allow us to build the relationship between the observed luminescence and the type of element that is responsible for it, and predict the chemical environment that leads to such luminescence. This is particularly valuable when analysing the role of dopant or structural defect luminescence [35, 36], as well as identifying the light-emitting component in a mixture of materials [24, 32].

Figure 4 shows a schematic layout of a synchrotron radiation endstation for conducting such experiment. We scan the incoming X-ray energy from below to above the absorption edge, the electron current generated by photoelectrons and secondary electrons is recorded as TEY, the emitted X-ray fluorescence photon is recorded as FY, and the amount of optical photon generated due to valence hole-conduction electron radiative recombination is recorded as photoluminescence yield (PLY). PLY can be collected for the entire wavelength region (200–900 nm) or at selected wavelengths. Using an energy/wavelength dispersive spectrometer, we could further gain a luminescence spectrum at each energy step. This will generate a 3D graph, which contains both the absorption behavior together with the associated luminescence. As shown in **Figure 5**, the color-coded map has a wavelength and excitation energy axis, the



Figure 3. Illustration of a XEOL process from shallow core levels.

Luminescence from TiO₂ Nanotubes and Related Nanostructures Investigated Using Synchrotron X-Ray... 197 http://dx.doi.org/10.5772/intechopen.72856



Figure 4. Experimental setup for XANES-XEOL measurements at synchrotron beamline endstation.



Figure 5. 2D XANES-XEOL map of TiO_2 nanowires. The x-axis is the luminescence wavelength, and the y-axis is the excitation photon energy. Color-coded z-axis is the luminescence intensity. A horizontal cut from the map (top panel) is XEOL at selected excitation energy and a vertical cut (right panel) is optical XANES of a selected luminescence wavelength.

vertical cut is a typical XANES spectrum, and the horizontal cut is a XEOL spectrum. In this way, both the change of absorption coefficient as well as the luminescence as a function of excitation energy can be tracked. This is the 2D XANES-XEOL.

3. Phase transformation and luminescence from TiO₂ nanotubes

 TiO_2 NT made by anodization has an amorphous structure. Upon annealing, they crystalize into anatase structure, and when temperature increases further, phase transformation occurs and anatase gradually turns into rutile. The morphology of the nanotube retains at the amorphous and anatase phase, but entirely collapses when rutile phase dominates. **Figure 6** shows the morphology evolution of TiO_2 NT undergoing phase transformation [37]. The tubular structure gradually collapses and fused into bulky columns. The phase transformation in nanostructured TiO_2 has been reasonably well studied. Although the exact temperature for phase transformation to occur depends on material morphology, the anatase to rutile transformation is the common outcome when the calcination temperature increases.



Figure 6. Scanning electron microscopy (SEM) images of TiO_2NT at different calcination temperatures. (a) as-prepared (inset is the cross section), (b) 500°C, (c) 650°C, and (d) 800°C. (Adapted from Ref. [37]).

Figure 7a shows the evolution of XANES of TiO_2 NT as calcinated temperature increases. The as-prepared TiO_2 NT exhibits broad features due to its amorphous form. The e_g peak starts to show splitting at calcination temperature above 400°C indicating the formation of anatase phase, and the more intense b_1 than b_2 in the e_g splitting corresponds to anatase features. As the temperature increases, the b doublet persists, but the b_1/b_2 intensity varies. At 650°C, b_1 and b_2 exhibit similar intensities, indicating a mixed phase of roughly equal concentration. Higher temperature calcination produces a pure rutile phase. A linear combination fit can be conducted using XANES of anatase and rutile standards (e.g. **Figure 2**), as shown in **Figure 7b**.

Upon X-ray excitation, TiO_2 NT emits light. The luminescence properties of TiO_2 NT depend on both the crystal phases of the sample as well as the excitation energy. For nanostructures, it also depends on the size since the complete thermalization path in nanostructures can be truncated if the nanostructure is smaller than the thermalization path which can be tracked by the universal kinetic energy-dependent escape depth of electrons. For site specificity, we record the optical spectra (i.e. XEOL) using a fixed excitation energy just about the edge of interest, so that the site of interest can be preferentially excited. For example, XEOL can be recorded by selecting excitation energy above the O K-edge at 580 eV. In this circumstance, both the Ti 2p electrons and the O 1 s electrons can be excited, and more core holes can be thermalized, opening up both site-specific optical channels.

Figure 8 shows the XEOL profile of TiO_2 NT calcinated at elevated temperatures. Visible luminescence at the green region starts to appear when amorphous TiO_2 NT begins to crystalize into anatase, and the intensity gradually increases as the crystallinity improves. A minor high energy shift is also seen as the calcination temperature increases. The emergence of rutile phase is accompanied by an intense near-IR emission [37]. Its intensity increases with increased rutile concentration but the wavelength persists. The observation is in agreement with the ones reported using conventional laboratory PL [21, 22]. Both emissions are below the



Figure 7. (a) XANES spectra of as-prepared and calcinated TiO_2 NT and (b) crystal phases' composition derived from linear combination fit.



Figure 8. XEOL spectrum of TiO₂NT calcinated at different temperatures. (Adapted from Ref. [37]).

bandgap of anatase and rutile, so they are of defect origin. The visible emission is usually attributed to the oxygen vacancies as well as surface hydroxyl groups in the TiO_2 lattice, while the near-IR emission from rutile is from an intrinsic defect that the deep electron trap recombines with holes [22, 38]. Luminescence defected using X-ray as excitation source is similar to the one reported using laboratory PL; therefore, the experimental results obtained using the two techniques are comparable. However, XEOL can characterize luminescence from a second dimension, that is, for a fixed sample, tracking the evolution of luminescence intensity as a function of excitation energy.

Figure 9 shows the luminescence response of TiO₂ NT calcinated at 400, 600, and 700°C leading to the formation of anatase, mixed anatase and rutile, and rutile phase, respectively



Figure 9. PLY spectra at the Ti $L_{3,2}$ -edge in comparison with XANES obtained in TEY mode. (a) 400°C, (b) 600°C, and (c) 700°C. (Adapted from Ref. [37]).
with excitation energy across the Ti $L_{3,2}$ - edge. This is done by the following: at each energy step, sum up the total optical photon counts (zero order PLY) or the photon counts within a selected wavelength window (partial PLY), and the final spectrum is a photon counts versus excitation energy plots. We can then compare the PLY spectra with the corresponding XANES spectra to obtain the relationship between structure and luminescence, so PLY is also called as the "optical XANES".

When TiO_2 NT only contains one emission peak at the green region, the PLY has the same profile as XANES, meaning that the radiative recombination site originates from the hybridized Ti 3d and O 2p states, and the intensity of the luminescence is proportional to the absorption coefficient of the element probed. This means, the decay of Ti 2p hole contributes to the luminescence positively. However, the PLY of the near IR emission from rutile retains all the features in XANES but completely inverted.

The inversion of PLY is not an unusual phenomenon. XEOL is produced by electron hole recombination near the bandgap via excitonic transition or energy transfer to defect states, but they are produced by thermalization following the decay of a core hole. The luminescence intensity can decrease if the energy transfer to the optical channel becomes less efficient, for example, the sampling depth decreases (increasing absorption) abruptly above the edge reducing the thermalization path. This is not uncommon for nanostructures since at these soft X-ray excitations, the specimen absorbs all the X-rays and above the absorption edge, the penetration depth of the X-ray reduces markedly, for example, just above and below the Ti L₃ edge, the one absorbed in the near surface region (0.13 μ m) as compared to the penetration depth just below (0.85 μ m).¹ As a result, at excitation energy above the edge, a significant fraction of the energetic electrons created at or near the surface escape the sample without contributing fully to thermalization. If the luminescence has a bulk origin, like a deep level defect, hitting the absorption edge will decrease the luminescence.

Following this theory, the visible green band can be attributed to a surface-related defect of anatase origin, while the near IR emission is from bulk defect of rutile. This is also true when TiO_2 NT has more than one type of defect, as can be seen from the TiO_2 NT containing mixed phases, both visible green and near IR emission is present (**Figure 9b**). If we track each emission band individually using wavelength-selected PLY, we are able to distinguish between the optical responses from each emission band. As shown in **Figure 9b**, although the overall PLY exhibits a total inversion, the visible green component maintains the positive response. This means that the two emission bands have different origin and are from different region of the specimen. The surface-related defect is from the anatase phase, once it converts to rutile, only bulk defect is present. As a result, by using optical XANES (both total PLY and wavelength-selected PLY), one can investigate multicomponent emission separately and track the luminescence to its origin.

Since the degree of PLY inversion is thickness dependent, we can also correlate the observed emission to the location of the sample. In the abovementioned example, TiO_2 NT gradually

¹Data obtained from X-ray calculator: http://henke.lbl.gov/optical_constants/

transform from anatase to rutile at elevated temperature, with the disappearing of the visible luminescence and emerging of the near IR emission. The PLY of visible emission (anatase phase) always exhibits a positive jump, meaning that anatase phase remains on the surface. On the other hand, as soon as rutile appears, it has an inverted PLY. If rutile appears on the surface of the tube, the thickness effect should be avoided, and PLY should have a normal positive jump. The observation suggests that the phase transformation of TiO₂ NT during calcination starts from the bottom to the top, from inside to the outside. This conclusion is later confirmed using scanning transmission X-ray microscopy that measures XANES from the top and the bottom of nanotubes separately in a mixed phase TiO₂ NT [39].

4. Luminescence from TiO₂ hierarchical nanostructures

When anodization is conducted at a high voltage (e.g. above 70 V), the nanotubular structure starts to break down due to the constant thinning of the tube walls, leading to the formation of a nanograss (NG)-nanotube (NT) hierarchical structure [20], shown in **Figure 10**. Although the formation of nanograss has long been observed, they are unzipped nanotube with reduced strain, and are often overlooked and treated as the by-product during TiO_2 NT formation. Recent findings suggest that the NG-on-NT hierarchical membrane exhibits interesting optical properties, which bring more potential applications of this material [40].

The most interesting observation from this structure is that the band emission is observed from the amorphous NG, while NT does not exhibit bandgap luminescence. TiO₂ is an indirect bandgap material, and the most commonly observed emission is from defects. A recent XEOL study on the amorphous TiO₂ NG, however, detected the weak but clear luminescence from it [20]. TiO₂ NG is excited with energy from below to above the Ti L_{3,2}-edge. As shown in **Figure 11**, the emission contains a broad peak centered at 3.30 eV when the excitation energy is below and well above the edge, while a second peak at 3.76 eV appears only when the



Figure 10. SEM images of nanograss-nanotube hierarchical structure. (a) Top/side view and (b) bottom view. (Adapted from Ref. [20]).

Luminescence from TiO₂ Nanotubes and Related Nanostructures Investigated Using Synchrotron X-Ray... 203 http://dx.doi.org/10.5772/intechopen.72856



Figure 11. Top panel: Ti $L_{3,2}$ -edge XANES of as-prepared nanograss. Bottom panel: XEOL spectra of nanograss under selected excitation energies indicated in the top panel. (Adapted from Ref. [20]).

energy just passes the edge. The 3.30 eV emission matches the value of bandgap measured by UV-vis absorption, and similar emission, although rare, has been reported from nanoparticles [41]. The 3.76 eV, however, is a unique band, and only appears when transition of the Ti 2p electron takes place. This band is hence a site-specific luminescence form NG and has been attributed to an up-conversion emission due to size effect [20].

Meanwhile, with two different nanostructures present, the hierarchical nanotubes exhibit unique phase transformation-induced light emission. A 2D XANES-XEOL study tracks the luminescence of NG and NT, after calcination at different temperatures, as a function of excitation energy is shown in **Figure 12** [40]. This map provides luminescence property in both energy space and wavelength space. Although anatase-to-rutile is a common trend at increased calcination temperature, NG can tolerate a much higher temperature (as high as 850°C) and remain anatase-like. The representative near-IR emission for rutile only shows up when the sample is calcinated at 900°C. In normal NT, a complete phase transformation usually occurs at temperature around 650°C [37].

Thus, 2D XANES-XEOL provides a clear view of the evolution of the luminescence, hence the structure. A hierarchical structure, which is made of the same material but of different morphologies, exhibits independent luminescence from the top and the bottom of the membrane.



Figure 12. 2D XANES-XEOL plot of TiO₂ hierarchical structures annealed at different temperatures.

This technique sheds light on tracking the fabrication of light-emitting devices with spatially separated luminescence.

 TiO_2 NT can also serve as a substrate for nanoparticle deposition. Noble metal loaded TiO_2 NT has been used in photocatalysis [42, 43] because the electron-hole recombination in TiO_2 can be effectively retarded with the presence of noble metal, leading to an enhanced photocatalytic efficiency [44]. The role of noble metal nanoparticles in modifying electronic structure of TiO_2 is investigated using XEOL-XANES. An example shows the study of Pd nanoparticles (PdNP)-loaded TiO_2 NT compared with pristine TiO_2 NT [19]. PdNP is deposited on TiO_2 NT by hydrothermal method, and the morphology is shown in **Figure 13a**.

Upon coating, the luminescence of TiO_2 NT changes. XEOL spectra, recorded with excitation energy above the O K-edge, are shown in **Figure 13b**. A decrease in intensity and a slight shift



Figure 13. (a) The morphology of TiO_2NT after Pd deposition. (b) XEOL of $TiO_2 NT$ with and without Pd nanoparticlet coating. (Adapted from Ref. [39]).

of the emission wavelength are observed in Pd-loaded TiO_2 NT. The presence of Pd has two roles such as modifies the defect states of TiO_2 on the surface and quenches the radiative recombination channel in TiO_2 by acting as an electron sink. Because of this, the photocatalysis efficiency can be improved with introducing PdNP.

5. Concluding remarks

 TiO_2 NT is a versatile material. It could be directly used in batteries, photocatalysis, solar cells on their own, and it can also serve as substrate for further decorating of nanoparticles or bioactive compounds. Understanding the electronic structure of TiO_2 NT-based materials and controlling their electronic and optical properties is hence crucial for integrating them into practical application. Both anatase and rutile nanostructures have their characteristic luminescence at visible green and near IR regions, respectively. The visible green luminescence in NT is of a surface origin, and it is highly sensitive to surface defect and surface modification. Near IR emission, on the other hand, is of bulk origin of rutile. It is independent of material morphology and always appears as long as rutile phase is present, even in a mixed structure. Thus XEOL in combination with XANES is a unique and powerful technique which tracks the relationship of the observed luminescence and the specific local chemical structure that is responsible for it. It is hence useful in analyzing the luminescence origin of novel TiO_2 nanostructures and related materials.

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References

- [1] O'Regan B, Gratzel M. Synthesis of nanocrystalline titanium dioxide dye sensitized solar cell. Nature. 1991;**353**:737
- [2] Fujishima A, Honda K. Electrochemical photolysis of water at a semiconductor electrode. Nature. 1972;238:37
- [3] Varghese OK, Gong D, Paulose M, Ong KG, Dickey EC, Gremes CA. Extreme changes in the electrical resistance of titania nanotubes with hydrogen exposure. Advanced Materials. 2003;15:624

- [4] Zhou JG, Fang HT, Maley JM, Murphy MW, Ko JYP, Cutler JN, Sammynaiken R, Sham TK, Liu M, Li F. Electronic structure of TiO₂ nanotube arrays from X-ray absorption near edge structure studies. Journal of Materials Chemistry. 2009;19:6804
- [5] Tsuchiya H, Macak JM, Muller L, Kunze J, Muller F, Greil P, Virtanen S, Schmuki P. Hydroxyapatite growth on anodic TiO₂ nanotubes. Journal of Biomedical Materials Research. Part A. 2006;77:534
- [6] Buin A, Constas S, Sham TK. Mechanisms of phase transformations of TiO₂ nanotubes and nanorods. Journal Physical Chemistry C. 2011;115:22257
- [7] Li J, Wan W, Zhou H, Li J, Xu D. Hydrothermal synthesis of TiO₂(B) nanowires with ultrahigh surface area and their fast charging and discharging properties in Li-ion batteries. Chemical Communications. 2011;47:3439
- [8] Aravindan V, Shubha N, Ling C, Madhavi S. Constructing high energy density nonaqueous Li-ion capacitors using monoclinic TiO₂-B nanorods as insertion host. Journal of Materials Chemistry A. 2013;1:6145
- [9] Zhang J, Li M, Feng Z, Chen J, Li C. UV Raman spectroscopic study on TiO₂. I. Phase transformation at the surface and in the bulk. The Journal of Physical Chemistry. B. 2006;110:927
- [10] Shannon RD, Pask JA. Kinetics of the anatase-rutile. Journal of the American Ceramic Society. 1965;48:391
- [11] Gribb AA, Banfield JF. Particle size effects on transformation kinetics and phase stability in nanocrystalline TiO₂. American Mineralogist. 1997;82:717-728
- [12] Gouma PI, Mills MJ. Anatase-to-rutile transformation in titania powders. Journal of the American Ceramic Society. 2001;84:619-622
- [13] Ghosh TB, Dhabal S, Datta AK. On crystallite size dependence of phase stability of nanocrystalline TiO₂. Journal of Applied Physics. 2003;94:4577-4582
- [14] Yan M, Chen F, Zhang J, Anpo M. Preparation of controllable crystalline titania and study on the photocatalytic properties. Journal of Physical Chemistry B. 2005;109:8673-8678
- [15] Li G, Gary KA. The solid-solid interface: Explaining the high and unique photocatalytic reactivity of TiO₂-based nanocomposite materials. Chemical Physics. 2007;**339**:173-179
- [16] Roy P, Berger S, Schmuki P. TiO₂ nanotubes: Synthesis and applications. Angewandte Chemie, International Edition. 2011;50:2904-2939
- [17] Lee K, Zazare A, Schnuki P. One-dimensional titanium dioxide nanomaterials: Nanotubes. Chemical Reviews. 2014;114:9385-9454
- [18] Ali G, Kim HJ, Kim JJ, Cho SO. Controlled fabrication of porous double-walled TiO₂ nanotubes via ultraviolet-assisted anodization. Nanoscale. 2014;6:3612

- [19] Li J, Sham TK, Ye Y, Zhu J, Guo J. Tracking the local effect of fluorine self-doping in anodic TiO₂ nanotubes. Journal of Physical Chemistry C. 2015;119:2222-2230
- [20] Liu L, Li J, Sham TK. Near-band-gap luminescence from TiO₂ nanograss-nanotube hierarchical membranes. Canadian Journal of Chemistry. 2015;93:106-112
- [21] Knorr FJ, Zhnag D, McHale JL. Influence of TiCl₄ treatment on surface defect photoluminescence in pure and mixed-phase nanocrystalline TiO₂. Langmuir. 2007;23:8686-8690
- [22] Shi J, Chen J, Feng Z, Chen T, Lian Y, Wang X, Li C. Photoluminescence characteristics of TiO₂ and their relationship to the photoassisted reaction of water/methanol mixture. Journal of Physical Chemistry C. 2007;111:693-699
- [23] Wang Z, Gou XX, Sham TK. 2D XANES-XEOL mapping: Observation of enhanced band gap emission from ZnO nanowire arrays. Nanoscale. 2014;6:6531-6536
- [24] Ward MJ, Han WQ, Sham TK. 2D XAFS-XEOL mapping of Ga_{1-x}Zn_xN_{1-x}O_x nanostructured solid solutions. Journal of Physical Chemistry C. 2011;115:20507-20514
- [25] Thomas JM, Sankar G. The role of synchrotron-based studies in the elucidation and design of active sites in titanium–silica epoxidation catalysts. Accounts of Chemical Research. 2001;34:571-581
- [26] Germack DS, Chan CK, Hamadani BH, Ritcher LJ, Fischer DA, Gundlach DJ, DeLongchamp DM. Substrate-dependent interface composition and charge transport in films for organic photovoltaics. Applied Physics Letters. 2009;94:233303
- [27] Wang D, Liu L, Sun X, Sham TK. Observation of lithiation-induced structural variations in TiO₂ nanotube arrays by X-ray absorption fine structure. Journal of Materials Chemistry A. 2015;3:412-419
- [28] Gorlin Y, Lassalle-Kaiser B, Benck JD. In situ X-ray absorption spectroscopy investigation of a bifunctional manganese oxide catalyst with high activity for electrochemical water oxidation and oxygen reduction. Journal of the American Chemical Society. 2013;135: 8525-8534
- [29] Yoon WS, Grey CP, Balasubramanian M, Yang XQ, McBreen J. In situ X-ray absorption spectroscopic study on LiNi0.5Mn0.5O₂ cathode material during electrochemical cycling. Chemistry of Materials. 2003;15:3161-3169
- [30] Kinyangi J, Solomon D, Liang BI, Lerotic M, Wirick S, Lehmann J. Nanoscale biogeocomplexity of the organomineral assemblage in soil. Soil Science Society of America Journal. 2006;70:1708-1718
- [31] Lawrence JR, Swerhone GDW, Leppard GG, Araki T, Zhang X, West MM, Hitchcock AP. Scanning transmission X-ray, laser scanning, and transmission electron microscopy mapping of the exopolymeric matrix of microbial biofilms. Applied and Environmental Microbiology. 2003;69:5543-5554

- [32] Wang ZQ, Wang W, Sham TK, Yang SG. Origin of luminescence from ZnO/CdS core/shell nanowire arrays. Nanoscale. 2014;6:9783-9790
- [33] Kim KT, Ali G, Chung KY, Chong SY, Yashiro H, Sun YK, Lu J, Amine K, Myung ST. Anatase titania nanorods as an intercalation anode material for rechargeable sodium batteries. Nano Letters. 2014;14:416-422
- [34] Okumura T, Fukutsuka T, Yanagihara A, Orikasa Y, Arai H, Ogumi Z, Uchimoto Y. Electronic and local structural changes with lithium-ion insertion in TiO₂-B: X-ray absorption spectroscopy study. Journal of Materials Chemistry. 2011;21:15369-15377
- [35] Ko JYP, Yiu YM, Liang HB, Sham TK. X-ray absorption and luminescence studies of Ba2Ca(BO₃)2:Ce₃+/Na+ phosphors. The Journal of Chemical Physics. 2010;132:234701
- [36] Wang DN, Yang JL, Li XF, Wang JJ, Li RY, Cai M, Sham TK, Sun XL. Observation of surface/defect states of SnO₂ nanowires on different substrates from X-ray excited optical luminescence. Crystal Growth & Design. 2012;12:397-402
- [37] Liu L, Chan J, Sham TKJ. Calcination-induced phase transformation and accompanying optical luminescence of TiO₂ nanotubes: An X-ray absorption near-edge structures and X-ray excited optical luminescence study. Physical Chemistry C. 2010;114:21353-21359
- [38] Wang X, Feng Z, Shi J, Jia G, Shen S, Zhou J, Li C. Trap states and carrier dynamics of TiO(2) studied by photoluminescence spectroscopy under weak excitation condition. Physical Chemistry. 2010;12:7083-7090
- [39] Li J, Wang Z, Wang J, Sham TK. Unfolding the anatase-to-rutile phase transition in TiO₂ nanotube using X-ray spectroscopy and spectromicroscopy. Journal of Physical Chemistry C. 2016;120:22079-22087
- [40] Li J, Liu L, Sham TK. 2D XANES-XEOL spectroscopy studies of morphology-dependent phase transformation and corresponding luminescence from hierarchical TiO₂ nanostructures. Chemistry of Materials. 2015;27:3021-3029
- [41] Abazovic ND, Comor MI, Dramicanin MD, Jovanovic DJ, Ahrenkiele SP, Nedeljkovic JM. New paradigms for active site engineering in titanium dioxide photocatalysts. Journal of Physical Chemistry B. 2006;110:25366
- [42] Li XH, Chen GY, Yang LB, Lin Z, Liu JH. Multifunctional Au-coated TiO₂ nanotube arrays as recyclable SERS substrates for multifold organic pollutants detection. Advanced Functional Materials. 2010;20:2815-2824
- [43] Lin CH, Lee CH, Chao JH, Kuo CY, Cheng YC, Huang WN, Chang HW, Huang YM, Shih MK. Photocatalytic generation of H₂ gas from neat ethanol over Pt/TiO₂ nanotube catalysts. Catalysis Letters. 204;98:61–66
- [44] Ye MD, Gong JJ, Lai YK, Lin CJ, Lin ZQ. High-efficiency photoelectrocatalytic hydrogen generation enabled by palladium quantum dots-sensitized TiO₂ nanotube arrays. Journal of the American Chemical Society. 2012;134:15720-15723

Photocatalytic Applications

Titanium Dioxide Films for Photocatalytic Degradation of Methyl Orange Dye

Rodrigo Teixeira Bento and Marina Fuser Pillis

Additional information is available at the end of the chapter

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Abstract

The aim of this work was to characterize and evaluate the influence of the thickness on the photocatalytic efficiency of titanium dioxide thin films on the degradation of methyl orange dye under UV light irradiation. The films of 280 and 468 nm thick were deposited on borosilicate substrates at 400°C by the MOCVD technique using titanium isoproxide IV as precursor. XRD analyses showed the formation of anatase-TiO₂ phase. Crosssectional FE-SEM images show that the films presented a dense columnar structure and grown perpendicularly to the substrate surface. The photocatalytic activity of the catalysts was studied using UV-vis spectrophotometry The TiO₂ film with 468 nm of thickness presented higher photocatalytic activity exhibiting 69% of dye degradation. The increase of grain size and thickness of the films promoted an improvement of photocatalytic efficiency.

Keywords: TiO, films, MOCVD, photocatalytic activity

1. Introduction

The availability of water is of great importance for the development of economic activities and mainly for human health. However, the rapid increase in industrial production resulted in serious consequences to the environment by generating waste and contaminating the water reserves [1–3]. The pharmaceutical products, pesticides, azo dyes, herbicides, and hormones are the main contaminants in water [4–6]. The textile activities are responsible for 15% of the industrial consumption of water [7]. It is estimated that approximately 15–20% of the chemical species, including dyes, are disposed of as effluent after processing [8].

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Among the more than 10,000 types of dyes available [9], the azo compounds stand out and are characterized by the presence of one or more chromophore groups (-N=N-) in their chemical structure [10–12]. The intensity of absorption and also the shades of color vary according to the other electrons π and n which are in conjunction [13]. An example of azo dye is the methyl orange (MO).

Methyl orange dye ($C_{14}H_{14}N_3NaO_3S^-Na^+$) is a compound generally used as acid-base indicator [14]. Sha et al. [14] shows that a decrease in pH causes a shift in the absorption band of MO, and a change in its coloration occur, being orange in basic pH and red in acidic condition [15]. The MO structure is characterized by the azo group among the aromatic rings [15, 16] and is shown schematically in **Figure 1**.

Several researches have been done to develop new technologies to remove dyes and others pollutants from wastewater effluent. Hassan et al. [17] studied the use of heterogeneous photocatalysis for the treatment of landfill leachate, comparing the efficiency of this technique to other methods, besides the parameters that influence the process results. The study revealed to be possible to remove pollutants found in landfill leachate using TiO, as catalyst. The best photocatalytic results were obtained for anatase and anatase-rutile mixture. Jorfi et al. [18] developed TiO₂ catalyst supported on magnetic activated carbon for the oxidative degradation of benzotriazole (BTA) by UV-Fenton process. According to the authors, the catalyst showed good reusability, since after five cycles of reuse, the efficiency in the degradation of BTA dropped from 92.2 to 71.6%. Konstantinou and Albanis [19] and Sleiman et al. [20] evaluated the photocatalytic degradation of azo dyes by photocatalytic oxidation using TiO₂ under UV-vis irradiation. Both works state the efficiency of the heterogeneous photocatalysis method in water treatment. Akrout and Bousselmi [21] carried out the electrochemical degradation of synthetic wastewater containing biazo dye on boron-doped diamond anode (BDD) at current densities from 8 to 48 Am⁻². The authors verified the influence of pH and of the applied current density on degradation. The decrease of pH and the increase of current density showed a positive effect on the oxidation. Vallejo et al. [22] presented a review about the capacity for polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) remediation by means of Advanced Oxidation Processes.

Advanced Oxidation Processes (AOPs) are the most attractive methods used to degrade polluting compounds based on the use of highly oxidizing species to promote greater efficiency in the treatment process [23].

AOPs are characterized by generating free radicals, especially the hydroxyl radical (OH[•]), transforming the organic contaminants in simpler species, such as carbon dioxide, water, and inorganic anions [24]. Hydroxyl radicals can be generated from reactions involving ozone (O_3) and hydrogen



Figure 1. Structure of the methyl orange dye molecule.

peroxide (H_2O_2) —oxidants with high degrading power—semiconductors such as titanium dioxide (TiO₂) and ultraviolet irradiation (UV) [25, 26]. **Figure 2** presents the main techniques of AOP [22].

The first studies in photocatalysis were developed by Fukushima and Honda [27], when they observed that TiO_2 exposed to the sunlight could produce the photocatalytic dissociation of water, producing hydrogen. Recent researches deal with heterogeneous photocatalysis for applications in water treatment [2, 6, 23, 26]. **Figure 3** shows the schematic diagram of photocatalytic process, showing the photoactivation of a catalyst semiconductor and the production of oxidizing radicals. This process is based on the electronic excitation of certain semiconducting oxides (catalyst) by means of radiant energy—visible or UV light [28, 29]. The reaction is activated by absorption of a photon with energy equal or higher than the bandgap energy (E_{bg}) of the catalyst [5]. When an electron is promoted from the valence band (VB) to the conduction band (CB), a hole (h+) is generated in the VB (Eq. (1)). The electrons transferred to CB are responsible for reduction reactions, producing gaseous hydrogen and other oxidizing species (Eqs. (2) and (3)). The holes react with the adsorbed water molecules on the surface of the photocatalyst to generate OH[•] radicals (Eqs. (4) and (5)), allowing the oxidation of organic molecules and ionized species [5, 6].

$$Photocatalyst + hv \rightarrow Photocatalyst(e_{ch}^{-} + h_{rh}^{+})$$
(1)

$$Photocatalyst(e_{cb}^{-}) + 2H_{(ads)}^{+} \rightarrow H_{2}$$

$$\tag{2}$$

$$Photocatalyst(e_{cb}^{-}) + H_2O_{(ads)} \rightarrow H^+ + OH$$
(3)

$$Photocatalyst(h_{vh}^{+}) + H_2O_{(ads)} \rightarrow H^{+} + OH^{\bullet}$$
(4)

$$Photocatalyst(h_{vb}^{+}) + OH_{(ads)}^{-} \rightarrow OH^{\bullet}$$
(5)



Figure 2. Principal advanced oxidation processes.



Figure 3. Schematic diagram of photocatalytic process and bandgap of TiO₂ semiconductor.

The main factors that influence the photocatalytic degradation are pH, initial concentration of dyes, reaction temperature, catalyst concentration, oxidizing agents, light intensity, and irradiation time [6, 17, 20]. Acid pH is more favorable for photocatalytic applications than neutral or alkaline pH [30]. Chanathaworn et al. [31] studied the effects of irradiation intensity of black light lamp on the degradation of the Rhodamine B. According to the results, an increase in the irradiation intensity intensified the dye degradation.

Titanium dioxide (TiO₂) is the most crystalline semiconductor used in photocatalytic process [26, 32]. It presents three polymorphic phases: anatase and rutile, with tetragonal structure; and brookite, orthorhombic [33, 34], being anatase the phase of greater degradative efficiency [17]. Due to the TiO₂ bandgap energy being relatively wide ($E_g = 3.2 \text{ eV}$ for anatase; $E_g = 3.0 \text{ eV}$ for rutile; $E_g = 3.1 \text{ eV}$ for brookite) [6, 33, 34], the material can only be activated by UV irradiation with $\lambda < 380 \text{ nm}$ [35].

Absalan et al. [36] developed TiO_2 nanoparticles in anatase, rutile, and brookite phases by solgel method using different calcination temperature and time and doped by transition metals (cadmium, chromium, nickel, manganese, iron, and cobalt). According to the authors, the proportion of anatase phase increased after doping process, besides improving the photocatalytic efficiency. According to Carp et al. [37], the doping process reduces the bandgap, making the material active in the region of the visible spectrum of light.

Among several techniques used on the synthesis of TiO_2 [38–41], the chemical vapor deposition (CVD) is widely employed [42]. Pierson [43] defines CVD as the deposition of a solid on a heated surface from a chemical reaction in the vapor phase. In this process, the vapor of a volatile compound reacts near or over the surface to be coated (substrate), forming a solid deposit by nucleation of the chemical element that composes the material to be deposited, from a movement governed by processes of diffusion and convection of matter [43].

The crystalline structure, grain size, and, mainly, the chemical composition and the thickness of the films are essential parameters to define its properties and applications [44]. The present research aims the structural and morphological characterization of TiO_2 thin films grown at 400°C by MOCVD process and to study the influence of the thickness on the photocatalytic efficiency to degrade methyl orange dye under UV light.

2. Experimental procedure

The growth of TiO₂ thin films was realized by metalorganic chemical vapor deposition (MOCVD) in a conventional horizontal reactor at 400°C under a pressure of 50 mbar. Titanium(IV) isopropoxide (*Sigma-Aldrich*, 99.999%) was used as precursor of titanium and oxygen. Nitrogen (flow rate of 0.5 mL min⁻¹) was used as carrier and purge gas. The borosilicate substrates ($25 \times 76 \times 1 \text{ mm}$) were previously cleaned in a 5% H₂SO₄ aqueous solution, rinsed in deionized water, dried in nitrogen, and immediately inserted into the reactor. **Figure 4** shows schematically the MOCVD equipment [45]. The main components are the reaction chamber, which consists of a quartz tube heated by an infrared oven containing the sample holder, and a vacuum pump that keeps the reaction chamber under a pressure below the atmospheric. The TTiP is maintained in a bubbler heated to 39°C. The gas conduction lines are made of stainless steel and are kept heated to prevent condensation and premature pyrolysis of the precursor.

2.1. Characterization of the films

X-ray diffraction (XRD) diagrams, obtained in a *Rigaku Multiflex* equipment using CuK α radiation (λ = 1.54148 Å), incidence angle of 2.5°, and scan rate of 0.02°, were used to identify the phases formed. Measurements of surface roughness and mean grain size were performed by atomic force microscopy (AFM) operating in the Tapping mode (*SPM Bruker NanoScope IIIA*), employing a silicon tip with a curvature radius of 15 nm. The thickness of the films was measured in the cross section of the samples by using a field emission scanning electron microscope (FE-SEM) *JSM6701F* X-ray photoelectron spectroscopy (XPS) measurements with spot size beam of 400 μ m were conducted in order to determine the chemical state of



Figure 4. MOCVD equipment shown schematically (adapted from reference 45).



Figure 5. Schematic diagram of the photocatalytic reactor.

the species near the solid surface. A *Thermo Scientific, K-Alpha model* equipment was used. After the acquisition of the high-resolution spectra, the deconvolution was done using the algorithm Smart in the software Avantage[®]. The binding energies were corrected considering the C1s reference peak at 214.8 eV.

2.2. Photocatalytic tests

The photocatalytic activities of the TiO₂ films were estimated by measuring the degradation of methyl orange dye (MO, 5 mg L⁻¹) in an aqueous solution (pH = 2), under UV light irradiation (Sankyo Denki Co., Ltd., 15 W, λ = 352 nm). The changes in the MO concentration were monitored using a UV-vis spectrophotometer (*Global Trade Technology*). For this purpose, the films were placed in a reactor (**Figure 5**) containing 40 mL of the dye solution and were illuminated by two tubular UV lamps for 300 min. Synthetic air (N₂/20 wt.% O₂) was bubbled into the solution during the tests.

The photocatalytic reactor consists of a glass chamber containing the MO dye solution to be degraded, the TiO_2 catalyst supported in borosilicate, and the source of radiation. The components of the photoreactor were arranged in a box to prevent loss of photons and to protect users against the emitted UV radiation. The distance between the photocatalyst and the UV lamps was set at 25 cm.

3. Results and discussion

The cross section of the samples was observed and the thickness of the TiO_2 films grown on borosilicate was measured. **Figure 6a** shows the FE-SEM image of the 280 nm thick film, revealing the formation of a dense film. The AFM image (**Figure 7a**) shows that the film presents homogeneous morphology, composed of rounded grains of 124 nm mean size and of 19 nm RMS roughness, which can be considered favorable for photocatalytic applications [37], since it facilitates the contact of the adsorbed substances with the film, increasing its photocatalytic efficiency [46].



Figure 6. FE-SEM fracture images for TiO, films: (a) thickness of 280 nm and (b) thickness of 468 nm.



Figure 7. AFM images of TiO₂ film with thickness of 280 nm: (a) topography and (b) 3D image.

The RMS (*Root Mean Square*) roughness expresses the values of a roughness profile that moves away from the midline, in other words, it is the standard deviation of the mean height *Z* [47], being mathematically expressed as:

$$RMS = \sqrt{\frac{\sum_{N=1}^{N} (Z_N - Z)^2}{N - 1}}$$
(6)

where N is the number of peaks; Z_N is the height of each peak; and Z is the mean height of N peaks.

The morphology of the surface of the TiO₂ film grown with thickness of 468 nm (**Figure 8a**) presents a mean grain size of 214 nm and roughness values of the order of 16 nm (**Table 1**). It can be observed as a dense film with columnar structure (**Figure 6b**). Results presented by Krumdieck et al. [48] showed that the increase of the thickness of the films caused a decreased of the roughness, similar trend with the values exhibited in the present work. The results clearly show that the increase of the growth time (**Table 1**) caused an increase in the film thickness, as evidenced by Antunes et al. [49].



Figure 8. AFM images of TiO, film with thickness of 468 nm: (a) topography and (b) 3D image.

| Temperature of deposition [°C] | Growth time [min] | Film thickness [nm] | Mean grain size [nm] | RMS roughness [nm] |
|-----------------------------------|----------------------|------------------------|-------------------------|--------------------|
| 400 | 30 | 280 | 124 | 19 |
| 400 | 40 | 468 | 214 | 16 |

Table 1. Characteristics of TiO₂ films grown by MOCVD on borosilicate.

Figure 9 shows the XRD patterns of TiO_2 films grown at 400°C with different thickness. The characteristic peaks correspond to the crystalline anatase phase (JCPDS 21–1272).

Figure 10 shows the XPS spectra of the 280 nm TiO_2 thin film. The surface of the films contains high quantities of Ti and O elements and C (**Figure 10a**). According to Liu et al. [50] and Babelon et al. [51], the presence of C1s peak was ascribed to the residual carbon from the metalorganic precursor and to surface pollution provoked for the sample exposition to air before the XPS experiments. Ti2p spectrum (**Figure 10b**) appeared at 459.5 and 465.2 eV attributed, respectively, to Ti2p_{3/2} and Ti2p_{1/2} peaks of O–Ti–O in TiO₂ [50, 52]. Bharti et al. [53] and Lin et al. [54] suggested that these peaks are consistent with Ti⁴⁺ in TiO₂ lattice. The O1s spectrum (**Figure 10c**) reveals two peaks at 530.7 and 532.4 eV. The first one can be attributed to the oxygen present in the TiO₂ lattice, and the other one represents the surface oxygen [52].

Figure 11 exhibits the C/C_0 graphs as a function of the time of exposure to UV radiation, where *C* represents the dye concentration at each time interval and C_0 is the initial concentration. The photolysis curve demonstrates that without the presence of the catalyst (TiO₂ film) there was no degradation of the dye. The TiO₂ film with thickness of 280 nm degraded 28% of MO dye for a total test time of 300 minutes while the TiO₂ film with 468 nm of thickness, showed 69% of dye degradation in the same condition, that is, it was approximately 2.5× more efficient.

A large surface area is necessary for the light irradiation and the photocatalyst contacting with pollutant compound and, consequently, the photocatalysis efficiency of the TiO₂ films



Figure 9. XRD patterns of the TiO_2 films grown on borosilicate at 400°C.



Figure 10. XPS spectra of the 280 nm TiO₂ films (a) survey; (b) Ti2p, and (c) O1s.



Figure 11. MO dye concentration as a function of the time of exposure to UV irradiation (λ = 352 nm) with and without the presence of TiO₂ films grown by MOCVD.

is intensified [55, 56]. The increase in thickness is also favorable for the photocatalytic performance, since thinner films have a higher electron recombination rate than thicker films [57].

4. Conclusions

 TiO_2 films grown by MOCVD process were demonstrated to be effective for methyl orange dye degradation under UV irradiation. The films presented the formation of anatase phase, and surface morphology composed of rounded grains. The methyl orange dye does not degrade under UV radiation without the presence of the TiO_2 photocatalyst. The best photocatalytic result occurred for the film with thickness of 468 nm, which exhibited 69% of dye degradation in 300 minutes. The results suggest that the morphology and structural characteristics influence the photocatalytic activity of the TiO₂ films.

Conflict of interest

The authors declare that there is no conflict of interest regarding the publication of this chapter.

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References

- Khaoulani S, Chaker H, Cadet C, Bychkov E, Cherif L, Bengueddach A, Fourmentin S. Wastewater treatment by cyclodextrin polymers and noble metal/mesoporous TiO₂ photocatalysts. Comptes Rendus Chimie. 2015;18:23-31
- [2] Tsoumachidou S, Lambropoulou D, Poulios I. Homogeneous photocatalytic oxidation of UV filter paraaminobenzoic acid in aqueous solutions. Environmental Science and Pollution Research. 2017;24:1113-1121
- [3] Josephine GAS, Nisha UM, Meenakshi G, Sivasamy A. Nanocrystalline semiconductor doped rare earth oxide for the photocatalytic degradation studies on acid blue 113: A diazo compound under UV slurry photoreactor. Ecotoxicology and Environmental Safety. 2015;121:67-72
- [4] Horáková M, Klementová S, Kriz P, Balakrishna SK, Spatenka P, Golovko O, Hájková P, Exnar P. The synergistic effect of advanced oxidation processes to eliminate resistant chemical compounds. Surface & Coatings Technology. 2014;241:154-158
- [5] Akpan UG, Hameed BH. Parameters affecting the photocatalytic degradation of dyes using TiO₂-based photocatalysts: A review. Journal of Hazardous Materials. 2009; 170:520-529
- [6] Reza KM, Kurny ASW, Gulshan F. Parameters affecting the photocatalytic degradation of dyes using TiO₂: A review. Applied Water Science. 2017;7:1569-1578
- [7] Silva MC, Corrêa AD, Torres JA, Amorim MTSP. Descoloração de corantes industriais e efluentes têxteis simulados por peroxidase de nabo (Brassica campestre). Química Nova. 2012;35:889-894
- [8] Jin XC, Liu GQ, Xu ZH, Tao WY. Decolorization of a dye industry effluent by Aspergillus fumigatus XC6. Applied Microbiology Biotechnology. 2007;74:239-243
- [9] Wang C, Yediler A, Linert D, Wang Z, Kettrup A. Toxicity evaluation of reactive dyestuffs, auxiliaries and selected effluents in textile finishing industry to luminescent bacteria *Vibrio fischeri*. Chemosphere. 2002;**46**:339-344
- [10] Kasic H, Bozic AL, Koprivanace N. Heterogeneous photocatalytic treatment of textile dye effluent containing Azo dye: Direct Crysophenine G. Der Chemica Sinica. 2011;2:37-46

- [11] Saratale RG, Saratale GD, Chang JS, Govindwar SP. Bacterial decolorization and degradation of azo dyes: A review. Journal of the Taiwan Institute of Chemical Engineers. 2011;42:138-157
- [12] Kaur N, Dhaka G, Singh J. Simple naked-eye ratiometric and colorimetric receptor for anions based on azo dye featuring with benzimidazole unit. Tetrahedron Letters. 2015; 56:1162-1165
- [13] Aljamali N. Review in azo compounds and its biological activity. Biochemistry & Analytical Biochemistry. 2015;4:1000169
- [14] Sha Y, Mathew I, Cui Q, Clay M, Gao F, Zhang XJ, Gu Z. Rapid degradation of azo dye methyl orange using hollow cobalt nanoparticles. Chemosphere. 2016;144:1530-1535
- [15] Guettai N, Amar HA. Photocatalytic oxidation of methyl orange in presence of titanium dioxide in aqueous suspension. Part I: Parametric study. Desalination. 2005;185:427-437
- [16] Kaur J, Singhal S. Facile synthesis of ZnO and transition metal doped ZnO nanoparticles for the photocatalytic degradation of methyl Orange. Ceramics International. 2014;40:7417-7424
- [17] Hassan M, Zhao Y, Xie B. Employing TiO₂ photocatalysis to deal with landfill leachate: Current status and development. Chemical Engineering Journal. 2016;285:264-275
- [18] Jorfi S, Kakavandi B, Motlagh HR, Ahmadi M, Jaafarzadeh N. A novel combination of oxidative degradation for benzotriazole removal using TiO₂ loaded on Fe^{II}Fe₂^{III}O₄@C as an efficient activator of peroxymonosulfate. Applied Catalysis B: Environmental. 2017;**219**:216-230
- [19] Konstantinou IK, Albanis TA. TiO₂-assisted photocatalytic degradation of azo dyes in aqueous solution: Kinetic and mechanistic investigations—A review. Applied Catalysis B: Environmental. 2004;49:1-14
- [20] Sleiman M, Vildozo D, Ferronato C, Chovelon JM. Photocatalytic degradation of azo dye Metanil Yellow: Optimization and kinetic modeling using a chemometric approach. Applied Catalysis B: Environmental. 2007;77:1-11
- [21] Akrout H, Bousselmi L. Water treatment for color and COD removal by electrochemical oxidation on boron-doped diamond anode. Arabian Journal of Geosciences. 2012;6:1-9
- [22] Vallejo M, Román MFSR, Ortiz I, Irabien A. Overview of the PCDD/Fs degradation potential and formation risk in the application of advanced oxidation processes (AOPs) to wastewater treatment. Chemosphere. 2015;118:44-56
- [23] Guz R, De Moura C, Da Cunha MAA, Rodrigues MB. Factorial design application in photocatalytic wastewater degradation from TNT industry—Red water. Environmental Science Pollution Research International. 2016;24:6055-6060
- [24] Pignatello JJ, Oliveros E, Mackay A. Advanced oxidation processes for organic contaminant destruction based on the Fenton reaction and related chemistry. Critical Reviews in Environmental Science and Technology. 2006;36:1-84

- [25] Azbar N, Yonar T, Kestioglu K. Comparison of various advanced oxidation processes and chemical treatment methods for COD and color removal from polyester and acetate fiber dyeing effluent. Chemosphere. 2004;55:35-43
- [26] Ângelo J, Magalhães P, Andrade L, Mendes A. Characterization of TiO₂-based semiconductors for photocatalysis by electrochemical impedance spectroscopy. Applied Surface Science. 2016;387:183-189
- [27] Fujishima A, Honda K. Electrochemical photolysis of water at a semiconductor electrode. Nature. 1972;238:37-38
- [28] Athalathil S, Erjavec B, Kaplan R, Stuber F, Bengoa C, Font J, Fortuny A, Pintar A, Fabregat A. TiO₂-sludge carbon enhanced catalytic oxidative reaction in environmental wastewaters applications. Journal of Hazardous Materials. 2015;**300**:406-414
- [29] Gomes O Jr, Borges Neto W, Machado AEH, Daniel D, Trovó AG. Optimization of fipronil degradation by heterogeneous photocatalysis: Identification of transformation products and toxicity assessment. Water Research. 2017;110:133-140
- [30] Shao C, Zhou G, Li Z, Wu Y, Xu D, Sun B. Fabrication of large-diameter tube-like mesoporous TiO₂ via homogeneous precipitation and photocatalytic decomposition of papermaking wastewater. Chemical Engineering Journal. 2013;230:227-235
- [31] Chanathaworn J, Bunyakan C, Wiyaratn W, Chungsiriporn J. Photocatalytic decolorization of basic dye by TiO₂ nanoparticle in photoreactor. Songklanakarin Journal of Science & Technology. 2012;34:203-210
- [32] Zhao F, Dong B, Gao R, Su G, Liu W, Shi L, Xia C, Cao L. A three-dimensional graphene-TiO₂ nanotube nanocomposite with exceptional photocatalytic activity for dye degradation. Applied Surface Science. 2015;**351**:303-308
- [33] Hanaor DAH, Sorrell CC. Review of the anatase to rutile phase transformation. Journal of Materials Science. 2011;46:855-874
- [34] Guo T-L, Li J-G, Sun X, Sakka Y. Photocatalytic growth of Ag nanocrystals on hydrothermally synthesized multiphasic TiO₂/reduced graphene oxide (rGO) nanocomposites and their SERS performance. Applied Surface Science. 2017;423:1-12
- [35] Dhayal M, Kapoor R, Sistla PG, Pandey RR, Kar S, Saini KK, Pande G. Strategies to prepare TiO₂ thin films, doped with transition metal ions, that exhibit specific physicochemical properties to support osteoblast cell adhesion and proliferation. Materials Science and Engineering. C. 2014;**37**:99-107
- [36] Absalan Y, Bratchikova IG, Lobanov NN, Kovalchukova OV. Novel synthesis method for photo-catalytic system based on some 3d-metal titanates. Journal of Materials Science: Materials in Electronics. 2017;28:18207-18219
- [37] Carp O, Huisman CL, Reller A. Photoinduced reactivity of titanium. Progress in Solid State Chemistry. 2004;32:33-177

- [38] El-Sheikh SM, Khedra TM, Hakkib A, Ismaila AA, Badawy WA, Bahnemann DW. Visible light activated carbon and nitrogen co-doped mesoporous TiO₂ as efficient photocatalyst for degradation of ibuprofen. Separation and Purification Technology. 2017;**173**:258-268
- [39] Benetti D, Dembele KT, Benavides J, Zhao H, Cloutier S, Concina I, Vomiero A, Rosei F. Functionalized multi-wall carbon nanotubes/TiO₂ composites as efficient photoanodes for dye sensitized solar cells. Journal of Materials Chemistry C. 2016;4:3555-3562
- [40] Mutuma BK, Shao GN, Kim WD, Kim HT. Sol–gel synthesis of mesoporous anatase– brookite and anatase–brookite–rutile TiO₂ nanoparticles and their photocatalytic properties. Journal of Colloid and Interface Science. 2015;442:1-7
- [41] Fakhouri H, Arefi-Khonsari F, Jaiswal AK, Pulpytel J. Enhanced visible light photoactivity and charge separation in TiO₂/TiN bilayer thin films. Applied Catalysis A: General. 2015;492:83-92
- [42] Li X, Colombo L, Ruoff RS. Synthesis of Graphene films on copper foils by chemical vapor deposition. Advanced Materials. 2016;28:6247-6252
- [43] Pierson HO. Handbook of Chemical Vapor Deposition (CVD)—Principles, Technology and Applications. 2nd Ed. Norwich, NY: William Andrew Publishing/Noyes; 1999
- [44] Bento RT, Ferrus Filho A, Pillis MF. Microstructural characterization of TiO₂ thin films: A review. Revista Brasileira de Inovação Tecnológica em Saúde. 2017;7:4-17
- [45] Marcello BA, Geribola GA, Pillis MF. Caracterização de filmes finos de TiO₂ crescidos sobre borossilicato. In: XXI Congresso Brasileiro de Engenharia e Ciência dos Materiais. Cuiabá: Proceedings of XXI CBECIMAT. Vol. 1. 2014. pp. 768-775
- [46] Zhou M, Yu J, Liu S, Zhai P, Jiang L. Effects of calcination temperatures on photocatalytic activity of SnO₂/TiO₂ composite films prepared by an EPD method. Journal of Hazardous Materials. 2008;154:1141-1148
- [47] Whitehouse DJ. Handbook of Surface Metrology. Vol. 988. London: IOP Publishing Ltd; 1994
- [48] Krumdieck S, Gorthy R, Gardecka AJ, Lee D, Miya SS, Talwar SD, Polson MIJ, Bishop C. Characterization of photocatalytic, wetting and optical properties of TiO₂ thin films and demonstration of uniform coating on a 3-D surface in the mass transport controlled regime. Surface and Coatings Technology. 2017;326:402-410
- [49] Antunes RA, Oliveira MCL, Pillis MF. Effect of the deposition temperature on the corrosion stability of TiO₂ films prepared by metal organic chemical vapor deposition. International Journal of Electrochemical Science. 2013;8:1487-1500
- [50] Liu R, Zhou X, Yang F, Yu Y. Combination study of DFT calculation and experiment for photocatalytic properties of S-doped anatase TiO₂. Applied Surface Science. 2014; 319:50-59
- [51] Babelon P, Dequiedt AS, Mostéfa-Sba H, Bourgeois S, Sibillot P, Sacilott M. SEM and XPS studies of titanium dioxide thin films grown by MOCVD. Thin Solid Films. 1998; 332:63-67

- [52] Georgios P, Wolfgang SM. X-ray photoelectron spectroscopy of Anatase-TiO₂ coated carbon nanotubes. Solid State Phenomena. 2010;**162**:163-177
- [53] Bharti B, Kumar S, Lee H-N, Kumar R. Formation of oxygen vacancies and Ti³⁺ state in TiO₂ thin film and enhanced optical properties by air plasma treatment. Scientific Reports. 2016;6:32355
- [54] Lin L, Wang H, Luo H, Xu P. Enhanced photocatalysis using side-glowing optical fibers coated with Fe-doped TiO₂ nanocomposite thin films. Journal of Photochemistry and Photobiology A: Chemistry. 2015;**307-308**:88-98
- [55] Wang F, Li F, Zhang L, Zeng H, Sun Y, Zhang S, Xu X. S-TiO₂ with enhanced visiblelight photocatalytic activity derived from TiS₂ in deionized water. Materials Research Bulletin. 2017;87:20-26
- [56] Hu B, Liu Y. Nitrogen-doped Nb₂O₅ nanobelt quasi-arrays for visible light photocatalysis. Journal of Alloys and Compounds. 2015;635:1-4
- [57] Mourão HAJL, De Mendonça VR, Malagutti AR, Ribeiro C. Nanostructures in photocatalysis: A review about synthesis strategies of photocatalysts in nanometric size. Química Nova. 2009;32:2181-2190

Preparation of Blue TiO₂ for Visible-Light-Driven Photocatalysis

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Abstract

Titanium dioxide (TiO_2) , which is regarded as a semiconductor photocatalyst, has drawn attention in the applications of photocatalysis, including hydrogen evolution reaction, carbon dioxide reduction, pollutant degradation, and biocatalytic or dye-sensitized solar cells due to its low toxicity, superior photocatalytic activity, and good chemical stability. However, there are still some disadvantages such as too large energy bandgap (~3.34 eV and ~3.01 eV for anatase and rutile phases, respectively) in the absorbance of all ranges of lights, which limits the photoelectrochemical performance of TiO₂. Herein, we like to introduce photocatalytic blue TiO₂ that is obtained by the reduction of TiO₂. The blue TiO₂ consists of Ti³⁺ state with high oxygen defect density that can absorb the visible and infrared as well as ultraviolet light due to its low energy bandgap, leading to enhance a photocatalytic activity. This chapter covers the structure and properties of blue TiO₂/ its possible applications in visible-light-driven photocatalysis, and mainly various synthetic methods even including phase-selective room-temperature solution process under atmospheric pressure.

Keywords: blue titanium dioxide, black titanium, synthesis method, photocatalysis, visible light

1. Introduction

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 TiO_2 is an extraordinarily versatile material. In 1964, Kato et al. used a TiO_2 suspension for the photocatalytic oxidation of tetralin (1,2,3,4-tetrahydronaphthalene) [1]. In 1972, the "Honda-Fujishima Effect" first described by Fujishima and Honda intensively promoted the photocatalytic field [2]. This discovery led to a new application of TiO_2 in water splitting using solar energy as the driving force of the process as well as solar energy conversion.

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To date, TiO_2 nanomaterials have attracted the interest of many scientists. The focus is to modify TiO_2 structural properties or to combine supportive materials to demonstrate that TiO_2 nanomaterials are excellent photocatalysts, which can be used as dopants in novel metal- TiO_2 systems such as Pt-doped TiO_2 [3], Au-doped TiO_2 , or graphene/ TiO_2 /carbon dot composites developed as visible light photocatalysts [3, 4].

In this chapter, we focus on blue TiO_2 as a visible-light-driven photocatalyst and its preparation methods. The blue TiO_2 nanomaterial contains Ti^{3+} with an abundant oxygen vacancy, which can absorb visible and infrared light as well as UV light, producing more electrons and holes and also facilitating better electrical conductivity than pristine TiO_2 [5]. In the future, we would like to further address the beneficial applications in clean energy storage media and protecting the environment, including the hydrogen evolution reaction, carbon dioxide reduction, and degradation of pollutants by using noble blue TiO_2 under visible light.

2. General structure and properties of TiO,

 TiO_2 belongs to the transition metal oxide family. There are four different polymorphs of TiO_2 found in nature such as anatase (tetragonal), rutile (tetragonal), brookite (orthorhombic), and TiO_2 (B) (monoclinic) [6], the most important of which are anatase and rutile. With calcination at high temperatures exceeding ~600°C, the brookite and anatase polymorphs will transform into the thermodynamically stable rutile polymorph [5].

The tetragonal anatase bulk unit cell has dimensions of a = b = 0.3733 nm and c = 0.9370 nm, and the rutile bulk unit cell has dimensions of a = b = 0.4584 nm, and c = 0.2953 nm (**Table 1**). In both structures, the octahedral distortions create the basic building units [7, 8]. The lengths and angles of octahedral coordinated Ti atoms, therefore, dictate stacking in both structures, as shown in **Figure 1**.

3. The advanced structure and properties of blue TiO_2

Zhang et al. [9] discovered that the color and crystalline phase of white P_{25} (70% anatase and 30% rutile) changed into blue color by the treatment of lithium in an ethylenediamine (Li-EDA) solution, which is the first achievement in making blue TiO₂ under atmospheric

| Properties | Crystalline forms | | | | |
|---|---|--|---|--|--|
| | Anatase | Rutile | Brookite | | |
| Crystalline structure Lattice constants (nm) | Tetragonal α = b = 0.3733 c = 0.9370 | Tetragonal a = b = 0.4584 c = 0.2953 | Rhombohedral a = 0.5436 b = 0.9166 | | |
| Bravais lattice Density (g/cm ⁻³) Meltine point (°C) | Simple, Body centred 3.83 Turning into rutile | Simple, body centred 4.24 1870 | c=0.5135 Simple 4.17 Turning into rutile | | |
| Boiling point (°C) Band gap (eV) Refractive index (n _a) Standard heat capacity, C ^o p | 2927* 3.2 2.5688 55.52 | - 3.0 2.9467 55.60 | 2.8090 | | |
| Dielectric constant | 55 | 110-117 | 78 | | |

^a Pressure at pO₂ is 101.325 KPa.

Table 1. Crystal structure data for TiO₂ Copyright (2014), Elsevier [15].



Figure 1. Bulk structures of anatase and rutile TiO2. Copyright (2003), Elsevier [18].

pressure at room temperature in solution and also the phase-selective reduction between anatase and rutile TiO_2 phases. They showed that the white anatase TiO_2 phase was not changed, while the rutile TiO_2 phase changed into black color. In the case of P_{25} TiO₂, the blue colored TiO₂ appeared as a result of the combination of white and black colors (**Figure 2**) [9].

The unit cell parameters and nanocrystalline size profiles of white P_{25} and blue TiO₂ are shown in **Table 2**. These results show that a slight change occurred along the a and b directions, but there was significant expansion in the c direction, and as a result, the unit cell volume expanded significantly as well [10].



Figure 2. Schematics of TiO_2 (white P_{25}) (left) and blue TiO_2 crystals (right). The black color corresponds to the visual color of the reduced rutile TiO_2 . Copyright (2016), Royal Society of Chemistry [9].

| samples | cell parameter $a, b/Å$ (a = b) | cell parameter c/Å | cell volume/ Å ³ | crystalline size (nm) |
|---------------------------|------------------------------------|--------------------------|-----------------------------------|--------------------------|
| white TiO ₂ | 4.612 30 | 2.952 47 | 62.8088 | 8.774 |
| blue TiO ₂ | 4.611 07 | 2.971 47 | 63.1793 | 7.650 |

Table 2. Unit cell parameters of TiO₂ (white P₂₅) and blue TiO₂ Copyright (2014), American Chemical Society [10].



Figure 3. XRD patterns of different shapes. Experimental (thick black lines) and simulated (thin colored lines) plots for TiO_2 nanocrystals. The insets showed accurate percentages of the {001} and {101} facets of atomistic models. Copyright (2012), American Chemical Society [12].



Figure 4. Color change of white P_{25} (left) to blue TiO₂ (right) and UV-vis absorption spectra of pristine TiO₂ (P-TiO₂) and reduced anatase TiO₂ (R-TiO₂). Copyright (2017), American Chemical Society [14].

Recent publications showed that the morphology of TiO_2 materials resulted in differences of the enhanced photocatalytic activity for the production of hydrogen between the {101} and {001} facets of anatase tetragonal bipyramidal nanocrystals [11–13]. Based on the XRD simulation,

the length and width of the peaks were calculated to confirm the percentages of the {101} and {001} facets (**Figure 3**). Their research well defined the optimum nanosize as well as the shape of TiO₂ crystals, suggesting that the {101} facets are more photocatalytically active than the {001} facets for the evolution of H₂ (up to 2.1 mmol h⁻¹ g⁻¹) under simulated solar illumination, while the blue coloration results from oxygen vacancies in the TiO₂ lattice [12].

The blue TiO_2 has excellent absorption over a much wider spectral range than white TiO_2 due to the excitation of conduction band electrons. Therefore, it should exhibit much better photocatalytic activity under visible light or the full spectrum of solar irradiation (**Figure 4**) [9, 14].

4. Electronic properties of blue TiO, in photocatalysis

Semiconductor materials, TiO₂ in particular, are widely used in the applications of photocatalysis. As shown in **Figure 5**, the reduction potential of photogenerated electrons is defined by the energy level at the bottom of the conduction band (CB), while the oxidizing ability is the energy level at the top of the valence band (VB). Because the CB energy level of TiO₂ is higher than the reduction potential levels of NHE references, semiconductors as well as TiO₂ nanomaterials can be used as a catalyst for hydrogen evolution, CO₂ conversion, or pollutant degradation [15].

Photocatalytic reactions occur as a material interacts with light, which provide higher energy than the bandgap of the semiconductor to create reactive oxidizing species, leading to the photocatalytic transformation of a compound.

The basics of the photocatalytic process can be summarized as follows:

- (1) TiO, absorption of photons with sufficient energy and generation of electron-hole pairs.
- (2) Separation and transport of electron-hole pairs with electrons excited from the valence band (VB) to CB.
- (3) Chemical reaction on the surface-active sites with charge carriers.



Figure 5. Bandgap of TiO₂ and some photocatalysts with respect to the redox potential (vs. NHE) values of different chemical species measured at a pH of 7. Copyright (2014), Elsevier [11, 15, 16].



Figure 6. Schematic diagram of Ti³⁺ self-doped TiO₂ mechanism for visible light photocatalysis.

Meanwhile, electron-hole recombination is also possible depending on the competition between these processes.

Blue TiO_2 nanomaterials can overcome the limitations to enhance the photocatalytic performance due to the formation of oxygen vacancies (supports many free carriers charges). The oxygen vacancy is a positive charge. Then, Ti³⁺ from the center shifts away from the oxygen vacancy position, leading to an advanced sublevel electric state and excellently trapped holes, preventing the recombination of electrons and holes, even with the lower energy bandgap irradiation (~2.7 eV) compared to P₂₅ (3.2 eV). Blue TiO₂ could generate electrons in the wide open region of irradiation such as solar light, which contains most visible and infrared wavelengths as well as UV light [17, 19] (**Figure 6**).

5. Synthesis of blue TiO, nanomaterials for photocatalysis

5.1. Hydrogenation synthesis

 H_2 is the most common reagent used for the hydrogenation of TiO₂, which can react with the lattice oxygen, leading to the formation of abundant oxygen vacancies and Ti³⁺ in TiO₂ due to its facile activation by thermal or electromagnetic energy [4, 19]. The annealing time changes with the annealing temperature, where the blue color was maintained up to a longer time at 500°C. It readily changed to pale gray at 600°C due to the high concentration of Ti³⁺ in the bulk at the early stage of hydrogenation, which may absorb oxygen molecules and lead to O⁻ as a major species on the surface after prolonged hydrogenation (**Figure 7**) [20, 21]. In addition, hydrogenation processes require harsh synthetic conditions and/or a dangerous production process [4, 10, 19, 21–25]. Therefore, H₂ is introduced using different reducing agents such as NaBH₄ and TiH₂ [4, 26, 27] instead of an external dose of hydrogen gas. TiH₂ as a solid solution of hydrogen in Ti and P₂₅ was mixed and sealed in a quartz tube and calcined at 450°C for 10 h. After discarding most of the unreacted TiH₂ sediments, HCl and H₂O₂ solutions were then introduced to completely remove the residual TiH₂, during which the TiH₂ dissolved and a yellow solution was formed. After centrifugation and thorough



Figure 7. Photograph of H-aTiO₂ samples prepared with a H_2 gas flow at temperatures of 500–700°C. Gradual changes in color from blue to gray to a different degree are observed, depending on annealing temperatures and annealing time. Copyright (2013) American Chemical Society [21].

washing, TiH_2 was completely removed, and a well-crystallized bluish sample (TiO_{2-x} : H) was obtained [4]. Qiu et al. found that the TiO_{2-x} : H can efficiently enhance the visible- and infrared-light absorption and improve photocatalytic degradation of methyl orange (MO) and hydrogen production via water splitting by H doped into the well-crystallized lattice, which means that might be localized states in the bandgap was offered and has a relatively low recombination rate of electrons and holes. Moreover, we should note that the low concentration of hydrogen atoms in hydrogenated titania was found to be a unfavorable factor affecting the photocatalytic activity [21].

5.2. Hydro(solvo)thermal method

Hydrothermal and solvothermal methods have received some attention due to their simple and low-cost production routes and are suitable for large-scale production [28, 29]. Zhu et al. reported the synthesis of novel blue colored TiO_2 with abundant defects through a one-step solvothermal method using TiCl_3 and TiF_4 as precursors. The introduction of Ti^{4+} in the reaction system inhibits the oxidation of Ti^{3+} during the solvothermal treatment.

$$Ti^{3+}$$
 + oxygen species $\rightleftharpoons Ti^{4+}$ (1)

This process is governed by the Le Chatelier's principle. The oxygen vacancy formation dominantly resulting from Ti^{3+} will not be completely oxidized during the solvothermal process. Moreover, leaving behind a high concentration of bulk Ti^{3+} defects is very favorable for visible light photocatalytic reactions [29]. In addition, Fang et al. synthesized a variety of reduced TiO_2 samples by using Zn powder as the reducing agent and HF as the solvent for the stabilization of the formed Ti^{3+} species and oxygen vacancies in a simple one-pot hydrothermal process. At the same time, it should be noted that the Ti^{3+} introduced by Zn reduction is not stable and is likely to be oxidized in air [28].

5.3. Electrochemical reduction synthesis

Zhang et al. demonstrated that that electrochemical reduction method is a facile and effective strategy to induce in situ self-doping of Ti³⁺ into TiO, and the self-doped TiO, photoelectrodes showed remarkably improved and very stable water splitting performance [30]. The hierarchical TiO₂ NTs were fabricated by a two-step anodization process. In the first step of anodization, the as-prepared Ti sheet as an anode was anodized at 60 V for 30 min in electrolytes consisted of 0.5 wt% NH₄F in EG solution with 2 vol% water and a Pt mesh (Aldrich, 100 mesh) as a cathode, respectively. After the as-grown nanotube layer was ultrasonically removed in DI water, the second step of anodization was performed at 80 V for 5 min. Then, the prepared TiO, NT samples were cleaned and annealed in air at 450 degree for 1 h with a heating rate of 5 degree min⁻¹ [30]. In the electrochemical reduction processes, the TiO₂ NTs as the working electrode with an AgCl electrode and a Pt mesh formed a typical three-electrode system under a negative potential (0.4 V vs. the reversible hydrogen electrode (RHE)) in the supporting electrolyte of 1 M Na₃SO₄ for 30 min [30]. The electronic transition from the valence band to the Ti³⁺ induced interbands and/or from the energy band levels to the conduction band was considered to contribute to enhance the absorption in the visible region in the self-doped TiO,, which helps explaining the observed color change from the prime white of the TiO, NTs to the light blue of the ECR-TiO, NTs [30].

5.4. Metal reduction method

Zheng et al. proposed an approach to synthesize blue TiO_2 nanoparticles with abundant oxygen deficiencies/Ti³⁺ species through Al reduction of TiO₂ nanosheets at 500°C [31]. Zhang et al. developed a reduction method to synthesize a series of TiO_{2-x} samples with their color changing from white to dark blue, which possess a much higher surface area and visible light absorption compared to pristine TiO₂ (**Figure 8**) [32]. In a typical reduction process, crystalline



Figure 8. The route for the preparation of Ru/TiO_{2-x} ; photographs of P_{25} nanocrystals and TiO_{2x} . (a) P_{25} nanocrystals, (b) TiO-1-80-0.5, (c) TiO-1-80-1, (d) TiO-1-120-4, (e) TiO-1-150-4, (f) TiO-1-180-4, (g) TiO-2-180-4, (h) TiO-3-180-4, and (i) TiO-4-180-4. Reprinted with permission from [32]. Copyright (2017) The Royal Society of Chemistry.

 TiO_2 was milled with Na/NaCl fine powders with different weight ratio at a series of milling rates such as 80, 120, 150, and 180 rpm at room temperature under argon atmosphere for 0.25–4 h. After the Na and NaCl was removed, the obtained TiO_{2-x} products were dispersed in a small amount of deionized water and then vacuum-dried at room temperature to obtain TiO_{2-x} powders [32]. Moreover, the obtained TiO_{2-x} with a high surface area can be employed as an effective support for Ru particles and the Ru/TiO_{2-x} catalyst exhibited superior activity in the catalytic hydrogenation of N-methylpyrrole [32].

5.5. Phase-selective room-temperature solution processing

Until now, numerous methods to prepare blue TiO_2 have been reported, but all of them require high-temperature processing. Due to high-temperature processing, a phase-selective reduction between the anatase and rutile TiO_2 phases is almost impossible. For the first time, phase-selective "disorder engineered" Degussa P_{25} TiO_2 nanoparticles using simple room temperature solution processing was demonstrated as a very effective method to prepare modulatory TiO_2 [9]. The blue-colored TiO_2 nanoparticles were obtained by using a strong reducing agent consists of lithium in ethylenediamine (Li-EDA), which can disorder only the white rutile phase of P_{25} , while well maintaining white anatase TiO_2 [9]. Firstly, 14 mg metallic Li foil was dissolved in 20 ml ethanediamine to form a 1 mmol/ml solvated electron solution. Two hundred milligram of Degussa P_{25} (anatase, size: ~25 nm, rutile, size: ~140 nm, P25, size: 20–40 nm) was prepared after thorough drying and then added into the abovementioned solution and stirred for several days depending on the application. After sufficient reaction, the excess electrons and formed Li salts were quenched by slowly adding HCl into the mixture. Finally, the blue-colored TiO₂ nanoparticles were thoroughly rinsed by deionized water several times and dried at room temperature in a vacuum oven [9].

In their study, the blue TiO_2 showed drastically enhanced visible and near-infrared light absorption by induced abundant order/disorder junctions at the surface from selective disorder engineering, which means that it has well charge separation efficiency through type-II bandgap alignment and can effectively promote strong hydrogen evolution surface reaction [9]. Therefore, when the phase-selective disorder engineering of P_{25} TiO₂ nanoparticles as photocatalysts were used, they exhibited high stability and a high hydrogen evolution rate of 13.89 mmol h⁻¹ g⁻¹ using 0.5 wt% Pt (cocatalyst) and 3.46 mmol h⁻¹ g⁻¹ without using any cocatalyst under simulated solar light (**Figure 9**) [9].

5.6. Other methods

5.6.1. Sol-gelation hydrothermal technique and subsequent reduction treatment method

Ti³⁺ self-doped blue TiO₂ (B) single-crystalline nanorods (b-TR) were synthesized *via* three steps, in which the titanium dioxide powder was prepared via the sol-gelation approach followed by hydrothermal treatment. Blue TiO₂ (B) single-crystalline nanorods were obtained by further annealing at 350°C in Ar [33]. Under visible light illumination, the degradation rate of RhB reached 97.01% by b-TR and the photocatalytic hydrogen evolution rate was as high as 149.2 µmol h⁻¹ g⁻¹ under AM 1.5 irradiation [33]. The mechanistic



Figure 9. (a) Comparison of the hydrogen generation and cycling performance of 0.5 wt% platinized P_{25} nonplatinized P_{25} and nonplatinized blue P_{25} after 1 day of continuous reaction using methanol as a sacrificial agent. A simulated full solar spectrum was used as the excitation source, which produced approximately 100 mW cm⁻² in the samples, which consisted of various TiO₂ nanocrystals in a 100 mL quartz reactor filled with 70 mL of solution. (b) Proposed mechanism for charge separation and H_2 generation in blue P_{25} (green part: ordered TiO₂, gray part: disordered TiO₂). Copyright (2016), Royal Society of Chemistry [9].

analysis and characterization results showed that the synergetic action of the special TiO_2 (B) phase, Ti^{3+} self-doping, and the 1D rod-shaped single-crystalline nanostructure resulted in a narrowed bandgap of 2.61 eV, which enhanced the photocatalytic and photoelectrochemical performances [33] (**Figure 10**).

5.6.2. Ice-water quenching

Liu et al. applied ice-water quenching as a facile strategy for the synthesis of blue color of Ti^{3+} self-doped TiO_2 [23]. In the typical process, commercial P_{25} materials were quenched in



Figure 10. Diagrammatic sketch for the formation of blue TiO₂ (B) single-crystalline nanorod. Copyright (2016) American Chemical Society [33].


Figure 11. (A) Digital pictures of q-TiO₂ and n-TiO₂ samples prepared from the commercial P_{25} powders after being subjected to pre-annealing at different temperatures. (B) Digital picture of just-quenched TiO₂ sample on filter paper, which shows the blue color in the inner side of the sample [23]. Copyright (2017) American Chemical Society.

ice-water after pre-annealing at a high temperature. Then, the obtained powders were filtered and dried at 80°C for 12 h for further use [23]. Digital pictures of q-TiO₂ (quenched TiO₂) show that the color changed to pale blue when subjected to a temperature higher than 900°C, which confirmed the presence of Ti³⁺ in TiO₂ after ice-water quenching (**Figure 11**), implying that the d-d might be a transition from Ti³⁺ band gap states to their resonant excited states and extended light absorption together with near-IR absorption [23]. In addition, the surface distortion and the associated oxygen defects were considered to be contributed to the substantially enhanced photocatalytic activity [23]. It should be pointed out that the quenched TiO₂ cannot absorb much visible light, which means that the photoexcited electrons at the Ti³⁺ defect level cannot transfer outside [23].

6. Conclusions and development

In this chapter, blue TiO, that has a low energy bandgap is introduced as an advanced semiconducting material for possible applications in the visible-light-driven photocatalysis. A variety of preparation methods for blue TiO, photocatalysts with Ti³⁺ states of a high oxygen defect density have been successfully introduced. For the synthesis of the blue TiO₂ in the applications of photocatalysis, hydrogenation method using TiO₂ with hydrogen at 500°C or with hydride reducing agent at 450°C, hydrothermal method using Ti precursors or Zn powder reducing agent under HF solvent, electrochemical reduction method using anodizing TiO₂ at 60 and 80 V and then annealing at 450°C, and metal reduction method using Al at 500°C, Na and NaCl solid milling, or Li-EDA solution at room temperature and atmospheric pressure. For the preparation of blue TiO,, the most recently developed metal solution room temperature method can give phase-selective reduction between the anatase and rutile TiO, phases. For the first time, the phase selective "disordered rutile and crystalline anatase" $P_{\rm 25}$ TiO₂ nanoparticles are reported, which turns out that it is a very effective photocatalyst for hydrogen evolution reaction and removal of algae under solar irradiation. However, how to quantitatively control surface defects and the properties of the interface between the order and disorder surface layer still remain as important challenges to understand the true physicochemical properties of blue TiO₂.

As mentioned in the introduction, in the near future, we would like to further address beneficial applications in clean energy conversion and storage media and protecting the environment, including the hydrogen evolution reaction, carbon dioxide reduction, and degradation of pollutants by using noble blue TiO₂ under visible light.

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References

- Gupta SM, Tripathi M. A review of TiO₂ nanoparticles. Chinese Science Bulletin. 2011; 56(16):1639-1657
- [2] Fujishima A, Honda K. Electrochemical photolysis of water at a semiconductor electrode. Nature. 1972;**238**:37
- [3] Banerjee B et al. Green synthesis of Pt-doped TiO_2 nanocrystals with exposed (001) facets and mesoscopic void space for photo-splitting of water under solar irradiation. Nanoscale. 2015;7(23):10504-10512
- Buso D et al. Gold-nanoparticle-doped TiO₂ semiconductor thin films: Optical characterization. Advanced Functional Materials. 2007;17(3):347-354
- [5] Hu Y, Tsai H-L, Huangk C-L. Effect of brookite phase on the anatase–rutile transition in titania nanoparticles. Journal of the European Ceramic Society. 2003;**23**:691-696

- [6] Mor GK et al. A review on highly ordered, vertically oriented TiO₂ nanotube arrays: Fabrication, material properties, and solar energy applications. Solar Energy Materials and Solar Cells. 2006;90(14):2011-2075
- [7] Qiu J. Hydrogenation synthesis of blue TiO₂ for high-performance lithiumion batteries. Journal of Physical Chemistry C. 2014;118:8824–8830
- [8] Khader MM, Kheiri FMN, El-Anadouli BE, Ateya BG. Mechanism of reduction of rutile with hydrogen. The Journal of Physical Chemistry. 1993;97:6074–6077
- [9] Zhang K et al. An order/disorder/water junction system for highly efficient co-catalyst-free photocatalytic hydrogen generation. Energy & Environmental Science. 2016;9(2):499-503
- [10] Qiu J et al. Hydrogenation synthesis of blue TiO₂ for high-performance lithium-ion batteries. The Journal of Physical Chemistry C. 2014;118(17):8824-8830
- [11] Pan J, Liu G, (Max) Lu GQ, Cheng H-M. On the true photoreactivity order of {001}, {010} and {101} facets of anatase TiO₂ crystals. Angewandte Chemie-International Edition. 2011;50(9): 2133-2137
- [12] Gordon TR et al. Nonaqueous synthesis of TiO₂ nanocrystals using TiF₄ to engineer morphology, oxygen vacancy concentration, and photocatalytic activity. Journal of the American Chemical Society. 2012;134(15):6751-6761
- [13] Liu X, Bi Y. In situ preparation of oxygen-deficient TiO₂ microspheres with modified {001} facets for enhanced photocatalytic activity. RSC Advances. 2017;7(16):9902-9907
- [14] Cushing SK et al. Effects of defects on photocatalytic activity of hydrogen-treated titanium oxide nanobelts. ACS Catalysis. 2017;7(3):1742-1748
- [15] Ola O, Maroto-Valer MM. Review of material design and reactor engineering on TiO₂ photocatalysis for CO₂ reduction. Journal of Photochemistry and Photobiology C: Photochemistry Reviews. 2015;24:16-42
- [16] Indrakanti VP, Kubicki JD, Schobert HH. Photoinduced activation of CO₂ on Ti-based heterogeneous catalysts: Current state, chemical physics-based insights and outlook. Energy & Environmental Science. 2009;2(7):745
- [17] Ishchenko OM. Semiconductor photocatalysis: Materials, mechanisms and applications. In: Caodoi W. editor. Chapter 2, Influences of Doping on Photocatalytic Properties of TiO₂ Photocatalyst. DOI: 10.5772/62774
- [18] Kim Y et al. Solar-light photocatalytic disinfection using crystalline/amorphous low energy bandgap reduced TiO₂. Scientific Reports. 2016;6:25212
- [19] Diebold U. The surface science of titanium dioxide. Surface Science Reports. 2003;48: 53-229
- [20] Zhu G et al. Hydrogenated blue titania with high solar absorption and greatly improved photocatalysis. Nanoscale. 2016;8(8):4705-4712

- [21] Su J, Zou X, Chen J-S. Self-modification of titanium dioxide materials by Ti³⁺ and/or oxygen vacancies: New insights into defect chemistry of metal oxides. RSC Advances. 2014;4(27):13979-13988
- [22] Yu X, Kim B, Kim YK. Highly enhanced photoactivity of anatase TiO₂ nanocrystals by controlled hydrogenation-induced surface defects. ACS Catalysis. 2013;3(11):2479-2486
- [23] Li JJ et al. Efficient promotion of charge transfer and separation in hydrogenated TiO₂/WO₃ with rich surface-oxygen-vacancies for photodecomposition of gaseous toluene. Journal of Hazardous Materials. 2018;**342**:661-669
- [24] Liu B et al. Ice-water quenching induced Ti³⁺ self-doped TiO₂ with surface lattice distortion and the increased photocatalytic activity. The Journal of Physical Chemistry C. 2017;121(36):19836-19848
- [25] Samsudin EM et al. Surface modification of mixed-phase hydrogenated TiO₂ and corresponding photocatalytic response. Applied Surface Science. 2015;359:883-896
- [26] Wang W et al. A new sight on hydrogenation of F and N-F doped {001} facets dominated anatase TiO₂ for efficient visible light photocatalyst. Applied Catalysis B: Environmental. 2012;127:28-35
- [27] Sun L et al. Design and mechanism of core-shell TiO₂ nanoparticles as a high-performance photothermal agent. Nanoscale. 2017;9(42):16183-16192
- [28] Fang W et al. Zn-assisted TiO_{2-x} photocatalyst with efficient charge separation for enhanced Photocatalytic activities. The Journal of Physical Chemistry C. 2017;121(32):17068-17076
- [29] Zhu Q et al. Stable blue TiO_{2-x} nanoparticles for efficient visible light photocatalysts. Journal of Materials Chemistry A. 2014;2(12):4429
- [30] Zhang Z et al. Electrochemical reduction induced self-doping of Ti³⁺ for efficient water splitting performance on TiO₂ based photoelectrodes. Physical Chemistry Chemical Physics. 2013;15(37):15637-15644
- [31] Zheng J et al. Facile aluminum reduction synthesis of blue TiO₂ with oxygen deficiency for lithium-ion batteries. Chemistry. 2015;21(50):18309-18315
- [32] Zhang M et al. Room temperature synthesis of reduced TiO₂ and its application as a support for catalytic hydrogenation. RSC Advances. 2017;7(8):4306-4311
- [33] Zhang Y et al. Ti³⁺ self-doped blue TiO₂(B) single-crystalline Nanorods for efficient solar-driven Photocatalytic performance. ACS Applied Materials & Interfaces. 2016;8(40): 26851-26859

Photocatalytic Degradation of Selected Organophosphorus Pesticides Using Titanium Dioxide and UV Light

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Additional information is available at the end of the chapter

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Abstract

The photocatalytic degradation of five selected organophosphorus pesticides (OPPs), azinphos methyl, azinphos ethyl, disulfoton, dimethoate, and fenthion, has been investigated using TiO₂ (photocatalyst) and UV irradiation. The addition of H₂O₂ (oxidant agent) into the illuminated aquatic suspensions was also surveyed. The degradation kinetics was studied under different experimental conditions such as pesticides' and catalyst's concentration. Experiments were performed in a Pyrex UV laboratory-constructed photoreactor equipped with 4 × 18 W low-pressure Hg lamps emitting at 365 nm (maximum intensity 14.5 mW cm⁻² at distance 15 cm). The concentration of pesticides was determined by GC-NPD means. The extent of pesticide mineralization was assessed through TOC measurements. The results demonstrated that photolysis of target organophosphates in the absence of catalyst or oxidant is a slow process resulting in incomplete mineralization. Contradictory, studied pollutants were effectively degraded in the presence of TiO₂; evolution of inorganic heteroatoms (SO₄²⁻, PO₄³⁻, NO₂⁻, NO₃⁻, and NH₄⁺) as final products provided evidence that pesticide deterioration occurred. The photolysis efficiencies decreased in the order: disulfoton > azinphos ethyl > azinphos methyl > fenthion > dimethoate. Furthermore, a synergistic effect was observed with the addition of H2O2 in the pesticide-TiO2 suspensions. In all cases examined, reduction process appeared to follow pseudo first-order kinetics (Langmuir-Hinshelwood model). In conclusion, both catalytic systems investigated (UV-TiO, and UV-TiO,-H₂O,) have good potential for small-scale applications.

Keywords: advanced oxidation processes, organophosphorus pesticides, water treatment, heterogeneous photocatalysis, TiO₂, mineralization

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1. Introduction

Several human activities may result in the presence of numerous and various types of emerging chemical contaminants and toxicants in water or wastewater. Pesticide is one of the most common groups of chemical pollutants found in wastewater effluents due to their widespread use in agriculture in order to maintain crop quality and quantity [1, 2]. Their widespread use for the prevention, control, or elimination of pests has led to public health concerns in recent years. According to an extended published literature, pesticides are usually detected in trace concentrations (ng L⁻¹ or μ g L⁻¹) and consequently are considered as micropollutants, which among other characteristics are specific water and wastewater constituents that cannot be removed by primary or secondary conventional treatment. As a result, the adaptation and application of advanced oxidation processes (AOPs) are necessary to decompose these persistent compounds from contaminated environmental matrices [3].

AOP is a class of oxidation techniques and procedures that are based on the in situ generation of highly reactive and oxidizing radical species (mainly powerful hydroxyl radicals ('OH)), which interact with the molecules of the organic pollutants and lead to their progressive degradation. AOPs can be classified as photochemical or non-photochemical processes that furthermore can be categorized either as homogeneous or heterogeneous. More specifically, heterogeneous AOPs require the addition of a solid semiconductor (such as metal oxides and sulfurs of Ti, Al, Zn, V, Cr, Mn, etc., or organometallic catalysts) to produce a colloidal suspension that is stable under radiation and is required to stimulate a photochemical reduction reaction in the solid/liquid interface (occurrence of accelerated photoreaction). In particular, illumination of the catalyst with radiation of the proper wavelength ($\geq E_{r}$, bandgap energy) generates electron and hole pairs (e⁻ and h⁺, respectively, acting as energy carriers) that can recombine or dissociate (both reactions take place in competition); when dissociation occurs, conduction band electrons and valence band holes are produced, which are able to migrate to the particle surface and interact with adsorbed electron acceptors (oxygen) and oxidize electron donors (-OH and H₂O) yielding in hydroxyl radicals. Compared with the homogeneous AOPs, the heterogeneous AOPs have the advantage of the easier separation from the product (meaning the treated effluents) [4, 5].

The use of heterogeneous photocatalysis has been shown as an ideal methodology for the decontamination and restoration of water contaminated with persistent organic pollutants (POPs) in developing countries [6–8]. Nowadays, among the most promising and successful applications of heterogeneous photocatalysis applied for the removal of various toxicants from water, photocatalysis over titanium dioxide (TiO₂) is included, since it has been demonstrated as one of the most frequently used methodologies employed for the treatment of chlorinated phosphate esters and carbamic, thiocarbamic, and triazine pesticides [4–6, 9–11].

The focus of the present chapter is to provide the results of the photocatalytic degradation study conducted with five selected organophosphorus pesticides (OPPs) (azinphos methyl, azinphos ethyl, disulfoton, dimethoate, and fenthion) by heterogeneous photochemical process using UV light and TiO_2 . The process of UV-TiO₂ system was applied to the photooxidation of all selected OPPs, while the UV-TiO₂-H₂O₂ system was applied only to degradation of dimethoate and fenthion as they proved to be more resistant in the previous set of photolysis

experiments. More specifically, the objectives of this work were (i) to evaluate and compare the kinetics of pesticide disappearance, (ii) to examine the influence of oxidant reagent (H_2O_2) added into the photocatalytic system of selected OPPs, and (iii) to investigate the potential of the catalytic systems studied to be applied in a small scale for the removal of OPPs, as, for instance, by research laboratories for purifying the wastewater they produce.

Disappearance of the investigated organophosphates contained in spiked water samples (that were irradiated) was detected by a gas chromatographic (GC) system equipped with a nitrogen-phosphorus detector (GC-NPD means). Degradation kinetics and obtained kinetic parameters, expressed as rate constant and half-life values, are presented. Moreover, mineralization of parent compounds during the batch photocatalytic experiments was assessed by quality and quantity determination of formed and released inorganic end products (evolution of heteroatoms at their highest oxidized states, such as SO_4^{2-} , NO_3^{-} , and PO_4^{3-}) along with TOC analyzer measurements. Based on the acquired results, the applicability of the UV-TiO₂ method that was employed in the present survey is discussed and compared with other successful applications and treatments reported in the literature.

2. Materials and methods

2.1. Test chemicals, reagents, and standards

High-purity analytical standards (>97.7%) of the five selected organophosphorus pesticides (azinphos methyl, azinphos ethyl, dimethoate, disulfoton, and fenthion) were purchased from Dr. Ehrenstorfer-Schäfers (Augsburg, Germany) and used without further purification. Their chemical structures and data for selected physicochemical properties of studied OPPs, taken from Ref. [12], are shown in Table 1. Titanium dioxide (TiO₂) catalyst was Degussa P-25 (Frankfurt, Germany). Hydrogen peroxide (30% solution H₂O₂) was obtained from Merck & Co (Darmstadt, Germany). Pesticide-grade and HPLC-grade solvents (acetone, hexane, methanol, and dichloromethane) were supplied from Labscan Ltd. (Dublin, Ireland). Organic-free water used for all aquatic solutions was of specific resistance greater than 18.2 M Ω cm (25°C) and was produced by a Milli-Q/Milli-RO water purification system (Millipore, USA). Individual pesticide stock solutions were prepared by gravimetric weighting of high-purity standards (to concentrations of approximately 1000 mg L^{-1}) in methanol (HPLC-grade) and were stored at -10°C in the dark. Working standard solutions of individual compounds were prepared by appropriate dilutions of the stock solutions. Other chemical reagents used (HCl, NaOH, Na,SO₄, and $C_8H_4K_2O_4$) were of analytical grade and procured from Merck (Merck, Germany).

2.2. Irradiation procedure

For the performance of photolysis experiments, a self-constructed illumination system was used which has been described in detail in the previous published survey of our laboratory [6]. In brief, the apparatus was a stainless steel illuminated box (chamber) irradiated by a set of UV low-pressure lamps (Hg-lamps manufactured in Philips TL-D, $4 \times 18 \text{ W}$, $\lambda_{uv} = 365 \text{ nm}$) that dominantly emitted radiation with maximum light intensity



Table 1. Chemical names, chemical formulas, and physicochemical properties of selected pesticides.

of 14.5 mW cm⁻² at 15 cm distance. Pyrex glass bottles with a capacity of 250 mL were employed as photoreactors, containing the pesticide solutions and placed in the center of the photolysis construction. Substrates were dissolved in distilled water at ppm (mg L⁻¹) levels, under their solubility levels by spiking the appropriate volume of a stock solution in methanol, so as to have a methanol content <0.05% [13]. Fortified aqueous solutions containing each tested insecticide individually (optimum pesticide's final concentration, 10 mg L⁻¹, unless otherwise stated), in the presence and absence of the photocatalyst, were prepared by dissolving the appropriate quantities of each one of the substances in water. When TiO₂ was used (optimum TiO₂ concentration, 100 mg L⁻¹, unless otherwise stated), the mixtures were magnetically stirred to obtain homogenization and a good dispersion of the catalyst and equilibrated in the dark for 30 min prior to illumination. Samples of 250 mL of the above-fortified solutions (in the absence of the photocatalyst) or suspensions (in the presence of the photocatalyst) were added to Pyrex bottles covered air tightly with caps and photolyzed. Finally, in the case that H_2O_2 was applied as an oxidant in the photolysis system, a certain volume of the stock solution of H_2O_2 was added into the mixtures to yield the desired concentration (optimum H_2O_2 concentration, 5 mM, unless otherwise stated). Immediately, after adding hydrogen peroxide, the UV lamps were turned on, and irradiation started. The irradiated samples were magnetically stirred throughout the experiment. Photolysis was carried out at a constant ambient temperature of $30 \pm 2^{\circ}$ C in the photolysis apparatus. Prior to the photolysis tests, the pH value of the samples was not adjusted unless otherwise stated. In such cases, the adjustment was accomplished by dropwise addition of 0.1 N HCl or 0.1 N NaOH solutions.

2.3. Analysis of the photolyzed solutions

At specific time intervals, samples were removed from the photoreactor, and 5 mL aliquots of the photolyzed aqueous matrices were withdrawn for further analysis. In order to remove TiO_{ν} samples were centrifuged at 8000 rpm for 15 min. OPP concentrations were determined after liquid-liquid extraction of the filtrated aqueous phases twice with 5 mL hexane or dichloromethane by vortex (1 min). Elimination of humidity in two combined extracts was accomplished by the addition of anhydrous Na₂SO₄, whereas 1 μ L of the organic extract was used for further analysis. Qualitative and quantitative determination of extracted pesticides' residues was performed on a Hewlett-Packard gas chromatographic (GC) system, model HP-5890, Series II, (Hewlett Packard, USA) equipped with a nitrogen-phosphorus detector (NPD). The chromatographic method and conditions applied are discussed in detail by Vagi et al. [14]. The validation of the method was carried out by the analysis of fortified water samples containing each target analyte at three different spiking levels in the range of 0.5–2 mg L⁻¹ and prepared in triplicate individual solutions [15]. Percentage recoveries for the five selected insecticides were above 95.2 \pm 2.4%, LOD values were 0.0050 µg L⁻¹ for dimethoate and 0.0025 μ g L⁻¹ for the other four selected organophosphates (azinphos methyl, azinphos ethyl, disulfoton, and fenthion), and LOQ for dimethoate was 0.0165 μ g L⁻¹, while for the rest four OPPs 0.0083 μ g L⁻¹ [14].

2.4. Evaluation of the extent of mineralization

Total organic carbon (TOC) measurements were performed with a Teledyne Instruments Tekmar TOC Combustion Analyzer (model Apollo 9000, Ohio, USA) calibrated with standard solutions of potassium phthalate [6]. Additionally, the release of inorganic anions containing the heteroatoms of the organophosphorus pesticides was monitored, such as phosphate (PO_4^{3-}), nitrate (NO_3^{-}), ammonium (NH_4^{+}), and sulfate (SO_4^{2-}) ions, as a function of irradiation time was performed spectrophotometrically by using UV/Vis spectrophotometer (Varian, model Cary 50, Australia) and by following the appropriate method of the American Standard Test Method (ASTM). Specifically, nitrate ion determination was performed according to the ASTM 4500- NO_3^{-} -E cadmium reduction method and ammonium ions according to ASTM 4500- NH_3 -F phenate method, whereas **sulfate** and phosphate ions according to ASTM 4500- SO_4^{2-} -E turbidimetric and ASTM 4500-P⁻-E ascorbic acid methods, respectively [16].

3. Results

3.1. Preliminary studies: control experiments

Two control experiments were performed under the same experimental conditions that were employed for photolysis experiments which are mentioned in detail in Section 2.2. More specifically, in order to estimate the thermal (dark) reactions between the solute and TiO_2 , a first set of experiments were carried out over the same periods as those used in the photolysis experiments, but in the dark (bottles were covered with aluminum foil for the protection against light interference). The second set of experiments involved the irradiation of the pesticide aquatic solutions without the presence of catalyst to account any direct photolysis of the studied substances.

3.1.1. Adsorption in the dark

As presented in a dotted line of **Figure 1** (curve A), the addition of the catalyst without UV radiation had a negligible effect on initial concentration of target analyte azinphos methyl (10 mg L⁻¹). The same trend was followed for the other four tested compounds (data not shown), and these observations suggest that within 48 h, which was the total duration of the experiments conducted for all of the examined substances, no obvious degradation in dark reaction occurred. Therefore, it can be concluded that negligible adsorbance of the compounds on the catalyst's surface took place and that hydrolytic processes during the experimental course can be neglected. Similar results have been previously published by several other authors [17, 18]. For example, Evgenidou and her co-workers reported that the addition of two metal oxide catalysts, TiO₂ and ZnO, without UV radiation had a negligible effect on dimethoate's photooxidation rate [17].



Figure 1. Disappearance of target pesticide azinphos-methyl (10 mg L⁻¹) in control as function of time. (Curve A) In the presence of the catalyst TiO₂ (100 mg L⁻¹) and in the absence of light (in the dark); (Curve B) in the absence of the catalyst TiO₂ and in the presence of light (λ_{UV} = 365 nm).

3.1.2. Direct photolysis: photodegradation in the absence of TiO,

The photolytic decomposition of the tested pesticides in the presence of UV light and in the absence of the catalyst TiO_2 was investigated. Experimental results for the case of azinphos methyl are illustrated in **Figure 1** (curve B). Direct photolysis of 10 mg L⁻¹ of studied OPPs under illumination of 365 nm did not decrease significantly pesticides' original concentrations. Obviously, under these experimental conditions and at the end of irradiation, the observed disappearance of the OPP compounds occurred at very slow rates. According to the acquired results (not shown for azinphos ethyl, dimethoate, disulfoton, and fenthion), reduction in pesticides' initial concentration varied from 6.03 (for azinphos ethyl) to 10.68% (for dimethoate), depending on the physicochemical properties of the studied OPP individually. Moreover, these results are in agreement with TOC changes of initial TOC during direct photolysis tests conducted in the current study (presented in Section 3.4.1.).

These results are conforming to other published data according to which direct photolysis is not expected to be an important process in water for several organophosphates, because their molecules do not absorb UV light at wavelengths greater than 290 nm, despite the fact that the most important wavelengths for the photolytic degradation of the majority of the organic pesticides are 280 and 320 nm [17, 19]. It should also be mentioned that the photocatalytic deterioration of numerous cases of organophosphates in the absence of several catalysts has been studied from researchers, such as fenitrothion [20], dimethoate [17], ethyl parathion, methyl parathion, ethyl bromophos, methyl bromophos, and dichlofenthion [13]. In all these data available in the literature, photolytic process was slower compared to photocatalytic decomposition of these substances.

3.2. Photocatalytic degradation of OPPs in UV-TiO₂ system

Figure 2 depicts the photodecomposition of the compounds studied in the presence of the semiconducting catalyst under UV illumination. It is clear that all investigated organophosphorus insecticides were sufficiently degraded in aqueous titanium dioxide (TiO₂) suspensions (100 mg L⁻¹) under illumination of UV light with wavelength of 365 nm.

It is well established in the bibliography that the rates of the photocatalytic reaction depend on several experimental parameters among which included initial concentration of illuminated solute reactant, radiant flux, wavelength, type and mass of catalyst, type of photoreactor, pH, and temperature. As a consequence, only the comparison between data measured for a given set of experimental conditions is meaningful and valuable.

Obtained experimental results demonstrated that under the employed set of conditions the decomposition efficiencies of OPPs in UV-TiO₂ system depended on the nature and the structure of tested compounds and decreased in the order: disulfoton > azinphos ethyl > azinphos methyl > fenthion > dimethoate. Semiconductor TiO₂ working as a catalyst with UV light to generate highly reactive oxidizing agents caused the total decomposition (100%) of disulfoton after 12 h of illumination, whereas complete disappearance of azinphos ethyl and azinphos methyl was achieved after 24 h of light exposure.



Figure 2. Photodegradation rates of studied OPPs in aqueous suspensions of the catalyst TiO₂ under UV light (pesticide's concentration, 10 mg L⁻¹; catalyst's concentration, 100 mg L⁻¹; pH_{22} , 6.06; λ_{1137} , 365 nm, in the presence of methanol).

On the contrary, fenthion and dimethoate proved to be very resistant to photocatalytic reduction, and even after 48 h of light exposure, 95 and 60% of their original concentration decomposed, respectively. That is the main reason that those two substances were selected for the study of photodegradation in the UV-TiO₂-H₂O₂ oxidation systems.

In general, the comparison of obtained results with other experimental data previously reported for other organic pesticide micropollutants shows that degradation rates estimated in the present survey are lower. This phenomenon can be ascribed to differences in the laboratory conditions used by other researchers. For instance, Echavia and co-workers [21] reported a complete (100%) decomposition of dimethoate within 60 min of irradiation, using TiO₂ immobilized on silica gel and UV light emitting mostly at 365 nm with light intensity of 1.4 mW cm⁻². Evgenidou and co-workers reported 65% reduction of dimethoate after 10 min of irradiation, using UV light with $\lambda > 290$ nm in the presence of TiO₂ 100 mg L⁻¹ [17].

3.2.1. Effect of the catalyst's concentration on photocatalytic degradation rate

The reaction rate of heterogeneous photodegradation as a function of the catalyst's concentration is very important and has been investigated in several other cases reported in the literature [5, 10, 22, 23]. Hence, the purpose of these experiments was to determine the optimum TiO_2 concentrations for subsequent experiments and to investigate how the TiO_2 concentration affected the photocatalytic decomposition pathway of selected toxicants. Therefore, photolytic procedures employing different concentrations of TiO_2 ranging from 0 to 500 mg L⁻¹ were conducted, whereas the initial concentration of the pesticide tested was maintained the same, 10 mg L⁻¹. The reaction rate (r) of the photocatalytic reactions was expressed as the change (decrease) in concentration of photolyzed pesticide reactants divided by the time interval during which this change was observed. Values of r were calculated by Eq. 1:

$$r = -\frac{\mathrm{d}\,C}{\mathrm{d}t} \tag{1}$$

where *r* is the reaction rate of photolysis (in mg L⁻¹ h⁻¹), *C* is the level of concentration of the degraded reactant (in mg L⁻¹), and *t* is the illumination time (in h). The initial reaction rates as a function of TiO₂ concentration for all cases investigated are depicted in **Figure 3**.

Obviously, as shown in **Figure 3**, the initial rate of photocatalytic degradation of all studied analytes decreased when TiO_2 concentration was increased from 0 to 10 mg L⁻¹ and then increased as the TiO_2 concentration was increased to 100 mg L⁻¹, where it seemed to level off. These trends and observations correspond with those of other researchers who have reported that this may be due to different contributions of distinct homogenous and heterogeneous photochemical reactions at different TiO_2 concentrations [17, 24–26]. More specifically, in the absence of TiO_2 , only the homogeneous photochemical reduction was



Figure 3. Effect of TiO₂ concentration on initial rate of photocatalytic degradation of studied OPPs (pesticide's concentration, 10 mg L⁻¹; catalyst's concentration, 0–500 mg L⁻¹; pH_{d'} 6.06; λ_{UV} 365 nm, in the presence of methanol).</sub>

possible. The downward trend in initial rates of pesticide's photocatalytic decomposition that is shown in **Figure 3**, when only a small amount of TiO_2 (<10 mg L⁻¹) was present, can be explained by the fact that the photocatalyst acted mainly to absorb and/or scatter UV light, thus inhibiting the homogenous reaction but not yet causing a significant heterogeneous reaction of photodegradation. However, at higher TiO₂ concentrations (>10 mg L⁻¹), an increase in the rate of the process was observed as the heterogeneous reaction increased in importance. Actually, from the obtained data, it became obvious that in this range of concentrations the reaction rate is directly proportional to the mass of the photocatalyst. This can be explained on the basis that with the increase in catalyst surface increases as well. However, above a certain value, the reaction rate leveled off and became independent of the TiO₂ concentration.

The eventual leveling off of the initial rates of photocatalytic deterioration (**Figure 3**) could be explained by the fact that suspended particles of TiO_2 were present at a high-enough concentration to block UV light passage to the interior parts of the reactor, increased the light scattering, and made the homogeneous reaction insignificant. Moreover, other phenomena such as particle-particle interactions (agglomeration) that may occur at high TiO_2 concentration (>100 mg L⁻¹) could result in a loss of surface area available for light harvesting and thus lead in a decrease of the photoreaction rates [17, 24]. Chen and Chou reported that further increase in TiO_2 catalyst amount beyond 200 mg L⁻¹ may result in the deactivation of activated molecules due to collision with the ground-state molecules [25] as shown in the chemical reaction (Eq. (2)):

$$\mathrm{TiO}_{2}^{\bullet} + \mathrm{TiO}_{2} \rightarrow \mathrm{TiO}_{2}^{\#} + \mathrm{TiO}_{2}$$

$$\tag{2}$$

where TiO_2^{\bullet} is the active species of the catalyst that is adsorbed on its surface, whereas $\text{TiO}_2^{\#}$ is the deactivated form of the catalyst [24].

The photocatalytic degradation of other organic pollutants has also exhibited the same dependency on catalyst dose [17, 24]. According to previous studies, the concentration of optimum catalyst was found to be dependent on the initial solute concentration of the photocatalyzed compound [17, 26].

In the present study, as it can be concluded from data illustrated in **Figure 3**, under the applied experimental conditions, the optimum value of catalyst's concentration TiO_2 P-25 on photocatalytic decomposition of investigated insecticides is 100 mg L⁻¹, and consequently, this amount was selected to work throughout the study. This result is in agreement with other studies [17].

3.2.2. Effect of the pesticides' initial concentration on photocatalytic degradation rate

In order to investigate the dependence of the photolysis rate (r_o) on the pesticide reactants' initial concentration (C_o) , a set of photodegradation experiments was carried out by varying the initial concentration of the solute from 5 to 60 mg L⁻¹ (a concentration range that

facilitated the procedure of LLE method), whereas the catalyst loading was maintained constant (100 mg L⁻¹). Throughout the performed tests, it was assumed that, in the first stages of irradiation ($\leq 20\%$ reduction), no variations took place resulting from other parameters such as competitive effects of intermediates, pH changes, etc. [6, 17]. The effect of the insecticides' initial concentration (C_o) of each individual pesticide reactant on the initial reaction rate (r_o) was independently obtained and illustrated in **Figure 4** (the inset of **Figure 4** is the linear transform of $1/r_o$ versus $1/C_o$ values).

From the depicted experimental data acquired in current investigation and are shown in **Figure 4**, it is obvious that the degradation rate increased with the increase of the concentration of all of the studied compounds until it reached a saturation value ($10 \text{ mg } \text{L}^{-1}$). At higher concentrations above that value (>10 mg L⁻¹), the initial rate started to become constant and independent of target solutes' concentration.

3.2.3. Photodegradation kinetics

According to several laboratory studies that have conducted, the use of Langmuir-Hinshelwood kinetics model and first-order rate equations provided reasonable simulations to the observed photocatalysis process of various organic pollutants over illuminated TiO_2 [5, 6, 13, 17]. Langmuir-Hinshelwood model is described by the following relationship:



Figure 4. Effect of initial concentration of selected OPPs on photocatalytic degradation rate (pesticide's concentration, 5–60 mg L⁻¹; catalyst's concentration, 100 mg L⁻¹; pH_{cr} , 6.06, λ_{11V} 365 nm, in the presence of methanol).

$$r = -\frac{\mathrm{d}\,C}{\mathrm{d}t} = \frac{k_r K C}{1 + K C} \tag{3}$$

where *r* is the rate of reaction (in mg L⁻¹ h⁻¹), *C* is the concentration at any time t during degradation (in mg L⁻¹), *t* is the irradiation time (in h), k_r is the limiting rate constant of reaction at maximum coverage under the employed experimental conditions (in mg L⁻¹ h⁻¹), and finally, *K* is the equilibrium constant for adsorption of the substrate onto catalyst TiO₂ particles (in mg⁻¹ L) [6]. The linear transformation of Eq. 3 is Eq. (4), which is used in the bibliography for demonstrating the linearity of data when plotted as the inverse rate versus inverse concentration (as in the inset of **Figure 4**, previously presented):

$$\left(\frac{1}{r}\right) = \left(\frac{1}{k_r}\right) + \left(\frac{1}{k_r K}\right) \left(\frac{1}{C}\right) \tag{4}$$

Integration of Eq. (3) yields Eq. (5):

$$\ln\left(\frac{C_o}{C}\right) + K\left(C_o - C\right) = k_r K t \tag{5}$$

When the initial concentration of the pesticide *Co* is very small (in millimolar solution as in the case), Eq. (5) is transformed into Eqs. (6) and (7):

$$ln\left(\frac{C_o}{C}\right) = k_r K t = K_{obs} t$$
(6)

$$C_t = C_o e^{-K_{obs} t} \tag{7}$$

where C_t represents the concentration at time t, C_o represents the initial concentration, and K_{obs} is the rate constant. In all cases, reduction process followed an apparent first-order rate reaction, and the calculations were performed using Eq. (7). The kinetic parameters calculated by Eqs. (4) and (7) are shown in **Table 2**. In this point, it must be mentioned that these constants reflect to the experimental conditions which have been used and are only useful for comparison between reactants that have been oxidized using the same catalyst and illumination source.

3.3. Photocatalytic degradation of OPPs in UV-TiO₂-H₂O₂ system

The addition of an oxidant into a semiconductor suspension has been proven to enhance the photodegradation of a variety of organic pollutants among which pesticides are included [8, 17, 27, 28]. In current study, the addition of hydrogen peroxide (H_2O_2) was evaluated only for the cases of dimethoate and fenthion as these compounds proved to be more resistant in the previous set of photocatalytic experiments. The initial concentration (5 mM) of H_2O_2 was chosen according to the results obtained in previously conducted experiments

employing different initial concentrations of the oxidant (not shown). This level of concentration of H_2O_2 is in accordance with relative published studies [17].

Blank experiments with the oxidant without the catalyst or UV light (not shown) proved a negligible reduction of OPPs studied. Experiments with UV light and the oxidant, without the catalyst, were performed too, are presented by the dotted lines of **Figure 5**, and showed that H_2O_2 is able to cause photooxidation of the pesticides tested. **Figure 5** illustrates the photocatalytic decomposition of fenthion and dimethoate in the UV-TiO₂-H₂O₂ system.

A significant enhancement on degradation efficiency was observed when 5 mM of H_2O_2 was added into the system. The kinetic parameters shown in **Table 3** demonstrated 18.20- and

| Pesticides | R^2 | k _r | | K | K | | t _{1/2} |
|-----------------|--------|---------------------------------------|--|----------------------|--------------------------------------|--------------------|------------------|
| | | (mg L ⁻¹ h ⁻¹) | (×10 ⁻⁶ M h ⁻¹) | (mg ⁻¹ L) | (×10 ⁻⁶ M ⁻¹) | (h ⁻¹) | (h) |
| Azinphos methyl | 0.9076 | 0.4569 | 1.4398 | 0.0894 | 0.2816 | 0.2293 | 3.02 |
| Azinphos ethyl | 0.8663 | 0.4574 | 1.3242 | 0.1320 | 0.3822 | 0.2378 | 2.91 |
| Dimethoate | 0.9612 | 0.0321 | 0.1402 | 0.0823 | 0.3592 | 0.0184 | 37.67 |
| Disulfoton | 0.9254 | 0.4553 | 1.6594 | 0.0789 | 0.2875 | 0.2587 | 2.68 |
| Fenthion | 0.9704 | 0.1289 | 0.4632 | 0.1203 | 0.4323 | 0.0535 | 12.96 |

Table 2. Photocatalytic kinetic parameters of selected pesticides in UV-TiO₂ (100 mg L⁻¹) system, in the presence of methanol, using a radiant UV energy of 14.5 mW cm⁻².



Figure 5. Effect of the addition of hydrogen peroxide on the photocatalytic degradation of dimethoate and fenthion (pesticide's concentration, 10 mg L⁻¹; catalyst's concentration, 100 mg L⁻¹; oxidant's concentration, 5 mM; pH_o, 6.06; λ_{UV} 365 nm, in the presence of methanol).

| Pesticide | R^2 | k_{obs} (h ⁻¹) | <i>t</i> _{1/2} (h) |
|------------|--------|------------------------------|-----------------------------|
| Dimethoate | 0.9907 | 0.0744 | 9.32 |
| Fenthion | 0.9838 | 0.9739 | 0.71 |

Table 3. Photocatalytic kinetic parameters of selected pesticides in UV-TiO₂ (100 mg L^{-1})-H₂O₂ (5 mM) system, in the presence of methanol, using a radiant UV energy of 14.5 mW cm⁻².

4.04-fold increase in rate constants, $k_{obs'}$ compared to the results obtained in UV-TiO₂ systems for fenthion and dimethoate, respectively.

The magnitude of enhancement is in agreement with other studies concerning phosphoruscontaining pesticides [27, 28]. This observation is explained by the fact that H_2O_2 can act as an alternative electron acceptor to oxygen (Eq. (8)) that is a thermodynamically more favorable reaction than oxygen reduction [29]. This should consequently promote the charge separation and accelerate the heterogeneous photocatalysis [30]. At the same time, hydroxyl radicals able to oxidize organic pollutants, such as pesticides, are generated by either the reduction of H_2O_2 at the conductance band [29] or the acceptance of an electron from superoxide again (chain reactions) (Eq. (9)) [31]. As a consequence, and regardless which conductance band reaction overrules, additional **•**OH oxidizing species may be produced resulting in the increase of the oxidizing power of the system [30]:

$$e_{CB}^{-} + H_2O_2 \rightarrow OH^- + OH^{\bullet}$$
(8)

$$O_2^{-} + H_2O_2 \rightarrow OH^- + OH^{\bullet} + O_2$$
(9)

Experimental data obtained proved that the addition of H_2O_2 in the aqueous suspensions of 100 mg L⁻¹ TiO₂/10 mg L⁻¹ OPPs was more effective on the photocatalytic oxidation of fenthion (100% decomposition in 5 h) rather than in the case of dimethoate (95% decomposition in 36 h). The $t_{_{1/2}}$ in the presence of both TiO₂ and H_2O_2 was 0.71 h (42.6 min) for fenthion and 9.32 h for dimethoate.

3.4. Mineralization studies

The general stoichiometric reaction proposed for the photocatalytic oxidation of the studied pesticides that leads to the conversion of all of their carbon atoms to gaseous CO_2 and the heteroatoms into inorganic anions at their highest oxidation states which remain in the solution is described by the following reaction (Eq. (10)). Consequently, in order to assess the extent of mineralization during photocatalysis of selected organic pollutants, TOC measurements were carried out along with determination of released inorganic anions containing the heteroatoms of the selected organics (**Figure 6**):

$$C_{x}H_{\psi}N_{\theta}O_{\omega}P_{z}S_{\phi} + [(2x+3\theta+4z+4\phi+1-\omega)/2]O_{2} \rightarrow xCO_{2} + \theta NO_{3}^{-} + zPO_{4}^{3-} + \phi SO_{4}^{2-} + H_{2}O + (\psi - 2)H^{+}$$
(10)

3.4.1. TOC content

As shown in **Figure 6**, in the presence of TiO_2 and under UV irradiation, the TOC concentration of the insecticides exhibited a constant decrease with time, reaching TOC reduction that ranged between 58 and 100% (total mineralization) after the end of illumination time. In addition, it can be seen that the rates of TOC reduction during irradiation of solutions of azinphos methyl, azinphos ethyl, and disulfoton were higher compared to those of dimethoate and fenthion, suggesting that former ones exhibit greater susceptibility to photocatalysis than the



Figure 6. Pesticide and TOC reduction and evolution of sulfate (SO_4^{2-}), phosphate (PO_4^{3-}), nitrite (NO_2^{-}), nitrate (NO_3^{-}), and ammonium (NH_4^{+}) ions originating from photocatalytic degradation of selected pesticides as a function of irradiation time (pesticide's concentration level, 10 mg L⁻¹; TiO₂, 100 mg L⁻¹; H₂O₂, 5 mM; λ_{UV} 365 nm, in the presence of methanol).

latter. Furthermore, these results are confirming the kinetic data acquired in the current study from the application of Langmuir-Hinshelwood model. The addition of H_2O_2 in the irradiated photocatalytic media of dimethoate and fenthion not only enhanced the removal of TOC in both cases but also resulted in almost total decomposition of target pesticide pollutants.

In general, the trend in TOC reduction was similar to that observed in pesticide disappearance. However, when the obtained k_{abs} values of these two studied processes were compared, the reduction in TOC content of irradiated solutions was found to be a slower phenomenon than the photodecomposition of the parent pesticides. This observation can be explained by the fact that the photocatalytic decomposition of the parent compounds occurred through the formation of various organic intermediates and not instantaneously. Moreover, taking into consideration the complex nature of photocatalysis and the wide variety of stable and unstable photoproducts that can be formed, rate of TOC reduction depended on the individual tested organophosphate. The same behavior has been observed in numerous irradiated pesticide solutions reported in the available literature; for instance, the formation and evolution of several carboxylic acids (such as formic, acetic, glycolic, and cyanuric acids) as transient intermediates of photocatalytic reaction, which could eventually undergo complete mineralization as irradiation progresses, have been published [4, 5, 9, 21]. Formation of oxon derivatives (such as paraoxon ethyl, pirimiphos-oxon, fenthion-oxon), corresponding phenols (e.g., nitrophenol), various and different trialkyl and dialkyl phosphorothioate or phosphate esters, and quinonidal compounds has also been observed and detected as major intermediate photoproducts that subsequently underwent mineralization [5]. On the contrary, in the absence of UV light (dark condition, not presented in TOC reduction data), no significant percent reduction in TOC of studied compounds occurred, suggesting negligible adsorbance of the pesticides on TiO₂ surface.

3.4.2. Mineral inorganic ions

Evolution of the heteroatoms at their highest oxidation states such as SO_2^{4-} , NO_3^{-} , and PO_4^{3-} provides evidence that pesticide degradation occurred primarily through photocatalytic oxidation reactions [21]. Therefore, in order to further confirm the extent of photocatalytic reduction and better understand the reaction mechanisms involved, the formation of inorganic anions containing the heteroatoms of the selected organophosphorus compounds was surveyed. More specifically in the present study, the formation of sulfate (SO_4^{2-}), phosphate (PO_4^{3-}), nitrite (NO_2^{-}), nitrate (NO_3^{-}), and ammonium (NH_4^{+}) ions, originating from photocatalytic degradation of selected toxicants under UV irradiation, was investigated.

As illustrated in **Figure 6**, photocatalytic treatment of target pesticides resulted in the destruction of the parent molecules as evidenced by the evolution of monitored inorganic anions. Decomposition of all five tested organophosphates released SO_2^{-4} and PO_4^{3-} , while that of the three nitrogen-containing molecules, azinphos methyl, azinphos ethyl, and dimethoate (chemical formulas in **Table 1**), liberated NO_2^{-} , NO_3^{-} , and NH_4^{+} ions as well. These findings are consistent with published works involving mineralization studies of other organophosphorus pesticides during heterogeneous photolysis over TiO_2 suspensions. It is well documented that the pesticides containing sulfur atoms are mineralized into sulfate ions [5, 17, 20, 21]. Overall, the monitoring of SO_2^{-4} ions showed that a rapid increase in their concentration was observed achieving finally (in the final stages of irradiation treatment) their expected amounts according to the stoichiometry proposed in the reaction (10). Formation of sulfate ions took place by the rupture of the sulfur group from the P=S and P-S bonds, which occurred firstly in the case of phosphorothioates, leading to the formation of oxon intermediate derivatives as reported in previous studies [5, 13].

Acquired results are in accordance with several experimental results, which have shown that photodecomposition of several organophosphorus substances in the presence of TiO₂ suspensions produces phosphate ions [5, 17, 20]. Release of phosphate ions occurred by the cleavage of the phosphorus atom from the P=S, P–S, and P–O bonds caused by the continuous oxidation attack of the *OH radicals. However, according to other reported studies, non-detection of PO₄³⁻ ions in the irradiated solutions of phosphorus-containing pesticides, such as acephate and dimethoate, is possible due to incomplete mineralization of the pesticides as well as competitive adsorption of PO₄³⁻ on the photoactivated reaction sites of the catalyst TiO_{2'} a strong phenomenon in the pH range used, that partially inhibits the reaction rate of deterioration (20–70% reduction at levels of greater than 10⁻³ mol dm⁻³) [5, 21].

The formation of nitrite, nitrate, and ammonium ions was also monitored for the three selected nitrogen-containing molecules, since these compounds could give rise to these ions [5, 32], based on relative literature, even N, gas can be generated mainly from the photodegradation of the -N = N- double bond moieties contained in aliphatic or heterocyclic nitrogen-containing compounds, such as azinphos methyl and azinphos ethyl. Obviously, the release of NO_2^- that was observed in the first stage of irradiation can be ascribed to the fact that these ions are formed as an intermediate of NO_3^- , which was demonstrated by the disappearance of NO_2^- and concomitant formation of NO₃⁻ after longer irradiation periods. Generally, it has been found that nitrate anions, probably formed through oxidation pathways, have little effect on the kinetics of reaction [5], whereas ammonium ions are relatively stable cations released from reduction processes [5]. The molar ratio of NO_3^- and NH_4^+ concentration (NO_3^-/NH_4^+) depends mainly on the nature of the N-containing organic compounds and the initial oxidation state of nitrogen and some experimental conditions, including the irradiation time, the pH of the solution, and the substance concentration [5, 32]. Under the employed experimental conditions, higher nitrate-to-ammonium concentration ratio was produced for the cases of azinphos methyl and azinphos ethyl that contained ring nitrogen converted mainly into $NO_3^-([NO_3^-] > [NH_4^+])$ than for dimethoate in which the contained amino group was predominantly mineralized into NH_4^+ species ($[NO_3^-] < [NH_4^+]$).

Mineralization studies of dimethoate and fenthion during photocatalysis were also conducted in the presence of oxidant (H_2O_2) (**Figure 6**). Based on the kinetics of formation and disappearance of mineral ions, it is obvious that the addition of the oxidant enhanced the transformation of both parent compounds and was able to achieve higher mineralization. This is in agreement with previous studies supporting that the final products of organophosphorus pesticides photooxidation are eventually carbon dioxide and inorganic ions containing the heteroatoms [18].

4. Conclusions

Based on the results of the current study concerning the photocatalytic decomposition of five selected organophosphorus insecticides contained individually in aqueous solutions and by using the heterogeneous systems of UV-TiO₂ and UV-TiO₂-H₂O₂, it appeared that TiO₂ is a semiconductor with high catalytic activity; photodegradation of all studied compounds proceeded at higher reaction rates in its presence than in its absence (direct photolysis). Total decomposition

in UV-TiO₂ system was accomplished for the three cases of azinphos ethyl, azinphos methyl, and disulfoton after illumination time that depended on the tested organophosphate, whereas longer irradiation time for the cases of dimethoate and fenthion is probably needed. With the addition of H_2O_2 into illuminated TiO₂ suspensions, a synergistic effect was observed, which led to an enhancement of the photolytic process, achieving total disappearance of dimethoate and fenthion. Finally, the experimental data revealed that both catalytic systems investigated have good potential for small-scale applications, such as the wastewater purification systems of research laboratories or agrochemical manufacturer, formulators, and producer companies. The advantages of the proposed photocatalytic systems among others include simplicity in design because they give the opportunity to employ UV lamps easily found in the market and semiconductor powder (TiO₂) of low cost as catalyst.

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References

- [1] Ternes T. The occurrence of micropollutants in the aquatic environment: A new challenge for water management. Water Science and Technology. 2007;55:327-332
- [2] Schwarzenbach RP, Egli T, Hofstetter TB, von Gunten U, Wehrli B. Global water pollution and human health. Annual Review of Environment and Resources. 2010;**35**:109-136
- [3] Bahnemann DW, Cunningham J, Fox MA, Pelizzetti E, Pichat P, Serpone N. Photocatalytic Treatment of Waters. In: Heltz GR, Zepp RG, Crosby DG, editors. Aquatic and Surface Photochemistry, Boca Raton, FL: CRC Press; 1993. 567 pp. ISBN: 9780873718714
- [4] Malato S, Blanco J, Caceres J, Fernres718714L AR, Aguera A, Rodriguez A. Photocatalytic treatment of water soluble pesticides by photo-Fenton and TiO₂ using solar energy. Catalysis Today. 2002;**76**:209-220
- [5] Konstantinou IK, Albanis TA. Photocatalytic transformation of pesticides in aqueous titanium dioxide suspensions using artificial and solar light: Intermediates and degradation pathways-review. Applied Catalysis B: Environmental. 2003;42:319-335

- [6] Petsas AS, Vagi MC, Kostopoulou MN, Lekkas TD. Photocatalytic degradation of the organophosphorus pesticide fenthion in aqueous suspensions of TiO₂ under UV irradiation. Proceedings of the 13rd International Conference of Environmental Science and Technology. 2013. Available from http://www.gnest.org/proceedings/cest2013/public_ html/papers/0514.pdf? [Accessed 2017-30-10]
- [7] Zwiener C, Frimmel FH. Water quality. In: Kleiböhmer W, editor. Environmental Analysis, Vol 3. Handbook of Analytical Separations, 1st ed. Amsterdam, The Netherlands: Elsevier Science; 2001. pp. 277-318. ISBN: 9780444500212
- [8] Ollis DF, Pelizzetti E, Serpone N. Destruction of water contaminants. Environmental Science & Technology. 1991;25(9):1522-1529
- [9] Tamimi M, Qourzal S, Assabbane A, Chovelon JM, Ferronato C, Ait-Ichou Y. Photocatalytic degradation of pesticide methomyl: Determination of the reaction pathway and identification of intermediate products. Photochemical & Photobiological Sciences. 2006;5:477-482
- [10] Bahnemann D, Bockelmann D, Goshlich R. Mechanistic studies of water detoxification in illuminated TiO₂ suspensions. Sol. Energy Maternité. 1991;24:564-583
- [11] Vagi MC, Petsas AS. Advanced oxidation processes for the removal of pesticides from wastewater: recent review and trends. 2017. Proceedings of the 15th International Conference of Environmental Science and Technology. Available from https://cest. gnest.org/sites/default/files/presentation_file_list/cest2017_01225_oral_paper.pdf [Accessed 2017-30-10]
- [12] Tomlin CDS. The Pesticide Manual: A World Compendium. 11th ed. Farnham, Surrey, UK: British Crop Protection Council; 1997. 1606 pp. ISBN:1901396118
- [13] Konstantinou IK, Sakellarides TM, Sakkas VA, Albanis TA. Photocatalytic degradation of selected s-triazine herbicides and organophosphorus insecticides over aqueous TiO₂ suspensions. Environmental Science & Technology. 2001;35:398-405
- [14] Vagi MC, Petsas AS, Kostopoulou MN, Lekkas TD. Adsorption and desorption processes of the organophosphorus pesticides, dimethoate and fenthion, onto three Greek agricultural soils. International Journal of Environmental Analytical Chemistry. 2010; 90(3-6):369-389
- [15] Huber L. Validation of analytical methods: Review and strategy. LC-GC International. 1998;11(2):96-105
- [16] APHA, AWWA, WEF. Standard Methods for Examination of Water and Wastewater. 22nd ed. Washington: American Public Health Association; 2012, 1360 pp. ISBN 978-087553-013-0. Available from: http://www.standardmethods.org/ [Accessed 2017-20-9]
- [17] Evgenidou E, Fytianos K, Poulios I. Photocatalytic oxidation of dimethoate in aqueous solutions. Journal of Photochemistry and Photobiology A: Chemistry. 2005;**175**:29-38

- [18] Oreopoulou A, Philippopoulos C. Photocatalytic oxidation of agrochemical industry liquid wastewaters. Proceedings of the 8th International Conference on Environmental Science and Technology. 2003. pp. 674-681. ISBN: 9607475240
- [19] Gore RC, Hannah RW, Pattacini SC, Porro TJ. Infrared and ultraviolet spectra of seventy-six pesticides. Journal of the Association of Official Analytical Chemists. 1971; 54(4):1040-1082
- [20] Kormali P, Dimoticali D, Tsipi D, Hiskia A, Papaconstantinou E. Photolytic and photocatalytic decomposition of fenitrothion by PW₁₂O₄₀³⁻ and TiO₂: A comparative study. Applied Catalysis B: Environmental. 2004;48:175-183
- [21] Echavia GRM, Matzusawa F, Negishi N. Photocatalytic degradation of organophosphate and phosphonoglycine pesticides using TiO₂ immobilized on silica gel. Chemosphere. 2009;76:595-600
- [22] Mills A, Le Hunte S. An overview of semiconductor photocatalysis. Journal of Photochemistry and Photobiology A: Chemistry. 1997;108:1-35
- [23] Herrmann JM. Heterogeneous photocatalysis: Fundamentals and applications to the removal of various types of aqueous pollutants. Catalysis Today. 1999;53:115-129
- [24] Shankar MV, Cheralethan KK, Arabindoo B, Palanichamy M, Murugesan V. Enhanced photocatalytic activity for the destruction of monocrotophos pesticide by TiO₂/Hβ. Journal of Molecular Catalysis A: Chemical. 2004;**223**:195-200
- [25] Chen LC, Chou TC. Photobleaching of methyl orange in titanium dioxide suspended in aqueous solution. Journal of Molecular Catalysis. 1993;85:201-214
- [26] Sakthivel S, Neppolian B, Shankar MV, Arabindoo B, Palanichamy M, Murugesan V. Solar photocatalytic degradation of azo dye: Comparison of photocatalytic efficiency of ZnO and TiO₂. Solar Energy Materials & Solar Cells. 2003;77:65-82
- [27] Harada K, Hisanaga T, Tanaka K. Photocatalytic degradation of organophosphorous insecticides in aqueous semiconductors suspensions. Water Research. 1990;**24**(11):1415-1417
- [28] Chen T, Doong R, Lei W. Photocatalytic degradation of parathion in aqueous TiO₂ dispersion: The effect of H₂O₂ and light intensity. Water Science and Technology. 1998;37:187-194
- [29] Wang Y, Hong CS. Effect of hydrogen peroxide, periodate and persulfate on photocatalysis of 2-chlorobiphenyl in aqueous TiO₂ suspensions. Water Research. 1999;33:2031-2036
- [30] Cornish BJPA, Lawton LA, Robertson PKJ. Hydrogen peroxide enhanced photocatalytic oxidation of microcystin-LR using titanium dioxide. Applied Catalysis B: Environmental. 2000;25(1):59-67
- [31] Crittenden JC, Hu S, Hand DW, Green SAA. Kinetic model for H₂O₂/UV process in a completely mixed batch reactor. Water Research. 1999;33:2315-2328
- [32] Jing J, Liu M, Colvin VL, Li W, Yu WW. Photocatalytic degradation of nitrogen-containing organic compounds over TiO₂ review. Journal of Molecular Catalysis A. 2011;**351**:17-28

Photocatalytic TiO₂: From Airless Jet Spray Technology to Digital Inkjet Printing

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Abstract

 TiO_2 powders can be employed as both photocatalytic and structural materials, leading to applications in external coatings or in interior furnishing devices, including cement mortar, tiles, floorings, and glass supports. The technology of photocatalytic building materials is connected with the widespread production of photocatalytic active tiles. All the techniques proposed in the study involve the employment of nanosized TiO₂: this represents a new problem to be dealt with, as inhaling nanoparticles exposes workers during industrial production and people in everyday locations to their dangerousness. Only very recently the employment of microsized TiO_2 has been proposed, and the authors in this manuscript report the use of micrometric titania materials, but employing a new deposition technique, which is digital inkjet printing. It represents an improvement of the classical spray coating methods, as it requires piezoelectric heads to precisely direct the deposition of the suspension with an electrostatic field. The mixture contains aqueous/ organic components containing micrometric TiO₂: to form a suspension, which is printed onto the surface of porcelain grès, large slabs using a digital printer. Many advantages are immediately evident, namely rapid and precise deposition, (almost) no waste of raw materials, thereby highlighting the economy, environmental friendliness, and sustainability of the process. All the materials we obtained have been thoroughly characterized by means of several experimental physico-chemical techniques, such as Raman microspectroscopy and scanning electron microscopy coupled with elemental analysis. Two different model VOCs, ethanol and toluene, and NOx have been selected to test the



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photocatalytic performances of the abovementioned tiles. Moreover, the antibacterial properties of the tiles have been determined, using *Escherichia* coli as example. Life cycle assessments (LCAs) for the two processes were modeled for 1 m² of tiles produced in Modena, Italy. The impact assessments revealed that jet spraying exhibited uniformly greater impacts than digital inkjet printing and that the principal impacts were in human toxicity, cancer effects, freshwater ecotoxicity, and climate change. Most of the impacts were associated with the energy required for the production processes. Further considerations revealed that jet spraying is projected to generate twice as much CO_2 and 30% more NOx than digital inkjet printing.

Keywords: TiO_2 , titania, digital inkjet printing, jet spraying, VOCs, NO_x , E. coli, life cycle assessment, impact assessments

1. Introduction

1.1. Pollution

The WHO (World Health Organization) estimates that 12.6 million deaths each year are attributable to unhealthy environments [1], confirming the urgent need for investment in strategies to reduce environmental risks in cities, homes, and workplaces. Of these deaths, 4.3 million (34%) and 3.7 million (29%) have been linked to exposure to indoor and outdoor pollution, respectively [2]. More broadly, it is considered that 92% of the population lives in areas that are exposed to respirable particulate matter of <2.5 µm in diameter (PM_{2.5}) at an annual mean concentration of >10 µg/m³ (or a 24 h mean of >25 µg/m³), which exceeds the WHO Air Quality Guidelines (AQG). The worst affected areas are China, the Indian subcontinent, the Middle East, and northern Africa.

Particulate and gaseous air pollution results largely from industrial and motor vehicular sources, although these emissions are exacerbated by those generated by heating [3]. The combustion of solid biomass and impure liquid fuels is the main source of pollution leading to health problems, as evidenced by numerous recent studies. For example, in Ethiopia, the average concentration of respirable particulate matter of diameter of $\langle PM_{2.5} \rangle$ reaches as high as a 24-h mean concentration of 280 μ g/m³, indoor CO levels are greater than the regulatory limits for the US, and the average NO2 level is 97 ppb [4]. In Southeast Asia, the large-scale burning of biomass causes heavy emissions of combustion by-products, which photochemically transform to other more dangerous molecules [5], such as polycyclic aromatic hydrocarbons (PAHs) [6]. Europe is affected mainly by emissions of nitrogen oxides (NO_x) [7]. Although outdoor pollution tends to be a focal point, indoor air in the US can be two to five times more harmful than outdoor air [8]. Almost 96% of houses in North America are reported to have at least one indoor air quality problem [9]. Cigarette smoke contains more than 7000 chemicals, of which 69 are known to be carcinogenic and many more to be poisonous [10]. Household items, such as cleaning products, air fresheners, and sanitation products, also contribute to indoor pollution by releasing chemicals. Consequently, there are environmental health imperatives to develop technologies that address these while satisfying other demands in the areas of energy efficiency, economic efficiency, utility, and esthetics.

1.2. Photocatalytic TiO₂ and its applications

Semiconductor photocatalysis involves the activation of a photocatalytic material, such as titania (TiO₂), by the action of light to produce charge carriers that undergo redox reactions with water and oxygen molecules [11]. This property allows these materials to decompose organic contaminants ideally into CO_2 and water, thus allowing applications in self-cleaning, anti-fogging, corrosion prevention, and air and water purification [12]. Although there are many scientific and technical requirements for effective photocatalytic performance [13], there are also numerous practical challenges that must be met. One of these is catalyst immobilization [14] because it generally must balance the requirements of achievement of a robust chemical bond to a substrate, the retention of sufficient exposed surface area, and the minimization of contamination from the substrate.

There has been an increase in the sales of TiO_2 -based products for self-cleaning and air and water purification owing to growing environmental concerns [15]. One of the key product developments was photocatalytic building materials, which appeared on the market at the beginning of the 1990s [16]. TiO_2 can be applied either in exterior construction or in interior furnishing materials, including concrete, mortar, tiles, flooring, and glass. In the early 2000s, the sales of photocatalytic building materials accounted for ~60% of the total market for photocatalytic materials [17]. Recent market projections to 2020 foreshadow increasing demand in the construction sector for self-cleaning coatings and other technologies for improving air quality, leading to a global market for photocatalyst-based products of ~\$2.9 billion [18]. At present, TiO_2 -based photocatalyst products constitute 97.6% of the market, and this dominance is a result of TiO_2 's low cost, ready availability, and well-documented performance data.

Many studies have demonstrated the effectiveness of photocatalytic materials for pollution abatement of the volatile organic compounds (VOCs) and nitrogen oxides (NO_x) that represent widespread risks to health. For example, concrete paving blocks with TiO₂ added directly to the mix were able to remove 4.01 mg/h/m² of NO [19]. However, similar work demonstrated that the efficiency of NO_x photodegradation varied significantly according to preparation method and resultant microstructure, with some products achieving 40% photodegradation while others showed almost no effect [20]. A comparison between pure TiO₂ and TiO₂ embedded in neat hydrated cement revealed that the photocatalytic activity was three to 10 times lower for the latter, which was attributed to the agglomeration of the TiO₂ powder [21]. TiO₂ also has been applied as surface coatings on roofing tiles and corrugated sheet and found to achieve gaseous toluene removal efficiencies as high as 78 ± 2%, although this was limited by gas concentration and residence time [22].

It is clear that the permanence and performance of TiO_2 -containing construction products depend significantly on the method used to immobilize the photocatalyst, whether in the bulk or on the surface. Other factors of importance include the type of substrate and the method of TiO_2 application [23]. Hence, there has been a commensurate focus on the design of such building products and their manufacture in order to obtain maximal lifetimes and efficiencies. An additional consideration is the potential alteration of the photocatalyst by fouling, which can block the active sites and reduce or prevent photocatalysis [24]. Finally, there are also potential health issues associated with the formation of chemical intermediates [25] and the respirability of nanoparticulates [26].

1.3. TiO₂ coatings

One of the most promising areas in photocatalytic building materials is photocatalytically active tiles, which are self-cleaning but also can decompose air pollutants. The standard approach has been to apply TiO₂-based materials on ceramic surfaces and to attempt to immobilize the TiO₂ at as low a temperature as possible. In the case of spray coating of aqueous dispersions of TiO₂ on clay roofing tiles, the heating temperature was 290°C [27]. Chemical vapor deposition (CVD) using gaseous precursors, following by heating at 550°C, also has been investigated [28] but these films suffered from poor adhesion. By contrast, plasma-enhanced chemical vapor deposition (PECVD), involving reheating at 400°C, yielded high-quality materials [29]. Aerosol flame synthesis (temperature probably <700°C) has been used to produce ultra-fine TiO₂ nanoparticles that could be deposited directly on supports [30]. Sol-gel TiO₂ precursors have been coated on cement-based materials by dipping and heating at 500°C [31]. TiO₂ suspensions in water or alcohol also have been sprayed on limestone with no subsequent heating since the porous microstructure immobilized the powder [32]. All of these approaches used nanosized TiO₂.

Although spray coating remains the simplest and least expensive coating technique, recent work [33] reports the functionalization of commercial glazed ceramic tiles with pigment-grade, microsized, anatase (Kronos 1001) using an industrial-type process. This method offers a reduction in the risk of inhalation as it does not involve the use of nanosized TiO_2 powders. The TiO_2 powder was deposited by airless jet spraying aqueous suspensions containing a silica-based commercial product as binder. The tiles were dried and then fired at 680°C in an industrial kiln for 80 min (cold-to-cold cycle).

This work reports a new deposition technique, which is digital inkjet printing. Despite the advantages of conventional spray coating methods, digital inkjet printing offers an advantageous, precise, coating technique that utilizes piezoelectric heads to effect directional deposition of an aqueous/organic ink suspension within an electrostatic field [34]. The suspension contained pigment grade, microsized anatase (Kronos 1077), and this was printed on the surface of porcelain grès (*viz.*, stoneware) tiles using a digital printer. This process has several advantages, including rapid and precise and more uniform deposition and essentially no waste of raw materials, which are favorable for both the economics of the process and the environment. Moreover, with this technique, slabs of large size up to 120×360 cm can also be activated. The data for the thin films deposited by digital inkjet printing are contrasted with those for the more conventional method of jet spraying.

2. Materials and methods

2.1. Microsize TiO₂ and porcelain grès tiles

The TiO₂ powder was Kronos 1077, which is \geq 98.5% anatase and has a particle size range of 110–130 nm, a BET surface area of 12 m²/g, a true density of 3800 kg/m³, and an optical indirect band gap of 3.15 eV [35, 36].

The TiO_2 was deposited on porcelain grès tiles that were manufactured by GranitiFiandre S.p. A. These are dry-pressed tiles fired at 1200–1300°C. The phase assemblage as such consists of glass, mullite, and quartz.

2.2. Digital inkjet printing and airless jet spraying procedures

Conventional, industrial-scale, airless, jet spray deposition was used for the deposition of coatings, as described in brief previously by the authors [37]. However, with the new, innovative, automated decoration of ceramic surfaces by digital instruments, it has become possible to manufacture products of considerably superior quality. Consequently, this work also reports an investigation of the deposition of coatings of photocatalytic TiO_2 by digital inkjet printing using a proprietary ink containing suspended microsized TiO_2 particles.

A prototype digital printer manufactured by Projecta S.p.A. was used to apply the suspensions. Following deposition, the tiles were calcined at 680°C for 80 min using an industrial-scale kiln designed to avoid thermal shock. The cooled tiles then were washed with water, brushed vigorously to remove loose particles, and air jet dried. The process is summarized in **Figure 1**. The water used for degreasing was recovered and purified prior to recycling; any damaged tiles were recycled.



Figure 1. Summary of digital inkjet printing process.

2.3. Characterization

Mineralogical analyses were done by laser Raman microspectroscopy (Raman; inVia Raman Microscope, green laser, 514 nm, 20×, 1.5-µm beam diameter, Renishaw, Wotton-under-Edge, Gloucestershire, UK). Microstructural analyses were done by field emission gun scanning electron microscopy (Field emission gun scanning electron microscopy (FEG-SEM); LEO 1525, 15, or 20 kV accelerating voltage, LEO Electron Microscopy Inc., Thornwood, NY, USA). Elemental analyses were done by paired energy dispersive spectroscopy (EDS; Bruker Quantax, Bruker Italia S.r.l., Milan, Italy).

2.4. Photocatalysis testing

2.4.1. Volatile organic compounds

VOC photodegradation reactions were conducted in a Pyrex glass cylindrical reactor with a diameter of 200 mm and an effective volume of 5 L [38]. A 100-cm² digital inkjet-printed sample or jet-sprayed sample was placed at the bottom of the reactor and exposed to a 500-W iron halogen lamp (HG 500, 315–400 nm, UV-A, Jelosil, Milan, Italy). The reactor had two entrances, one for VOC loading and the other for sampling by a gas chromatograph (490 Micro GC System, Agilent Technologies Italia S.p.A, Milan, Italy).

Ethanol and toluene were selected as model pollutants, and the initial concentration for both was 400 ppm for each test. The photodegradation tests were conducted for 6 h.

2.4.2. Nitrogen oxides

Two different setups were used - one under static conditions [39] and the other under flowing conditions [40]. A chemiluminescence NO_x monitor (Teledyne API, Model 200E, San Diego, CA, USA) provided online detection of NO and NO_2 concentrations. The batch reactor consisted of a Pyrex glass cylinder of volume of 25 L; this is described elsewhere [39]. The tile $(2 \times 20 \text{ cm})$ was located at the bottom of the cylinder and an overhead 500-W iron halogenide lamp (HG 500, 315–400 nm, UV-A, Jelosil, Milan, Italy) provided irradiation of 20 W/m². The inlet gas consisted of NO_2 (0.6% in N_2) mixed with air of relative humidity (RH) 40%, which allowed equilibration between NO and NO₂ to be reached quickly. The NO₂ concentration was set at 1000 ppb (static) or 250 ppb (flowing) and tests lasted 6 h each. The continuous flow reactor allowed testing of larger tiles (60×60 cm) [40]. A Thermo-Hygro Meter (HT-3006A, Metravi, Calcutta, India) measured both temperature and relative humidity, which ranged between 40 and 50%. Two iron halogen lamps (Jelosil, model HG 500), at 770-mm center-tocenter distance, which was designed to irradiate the sample surface with the same 20 W/m^2 light intensity, were used. The total NO_x gas flow was in the range of 140–180 NL/h, which is in accordance with the standard concentration based on the limiting values specified in Directive 2008/50/EC of the European Parliament and of the Council on Ambient Air Quality and Cleaner Air for Europe (range 100–200 ppb).

2.5. Antibacterial effects

The photocatalytic tiles were tested using Escherichia coli (E. coli, ATCC 8739) according to *ISO* 27447:2009 *Fine Ceramics—Test Method for Antibacterial Activity of Semiconducting Photocatalytic Materials*. Each strain was inoculated into a nutrient agar slant, incubated for 16–24 h at 37 \pm 1°C, and then transferred to a new nutrient agar slant and again held at 37 \pm 1°C for 16–24 h. An appropriate quantity of bacteria was dispersed in 1/500 nutrient broth (NB) to obtain a count of 6.7 \times 10⁵ to 2.6 \times 10⁶ cells/mL. Tile samples of dimensions 50 \times 50 mm were rinsed with distilled water and autoclaved at 121°C for 30 min prior to testing in order to remove any organic residue on the surfaces. For each strain, six tile samples without (controls) and six with photocatalytic coating were investigated. A volume of 0.15 mL of bacterium suspension was placed on each specimen and covered with an inert and non-water adsorbent film of dimensions 40 \times 40 mm; the film transmitted >85% of radiation in the range of 340–380 nm. Each specimen was placed in a 100-mm diameter Pyrex Petri dish containing a moistened paper filter to prevent drying of the suspension of >85% in the range of 340–380 nm.

A fluorescent UV lamp (18 W, Royal Philips, Amsterdam, Netherlands) was used for the testing at an intensity of 0.25 mW/cm² for 8 h. A viability count was performed by dilution and plating on nutrient agar incubated at 37°C for 48 h. More details are reported elsewhere [37].

3. Results and discussion

3.1. Characterization

3.1.1. Field emission gun scanning electron microscopy

The FEG-SEM images shown in **Figure 2** reveal a relatively widespread, homogeneous, and thick deposition of TiO_2 on the digital inkjet-printed tile surface in comparison to the jet-sprayed tile surface, which shows that voids are present. The EDS data confirmed a greater areal extent of coverage by TiO_2 for digital inkjet printing. However, it is significant that the digital inkjet-printed coating exhibits a considerably lower degree of agglomeration than does the jet-sprayed coating. The former can be expected to provide a greater surface area and associated density of photocatalytically active sites. The reason for this difference is the superior dispersion of the TiO_2 powder by the inclusion of a dispersant in the ink, which reduced the formation of soft agglomerates. Further, it is likely that the included organic phases played a key role in the development of this microstructure through separation of the particles and consequent surface exposure during pyrolysis. Consequently, digital inkjet printing can be expected to exhibit a superior photocatalytic performance owing to the greater volume of deposited TiO_2 , the extent of areal coverage of the tile, and exposed surface area.



Figure 2. FEG-SEM micrographs digital inkjet-printed coating at (A) low magnification and (B) high magnification and jet-sprayed coating at (C) low magnification and (D) high magnification.

3.1.2. Laser Raman microspectroscopy

In the optical micrographs taken by Raman, shown in **Figure 3**, the lighter rougher regions consist of TiO₂ and the darker regions are the exposed porcelain grès substrates. These images confirm that the TiO₂ deposited by digital inkjet printing is more widespread than that by jet spraying. **Figure 4** shows that the Raman spectra of the digital inkjet-printed and the jet-sprayed coatings are significantly different. The intensities of the peaks and the slopes of the baselines indicate the TiO₂ content of the coating and the glass content, respectively, for each sample. That is, lower peak intensities indicate a low amount of TiO₂ and/or a low degree of crystallinity and the sloped baseline indicates a high glass content in the vitreous tile. The greater peak intensities and flat baseline for the digital inkjet-printed coating confirm the greater extent of coverage of the tile by TiO₂, whereas the low peak intensities and sloped baseline for the jet-sprayed coating confirm the low areal distribution of TiO₂. Since laser Raman microspectroscopy does not analyze amorphous materials accurately, the peak at 510 cm⁻¹ is attributed to albite feldspar and the peak at 610 cm⁻¹ to α -quartz. The two other small but relatively sharp peaks at 439 and 356 cm⁻¹ could not be identified.



Figure 3. Optical micrographs of (A) digital inkjet-printed coating and (B) jet-sprayed coating.



Figure 4. Laser Raman microspectra of (A) digital inkjet-printed coating and (B) jet-sprayed coating.

3.2. Photocatalytic testing

3.2.1. VOC photodegradation

Figure 5 shows the UV photodegradation of ethanol and toluene. Both sets of data demonstrate the superior photocatalytic performance of the digital inkjet-printed coating. While similar testing of Kronos 1077 bulk powder has been shown to decompose ethanol completely in 1 h [37], this work for the deposition of this TiO_2 powder as a digital inkjet-printed coating shows that nearly complete decomposition (~97%) requires 6 h. By contrast, the jet-sprayed coating decomposes only ~47% of the ethanol after 6 h. Interestingly, both coatings outperform the powder when decomposing the more stable aromatic toluene ring. While Kronos 1077 bulk



Figure 5. Photodegradation over time by digital inkjet-printed and jet-sprayed coatings of (A) ethanol, (B) toluene, (C) static NO_{xv} and (D) flowing $NO_{x.}$

powder decomposed only ~43% of toluene after 6 h, the digital inkjet-printed coating decomposes ~84% and the jet-sprayed coating decomposes ~75%. It is probable that the difference in results for ethanol and toluene is that while both involved decomposition by photocatalysis, the latter also included a contribution from direct photolysis, which was enhanced by the greater surface area of the coating exposed to UV in comparison to that of a powder bed. This component may be significant because the difference between the two coating techniques is less than that for ethanol photodegradation.

These data confirm that the photocatalytic performance of the digital inkjet-printed coating is superior to that of the jet-sprayed coating for VOC decomposition. This is a result of the greater extent of coverage, more even areal distribution, a reduced agglomeration, a greater extent of exposed particle surface area, and a greater crystallinity of the TiO_2 in the digital inkjet-printed coating.

3.2.2. NO_x photodegradation

Figure 5 also shows the UV photodegradation of NO_x in both batch and continuous-flow reactors. Again, the digital inkjet-printed coating outperforms the jet-sprayed coating. After 6 h under static conditions, the digital inkjet-printed coating decomposes ~90% of the NO_x

while the jet-sprayed coating decomposes only ~56%. After 6 h under flowing conditions, the performances were closer, with the digital inkjet-printed and jet-sprayed coatings decomposing ~80 and ~74% of the NO_x, respectively. It is clear that the maximal levels of decomposition were attained relatively quickly and they were maintained such that no deactivation was observed.

The larger dimensions (60×60 cm) of the tiles and the lower NO_x concentration used during the testing under flowing conditions provide a better simulation of real environmental conditions [40]. It may be noted that this digital inkjet-printing technology is capable of coating dimensions as large as 150 by 300 cm.

3.3. Antibacterial testing

Table 1 summarizes the results of the antibacterial testing, which reveals that both types of coatings were highly effective in destroying *E. coli* (gram-negative), which is part of the bacterial flora of human and animal intestines and hence a suitable indicator of potential contamination of drinking water and food. These data show that UV irradiation alone is capable of destroying ~45–72% of the bacteria while both photocatalytic coatings destroy essentially all of the bacteria. After photocatalysis (R_L), the digital inkjet-printed and jet-sprayed coatings are essentially equivalent. However, with photocatalysis (ΔR), the digital inkjet-printed coating clearly outperforms the jet-sprayed coating. Hence, these data are in basic agreement with those for the photodegradation of ethanol and toluene. However, they must be interpreted in light of the different surface topographies, where **Figures 2** and **3** show that the jet-sprayed coating provides less homogeneous coverage and hence presents a more

| Antibacterial activity of photocatalytic coatings using E. coli ATCC 8739 | | | | | |
|---|---|----------|-----------------------------|------------------|--|
| Symbol | Parameter | Units | Uncoated tile 1 | Uncoated tile 2 | |
| Uncoated p | vorcelain grès tile controls | | | | |
| Ν | Number of live bacteria | Cells | 1,900,000 | 1,100,000 | |
| А | Number of live bacteria after inoculation | Cells/mL | 280,000 | 160,000 | |
| B _D | Number of live bacteria before UV irradiation | Cells/mL | 220,000 | 600,000 | |
| $B_{\rm L}$ | Number of live bacteria after UV irradiation | Cells/mL | 120,000 | 170,000 | |
| - | Reduction in bacterial count after UV irradiation | % | 45.45 | 71.67 | |
| TiO ₂ -coate | d porcelain grès tiles | | | | |
| Symbol | Parameter | Units | Digital inkjet-printed tile | Jet-sprayed tile | |
| C _D | Number of live bacteria before photocatalysis | Cells/mL | 180,000 | 130,000 | |
| C _L | Number of live bacteria after photocatalysis | Cells/mL | 10 | 10 | |
| - | Reduction in bacterial count after photocatalysis | % | 99.99 | 99.99 | |
| R _L | Antibacterial activity after photocatalysis | _ | 4.1 | 4.2 | |
| ΔR | Antibacterial activity with photocatalysis | _ | 4.1 | 3.6 | |

Table 1. Summary of the antibacterial testing results on sprayed and digital printed tiles.

uneven surface that is likely to be more amenable to cell attachment and proliferation [41]. A second factor is the sizes of the species that were examined, where **Table 2** [42, 43] contextualizes the view that the photocatalytic performance is correlated through size similarities between the photocatalyst and the species [42].

$$R_{L} = \log_{10} (B_{L}/C_{L})$$
(1)

$$\Delta R = \log_{10} (B_{\rm L}/C_{\rm L}) - \log_{10} (B_{\rm D}/C_{\rm D})$$
⁽²⁾

3.4. Life cycle assessment

In 1993, the Society of Environmental Toxicology and Chemistry (SETAC) standardized the process for life cycle assessment (LCA) to include four components: (1) goal and scope, (2) inventory, (3) impact assessment, and (4) data interpretation [44]. LCA normally is applied to early-stage plants in order to investigate environmental hot spots arising from new technologies [45] or to establish industrial-scale processes for the comparison of divergent designs and optimization of environmental profiles [46]. In this work, the LCA has been modeled for the production of photocatalytic ceramic tiles by digital inkjet printing and jet spraying.

The approach applies *gate-to-gate* boundaries using a functional unit of 1 m² of tiles produced in Modena, Italy. *SimaPro* (Version 8.3.0.0) extracted the secondary data from the *Ecoinvent* 3 database. *ILCD 2011 Midpoint* + (Version 1.08) and *IPCC 2013 GWP 100a* methods were used to calculate the impacts, which are given in terms of micro-eco-points (μ Pt). An eco-point is defined as one thousandth of the total environmental impact caused by a statistical European citizen per year [47]. The LCA was done in accordance with the *ISO/TC 207/SC 5 Life Cycle Assessment* methodologies for the principles and framework as well as the requirements and guidelines. For the inventory phase, these two processes were divided into substeps.

In order to highlight the differences between the two production processes, LCA comparison calculations were performed using the *ILCD 2011 Midpoint* + method, weighting the results for the 16 impact categories that were considered. **Figure 6** shows the results graphically and **Table 3** lists them numerically.

| Species | Size (nm) | Reference |
|------------------|---------------------|-----------|
| Ethanol | 0.437 | [43] |
| Toluene | 0.564 | [43] |
| E. coli | $1000\times 3000^*$ | [42] |
| Viruses | 10–300 | [42] |
| Bacteria | 500-5000 | [42] |
| Fungi | 5000-15,000 | [42] |
| *Rod-like shape. | | |

Table 2. Sizes of tested and other relevant species.
Photocatalytic TiO₂: From Airless Jet Spray Technology to Digital Inkjet Printing 273 http://dx.doi.org/10.5772/intechopen.72790



Figure 6. Graphical data for impact (µPt) assessments of digital inkjet-printed and jet-sprayed coatings.

| Impact category | Jet sprayed | Digital inkjet printed | Difference (%) | |
|--|-------------|------------------------|----------------|--|
| Human toxicity, cancer effects | 83.83 | 42.49 | 49.31 | |
| Freshwater ecotoxicity | 48.74 | 27.41 | 43.76 | |
| Climate change | 24.68 | 11.82 | 52.11 | |
| Human toxicity, non-cancer effects | 19.35 | 10.62 | 45.10 | |
| Mineral, fossil and resource depletion | 14.44 | 3.69 | 74.41 | |
| Freshwater eutrophication | 12.99 | 8.36 | 35.62 | |
| Acidification | 12.14 | 6.13 | 49.50 | |
| Particulate matter | 10.70 | 5.40 | 49.56 | |
| Photochemical ozone formation | 9.17 | 5.04 | 45.03 | |
| Ionizing radiation, human health | 7.44 | 5.85 | 21.42 | |
| Water resource depletion | 4.38 | 2.76 | 36.90 | |
| Marine eutrophication | 3.52 | 2.77 | 21.36 | |
| Terrestrial eutrophication | 3.48 | 2.75 | 20.95 | |
| Land use | 2.04 | 1.18 | 42.40 | |
| Ozone depletion | 1.16 | 0.70 | 39.99 | |
| Ionizing radiation, ecosystems (interim) | 0.00 | 0.00 | 0.00 | |

Table 3. Numerical data for impact (μPt) assessments of digital inkjet-printed and jet-sprayed coatings.

These data show that jet spraying makes consistently greater impacts than digital inkjet printing does, with the most significant impacts being on human toxicity, cancer effects, freshwater ecotoxicity, and climate change. The first two of these categories have been examined in more detail using *USEtox* calculations and the third category also has been examined using *IPCC 110a* calculations. These analyses reveal that their impacts derive almost entirely from the energy required by the production processes. This explains why jet spraying projects very high impact values since this process also is relatively energy-intensive. It is notable that the impacts of climate change and mineral, fossil and resource depletion reveal differences of >50% between the two production methods. Again, these significant differences are attributed to energy requirements. Three other categories (human toxicity, cancer effects, acidification, and particulate matter) also show nearly the same differential of ~50%. The single-score analysis, which is the average of all values in the 16 categories, shows that digital inkjet printing is ~46% lower than jet spraying.

Further, the calculation of the CO_2 equivalents, carried out by the *IPCC 100a* method, demonstrates that jet spraying has a greater impact than digital inkjet printing by a difference of 3.42 kg CO_2 versus 1.63 kg CO_2 . A final point of difference is that the application of the *ILCD* method reveals that NO_x production demonstrates the same trend, with 2.10 g NO_x from jet spraying and 1.65 g NO_x from digital inkjet printing.

The preceding LCA data suggest that the traditional method of jet spraying is considerably inferior to that of digital inkjet printing and that further detailed analysis of each step of the process is likely to improve the process and its outcomes commercially, environmentally, and performatively.

4. Conclusions

This work reports design, synthesis, and characterization of photocatalytic TiO_2 -coated tiles fabricated by the conventional jet spraying technique and the new technique of digital inkjet printing. The latter represents a significant improvement over the former, in that (1) it provides a more precise deposition as it utilizes piezoelectric heads to direct the suspension within an electrostatic field, (2) the microsized TiO_2 powder strikes a medium that balances the small size advantageous for photocatalytic performance and the ability to resist solubility in the glass bonding to the tile against the large size that inhibits respirability, and (3) the topography of the digital inkjet-printed coating is less amenable to cell attachment and proliferation than those of the jet-sprayed coating.

The performance data show that the digital inkjet-printed coating was significantly more effective than the jet-sprayed coating in ethanol photodegradation. While the same trend was observed for toluene photodegradation, the difference was not as significant owing to direct photolysis of this aromatic compound. Both coatings were highly effective in destroying E. coli but the antibacterial activity with photocatalysis (ΔR) of the digital inkjet-printed coating was significantly superior to that of the jet-sprayed coating. Similarly, the LCA analysis of the impact assessments reveals the multifarious advantages of the digital inkjet-printed tile.

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References

- Prüss-Ustün A, Wolf J, Corvalán C, Bos R, Neira M. Preventing Disease through Healthy Environments: A Global Assessment of the Burden of Disease from Environmental Risks. Geneva, Switzerland: World Health Organization (WHO); 2016
- [2] Anonymous. Ambient Air Pollution: A Global Assessment of Exposure and Burden of Disease. Geneva, Switzerland: World Health Organization (WHO); 2016
- [3] Martin WJ II, Glass RI, Araj H, Balbus J, Collins FS, Curtis S, Diette GB, Elwood WN, Falk H, Hibberd PL, Keown SEJ, Mehta S, Patrick E, Rosenbaum J, Sapkota A, Tolunay HE, Bruce NG. Household air pollution in low- and middle-income countries: Health risks and research priorities. PLOS Medicine. 2013;10:paper 1001455 (8 pp)
- [4] Tefera W, Asfaw A, Gilliland F, Worku A, Wondimagegn M, Kumie A, Samet J, Berhane K. Indoor and outdoor air pollution—Related health problem in Ethiopia: Review of related literature. Ethiopian Journal of Health Development. 2016;30(special issue):5-16

- [5] Chen A, Cao Q, Zhou J, Yang B, Chang V, Nazaroff WW. Indoor and outdoor particles in an air-conditioned building during and after the 2013 haze in Singapore. Building and Environment. 2016;99:73-81
- [6] Phoothiwut S, Junyapoon S. Size distribution of atmospheric particulates and particulatebound polycyclic aromatic hydrocarbons and characteristics of PAHs during haze period in Lampang Province, Northern Thailand. Air Quality, Atmosphere and Health. 2013;6:397-405
- [7] Beelen R, Hoek G, Vienneau D, Eeftens M, Dimakopoulou K, Pedeli X, Tsai M-Y, Künzli N, Schikowski T, Marcon A, Eriksen KT, Rasschou-Nielsen O, Stephanou E, Patelarou E, Lanki T, Yli-Tuomi T, Declercq C, Falq G, Stempfelet M, Birk M, Cyrys J, von Klot S, Nádor G, Varró MJ, Dèdelė A, Gražulevičienė R, Mölter A, Lindley S, Madsen C, Cesaroni G, Ranzi A, Badaloni C, Hoffmann B, Nonnemacher M, Krämer U, Kuhlbusch T, Cirach M, de Nazelle A, Nieuwenhuijsen M, Bellander T, Korek M, Olsson D, Strömgren N, Dons E, Jerrett M, Fisher P, Wang M, Brunekreef B, de Hoogh K. Development of NO₂ and NO_x land use regression models for estimating air pollution exposure in 36 study areas in Europe–The ESCAPE project. Atmospheric Environment. 2013;72:10-23
- [8] Environmental Protection Agency (EPA). https://cfpub.epa.gov/roe/chapter/air/indoorair.cfm
- [9] Dales R, Liu L, Wheeler AJ, Gilbert NL. Quality of indoor residential air and health. CMAJ·JAMC. 2008;179:147-152
- [10] American Lung Association. http://www.lung.org/stop-smoking/smoking-facts/
- [11] Ren H, Koshy P, Chen W-F, Qi S, Sorrell CC. Photocatalytic materials and technologies for air purification. Journal of Hazardous Materials. 2017;325:340-366
- [12] Fujishima A, Zhang X, Tryk DA. TiO₂ photocatalysis and related surface phenomena. Surface Science Reports. 2008;63:515-582
- [13] Bak T, Nowotny J, Rekas M, Sorrell CC. Photo-electrochemical hydrogen generation from water using solar energy. Materials-related aspects. International Journal of Hydrogen Energy. 2002;27:991-1022
- [14] Fujishima A, Nakata K, Ochiai T, Manivannan A, Tryk DA. Recent aspects of photocatalytic technologies for solar fuels, self-cleaning, and environmental cleanup. Electrochemical Society Interface. 2013;22:51-56
- [15] Chong MN, Jin B, Chow CWK, Saint C. Recent developments in photocatalytic water treatment technology: A review. Water Research. 2010;44:2997-3027
- [16] Chen J, Poon C-S. Photocatalytic construction and building materials: From fundamentals to applications. Building and Environment. 2009;44:1899-1906
- [17] Fujishima A, Zhang X. Titanium dioxide photocatalysis: Present situation and future approaches. Comptes Rendus Chimie. 2006;9:750-760
- [18] Gagliardi M. Photocatalysts: Technologies and Global Markets. Market Research Report AVM069B. Wellesley, MA, USA: BCC Research LLC; 2015

- [19] Poon CS, Cheung E. NO removal efficiency of photocatalytic paving blocks prepared with recycled materials. Construction and Building Materials. 2007;**21**:1746-1753
- [20] Hüsken G, Hunger M, Brouwers HJH. Comparative study on cementitious products containing titanium dioxide as photo-catalyst. In: Baglioni P, Cassar L, editors. International RILEM Symposium on Photocatalysis, Environment and Construction Materials. Bagneux, France: RILEM Publications; 2007. pp. 147-154
- [21] Strini A, Cassese S, Schiavi L. Measurement of benzene, toluene, ethylbenzene and oxylene gas phase photodegradation by titanium dioxide dispersed in cementitious materials using a mixed flow reactor. Applied Catalysis B: Environmental. 2005;61:90-97
- [22] Demeestere K, Dewulf J, De Witte B, Beeldens A, Van Langenhove H. Heterogeneous photocatalytic removal of toluene from air on building materials enriched with TiO₂. Building and Environment. 2008;43:406-414
- [23] Rachel A, Subrahmanyam M, Boule P. Comparision of photocatalytic efficiencies of TiO₂ in suspended and immobilised form for the photocatalytic degradation of nitrobenzenesulfonic acids. Applied Catalysis B: Environmental. 2002;37:301-308
- [24] Yu JC-M. Deactivation and Regeneration of Environmentally Exposed Titanium Dioxide (TiO₂) Based Products. Departmental Order Ref. No.: E183413. Chinese University of Hong Kong, Hong Kong: Environmental Protection Department, HKSAR; 2003
- [25] Auvinen J, Wirtanen L. The influence of photocatalytic interior paints on indoor air quality. Atmospheric Environment. 2008;42:4101-4112
- [26] Wang J, Chen C, Liu Y, Jiao F, Li W, Lao F, Li Y, Li B, Ge C, Zhou G, Gao Y, Zhao Y, Chai Z. Potential neurological lesion after nasal instillation of TiO₂ nanoparticles in the anatase and rutile crystal phases. Toxicology Letters. 2008;183:72-80
- [27] Radeka M, Markov S, Lončar E, Rudić O, Vučetić S, Ranogajec J. Photocatalytic effects of TiO₂ mesoporous coating immobilized on clay roofing tiles. Journal of the European Ceramic Society. 2014;34:127-136
- [28] Powell MJ, Quesada-Cabrera R, Taylor A, Teixeira D, Papakonstantinou I, Palgrave RG, Sankar G, Parkin IP. Intelligent multifunctional VO₂/SiO₂/TiO₂ coatings for self-cleaning, energy-saving window panels. Chemistry of Materials. 2016;28:1369-1376
- [29] Martinet C, Paillard V, Gagnaire A, Joseph J. Deposition of SiO₂ and TiO₂ thin films by plasma enhanced chemical vapor deposition for antireflection coating. Journal of Non-Crystalline Solids. 1997;216:77-82
- [30] De Falco G, Porta A, Del Gaudio P, Commodo M, Minutolo P, D'Anna A. Antimicrobial activity of TiO₂ coatings prepared by direct thermophoretic deposition of flamesynthesized nanoparticles. Nanomater. 2017;2:1493-1498
- [31] Jafari H, Afshar S, Zabihi O, Naebe M. Enhanced photocatalytic activities of TiO₂–SiO₂ nanohybrids immobilized on cement-based materials for dye degradation. Research on Chemical Intermediates. 2016;42:2963-2978

- [32] Calia A, Lettieri M, Masieri M, Pal S, Licciulli A, Arima V. Limestones coated with photocatalytic TiO₂ to enhance building surface with self-cleaning and depolluting abilities. Journal of Cleaner Production. 2017;**165**:1036-1047
- [33] Tobaldi DM, Graziani L, Seabra MP, Hennetier L, Ferreira P, Quagliarini E, Labrinch JA. Functionalised exposed building materials: Self-cleaning, photocatalytic and biofouling abilities. Ceramics International. 2017;43:10316-10325
- [34] Morita N, Khalate AA, van Buul AM, Wijshoff H. Inkjet printheads. In: Hoath SD, editor. Fundamentals of Inkjet Printing: The Science of Inkjet and Droplets. Weinheim, Germany: Wiley-VCH Verlag GmbH & Co. KGaA; 2016
- [35] Bianchi CL, Pirola C, Galli F, Stucchi M, Morandi S, Cerrato G, Capucci V. Nano and micro-TiO₂ for the photodegradation of ethanol: Experimental data and kinetic modelling. RSC Advances. 2015;5:53419-53425
- [36] Bianchi CL, Gatto S, Pirola C, Naldoni A, Di Michele A, Cerrato G, Crocellà V, Capucci V. Photocatalytic degradation of acetone, acetaldehyde and toluene in gas-phase: Comparison between nano and micro-sized TiO₂. Applied Catalysis B: Environmental. 2014;146: 123-130
- [37] Bianchi CL, Pirola C, Stucchi M, Sacchi B, Cerrato G, Morandi S, Di Michele A, Carletti A, Capucci V. A new frontier of photocatalysis employing micro-sized TiO₂: Air/water pollution abatement and self-cleaning/antibacterial applications. In: Semiconductor Photocatalysis—Materials, Mechanisms and Applications. Cao, W. ed. InTech, London, UK, Chapter 23. 2016
- [38] Bianchi CL, Stucchi M, Pirola C, Cerrato G, Morandi S, Sacchi B, Vitali S, Di Michele A, Capucci V. Micro-sized TiO₂ catalyst in powder form and as coating on porcelain grès tile for the photodegradation of phenol as model pollutant for water phase. Advances in Materials Science. 2017;2:1-6
- [39] Bianchi CL, Pirola C, Galli F, Cerrato G, Morandi S, Capucci V. Pigmentary TiO₂: A challenge for its use as photocatalyst in NO_x air purification. Chemical Engineering Journal. 2015;261:76-82
- [40] Bianchi CL, Pirola C, Galli F, Vitali S, Minguzzi A, Stucchi M, Manenti F, Capucci V. NO_x degradation in a continuous large-scale reactor using full-size industrial photocatalytic tiles. Catalysis Science & Technology. 2016;6:2261-2267
- [41] Deligianni DD, Katsala ND, Koutsoukos PG, Missirlis YF. Effect of surface roughness of hydroxyapatite on human bone marrow cell adhesion, proliferation, differentiation and detachment strength. Biomaterials. 2001;22:87-96
- [42] Blake DM, Maness P-C, Huang Z, Wolfrum EJ, Huang J, Jacoby WA. Application of the photocatalytic chemistry of titanium dioxide to disinfection and the killing of cancer cells. Separation and Purification Methods. 1999;28:1-50

- [43] Marcus Y. The sizes of molecules–Revisited. Journal of Physical Organic Chemistry. 2003; 16:398-408
- [44] Klöpffer W. The role of SETAC in the development of LCA. International Journal of Life Cycle Assessment. 2006;11(Suppl. 1):116-122
- [45] Galli F, Pirola C, Previtali D, Manenti F, Bianchi CL. Eco design LCA of an innovative lab scale plant for the production of oxygen-enriched air. Comparison between economic and environmental assessment. Journal of Cleaner Production. 2018;171:147-152
- [46] Curran MA. Life cycle assessment: A review of the methodology and its application to sustainability. Current Opinion in Chemical Engineering. 2013;2:273-277
- [47] Grzesik K, Usarz M. A life cycle assessment of the municipal waste management system in Tarnów. Geomatics and Environmental Engineering. 2016;**10**:29-38

Influence of the Synthesis Method on the Preparation Composites Derived from TiO₂-LDH for Phenol Photodegradation

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Abstract

Three different TiO₂ catalysts are prepared using different methods. MgAl-CO₃²⁻ layered double hydroxides (LDH) were obtained by the sol-gel method. In the preparation of the composites, the three photocatalysts were combined with LDH following different methodologies. The composites were characterized using X-ray diffraction (XRD), specific surface area (SA), atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS). The influence of the synthesis method on the preparation of the composites was evaluated by analyzing their photocatalytic activity against phenol as a model organic pollutant under UV irradiation. The photocatalytic activity of the composites improves when the chemical interaction, determined by XPS, between the TiO₂ and the LDH decreases. The same happens when the ratio of the anatase-rutile phases, determined by XRD, approaches optimum (80:20%). The effect of the composite concentration in the solution (0.5-2.0 g/L) was investigated, and the light-shielding phenomenon due to high composite concentration decreases the phenol photodegradation. The reduction of photocatalytic activity in reuse cycles is due to loss and partial deactivation of the material. The elimination of phenol is attributed primarily to the photocatalytic process due to the generation of •OH radicals and to a lesser extent the adsorption process also present in the samples.

Keywords: composites, photocatalyst, layered double hydroxides, TiO₂, phenol, degradation

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1. Introduction

Synthetic organic composites like phenol are widely used in a great variety of industries including paper, wood, paint, and fertilizers [1]. Wastewater from such industrial processes contains this kind of composite and poses a threat to aquatic life and the environment. It is therefore important to remove or degrade such composites before discharging the wastewater into the environment. Among the technologies used for the degradation of organic pollutants in aqueous media are advanced oxidation processes (AOPs), specifically heterogeneous photocatalysis, which promotes the degradation of several pollutants by broadband semiconductor excitation [2–5]. Photon adsorption by the semiconductor with higher bandgap energy leads to the formation of an electron-hole pair $(e_{RC}^-h_{RV}^+)$. The photogenerated holes in the valence band are powerful oxidants, while the conduction band electrons are good reducers. The formation of other highly oxidant species (mainly •OH radicals) can also occur; these redox-type reactions occur when the electron-hole recombination is minimized [6]. The use of TiO, as photocatalyst has caused great interest due to its high activity, resistance to mild chemical corrosion, low toxicity, and efficiency [7]. The anatase crystalline phase of TiO, is more effective than the rutile phase for the photodegradation of several contaminants [5]; however, photoactivity has been found to increase in mixed anatase-rutile phases [8]. One difficulty with the use of TiO, is its separation and recovery for possible reuse; the addition of a support material or coadsorbent to immobilize TiO, particles to facilitate recycling has been the subject of various investigations [9, 10].

Layered double hydroxides (LDHs) are synthetic composites belonging to the anionic clay family, having a hexagonal or octahedral crystalline structure. They consist of layers of positively charged metal cations, where the surface of the layers is occupied by hydroxyl groups, anions, and water molecules. LDHs are the result of isomorphic variations of brucite-type layers (Mg(OH)₂) when Mg²⁺ cations are substituted by Al³⁺ cations, thereby generating a positive charge residue which is offset by the presence of intercalated anions, carbonate (CO₃²⁻) being the predominant anion [11]. Hydrotalcite is an LDH-type layered material, with the chemical formula $[M^{2+}_{1-x}M^{3+}_x(OH)_2]_x(A^{n-})_{x/n} \circ mH_2O$, where M^{2+} and M^{3+} are di- and trivalent cations (Mg²⁺ and Al³⁺) and Aⁿ⁻ is the intercalated anion. LDH and its calcined products are porous materials with large surface area, have the capacity to adsorb pollutants, and have proven suitable for immobilizing TiO₂ particles for the photodegradation of organic pollutants [12, 13].

The aim of this work is to synthesize composites derived from the TiO_2 photocatalyst and the LDH anionic clays to study the influence of the preparation method on the photocatalytic capacity of those composites in a phenol solution. Two groups of synthesis methods were used: the first one is to obtain the TiO_2 photocatalyst, and the second one is in the preparation of the TiO_2 -LDH composites. The LDH was prepared by the sol-gel method, according to previously optimized procedures [14, 15] in relation to its photoactivity evaluated with the degradation of phenol. The synthesized composites in this work were also tested for phenol photodegradation in aqueous solution. These materials also showed advantages in their reusability and were able to be used in four photocatalytic cycles with a minimum loss in the photocatalytic activity at the end of the test.

2. Materials and methods

2.1. TiO₂ synthesis

The photocatalysts were synthesized using three methods. (i) First, following the sol–gel procedure [16], 5.25 mL of titanium isopropoxide (TTIP) Ti[OCH(CH₃)₂]₄ were added to 97% (Sigma-Aldrich) in 47 mL of ethanol (Civeq); the mixture was agitated for 3 hours after which 12.25 mL of deionized water were added. Agitation continued at 78°C for 20 hours. The solid was washed with deionized water by centrifugation and dried at 80°C during 1 hour. The resulting powder was ground and calcined (TiO₂I). (ii) In the second method, 90 mL of 1-butanol C₄H₁₀O (Sigma-Aldrich) were mixed with 120 mL of deionized water; both reagents were heated at 70°C in a water bath with continuous agitation and reflux system. Subsequently, 45 mL of titanium butoxide (TOBT) C₁₆H₃₆O₄Ti 97% (Sigma-Aldrich) were added by dripping. The mixture was aged during 24 hours at constant agitation and temperature. The resulting solid was recovered and washed by centrifugation using ethanol, dried during 24 hours at 100°C, and finally calcined (TiO₂B). (iii) The third method of obtaining TiO₂ was direct calcination of TTIP by placing 10 mL in mechanical agitation in air for 30 minutes, before being calcined (TiO₂T). In all cases, calcination took place at 550°C for 3.5 hours.

2.2. LDH synthesis

LDHs were synthesized by the sol–gel method [17], mixing 5.72 g of magnesium ethoxide $C_4H_{10}MgO_2$ (Aldrich) in 100 mL of ethanol CH_3CH_2OH (99.5%) (Civeq) and adding 8.8 mL of HCl (Fermont); the mixture was maintained at 80°C with reflux and agitation. The second solution was prepared by dissolving 5.4 g of aluminum acetylacetonate $C_{15}H_{21}AlO_6$ (Aldrich) in 80 mL of ethanol and added dropwise to the first solution maintaining pH 10 with a 3:1 solution of NH_4OH in water. The mixture was aged for 20 hours. The solid was separated by centrifugation and dried at 100°C for 24 hours (LDH). It was then calcined at 550°C for 3.5 hours (CLDH).

2.3. Synthesis of TiO₂-LDH composites

As previously reported, in the preparation of HDL-TiO₂ composites [15], the use of anionic clays synthesized by the sol-gel method has advantages over those prepared by the conventional coprecipitation method, because the sol-gel HDL possesses smaller crystal size, which offers a bigger dispersion of TiO₂ particles on the surface of material minimizing the photocatalyst screening phenomenon. In this work according to previous tests, three methodologies were chosen in the preparation of composites derived from TiO₂ and sol-gel HDL based on their photocatalytic efficiency, which are representative for the three different synthesized photocatalysts:

(i) In the first method, 2.0 g of TiO_2I catalyst were mixed with the gel during LDH synthesis, continuing with the methodology described in the previous paragraph. Finally, the solid was calcined at 550°C for 3.5 hours (TiO₂I-LDH).

(ii) In the second method, 2.0 g of the TiO_2B catalyst and 0.2 g of the CLDH solid were mixed in 20 mL of ethanol with mechanical agitation for 3 hours; the resulting paste was dried at 100°C for 20 hours (TiO_2B-LDH).

(iii) In the preparation of the third composite, 9 mL of TTIP were mixed with 0.5 g of CLDH, and the mixture agitated for 30 minutes in the air. The samples were then calcined at 550°C for 3.5 hours (TiO₂T-LDH). **Figure 1** illustrates the processes described above in the preparation of TiO₂-LDH composites.

2.4. Characterization

The materials obtained were characterized by XRD using Siemens D500 diffractometer (Cu $k\alpha \lambda = 1.54$ Å) at a scanning speed of 2(°2 θ)/min. The specific surface area was determined by N₂ adsorption using the BET method on BELSORP-max equipment. The surface analysis of the materials by the AFM technique was performed in an Oxford Asylum Research Cipher AFM at room conditions with noncontact mode with a Si tip of 10 nm radius and resonance frequencies from 180 to 240 kHz. The measurements were taken in a range of 500 × 500 nm. The composites were also analyzed by XPS using Thermo Scientific K-Alpha X-ray photoelectron spectrometer, using the Al $k\alpha$ radiation line (1487 eV) in standard mode, with 10 scans, tip size of 400 μ m, step voltage of 200.0 eV, and pass energy of 1.0 eV. All the characterization analysis was performed prior to the photocatalytic tests.

2.5. Phenol photodegradation and adsorption tests

The LDH, CLDH, TiO₂I, TiO₂B, and TiO₂T precursors and TiO₂I-LDH, TiO₂B-LDH, and TiO₂T-LDH composites were mixed separately with a phenol solution (Baker) ($C_0 = 10 \text{ mg/L}$). Air was pumped through each mixture to maintain constant agitation, and the solution was stabilized for 20 minutes. Three different conditions were evaluated: (i) under UV light with a UVS-18 EL ($\lambda = 264 \text{ nm}$, 8 w) lamp and in the absence of solid (photolysis), (ii) in the dark without UV irradiation and with the synthesized materials (adsorption), and (iii) under UV light with the presence of the synthesized solids (photocatalysis). The experiments were conducted for 120 minutes at room temperature (20°C) and without external pH variation. The effect of different concentrations of the prepared composites was also evaluated at concentrations of 0.5, 1.0, 1.5, and 2.0 g/L; aliquots were extracted at 0, 5, 10, 30, 50, 80, and 120 minutes during



Figure 1. Methodologies for TiO₂-LDH composite preparation.

the experiments. The phenol concentration was determined by UV-Vis spectrophotometry using the 4-aminoantipyrine method [18]. In order to determine the reuse capacity of the synthesized composites, photodegradation tests were conducted with UV irradiation using the same solid in consecutive rounds. At the end of a photodegradation cycle, the material was recovered from the solution by sedimentation and reused with a new phenol solution until four cycles were completed.

3. Results and discussion

3.1. Characterization

Figure 2 shows the X-ray diffraction patterns for the synthesized TiO₂ precursors along with the LDH and its calcined product CLDH. For the photocatalysts, the TiO₂I sample is composed mostly of the crystalline structure related to the TiO₂ anatase phase, presenting peaks at 25.4, 37.9, 48.1, 54.1, 55.2, and 62.6 °20 (JCPDS 01-089-4921), in addition to a peak related to the TiO₂ brookite phase at 30.9 °20 (JCPDS 00-029-1360). The diffractogram for the TiO₂T sample shows a bigger variety in the different crystalline structures that this photocatalyst possesses, with a main peak at 25.4 °20 and smaller peaks at 37.9, 48.1, 54.0, and 55.2 °20 referring to the TiO₂ anatase phase (JCPDS 01-089-4921). In smaller proportion characteristic, reflections of the TiO₂ phase with rhombohedral structure are observed in 32.9, 35.7, and 40.8 °20 (JCPDS 01-071-0146), a peak at 43.7 °20 of TiO with monoclinic structure (JCPDS 01-072-0020) and one lower peak associated with TiO₂ rutile phase referring to the TiO₂ anatase phase at 25.4 °20 (JCPDS 01-089-4921). The TiO₂ B sample shows peaks referring to the TiO₂ anatase phase at 25.4, 37.9, 48.1, 54.0, and 55.2 °20 (JCPDS 01-089-4921) and a signal at 30.9 °20 of the TiO₂ brookite with orthorhombic crystalline formation (JCPDS 00-029-1360), as well as peaks related to the TiO₂ rutile phase at 27.6 and 36.2 °20 (JCPDS 01-089-4920).

In a photocatalyst, the pure anatase phase is considered photocatalytically superior to the rutile phase, which, although more heat stable, at the same time has a higher rate of electron–hole recombination ($e_{BC}^--h_{BV}^+$) and a lesser affinity for the adsorption of organic compounds like phenol [19]. A key factor in the photocatalytic activity of TiO₂ is to obtain a mixed anatase-rutile material at an optimal ratio of about 80:20%, which has lower recombination rates ($e_{BC}^--h_{BV}^+$) due to the interconnection of the electronic bands, in which the rutile phase acts as e_{BC}^- collector. In the meanwhile, the anatase phase is the photocatalytically active part causing oxidation and reducing reactions, which are carried out separately, maximizing the photocatalytic mechanism [8]. The composition of the precursor photocatalysts in the anatase-rutile phases was determined by the Spurrs and Myers equation [20], finding that the optimal anatase-rutile phase ratio (80:20%) was close to be found in samples TiO₂T (82:18%) and TiO₂B (89:11%). Meanwhile, the rutile phase of TiO₂ was not observed in the TiO₂I photocatalyst; only the anatase and brookite phases were present. These results occasionally influence the performance of these materials and the composites used in the photocatalytic tests, as discussed later.



Figure 2. XRD patterns for TiO₂ and LDH compounds, with A (TiO₂ anatase), R (TiO₂ rutile), TiO m (TiO monoclinic crystalline structure), TiO, r (TiO, rombohedric crystalline structure), B (TiO, brookite) H (LDH), and O (MgO) peaks.

The diffraction pattern of LDH (**Figure 2**) shows the typical rhombohedral structure of an MgAl layered double hydroxide, where the diffraction at 11.3 °20 corresponds to the basal plane (003), defined as the distance between two adjacent layers. Harmonic reflections corresponding to planes (006), (009), (012), (015), and (110) can also be observed at 22.0, 34.6, 38.2, 47.8, and 61.0 °20, respectively (JCPDS 00-014-0191) [21]. The diffraction pattern for CLDH (**Figure 2**) shows the characteristic peaks of periclase MgO with crystallographic planes (200) and (220) at 42.9 and 62.3 °20, respectively (JCPDS 00-003-0998), which correspond to crystals of a MgAl mixed oxide associated with the collapse of the laminar structure of the LDH [21, 22].

Figure 3 shows the X-ray diffraction patterns for the synthesized TiO_2 -LDH composites. In the case of the TiO_2 T-LDH composite, the TiO_2 anatase phase and the mixed oxides can be observed separately; the reflections of the TiO_2 anatase phase are predominant at 25.4, 37.0, 37.9, 48.1, 54.0, and 55.2 °20 (JCPDS 01-089-4921). A less intense peak can be seen at 42.9 °20 (JCPDS 01-003-0998) corresponding to CLDH component and another peak at 32.9 °20 of the MgTi mixed oxide with rhombohedral crystalline structure (JCPDS 01-079-0831), thus confirming the immobilization of TiO_2 in the composite through the calcination process and achieving the diffusion of the photocatalyst in the composite [21, 23].

The TiO₂I-LDH composite mostly shows diffraction of the MgTiO₃ mixed oxide with rhombohedral structure, with a main peak located at 32.9 °2 θ and secondary peaks at 19.3, 21.3, 24.1, 35.7, 40.8, 49.3, 53.7, 62.1, and 63.8 °2 θ (JCPDS 01-079-0831). The crystal structure of monoclinic TiO presents two diffractions with peaks located at 42.1 and 43.1 °2 θ (JCPDS



Figure 3. XRD patterns for TiO_2 and LDH compounds, with A (TiO_2 anatase), R (TiO_2 rutile), TiO_2 m (TiO_2 monoclinic crystalline structure), B (TiO_2 brookite), O (MgO), and M (MgTiO₃ rombohedric crystalline structure) peaks.

01-072-0020). The TiO₂ anatase phase in this composite is seen in a small peak of (110) plane at 25.4 °20 (JCPDS 01-089-4921) suggesting that only a small part of Ti exists in this phase and the rest is dispersed over the MgAl mixed oxide [21]. Supporting the above statement, no diffraction spikes attributed to the MgAl mixed oxide can be observed, suggesting that the impregnated TiO₂ particles are disaggregated [24] when mixed with the LDH gel and prior to the heat treatment of the composite, achieving a chemical interaction between the composites resulting in the formation of the MgTiO₃ phase [25].

The diffraction pattern of the TiO₂B-LDH composite is mostly composed of diffractions with the TiO₂ anatase phase at 25.4, 37.9, 48.1, 54.1, 55.2, and 62.6 °2 θ (JCPDS 01-089-4921); similarly, it is possible to observe a peak relating to the TiO₂ rutile phase at 27.6 °2 θ (JCPDS 01-089-4920), a signal at 30.9 °2 θ of the TiO₂ brookite phase (JCPDS 00-029-1360), and a lesser intense peak at 42.9 °2 θ associated with the MgO oxide (JCPDS 00-003-0998). Reflections related to the formation of MgTiO₃ mixed oxide are absent.

These results confirm the addition of TiO_2 in the composites. In the case of $\text{TiO}_2\text{I-LDH}$, there are significant changes in the structure with respect to the precursors, whereas in the $\text{TiO}_2\text{T-LDH}$ and $\text{TiO}_2\text{B-LDH}$ samples, the components remain segregated.

Properties such as the photocatalytic crystalline phases, the proportion of each one, and the size of the crystals in photocatalysts are influential in the generation and/or recombination of electron–hole pairs. The formation of the different crystalline phases of a photocatalyst is related to the atomic arrangement and the facet that shows the crystals during irradiation in photocatalytic processes [16]. The crystal sizes of the synthesized samples are calculated using the Debye-Scherrer equation [26] and are given in **Table 1**. The preparation temperature on TiO_2 synthesis affects the formation of the anatase and rutile phases, which is reflected in the size of the crystal formed [27]. The crystal size for the composites is from 26 to 36 nm, observing that the different methodologies used to prepare the composites influence the size of the crystals formed. The TiO_2T -LDH and TiO_2B -LDH composites present a similar crystal size to the TiO₂T and TiO₂B photocatalysts, while the crystal size for TiO₂I-LDH

| Sample | Crystal size (nm) | AS _{BET} (m ² /g) | Total pore volume (cm ³ /g) | Average pore diameter (nm) |
|------------------------|-------------------|---------------------------------------|--|----------------------------|
| TiO ₂ T | 34 | 1.48 | 0.003 | 8.16 |
| TiO ₂ I | 16 | 62.99 | 0.180 | 11.40 |
| TiO ₂ B | 25 | 54.61 | 0.113 | 8.30 |
| LDH | 11 | 87.09 | 0.169 | 7.74 |
| CLDH | 43 | 77.47 | 0.151 | 7.80 |
| TiO ₂ T-LDH | 36 | 70.44 | 0.175 | 9.95 |
| TiO ₂ I-LDH | 31 | 90.12 | 0.239 | 10.61 |
| TiO ₂ B-LDH | 26 | 45.29 | 0.111 | 9.82 |

Table 1. Crystal size and textural characteristics of the composites.

is almost double that the TiO_{2}I sample. Similarly, the generation of nanometric crystals in LDH (11 and 43 nm of LDH and CLDH, respectively) that are obtained by sol-gel synthesis may enable a more homogeneous interaction with TiO_{2} compared to other methods of LDH synthesis [28–29].

The textural properties of a photocatalyst affect its contact with pollutants. The heterogeneous photocatalysis process performs better in photocatalysts with high surface area, which increases the probability that the molecules of the pollutant and its oxidation intermediates are in direct contact with the photogenerated holes during irradiation, thus enhancing the photodegradation process [19].

Table 1 shows the results of surface area, total volume, and mean pore diameter of the synthesized solids. The mean diameter of the samples is in the range of 2 to 50 nm assigning them mesoporous materials [22]. The N, adsorption-desorption isotherms that were obtained for the materials in all cases were type IV according to IUPAC classification, where a slow increase in the adsorption process can be observed, followed by a rapid adsorption typical of mesoporous materials. Furthermore, the hysteresis loop for all materials correspond to H3 type, which is associated with the filling and emptying of the mesopore by capillary condensation; this type of hysteresis is usually found in materials that form particle aggregates, which indicate the presence of asymmetric pores, with nonuniform size and shape [4, 30]. In the prepared composites, the presence of TiO₂ induces profound changes in the textural properties of the solids; TiO,I-LDH presents a bigger surface area (90.12 m²/g) compared to the TiO,I and LDH precursors (62.99 and 77.47 m²/g, respectively), attributed to the increase of the pore volume in samples [4]. The preparation of this composite entirely by a sol-gel route also accounts for the greater specific surface area of this sample. This behavior is not observed in TiO₂T-LDH, since it has a smaller surface area (70.44 m²/g), attributed to the contribution of the surface area of the photocatalyst TiO₂T used as precursor (1.48 m²/g), whereas the surface area for TiO₃B-LDH is reduced (45.29 m²/g) compared to the TiO₃B precursors and calcined LDH (54.61 and 77.47 m²/g, respectively), attributed to the reduced number of accessible pores, reflected in a slight reduction in pore volume [24].

The AFM characterization in noncontact mode of TiO_2 and CLDH precursors and the composites obtained is shown in the images in **Figure 4**. The surface morphology observed in the two- and three-dimensional (2D and 3D) images for the TiO_2T photocatalyst consists of spherical particle agglomerates with diameters in the range of 35 to 175 nm. As can be seen in the images, the particles for TiO_2I and TiO_2B precursors preserve their shape, while their size decreases considerably to diameters in the range of 15 to 50 nm as a result of the sol-gel process used to synthesize these two photocatalysts in particular [31], which is related to the crystal size obtained for these materials. The image for CLDH shows a topography formed by densely packed plate-shaped particles whose horizontal dimensions vary from 40 to 100 nm.

On the other hand, in the TiO_2T -LDH composites, a more uniform morphology can be seen on comparing TiO_2I -LDH and TiO_2B -LDH, where in the latter, it can be more clearly appreciated how the components contrast where the smaller spherical particles of TiO_2 are spread over the surface of the larger plates of the LDH component, thus confirming the formation of the composites.



Figure 4. AFM 3D–2D images and height profiles for (a) TiO_2T , (b) TiO_2I , (c) TiO_2B , and (d) CLDH samples and (e) TiO_2T -LDH, (f) TiO_2I -LDH, and (g) TiO_2B -LDH composites.

Surface roughness can be quantitatively identified using the data obtained from the AFM analysis through the definition of the quadratic mean, as follows [32]:

$$R_{rms} = \sqrt{\frac{\sum_{n=1}^{N} (z_n - z)^2}{N - 1}}$$
(1)

where R_{rms} is the roughness of the mean quadratic value, z_n is the height of the n_{th} data point, z is equal to the average height of the z_n values obtained by AFM topography, and N is the number of data points. The results of statistical analysis for the materials used are shown in **Table 2**.

| Muestra | TiO ₂ T | TiO ₂ I | TiO ₂ B | CLDH | TiO ₂ T-LDH | TiO ₂ I-LDH | TiO ₂ B-LDH |
|-----------------------|--------------------|--------------------|--------------------|-------|------------------------|------------------------|------------------------|
| R _{rms} (nm) | 32.54 | 6.72 | 4.56 | 18.44 | 18.75 | 40.84 | 39.71 |

Table 2. Roughness values of quadratic mean (R_{rms}) for the precursors and synthesized composites.

As observed in the surface profiles in **Figure 4**, all the samples presented roughness, the TiO_2T photocatalysts having a higher value compared to the TiO_2I and TiO_2B precursors. This trend coincides with the reduced particle size observed for these last photocatalysts, whereas the CLDH precursor presents a roughness with intermediate value compared to that obtained in the photocatalysts. The TiO_2T -LDH composite shows a decrease in the R_{rms} value compared to the value of TiO_2T ; a reduction in the roughness value is representative of the homogeneity of the particles [33], suggesting that the photocatalyst is diffused inside the composite, while the surface is constituted mostly by the CLDH component. This result is not observed in the AFM images for the TiO_2I -LDH and TiO_2B -LDH composites, indicating that in these materials the photocatalyst remains more superficially exposed.

The high-resolution XPS spectra for the O 1 s and Ti 2p regions of the TiO₂-LDH composites are presented in **Figure 5**. The O 1 s spectra signals for the TiO₂T-LDH material decompose into energy peaks at 529.48, 530.01, 531.77, and 532.87 eV attributed to the bonds in TiO_{2'} MgO, Al₂O_{3'} and CO, whereas the Ti 2p spectrum is resolved in the coordinations that form the Ti in Ti₂O₃ and TiO₂ (octahedral coordination) and the TiO₂/Al₂O₃ interaction, which are related to the binding energies 456.90, 458.15, and 458.89 eV, respectively [21, 34].

The XPS O 1 s spectrum for TiO₂I-LDH is resolved in spikes with binding energies of 529.66, 530.43, 532.10, and 533.37 eV which correspond to TiO₂, MgO, Al₂O₃, and CO composites. The resolution of the XPS spectrum of Ti 2p3/2 region shows spikes with binding energies of 456.93, 458.34, and 459.05 eV corresponding to Ti₂O₃ and TiO₂ (octahedral) and TiO₂/Al₂O₃; this latter as a result of the chemical interaction between the LDH oxides and the impregnated TiO₂ [12, 30, 34].

The resolution of the XPS spectra for the TiO₂B-LDH composite in the O 1 s region shows the contributions of O forming bonds in the MgO, TiO₂, Al₂O₃, and CO composites with peaks at 529.20, 529.99, 531.80, and 532.75 eV, respectively. The binding energies of the Ti 2p3/2 region found at 457.34, 458.74, and 460.34 eV indicate their presence forming the Ti₂O₃, TiO₂ (octahedral), and TiO₂ (tetragonal) composites, respectively [29, 34].

Similarly, in the XPS spectra of **Figure 5** corresponding to the Ti 2p region, a traditional Ti 2p spectrum can be observed, where the intensity of the Ti 2p3/2 peak is higher than for the Ti 2p1/2 peak. It can also be seen that in all the composites the neighboring distances between the main Ti 2p3/2 and Ti 2p1/2 peaks are close to 5.9+/-0.2 eV. This value indicates that the charged TiO₂ particles in the composite have an octahedral coordination typical of the anatase phase [12, 21, 35].

The XPS analysis shows the different types of Ti coordination in the samples; the octahedral TiO_2 coordination is predominant in all the samples. The chemical interaction of Ti with the



Figure 5. XPS spectra for Ti 2p and O 1s regions for TiO₂-LDH composites.

LDH also presents [12]. From these results, it can be deduced that the composites obtained are not mixtures of unrelated components, rather than there is a chemical interaction between them. According to the literature [36], chemical interaction reduces photocatalytic efficiency since the Ti is incorporated into the structure, remaining a lesser extent on the surface. This occurs with greater frequency in the TiO₂I-LDH composite where, based on the different Ti coordinations presented (see **Figure 6**), the chemical bond between the TiO₂-Al₂O₃ components occurs in 25.9%, whereas this contribution is lower (19.6%) for TiO₂T-LDH and is not observed in TiO₂B-LDH. However, TiO₂B-LDH is possible to observe the tetragonal TiOx coordination which may enhance photocatalytic efficiency in the degradation of phenolic composites [21], directly relating these results to the photocatalytic degradation rates of each of these materials as it is shown below.

Influence of the Synthesis Method on the Preparation Composites Derived... 293 http://dx.doi.org/10.5772/intechopen.72279



Figure 6. Contributions of Ti coordinations in TiO₂-LDH composites.

| Muestra | Mg | Al | Ti | С | 0 | Ti/(Mg + Al) |
|------------------------|-------|-------|-------|-------|-------|--------------|
| TiO ₂ T-LDH | 14.95 | 6.83 | 9.83 | 24.01 | 44.38 | 0.45 |
| TiO ₂ I-LDH | 30.54 | 10.06 | 5.31 | 9.11 | 44.98 | 0.13 |
| TiO ₂ B-LDH | 9.74 | 0.95 | 15.29 | 22.40 | 51.62 | 1.44 |

Table 3. Elemental analysis by XPS (% atom.) and relation Ti/(Mg+Al) for TiO2-LDH composites.

The elementary XPS study in terms of atomic percentage produces the results shown in **Table 3**. The presence of Ti in the composites is lower in TiO_2I -LDH, leading us to say that the methodology used in the preparation of this composite is not conducive to its incorporation on the surface, while for TiO_2T -LDH and TiO_2B -LDH, the percentage of surface Ti is higher (9.83 and 15.29%, respectively).

The loading of TiO₂ over the LDH surface can be determined by means of the Ti/(Mg + Al) ratio [36] through elementary XPS analysis, finding values of 1.44, 0.45, and 0.13 for TiO₂B-LDH, TiO₂T-LDH, and TiO₂I-LDH, respectively. The results are attributed to the synthesis methods used in the preparation of the materials, finding that the direct mixing of the TiO₂ and LDH solids as in TiO₂B-LDH leads to a lower Ti propagation inside this composite, enabling increased activity per unit of mass, reducing the agglomeration of photocatalytically active particles and the screening phenomenon, as well as allowing the easy separation and recovery of the solid at the end of its use in photocatalytic processes [36]. Contrary to the aforementioned, the TiO₂I-LDH sample presents a lower value in Ti loading, attributed to the direct mixing of the LDH gel with the TiO₂ solid, causing fewer particles of the TiO₂ photocatalyst to remain on the external surface, instead of being diffused in the interior causing lower photodegradation rates [12].

3.2. Photodegradation and phenol adsorption tests

In heterogeneous photocatalysis processes, several phenomena can occur. Direct photodegradation is where the adsorption of the organic pollutant on the surface of the catalyst promotes its decomposition by the action of the photogenerated holes. On the other hand, indirect photodegradation is based on the generation of •OH radicals which react with the organic matter degrading it. Other processes that may occur in phenol photodegradation are direct photolysis due to the presence of UV irradiation and photooxidation by the action of UV radiation and the oxidizing agent, but without any involvement from the photocatalyst [19].

As observed in Figure 7, after 120 minutes of photolytic reaction, degradation of phenol reaches 11.0% (1.1 mg/L). Since there is no absorption or light dispersion by the presence of any solid, majority of the photon flux was used for the photolytic reaction. This process reaches higher speed during the first 30 minutes of irradiation, and then the rate of photodegradation decreases but without reaching equilibrium, attaining the lowest level in all tests due to the lack of a material to act as photocatalyst and/or adsorbent [37]. For precursor photocatalysts, phenol degradation rates of 38.2 (3.8 mg/L), 41.8 (4.2 mg/L), and 54.6% (5.5 g/L) were obtained for TiO,T, TiO,I, and TiO,B, respectively, during 120 minutes of irradiation. Although the TiO, anatase phase predominates in all the photocatalysts, as shown in the DRX analysis, the higher performance of the TiO₂B sample is attributed to the anatase-rutile ratio of 88:12%, which is the closest to the optimal one (80:20%); the rutile phase acts as a e_{BC} collector reducing recombination rates with h_{RV}^+ and transferring the pollutant particles to the active TiO₂ anatase phase [38]. Another important difference is observed in the formation of crystalline phases of TiO, without photocatalytic properties [39], finding the presence of monoclinical TiO and rhombohedral TiO, in the TiO,T sample, while the TiO, brookite phase forms in TiO,I, resulting in lower photocatalytic efficiency and in TiO₂B the anatase and rutile phases they are present.

In addition, based on the particle size obtained for these photocatalysts, it is known that the optimum size in a TiO_2 photocatalyst is in the range of 20 to 30 nm, since this gives an optimum balance between the production of $e_{BC}^-h_{BV}^+$ pairs and the recombination process due to the surface/volume ratio becoming larger, enabling the timely use of the photogenerated



Figure 7. (a) Adsorption, (b) phenol photolysis, and photocatalytic degradation, with TiO, and LDH.

charges [39]. Considering the abovementioned, the particle size based on the AFM analysis is directly related to the percentage of photodegradation found in the photocatalysts, with the TiO_2T sample having the highest particle size (in the range of 35–175 nm), which is reflected in a lower photoactivity.

The adsorption rates found in the photocatalysts are lower and unrelated to the surface area of the materials, being slightly higher for TiO₂B (3.2%) 0.3 mg/L compared to TiO₂T (1.8%) and TiO₂I (1.5%), 0.2 and 0.1 mg/L, respectively. These results confirm the TiO₂B synthesis methodology as the most efficient for achieving maximum phenol degradation of 5.5 mg/L (54.6%). According to the XRD study, this is attributed mainly to the optimal anatase-rutile ratio of 88:12% and to smaller crystal size (25 nm), which is reflected in an optimal particle size range (15–50 nm), allowing $e^-_{BC}-h^+_{BV}$ recombination to be minimized [40].

There is evidence that although LDH and CLDH are not semiconductors, these materials can act as photocatalysts since, due to the presence of Mg^{2+} and Al^{3+} cations, other materials with photoinduced defects on the oxide surface can be obtained, which can act as active centers for the surface reactions, promoting the generation of e^-_{BC} - h^+_{BV} pairs where the electron is delocalized toward the deficient charge of the Al^{3+} and the hole oxidizes the surrounding hydroxyl groups allowing the formation of •OH radicals [41, 30]. This statement is not reinforced by the results obtained in this study, where it can be observed (**Figure 7**) that the percentage of phenol degradation by photocatalysis for LDH and CLDH reaches 15.9 (1.6 mg/L) and 17.1%, (1.7 mg/L), respectively, after 120 minutes of irradiation. This behavior is mostly attributed to the concurrence of the adsorption and photolysis phenomena. Furthermore, in the adsorption process, lower percentages of phenol removal 3.9 (0.4 mg/L) and 2.7% (0.3 mg/L) were observed, with the value achieved with LDH being higher than with mixed oxides (CLDH), attributed to the greater surface area and pore volume of LDH.

The photodegradation curves obtained for the prepared composites are shown in **Figure 8**. It can be seen that the composites present higher phenol degradation rates than the LDH and CLDH precursors. The photodegradation curves in the composites show bigger photocatalytic activity during the first minutes of the reaction, when there is less competition between the phenol molecules to be degraded; as the passing of time, the photodegradation intermediates produced limit the elimination of phenol by the supported photocatalyst. Over time, there is no appreciable decrease in the photodegradation rate with the exception of the TiO₂B-LDH solid, where it can be observed that after the first few minutes of irradiation, the gradient of the curve remains stable, leading to higher percentages of phenol photodegradation. The formation of •OH radicals can be affected by excess coverage of LDH over the TiO₂ particles, causing a blocking of the radiant energy to the molecules of the photocatalyst [13]. The abovementioned is manifested mainly in the TiO₂T-LDH and TiO₂I-LDH samples, coinciding with the results of the AFM characterization.

The effect of synergy between a support material and a catalyst is based on the active surface exposed during the photocatalytic process [24, 36]. Higher degradation percentages were obtained for the TiO_2B -LDH sample, attributed to the methodology used in preparing the composite, which effectively reduces agglomeration and at the same time minimizes the screening phenomenon of the photocatalyst during UV irradiation. This is supported by the XPS results obtained, where it can be observed that the proportion of chemical interaction



Figure 8. (a) Adsorption and (b) phenol photodegradation with TiO₂-LDH composites.

between Ti and mixed oxides (CLDH) is in direct relation to the photodegradation percentages, as observed for TiO₂T-LDH and TiO₂I-LDH, where there is a chemical interaction between Ti and the mixed oxides (CLDH), causing the impregnated Ti to be diffused to a greater degree inside the composite, with a lesser proportion to be spread over the surface [36]. The opposite can be seen in the TiO₂B-LDH sample, reflected in better photocatalytic performance.

Another possible cooperative effect between the TiO_2 mixed with LDH in the composites can be explained by the CLDH reconstruction process, since, when these are put in contact with an aqueous solution, they form highly hydroxylated species on the surface which can react with the photogenerated holes to promote •OH radical production, enabling them to attack the phenol more effectively [13].

The adsorptive capacity of the composites in general is minimal and is unrelated to the surface area of the materials; in the case of the TiO_2I -LDH sample, the percentage of phenol adsorbed is 1.5% (0.15 mg/L), in TiO_2T -LDH is 1.8% (0.18 mg/L), and in TiO_2B -LDH is 3.2% (0.32 mg/L).

Based on the results obtained, it can be assumed that, in general, phenol removal in the composites is attributed to indirect photocatalytic degradation through oxidation by •OH radicals as opposed to direct degradation by photogenerated holes due to the low adsorption rates of these materials [19].

The photocatalytic efficiency in the synthesized TiO_2 -LDH composites depends mainly on the degree of chemical interaction of the impregnated Ti, which is in direct relation to the proportion of Ti diffused into the composite and the presence of photocatalytically active phases found on the surface of the material leaving the catalyst more exposed to UV irradiation, avoiding agglomeration and the screening phenomenon.

3.3. Evaluation of the photocatalyst concentration

Figure 9 shows photocatalytic performance in terms of the concentration of the solid (0.5, 1.0, 1.5, and 2 g/L) obtained with the composites. In photocatalysts with surface areas between 50

Influence of the Synthesis Method on the Preparation Composites Derived... 297 http://dx.doi.org/10.5772/intechopen.72279



Figure 9. Composite concentration effect at photocatalytic yields.

and 200 m²/g, the optimal concentration was found in the 0.5 to 3.0 g/L range depending on the chemical characteristics and techniques of the irradiation system [19].

High or low dosages of the photocatalyst may lead to a decrease in the reaction rate, so it is advisable to use the concentration of the photocatalyst near the point where its steady state is reached, i.e., the optimal concentration will correspond to the minimum quantity for which the maximum reaction is obtained, which is the highest proportion of material that remains exposed during radiation [19]. For all the composites, this state is observed at a concentration of 1 g/L where the highest performance is reached. In all the samples analyzed, it is observed that in quantities of 0.5 g/L a limiting effect occurs between the number of photocatalytic sites available for the reaction and the amount of phenol to degrade resulting in lower degradation rates [42]. When increasing the concentration of the photocatalyst, the radiation screening and dispersal phenomena—due to turbidity by the particles in suspension—gradually start to become significant, preventing the complete illumination of the solid due to the filtering effect of the excess particles, which mask part of the photosensitive surface. In addition, a bigger amount of the photocatalyst can lead to the deactivation of active molecules by particle collision [19], as observed in the composites on increasing the concentration to 2 g/L.

3.4. Phenol photodegradation in cycles with TiO₂-LDH composites

One advantage of using TiO_2 composites is their easy recovery and reuse over several degradation cycles [43]. The results obtained on reusing a single solid from the synthesized composites over four rounds are shown in **Figure 10**, indicating the percentage of photodegraded phenol in each cycle. This behavior is favorable for the composites, since they can be reused, thereby demonstrating the synergy between mixed oxides derived from CLDH and TiO_2 , which, once they form the composite, cannot be separated and are therefore reusable.



Figure 10. Phenol photodegradation using reutilized composites.

The results show that the photocatalytic capacity of the materials is maintained without further decreasing the degradation performance. The decline of photocatalytic activity in successive photodegradation cycles, in general, is not significant and is attributed to the gradual deactivation of the catalyst in the composites and, to a lesser extent, the minimum quantity of solid lost after the aliquot is taken and that cannot be recovered at the end of the irradiation cycle [19].

4. Conclusions

TiO₂-LDH composites were prepared from TiO₂ using three different methodologies, and LDHs were obtained by sol-gel synthesis, which are combined following different procedures. The different methodologies used to prepare the photocatalysts and the composites influence the photocatalytic activity of the materials, giving them different characteristics, being the most significant generation of mixed crystalline phases of TiO₂ with photocatalytic properties (anatase and rutile) in a ratio close to that reported as adequate (\approx 80:20%), the absence of TiO₂ phases without photocatalytic properties, and the particle size (between 15 and 50 nm), which allows an optimal balance between the production and recombination of photogenerated electron-hole pairs. The TiO,B precursor was the photocatalyst whose characteristics were closest to those described to promote greater photocatalytic activity. The composites originate distinct forms of interaction between the components affecting their photoactivity. Based on the characterization results in the TiO,T-LDH and TiO,I-LDH composites, a bigger chemical interaction and larger crystals are observed, which indicates the degree of diffusion of TiO, inside the composite. Meanwhile, in the TiO,B-LDH sample, the components remain segregated, with less chemical interaction, at the same time allowing minimal agglomeration and screening of the photocatalyst enhancing the photocatalytic mechanism. For the composites obtained, phenol elimination is attributed mainly to the degradation process through oxidation reactions produced by the formation of •OH radicals, finding a minimal adsorptive capacity in the materials. In the analysis of the different concentrations of material, a dosage of 1 g/L was the most efficient, exposing the maximum amount of the composite to UV irradiation. In addition, the composites can be separated after use in the aqueous solution, allowing them to be reused with minimal loss of photocatalytic activity between each cycle.

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References

- Busca G, Berardinelli S, Resini C, Arrighi L. Technologies for the removal of phenol from fluid streams: A short review of recent developments. Journal of Hazardous Materials. 2008;160:265-288
- [2] Anwar DI, Mulyadi D. Synthesis of Fe-TiO₂ composite as a photocatalyst for degradation of methylene blue. Procedia Chemistry. 2015;17:49-54
- [3] Ba-Abbad MM, Kadhum AAH, Mohamad AB, Takriff M, Sopian K. Photochemical oxidation of concentrated chlorophenols under direct solar radiation. International Journal of Electrochemical Science. 2012;7:4871-4888
- [4] Bouberka Z, Benabbou KA, Khenifi A, Maschke U. Degradation by irradiation of an acid orange 7 on colloidal TiO₂/(LDHs). Journal of Photochemistry and Photobiology A: Chemistry. 2014;275:21-29
- [5] Lin SH, Chiou CH, Chang CK, Juang RS. Photocatalytic degradation of phenol on different phases of TiO₂ particles in aqueous suspensions under UV irradiation. Journal of Environmental Management. 2011;92:3098-3104
- [6] Hoffmann MR, Martin ST, Choi W, Bahnemann DW. Environmental applications of semiconductor Photocatalysis. Chemical Reviews. 1995;95:69-96
- [7] Linsebigler AL, Guangquan L, Yates JT. Photocatalysis on TiO₂ surfaces: Principles, mechanisms, and selected results. Chemical Reviews. 1995;95:735-758
- [8] Yuangpho N, Le STT, Treerujiraphapong T, Khanitchaidecha W, Nakaruk A. Enhanced photocatalytic performance of TiO₂ particles via effect of anatase–rutile ratio. Physica E. 2015;67:18-22
- [9] Zhou W, Pan K, Qu Y, Sun F, Tian C, Ren Z, Tian G, Photodegradation HF. Of organic contamination in wastewaters by bonding TiO₂/single-walled carbon nanotube composites with enhanced photocatalytic activity. Chemosphere. 2010;81:555-561
- [10] Chong M, Vimonses V, Lei S, Jin B, Chow C, Saint C. Synthesis and characterization of novel titania impregnated kaolinite nano-photocatalyst. Microporous and Mesoporous Materials. 2009;117:233-242
- [11] Vaccari A. Clays and catalysis: A promising future. Applied Clay Science. 1999:161-198
- [12] Huang Z, Wua P, Lu Y, Wang X, Zhu N, Dang. Z. Enhancement of photocatalytic degradation of dimethyl phthalate with nano-TiO₂ immobilized onto hydrophobic layered double hydroxides: A mechanism study. Journal of Hazardous Materials. 2013;**246-247**: 70-78
- [13] Paredes SP, Valenzuela MA, Fetter G, Flores SO. TiO₂/MgAl layered double hidroxides mechanical mixtures as efficient photocatalyst in phenol degradation. Journal of physics and Chemistry of solids. 2011;72:914-991

- [14] Contreras-Ruiz J, Martínez-Gallegos S, Ordoñez E. Surface fractal dimension of composites TiO₂-hydrotalcite. Materials Characterization. 2016;**121**:17-22
- [15] Contreras-Ruiz J, Martinez-Gallegos S, Ordoñez-Regil E, Gonzalez-Juarez J, Garcia-Rivas J. Synthesis of hydroxide–TiO2 compounds with photocatalytic activity for degradation of phenol. Journal of Electronic Materials. 2017;46(3):1658-1668
- [16] Araña J, Peña A, Doña J, Colón G, Navio J, Pérez J. FTIR study of photocatalytic degradation of 2-propanol in gas phase with different TiO₂ catalysts. Applied Catalysis B: Environmental. 2009;89:204-213
- [17] Valente J, Lima E, Toledo-Antonio J, Cortes-Jacome M, Lartundo-Rojas L, Montiel M, Prince J. Comprehending the thermal decomposition and reconstruction process of solgel MgAl layered double hydroxides. Journal of Physical Chemistry C. 2010;114:2089-2099
- [18] González-Juárez JC, Jiménez-Becerril J, Carrasco-Abrego H. Influence of pH on the degradation 4-chlorophenol by gamma radiocatalysis using SiO₂, Al₂O₃ and TiO₂. Journal of Radioanalytical and Nuclear Chemistry. 2008;275(2):257-260
- [19] Kish H. On the problem of comparing rates or apparent quantum yields in heterogeneous photocatalysis. Angewandte Chemie International Edition. 2010;49:9588-9589
- [20] Spurr RA, Myers H. Quantitative analysis of anatase rutile mixtures with an X-ray diffractometer. Analytical Chemistry. 1957;29:760-762
- [21] Mendoza-Damián G, Tzompantzi F, Mantilla A, Barrera A, Lartundo-Rojas L. Photocatalytic degradation of 2,4-dichlorophenol with MgAlTi mixedoxides catalysts obtained from layered double hydroxides. Journal of Hazardous Materials. 2013;263:67-72
- [22] Li B, Yuan SL. Synthesis, characterization, and evaluation of TiMgAlCu mixed oxides as novel SO_x removal catalysts. Ceramics International. 2014;40:11559-11566
- [23] Tzompantzi F, Mendoza-Damián G, Rico JL, Mantilla A. Enhanced photoactivity for the phenol mineralization on ZnAlLa mixed oxides prepared from calcined LDHs. Catalysis Today. 2014;56:220-222. 56-60
- [24] Seftel EM, Niarchos M, Mitropoulos CMM, Vansant EF, Cool P. Photocatalytic removal of phenol and methylene-blue in aqueous media using TiO₂@LDH clay nanocomposites. Catalysis Today. 2015;252:120-127
- [25] Petrović VV, Obradović S, Žorić A, Milošević H. Influence of synthesis parameters on electrical properties of sistems MgO-TiO₂. Contemporary Materials. II. 2011:51-54
- [26] West AR. Solid State Chemistry and its Application. New York: Wiley; 1984
- [27] Liu S, Yu J, Jaroniec M. Anatase TiO₂ with dominant high-energy {001} facets: Synthesis, properties, and applications. Chemistry of Materials. 2011;23:4085-4093
- [28] Othman MR, Helwani Z, Martunus WJN. Fernando, synthetic hydrotalcites from different routes and their application as catalysts and gas adsorbents: A review. Applied Organometallic Chemistry. 2009;23:335-346

- [29] Chubar N, Gerda V, Megantari O, Micušik M, Omastova M, Heister K, Man P, Fraissard J. Applications versus properties of mg–al layered double hydroxides provided by their syntheses methods: Alkoxide and alkoxide-frsol–gel syntheses and hydrothermal precipitation. Chemical Engineering Journal. 2013;234:284-299
- [30] Jacome-Acatitla G, Tzompantzi F, Lopez-Gonzalez R, Garcia-Mendoza C, Alvaroa JM, Gomez R. Photodegradation of sodium naproxen and oxytetracycline hydrochloride in aqueous medium using as photocatalysts mg-al calcined hydrotalcites. Journal of Photochemistry and Photobiology A: Chemistry. 2014;277:82-89
- [31] Peng F, Cai L, Huang L, Yu H, Wang H. Preparation of nitrogen-doped titanium dioxide with visible-light photocatalytic activity using a facile hydrothermal method. Journal of Physics and Chemistry of Solids. 2008;69(7):1657-1664
- [32] Leprince-Wang Y. Study of the growth morphology of TiO₂ thin films by AFM and TEM. Surface and Coatings Technology. 2001;140:155-160
- [33] Cedillo-Gonzalez EI, Montorsi M, Mugoni C, Montorsi M, Siligardi C. Improvement of the adhesion between TiO₂ nanofilm and glass substrate by roughness modifications. Physics Procedia. 2013;40:19-29
- [34] Naumkin AV, Kraut-Vass A, Gaarenstroom SW, Powell CJ. NIST X-ray Photoelectron Spectroscopy Database NIST Standard Reference Database 20, Version 4.1 febrero 2016. [Online]. Available: http://srdata.nist.gov/. [Accessed: 2016]
- [35] Kim LH, Kim K, Park S, Jeong YJ, Kim H, Chung DS, Kim SH, Park CE, Al₂O₃/TiO₂ nanolaminate thin film encapsulation for organic thin film transistors via plasma-enhanced atomic layer deposition. ACS Applied Materials & Interfaces. 2014;6:6731-6738
- [36] Seftel EM, Mertens M, Cool P. The influence of the Ti⁴⁺ location on the formation of selfassembled nanocomposite systems based on TiO₂ and Mg/Al-LDHs with photocatalytic properties. Applied Catalysis B: Environmental. 2013. 134-135. 274-285
- [37] Prince J, Tzompantzi F, Mendoza-Damián G, Hernández-Beltrán F, Valente JS. Photocatalytic degradation of phenol by semiconducting mixed oxides derived from Zn(Ga)al layered double hydroxides. Applied Catalysis B: Environmental. 2015;163:352-360
- [38] Pino E, Encinas MV. Photocatalytic degradation of chlorophenols on TiO₂-325 mesh and TiO₂-P25. An extended kinetic study of photodegradation under competitive conditions. Journal of Photochemistry and Photobiology A: Chemistry. 2012;**242**:20-27
- [39] Ahmad A, Hameed G, Aziz S. Syntesis and applications of TiO₂ nanoparticles. Engineering Advances. 2007;1:403-413
- [40] Bayal N, Jeevanandam P. Synthesis of TiO₂_MgO mixed metal oxide nano particles via a sol_gel method and studies on their optical properties. Ceramics International. 2014;40:15463-15477

- [41] Mantilla A, Jacome-Acatitla G, Morales-Mendoza G, Tzompantzi F, Gomez R. Degradation of 4-chlorophenol and p-cresol using MgAl hydrotalcite. Industrial & Engineering Chemistry Research. 2011;**50**:2762-2767
- [42] Shaban YS, El Sayed MA, El Maradny AA, Al Farawati RK, Al Zobidi MI. Photocatalytic degradation of phenol in natural seawater using visible light active carbon modified (CM)-n-TiO₂ nanoparticles under UV light and natural sunlight illuminations. Chemosphere. 2013;91:307-313
- [43] Bai X, Zhang X, Hua Z, Ma W, Dai Z, Huang X, Gu H. Uniformly distributed anatase TiO₂ nanoparticles on graphene: Synthesis, characterization, and photocatalytic application. Journal of Alloys and Compounds. 2014;599:10-18

TiO₂-Low Band Gap Semiconductor Heterostructures for Water Treatment Using Sunlight-Driven Photocatalysis

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Additional information is available at the end of the chapter

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Abstract

Heterogeneous photocatalysis is a promising advanced oxidation process for water purification, given its potential to fully oxidize organic pollutants and to inactivate microorganisms. Due to its versatility and high performance in a broad range of conditions, titanium dioxide (TiO2)-based photocatalysis has been systematically used at laboratory scale to treat water of different quality. Even though TiO, is an exceptional photocatalyst, its broad band gap value (3.2 eV) makes necessary the use of UV light to achieve the photoactivation. This results in the underutilization of the material in sunlight-driven photocatalysis schemes. In order to overcome this handicap, the synthesis of heterostructures using low band gap semiconductors coupled with TiO, has brought exceptional materials for visible light-driven photocatalysis. In this chapter, the fundamentals of the synthesis and photoactivation of TiO₂-low band gap semiconductor heterostructures are explored. The mechanisms leading to the increase of the photocatalytic activity of such heterostructures are described. A summary of the available data on the photocatalytic performance of TiO₂-based heterostructures is presented, in terms of degradation of organic pollutants in water using visible light and sunlight. A comparison of the depuration performance of powdered and thin film heterostructures is given at the end of the chapter.

Keywords: composites, heterojunctions, metallic oxides, organic pollutants, semiconductors, water treatment

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1. Introduction

Water and wastewater treatment brings new challenges due to the occurrence of new and refractory contaminants produced by anthropogenic activities [1, 2]. In the past few years, water depuration aimed to remove particles, the bulk of organic matter and inactivate microorganisms. However, nowadays, the degradation not only of organic pollutants at trace levels but its precursors and by-products is especially pursued in drinking water treatment systems. For instance, the biological and chemical degradation of fluoroquinolone antibiotics results in the generation of some by-products displaying antibiotic residual activity. Biological and abiotic degradation of personal care products, such as triclosan and triclocarban, leads to the emergence of polychlorinated biphenyls and dioxins. Some bacterial residues in surface water bodies, such as microcystin and geosmin, may impact in the organoleptic properties of drinking water as well as express toxicity, while some iodinated pharmaceuticals may be precursors of trihalomethanes. Under this scenario, the most advanced water treatment systems should aim to completely mineralize the organic pollutants, in order to take the risks of water contamination to the minimum. The complete mineralization of organic pollutants can be warranted by few processes, such as photocatalysis [3–7]. This process is based on the generation of highly reactive 'OH radicals, which are able to fully oxidize organic molecules. Heterogeneous photocatalysis process has shown to be efficient in the degradation of organic pollutants in water, avoiding the transport and use of potentially hazardous materials, such as acids or H₂O₂, while the catalyst can be recovered and reused in several cycles [8, 9].

TiO₂ is a widely used semiconductor in heterogeneous photocatalysis due to its high activity and stability [10–12]. This harmless material is currently used not only for water treatment but in food preparation and disinfection of surgical equipment. Anatase is the most photoactive phase of TiO₂, followed by rutile; however, the wide band gap value of both phases (3.0–3.2 eV) results in the activation of these materials under UV-A light irradiation [13]. In order to take the photocatalysis process toward sustainability, it is necessary to develop materials with high photo-response under sunlight irradiation. Given that sunlight comprises only 4–5% of UV-A light, the need to find nanostructures capable to absorb visible light-which composes 50% of the sunlight spectrum [14]-becomes imperative. A growing number of modifications of TiO₂ at nanometric scale have been performed in order to achieve the complete photoactivation of this semiconductor under visible light irradiation. Doping with nonmetal atoms has given partially positive results, since the redshift of the absorption edge of TiO, increases in turn the recombination rate of the hole-electron pair. The development of heterostructures based on TiO, coupled to low band gap semiconductors could be an efficient approach to improve the photocatalytic conversion of contaminants in water [12, 15, 16]. This chapter explores the fundamentals of the synthesis and photoactivation of the TiO₂-low band gap semiconductor heterostructures, and presents some of the reported data on the photocatalytic activity of these materials, in order to bring light on their potential use for water purification at a higher scale.

2. Fundamentals on the formation and photoexcitation of TiO₂-based heterostructures

A heterostructure or junction is defined as the interfacial union of two or more components. In photocatalysis, heterounions are formed to improve the efficiency of a semiconductor either by redshifting the light absorption or through the decrease of the recombination of the hole-electron pairs [12, 17, 18]. Heterostructures are commonly built up by combining a specific semiconductor with one or more materials, such as metals, semiconductors or organic molecules for example, azo dyes or polymers.

Semiconductor/metal junctions are heterostructures based on the deposition of metallic nanoparticles on crystalline semiconductors. Such union is able to hinder the electron/hole recombination through the sequestration of the photoelectrons from the conduction band of the semiconductor to the surface of the metallic nanoparticles [12] (Figure 1). The differences in the Fermi level reached in the semiconductor/metal junction triggers the sequestration of photoelectrons; although other factors, such as the higher work function and electronegativity of the metal, favor the transference of the charge carriers [16, 19, 20]. The defects created in the semiconductor/conductor junction are proposed as the main route of the electron transfer from one material to the other. The Schottky barrier created in the junction impedes the return of the charge carriers to the conduction band of the semiconductor. Typically, low loadings of metallic nanoparticles tend to be the optimal for achieving the highest potential of the electron trap process. However, when this optimal loading is surpassed, the electron traps are converted into charge carriers recombination sites, leading to the dramatic drop of the photocatalytic performance [21–23]. Even when the electron trap effect is unable to significantly redshift the light absorption of the heterostructure, some photocatalytic activity can be achieved by the surface plasmon resonance (SPR) effect, which is expressed by the oscillation of the electrons in the conduction band of the metallic nanoparticles when electromagnetic excitation at a determined wavelength is provided [24–26]. Some extent of photocatalytic activity has been attributed to SPR effect, although this cannot be considered as determinant in the photodegradation of pollutants in water when compared with that achieved under UV light irradiation.



Figure 1. Photoactivation and charge carriers transfer in a semiconductor/conductor heterounion.

The synthesis of semiconductor/semiconductor nanocomposites provides an efficient way to redshift the photoactivation of TiO_2 -based materials. When these materials are exposed to visible light, the low band gap semiconductor is activated, producing the hole–electron pair. Then, the photoelectrons migrate from the surface of the low band gap semiconductor to the conduction band of TiO_2 , as an effect of the difference in the redox potential between both semiconductors (**Figure 2**). The process leads to the drop of the hole-electron pair recombination rate, resulting in the oxidation process in the low band gap semiconductor, and the reduction process on the TiO₂ surface [17, 27].

When the composite is photoactivated under UV light irradiation, the hole-electron pairs are produced in the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of each semiconductor. Charge carriers are then transported and accumulated in the HOMO and LUMO of one of the semiconductors, as a function of gradient in the potential of the bands (**Figure 3**). For this kind of schemes, p-n heterostructures have shown the best results in the separation of the photo-formed charge carriers. However, in some cases, decreasing of the redox potential of charge carriers can occur, depending of



Figure 2. Photoactivation and charge carriers transfer in a TiO_2 -low band gap semiconductor heterounion when photoactivation with visible light occurs.



Figure 3. Photoactivation and charge carriers transfer in a TiO_2 -low band gap semiconductor heterounion when photoactivation with UV light occurs.
the HOMO and LUMO positions of the semiconductors in the heterostructure, leading to the decrement in the photocatalytic performance [15, 17, 18].

In some advanced approaches, metallic nanoparticles are settled in the heterounion of the two semiconductors. Noble metal nanoparticles can act as electron mediators, transporting the charge carriers from one semiconductor to another, increasing with this the electron trap effect. Heterostructures based on p-n semiconductors have shown a notable increase in the charge separation when noble metal nanoparticles are added in the semiconductor heterounion. These materials, known as all solid-state Z schemes, provide highly reductive photoelectrons and highly oxidative photo-holes by the process shown in **Figure 4** [28].

Photoelectrons are transported from semiconductor II to semiconductor I via the metallic nanoparticles. At the same time, photoelectrons are formed in semiconductor I and photoholes in the HOMO of semiconductor I are recombined with photoelectrons coming from the LUMO of semiconductor II. This kind of schemes impedes the recombination of the charge carriers with the highest oxidative and reductive potential, increasing not only the photocatalytic performance of the components, but bringing chances to photodegrade more recalcitrant pollutants because of the increment of the oxidative potential of the charge carriers.

When TiO_2 nanoparticles are deposited on graphene sheets, the semiconductor/polymer junction displays higher photocatalytic activity due to the transfer of the charge carriers from the semiconductor to the polymer, as shown in **Figure 5b**. Even when the lifetime of the charge carriers is increased, visible light-driven activity is not improved; however, graphene materials can be used as an excellent electron mediator in all solid Z schemes. On the other hand, organic molecules, which are able generate the triplet state under visible light irradiation, can act as sensitizers when deposited on the TiO_2 surface (**Figure 5a**). In this case, electrons are injected from the sensitized molecule to the LUMO of the semiconductor, triggering the photocatalytic process [29].

2.1. Classification of the semiconductors/semiconductor heterostructures

Semiconductor/semiconductor junctions can be classified depending on either the type of semiconductors that are being coupled or by the band structure they present. Considering the type of semiconductors, the semiconductor/semiconductor heterostructures can be classified



Figure 4. Photoactivation and charge carriers transfer in a TiO_2 based all solid Z scheme when photoactivation when UV light activation occurs.

either as anisotype—a p-n junction—, or isotype heterojunctions, in which both coupled semiconductors are n-type (n-n junction) or p-type (p–p junction). Some examples of n-type semiconductors include TiO_2 , WO_3 , ZnO, Fe₂O₃, CeO_2 , AgI, BiVO₄, CdS, CdSe, Bi₂WO₆, and ZnSe, while for p-type semiconductors Bi₂O₃, V₂O₅, BiOI, BiOBr, BiOCl, CuO, Cu₂O can be mentioned [18]. When semiconductor/semiconductor heterostructures are classified depending on the band position of the components, three main groups can be mentioned. **Figure 6** shows the three possible band alignments in semiconductor/semiconductor heterostructures.

In a type I heterostructure, also known as straddling alignment, the band gap value of the semiconductor B is smaller than that of semiconductor A (**Figure 6**). In this case, the potential of valence band of the semiconductor B is located at a higher position than that of semiconductor A, while conduction band of semiconductor A displays a lower potential than that of the conduction band of semiconductor B. In this scheme, electrons and holes are transferred from A to B, resulting in the accumulation of charge carriers in B [18]; this facilitates in turn the recombination of the charge carriers and decreases the photocatalytic activity. Obregon et al. [30] reported the formation of a type I heterojunction using monoclinic BiVO₄ and TiO₂. The 1 wt. % m-BiVO₄/TiO₂ nanocomposite was prepared by a simple impregnation method and was tested in the degradation of phenol. This system has been tested by other authors using different approaches and modification [31–33]. Other semiconductors that have been coupled to TiO₂ to form a type I heterojunction [18] are WO₃ [34, 35], Fe₂O₃ [36], MoS₂ [37] and BiOI [36].



Figure 5. Photoactivation and charge carriers transfer in a TiO₂-sensitized materials under visible light activation (a) and in TiO₂-graphene heterostructures when UV light occurs (b).



Figure 6. Classification of semiconductor/semiconductor heterostructures based on the band alignment of the components.

Type II heterostructure, or staggered lineup, represents the most efficient configuration for the charge carriers transfer. In this case, photo-generated electrons will be transferred from semiconductor B to semiconductor A, while the holes are moving from semiconductor A to semiconductor B. A more efficient charge separation is achieved, having both photoelectrons and photo-holes distributed in the two semiconductors. A large number of type II heterojunctions have been synthesized with TiO_2 , by the union with CdS [38], CdSe [39, 40], Bi₂S₃ [41], WS₂ [42], V₂O₅ [43], Bi₂O₃ [44], CuO [45], Cu₂O [45, 46], and CeO₂ [47].

Type III heterojunctions are similar in structure to the type II composites, but a wider difference in the position of bands between semiconductor A and B is observed. This type of heterojunctions is also known as broke-gap junction, which is highly recommended to the construction of all solid Z schemes. For instance, Heng et al. [48] prepared a type III heterojunction by incorporating $H_3PW_{12}O_{40'}$ TiO₂ and In_2S_3 . The authors propose that the $H_3PW_{12}O_{40}$ assists in the transfer of electronics from TiO₂ to In_2S_3 .

3. Synthesis methods to obtain TiO₂-based heterostructures

A wide variety of physical and chemical methods have been developed for the synthesis of TiO_2 based heterostructures, using a vast diversity of structures and morphologies. Some examples of such methods are sol-gel, solvothermal, impregnation, sputtering, dip-coating, co-precipitation, mechanical synthesis and chemical vapor deposition, among others. In many cases, a combination of two or more synthetic methods and reaction steps are needed in order to create a specific photocatalyst with the desired characteristics. The use of photocatalyst powders for water purification has been of great interest. This is because of the simplicity in the synthesis, the high exposition of the particle surface area to the target pollutants, as well as the high dispersion of the catalyst. In this section, some of the most used methods for the synthesis of TiO_2 -based heterostructures are explored.

Sol-gel: The sol-gel method consists of the acidic or basic hydrolysis of an organometallic precursor, followed by a slow polymerization. The obtained material is dried, allowing the decomposition and elimination of all the organic components present in the gel.

 WO_3/TiO_2 nanocomposites have been synthesized by the sol-gel method using $Ti(OBu_4)$ and ammonium tungstate as main precursors [35, 49]. The photocatalytic activity of the material was tested via the degradation of malathion using natural sunlight. The complete degradation of the pollutant was achieved after a 2 h irradiation and a mineralization rate of 63% upon 5 h. Yang et al. [47] reported the synthesis of different CeO₂/TiO₂ heterostructures by the sol-gel synthetic route, using Ti(OBu)₄ and Ce(NO₃)₃·6H₂O as precursors. The synthesized materials were tested for the degradation of methyl orange, noting the enhanced activity of the CeO₂/TiO₂ composite compared with unmodified TiO₂ and CeO₂.

Hydrothermal/solvothermal method: The solvothermal method allows the synthesis of crystalline materials by heating the precursors in solution inside a sealed reactor (autoclave). Water (hydrothermal) and several organic compounds such as ethylene glycol and glycerol (solvothermal) may be used as solvent during the reaction. The solvothermal method is one of the most common preparation techniques for heterostructures, since the variation of pressure and temperature parameters allows the formation of a wide diversity of crystal morphologies. The

products obtained are usually well dispersed in form and size. Also, some additives and templates may be added into de reaction mixture to favor a desired morphology or crystallite size. Xu et al. [50] synthesized a rutile/anatase TiO, heterostructure using titanium tetrachloride (TiCl₄), urea and cetyl trimethyl ammoniumbromide (CTAB) as a template. Reaction was carried out at 160°C for 12 h, resulting in rutile/anatase nanoflowers with high surface area -up to $106.29 \text{ m}^2/\text{g}$ – . CdS/TiO, composites were synthesized by Wu et al. [27] via the microemulsionmediated solvothermal method, allowing the formation of anatase nanoparticles with highly dispersed CdS nanocrystals on the surface. The modification of TiO, with CdS nanoparticles increased the absorption of visible light irradiation at 550 nm. Zhu et al. [51] prepared $Bi_2O_3/$ TiO₂ flower-like spheres, which displayed high photocatalytic activity due to an enhanced visible light absorption. TiO,@MoO, core@shell structures were synthesized by Li et al. [52] using a one-step hydrothermal method, while Liu et al. [53] used this method to achieve the formation of a series of Cu₂O@TiO₂ core@shell structures by coating different Cu₂O polyhedral nanoparticles on the TiO, surface. Cu,O/TiO, hollow spheres (HS) were synthesized by both solvothermal and sol-gel methods [54]. In a first step, TiO, HS were synthesized by a sol-gel method, using carbon nanospheres as a template. In the second step, the HS were mixed with a glucose solution, containing CuSO₄·5H₂O; then, the mixture was poured into a teflon-lined stainlesssteel autoclave. In this reaction, glucose took the role of reducing agent, which helped to reduce copper from Cu^{2+} to Cu^{1+} . These heterostructures were tested for the photocatalytic degradation of Rhodamine B under visible and sunlight irradiation, showing promising results.

Impregnation: This method consists of the saturation of one specific support—in this case TiO_2 —with a solution containing the desired precursor, usually a metal salt; this allows the metal ions to fill the support pores. Then, the material is dried and exposed to a thermal treatment.

Perales-Martínez et al. [55] reported the formation of the $InVO_4/TiO_2$ catalyst. In a first step, both $InVO_4$ and TiO_2 were prepared using the solvothermal method. Then, the composite was formed by suspending both oxides in methanol in order to achieve the impregnation assisted by ultrasonication. Lastly, the solvent was evaporated using a rotary evaporator. In another work, Maeda et al. [56] reported the formation of cobalt oxide nanoparticles supported on the surface of rutile TiO_2 (Co_3O_4/TiO_2 heterostructure). In this case, TiO_2 was impregnated with the $Co(NO_3)_2.6H_2O$ solution, followed by a thermal treatment in air atmosphere. Fe₂O₃/TiO₂ photocatalyst was prepared using a Fe(NO_3)₃.9H₂O ethanol solution, where TiO_2 powders were stirred and sonicated [57]. Peng et al. [58] reported that after calcination at 300°C for 6 h, the Fe₂O₃ was deposited on the surface of TiO_2 nanorods. In other report, the preparation of RuO₂/TiO₂ heterostructures was achieved by Uddin et al. [59] using ruthenium(III) pentan-2,4-dionate as RuO₂ precursor.

UV light irradiation: This method consists of the reduction and precipitation of one or more soluble precursors over the surface of $\text{TiO}_{2'}$ which acts as a support. The presence of UV light irradiation allows the photo-formation of electrons in the support, which are responsible of reducing the chemical species in the solution.

 MoS_2/TiO_2 and WS_2/TiO_2 have been synthesized by the photo-reduction of either $(NH_4)_2MoS_4$ or $(NH_4)_2WS_4$, directly on the surface TiO_2 particles [42]. These materials showed good efficiency in the degradation of methylene blue and 4-chlorophenol.

Electrosynthesis: The electrosynthesis method consists of the use of electrochemical cells to produce the desired material. Yang et al. [39] achieved the electrodeposition of CdSe nanoparticles on the surface and the inner space of TiO₂ nanotubes (TNTs). For this, three electrodes were used, namely a Pt wire (counter electrode), a saturated calomel electrode (reference electrode) and the TNTs (working electrode). The three electrodes were submerged in an electrolyte solution containing CdCl₂ and SeO₂. CdSe was deposited at -0.7 V, -6 V vs. reference electrode at room temperature. Well-dispersed CdSe nanoparticles deposited on TiO₂ were obtained.

Mechanical mixing: This is one of the simplest synthesis methods, which involves the direct mixing of the heterostructure precursors. Manual mixing usually results in long reaction times and low homogeneity of the products. In certain cases, binding agents may be added to the mixture in order to increase the stability of the heterostructure.

Shifu et al. [60] prepared the WO_3/TiO_2 heterostructure using the mechanical mixing method. The precise amounts of TiO_2 and WO_3 powders were mixed in an agate ball milling tank. The two oxides were mixed for 12 h at 300 rpm. A loading of 3% wt. of WO_3 presented the best efficiency for the degradation of monocrotophos. The coupled photocatalyst showed a redshift in its light absorption compared to pure TiO₂.

Precipitation and co-precipitation: Both precipitation and co-precipitation methods consist of the formation of an insoluble material, starting from one or several solutions containing the soluble precursors. Usually, an increase in the pH value of the solution helps in the formation of insoluble hydroxides, allowing the precipitation. Yu et al. [61] prepared an Ag/AgCl/TiO₂ heterostructure by the impregnation of TNTs with a 1 M HCl aqueous solution, followed by a second impregnation with a 0.1 M AgNO₃ solution. As a result, AgCl nanoparticles were precipitated on the TNTs. Lastly, UV irradiation was applied to achieve a partial reduction of the formed AgCl nanoparticles into metallic Ag.

Thin films: One of the main burdens of using powder photocatalysts is the need of including a separation step for the effluent in order to reuse the photocatalyst in further cycles. This step can become difficult and very expensive, making the photocatalytic process less viable in a plant scale approach. A feasible solution is the immobilization of the material in a suitable support, such as glass, quartz or polymer. Some synthetic routes for obtaining photocatalysts as thin films are described below.

Dip-coating: This is one of the most used methods for the synthesis of thin films, which consists of submerging, at a constant rate, the substrate in a solution containing the precursor of the semiconductor. After a certain dwell time, the substrate is pulled out of the solution. Lastly, the solvent is dried, and a thermal treatment can be applied to eliminate organic residuals and induce crystallization of the semiconductor in the film.

Spin Coating: This process consists of putting a small amount of a solution containing the precursor of the thin film material on the surface of the substrate. Then, the substrate is rotated at high speed, eliminating the excess solution and leaving a uniform film once the solvent is dried.

Sputtering: In this route, ionized atoms (e.g., Ar⁺) are accelerated into the surface of a cathodic material. This collision causes that some atoms are ejected from the surface of the electrode.

Subsequently, the ejected atoms are condensed on the surface of the substrate (anode), forming the thin film.

Chemical vapor deposition: This method uses volatile precursors at high temperature. The gaseous species react forming intermediates which are diffused and adsorbed on the surface of the substrate. Further reactions can take place on the surface on the substrate.

4. Photocatalytic activity of TiO₂-based heterostructures under visible and simulated sunlight

The coupling of TiO₂ with low band gap semiconductors leads to the activation of the photocatalyst material under visible light irradiation, as established earlier, resulting in turn in the generation of materials with high efficiency and stability. An important number of studies have reported the photocatalytic performance of these heterostructures, showing high conversion rates of organic and inorganic pollutants in water. Some of these results are shown in Table 1. As observed in the table, conversion of azo dyes molecules is the most used way to assess the photocatalytic activity of the synthesized materials. This is due to the easy analytical determination of such molecules in water—most of them for UV–vis spectroscopy—in comparison with uncolored molecules-such as phenols-organochlorinated compounds and pharmaceutical substances. However, as was recently pointed out, using azo dyes molecules in the evaluation of the photocatalytic performance of semiconductors may result in an artifact because of the sensitization of the semiconductors by the adsorbed organic molecules [62]. It is worth noting how the degradation rate constant is mostly determined using the pseudo first-order approach, forgetting the multiple phase conditions. In very few studies, other models-such as the Langmuir-Hinshelwood approximation-have been used [63]. Degradation yields is the most reported parameter in this kind of experiments. Very few studies follow the content of the total organic carbon throughout the process, ignoring with this the mineralization yield of the pollutants. This may lead to a miscalculation of the risk that treated water pose on the exposed organisms, since some of the photodegradation byproducts may be more toxic or recalcitrant than the parent compound. Examples of this are benzoquinone, which degradation requires more energy than phenol and triclosan, which degrades into a low toxicity dioxin.

In most cases reported in the literature, halogen lamps are the light sources in photocatalysis schemes, while the loading of the catalyst is maintained below 1 g/L, in order to avoid the screening of light due to the high turbidity in the suspension. Concentration of the organic pollutants is normally set at levels of mg/L, which are one to three magnitude orders higher than those observed in the environment, even in wastewater [1, 64, 65]. The use of such concentration levels enables the determination of the kinetic constants in the photocatalytic degradation of the pollutants in water. However, when experimental conditions require the use of complex liquid matrices, such as superficial water, groundwater or wastewater, the degradation rate is reduced, bringing the opportunity for lowering the initial concentration of the target compound toward environmentally relevant levels, such as μ g/L or even ng/L, with no impact in the study of the kinetic constants.

| Heterostructure components | Architecture | Pollutant removed | Reaction conditions | Performance | Reference |
|--|--------------|--|--|--|-----------|
| FeWO4/TiO2 Fe:Ti ratio = 95:5 | Composite | Salicylic acid (6.9 ppm) | 300 W Xe lamp (λ≥420 nm). 10 mg of composite were suspended in 50 mL. 120 min of irradiation time. | $k^* = 0.053 h^{-1}$ | [69] |
| FeWO ₄ /TiO ₂ /CdS Fe:Ti:Cd ratio = 5:94:1 | | | | $k^* = 0.099 h^{-1}$ | |
| 60 wt. % Cu ₂ S/TiO ₂ | | Orange II (15 ppm) | 150 W tungsten-halogen-lamp with UV cutoff filter at 475 nm. pH ~ 6.4. | $k^* \sim 6.1 \times 10^{-3} min^{-1}$ | [20] |
| Bi ₂ O ₃ /TiO ₂ Bi:Ti molar ratio = 1:100 | | <i>p</i> -chlorophenol (12.88 ppm) | 150 W xenon lamp (λ≥ 420 nm). 0.001 g mL ⁻¹ of catalyst. 6 h of irradiation time. | Degradation yield of 49% | [12] |
| TiO ₂ /Fe ₃ O ₄ (30:70) | | Cr(VI) (20 ppm of K ₂ Cr ₂ O ₇) | Mercury vapor lamp of 125 W with a broadband from 250 to 450 nm (maxima at 254, 312 and 365 nm). 30 mg of catalyst in 100 mL of solution. | Complete reduction to Cr(III) in 30 min. k = 0.91 ppm g ⁻¹ min ⁻¹ | [72] |
| Carbon-doped anatase/brookite TiO ₂ (80:20) | Composite | Methylene blue (3.2 ppm) | Solar simulator with filter for blue light. 0.06 g of powder in 100 mL solution. 60 min irradiation. | k = 0.008 min ⁻¹ | [73] |
| Rutile/anatase TiO ₂ | Nanoflowers | Methylene blue (15 ppm) | 350 W xenon lamp. 10 mg of catalyst. 120 min of irradiation time. | 72% degradation of degradation rate. | [50] |
| | | | Adding 0.5 mL of a 30% m/v $\rm H_2O_2$ solution. | ~88% of degradation rate. | |

| Heterostructure components | Architecture | Pollutant removed | Reaction conditions | Performance | Reference |
|---|--|---|--|--|-----------|
| BiVO ₄ @TiO ₂ | Core@shell | Methylene blue (5 ppm) | Osram Dulux S67 blue light Bulbs, with maximum emission at 450 nm. | ~85% of Degradation rate. | [74] |
| | | | 50 mg of the catalyst were dispersed in 150 mL. 120 min irradiation. | | |
| 5 wt. % WO ₃ /TiO ₂ | Composite | Methyl orange (20 ppm) 2,4-dichlorophenol (20 ppm) | 1000 W halogen lamp (λ > 420 nm). Catalyst loading of 1.1 g L ⁻¹ . 5 h of time irradiation. | 85% degradation 73% degradation | [34] |
| 12 wt. % Zn _x Cd _{1x} S/ TiO ₂ Cd:Zn ratio = 3:1 | Composite | Rhodamine B (4.8 ppm) | 500 W halogen lamp (420 nm $< \lambda < 800$ nm). 0.04 g of the catalyst was added to 80 mL of solution. | ~95% degradation | [75] |
| Cu_2O/TiO_2 | Cu ₂ O nanospheres decorated with TiO ₂ | Methyl Orange (30 ppm) | Lot full of nation of the control of | ~97% degradation r*≁12.825 mg g¹ min¹ | [76] |
| | nanoislands. | | 0.03 g of catalyst was dispersed in 150 mL of solution. 40 min of irradiation time. |) | |
| Cu ₂ O@TiO ₂ | Core@shell Polyhedra (cubes, cuboctahedra and octahedra) | Methylene Blue (3.2 ppm) | 300 W xenon lamp with a glass filter ($\lambda > 400$ nm). Light intensity of 23 mW cm ⁻² . | Up to 80% degradation for octahedra core-shell structure. | [53] |
| | | | Concentration to u.z. mg photocatalyst mL ⁻¹ . 4 h of irradiation time. | | |
| | | 4-Nitrophenol (10 ppm) | 0.02 g of photocatalyst was dispersed in 50 mL of solution. | Up to 50% degradation for octahedra core-shell structure. | |

| Heterostructure components | Architecture | Pollutant removed | Reaction conditions | Performance | Reference |
|---|---|---|--|--|-----------|
| Bi _z MoO ₆ /TiO ₂ Bi:Ti ratio = 1:2.6 | Nanofibers | Rhodamine B (10 ppm) | 150 W xenon lamp. 0.1 g of catalyst was suspended in 100 mL of the compound solution. 5 h of irradiation. | 92% degradation | [77] |
| 0.5 wt.% lnVO₄/TiO₂ | Composite | Phenol (30 ppm) | 300 W lamp with an intensity irradiation of 38.4 W m ⁻² . 0.05 g of catalyst dispersed in 50 mL of solution. 80 min of irradiation time | 100% of degradation rate. k ⁴ = 8.1×10 ⁻⁴ s ⁻¹ | [55] |
| $Polydopamine@TiO_2$ | Core@shell nanoparticles and brush-like structures. | Geosmin (1000 ppb) Fluorene (1000 ppb) | 350 W xenon lamp equipped with a 420 nm cutoff filter. 120 min of irradiation | 90% degradation 98% degradation | [78] |
| Bi _. O ₃ /TiO ₂ Bi:Ti ratio = 10% | Composite | Ofloxacin (25 ppm) | Solar irradiation with average light intensity of 70.3 K lux. Catalyst concentration of 0.5 g/L. 120 min of irradiation time | 92.4% degradation | [62] |
| 60 wt. % Sb ₂ S ₃ /TiO ₂ | Nanorods | p-hydroxyazobenzene (10 ppm). Methyl orange | 500 W halogen lamp with two cutoff filters (below 420 nm and above 850 nm). 40 mg of catalyst were dispersed in 80 mL. 5 h of irradiation time. | 89% of degradation rate 96% of degradation rate | [80] |
| Ag/AIO ₂ /TiO ₂ 90:10 AI:Ti mass ratio | Composite | Formaldehyde (10 ppm) | Sunlight irradiation with an intensity of 90 ± 15 mW/cm². 0.1 g of catalyst was dispersed in 100 mL of solution. 90 min of irradiation time. | 97.8% of degradation rate | [81] |

TiO₂-Low Band Gap Semiconductor Heterostructures for Water Treatment Using Sunlight... 317 http://dx.doi.org/10.5772/intechopen.76501

| Heterostructure components | Architecture | Pollutant removed | Reaction conditions | Performance | Reference |
|--|--------------------------------|---|--|---|-----------|
| Cu ₂ O/TiO ₂ | Nanotubes | Rhodamine B (5 ppm) | 500 W tungsten halogen lamp with an optical filter ($\lambda > 420$ nm). 120 min of irradiation time. | 31% of degradation rate k* = 0.00312 min⁻¹ | [82] |
| AgBr/Ag ₃ PO₄/TiO ₂ Ag:Ti molar ratio = 1:5 | Spheres | Methyl orange (8.2 ppm). | Simulated sunlight lamp with intensity of 4 W m ⁻² . 0.001 g of catalyst was dispersed in 6 mL of solution. 50 min of irradiation time. | ~90% of degradation rate k* = 0.1329 min ⁻¹ | [83] |
| | | Microcystin-LR (50 ppm) | 0.01 g of catalyst was dispersed in 30 mL of solution. | 100% of degradation after 5 min. k* = 0.6371 min ⁻¹ | |
| 7 wt. % Fe ₂ O ₃ @TiO ₂ | Core@shell | Rhodamine B (10 ppm) | 350 W xenon lamp. 5 mg of catalyst were dispersed in 50 mL of aqueous solution. 5 h of irradiation time. | 60% of degradation rate k* = 0.1605 h ⁻¹ | [84] |
| Cu ₂ 0/TiO ₂ | Octadecahedron/ Quantum Dot | Methyl orange (30 ppm) | 500 W xenon lamp with glass filter (λ > 400 nm) and intensity of 100 mW cm⁻². 25 mg of catalyst were dispersed in 100 mL of solution. 60 min of irradiation. | 97% of degradation rate k* = 0.055 min ⁻¹ | [85] |
| BiOBr/TiO ₂ molar ratio Ti:Bi = 2:1 | Nanorods | Rhodamine B (15 ppm) Cr (VI) (50 ppm K ₂ Cr ₂ O ₇ solution) | 300 W Xenon lamp with a cut-off glass filter (A > 420 nm). Illumination intensity of 7 × 10 ³ mW cm ⁻² . 70 mg of photocatalyst were dispersed in 70 mL of solution. | 99.9% of degradation after 10 min of irradiation. k = 0.49 min ⁻¹ 88.5% mineralization. 95.4% of conversion after 120 min irradiation. k = 0.025 min ⁻¹ | [86] |

| Heterostructure components | Architecture | Pollutant removed | Reaction conditions | Performance | Reference |
|--|---|---|--|---|-----------|
| Cu ₂ O/TiO ₂ | Nanoparticles/ nanotubes | p-nitrophenol (20 ppm) | Xe lamp ($\lambda > 420$ nm). with an intensity of 100 mW cm ⁻² . 210 min of irradiation. | 35-40% of degradation rate under visible light irradiation. >90% of degradation rate under sunlight irradiation. | [87] |
| Bi ₂ S ₉ /TiO ₂ | Fungus-like mesoporous Bi ₂ S ₃ / TiO ₂ nanotube | 2,4-dichlorophenoxyacetic acid (2,4-D) (10 ppm) 2,4-D and Cr(VI) (10 ppm) | Xenon lamp with a radiation intensity of 85 mW cm ⁻² . 180 min of irradiation time. | 71% degradation ~75% mineralization (after 360 min of irradiation) 81% degradation for 2,4-D Complete Cr(VI) reduction. | [41] |
| Cu ₂ O/TiO ₂ | Hollow spheres | Rhodamine B (5 ppm) | 300 W xenon lamp. 0.1 g of catalyst was dispersed in 200 mL of the compound solution. 120 min irradiation time 300 W Xenon lamp with a 420 nm cut off filter. 300 min time irradiation | ~ 88% of degradation rate. k* = 0.0165 min ⁻¹ ~ 92% of degradation rate. k* = 0.0081 min ⁻¹ | [54] |
| 1 wt. % Ag ₂ CO ₃ /TiO ₂ | Composite | Methyl orange (20 ppm) | 300 W iodine tungsten lamp. 0.05 g of catalyst was suspended in 80 mL of the compound solution. 5 h of irradiation time. | ~75% degradation k* = 0.24 min ⁻¹ | [88] |
| *Degradation rate const *Reaction rate (degrada *Kinetic constants of ph | ants approximated to the tion rate). otodegradation estimated | pseudo first-order kinetics. by the Langmuir-Hinshelwood n | nodel according to a first-order reacti | on. | |

Table 1. Degradation performance using TiO_2 -based heterostructures under different experimental conditions.

Even when for the results shown in **Table 1**, direct comparisons are difficult to be established, it seems clear that tailored heterostructures formed by TiO, and low band gap semiconductors are efficient to achieve high photocatalytic degradation yields under visible light irradiation when azo dyes are used as target pollutants. For most of the reported heterostructures, degradation yields above 80% were obtained; except for the Cu₂O/TiO₂ material, which performance was as low as 31%. On the other hand, very low photocatalytic efficiency is observed for refractory industrial pollutants, such as nitrophenols and chlorophenols. These compounds displayed degradation yields lower than 50% when Cu₂O-TiO₂ and Bi₂O₃/TiO₂ heterostructures were used in photocatalytic assays under visible light irradiation. Some environmentally relevant pollutants, which are commonly found in surface water sources, are efficiently removed by the visible light-driven photocatalysis process. A high concentration of microcystin, a toxin produced by cyanobacteria, is fully degraded in 5 min under visible light irradiation, when AgBr/Ag₄PO₄/ TiO, nanospheres are used as photocatalyst, while 90% of degradation of environmentally relevant concentrations of geosmin was achieved upon 120 min using core@shell polydopamine@ TiO₂ composites. Also, high loads of pharmaceutically active substances, bisfenol A and the widely used herbicide 2,4-D are efficiently removed from water under visible light by the TiO, based heterostructures. From these results, the use of these materials in advanced oxidation processes for ternary drinking water treatment sounds like a plausible option, keeping in mind that the high efficiency showed in these lab-scale studies can be affected by the complexity of the liquid matrix. Regarding heavy metals, the complete photocatalytic reduction of hexavalent chromium has been reported using Fe₂O₃/TiO₂ and Bi₂S₃/TiO₂ heterostructures in a very short time lapse, while BiOBr-based composites showed a slightly lower activity. For the studies reported in Table 1, the occurrence of synergistic effects was observed when the photocatalytic performance of the heterostructures and their single components was compared. For some cases, the increment in the degradation rate and degradation yields was found in the order of 1.5–5 fold, demonstrating that the efficiency of the heterostructure was significantly higher than the sum of the performance of the single components.

When the photocatalytic performance of thin films is assessed, a clear decrease in the degradation rate of organic pollutants is observed. This is because of the decrease in the number of active sites exposed to the aqueous matrix due to the immobilization of the photocatalyst on a substrate. Degradation rates as low as 30% in 15 h for of azo dyes have been reported using TiO_2 - $InVO_4$ thin films [66], although the efficiency can be improved by the deposition of noble metal nanoparticles on the film surface. Conversely, in other study [67], the complete degradation of methyl orange was achieved in 8 h of visible light irradiation by using BiOCl-TiO₂ thin films. This study reveals the importance of the charge carrier transference in the immobilized photocatalyst material. When this factor is taken into account, the reactivity of the thin film surface increases, leading to a higher photocatalytic activity and overcoming the mass transference hindrance.

In this sense, the arrangement of the heterostructure components is of high relevance since some approaches may favor the transfer of photo-holes or photoelectrons to the surface of the thin films. In this sense, Monfort et al. [68] tested the transfer of charge carriers in the $BiVO_4$ - TiO_2 heterostructure, noting the occurrence of oxidation reactions by photo-holes when $BiVO_4$ was located on the surface of the thin films, while reduction reactions given by photoelectron were prominent when TiO_2 was in contact with the aqueous matrix.

5. Conclusions

Even when TiO_2 displays an outstanding performance as photocatalyst, its limitation to absorb light and photoactivate under visible light irradiation makes necessary to develop a set of strategies to overcome this handicap. Coupling of low band gap semiconductors with TiO_2 nanoparticles is an auspicious approach not only to redshift the light absorption of the composite, but to reduce the recombination rate of the hole-electron pair by the transference of the charge carriers from one semiconductor to another, increasing the photocatalytic performance. This leads to the generation of materials with high photoactivity and stability under visible light and sunlight irradiation.

In order to obtain functional heterostructures, care must be taken in the selection of the composite components, in order to get the best alignment of the semiconductors bands and thus the optimal transference of the charge carriers from one component to the other. Type II and III heterostructures have shown the highest efficiency in the separation of the hole-electron pairs. The defects formed in the heterounion act as transference sites for the charge carriers; although it only works when tiny loadings of semiconductor particles are deposited on $TiO_{2^{\prime}}$ and recombination centers appear in the heterounion when the optimal loading is surpassed. The p-n heterostructures, specially the all solid Z schemes, have shown not only the efficient separation of the charge carriers in the composite, but the generation of highly oxidant photo-holes, which opens the opportunity to photodegrade highly recalcitrant organic pollutants in water. To date, very few TiO_2 -based Z schemes have been explored; thus, investigation should aim to develop new schemes, beyond the TiO_2 -Au-CdS approach, using nontoxic semiconductors, such as BiOI, ZnS, Ag₂O or graphene.

 TiO_2 -based heterostructures have shown a notable high performance in the photocatalytic removal of organic and inorganic pollutants in water under visible light irradiation. In some cases, removal yields surpass those observed for the individual components of the heterostructure, indicating the occurrence of a synergistic effect. New challenges are in the development of functional heterostructures in the form of thin films, which will optimize the energy and space consumption in photocatalytic water treatment systems.

The photocatalysis processes have the potential to move toward sustainability, through the development of sunlight active heterostructures, which simultaneously perform the oxidation of organic pollutants and the reduction of water molecule for hydrogen generation. This will lead to energy autonomous treatment systems based on sunlight-driven photocatalysis. Lastly, investigations should aim to the development of green synthesis methods, which optimize the energy consumption and minimize the use of harmful reagents.

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References

- [1] Richardson SD, Ternes TA. Water analysis: Emerging contaminants and current issues. Analytical Chemistry. 2014;86:2813-2848. DOI: 10.1021/ac500508t
- [2] Murray KE, Thomas SM, Bodour AA. Prioritizing research for trace pollutants and emerging contaminants in the freshwater environment. Environmental Pollution. 2010;158:3462-3471. DOI: 10.1016/j.envpol.2010.08.009
- [3] Oller I, Malato S, Sánchez-Pérez JA. Combination of advanced oxidation processes and biological treatments for wastewater decontamination–A review. Science of the Total Environment. 2011;409:4141-4166. DOI: 10.1016/j.scitotenv.2010.08.061
- [4] Andreozzi R, Vincenzo C, Insola A, Marotta R. Advanced oxidation processes (AOP) for water purification and recovery. Catalysis Today. 1999;53:51-59. DOI: 10.1016/S0920-5861(99)00102-9
- [5] Matilainen A, Sillanpää M. Removal of natural organic matter from drinking water by advanced oxidation processes. Chemosphere. 2010;80:351-365. DOI: 10.1016/j.chemosphere. 2010.04.067
- [6] Klavarioti M, Mantzavinos D, Kassinos D. Removal of residual pharmaceuticals from aqueous systems by advanced oxidation processes. Environment International. 2009;35: 402-417. DOI: 10.1016/j.envint.2008.07.009
- [7] Deng Y, Zhao R. Advanced oxidation processes (AOPs) in wastewater treatment. Current Pollution Reports. 2015;1:167-176. DOI: 10.1007/s40726-015-0015-z
- [8] Padmanaban VC, Giri Nandagopal MS, Madhangi Priyadharshini G, Maheswari N, Janani Sree G, Selvaraju N. Advanced approach for degradation of recalcitrant by nanophotocatalysis using nanocomposites and their future perspectives. International Journal of Environmental Science and Technology. 2016;13:1591-1606. DOI: 10.1007/s13762-016-1000-9
- [9] Hoffmann MR, Martin S, Choi W, Bahnemann DW. Environmental applications of semiconductor photocatalysis. Chemical Reviews. 1995;95:69-96. DOI: 10.1021/cr00033a004
- [10] Kumar SG, Rao KSRK. Comparison of modification strategies towards enhanced charge carrier separation and photocatalytic degradation activity of metal oxide semiconductors (TiO₂, WO₃ and ZnO). Applied Surface Science. 2017;**391**:124-148. DOI: 10.1016/j. apsusc.2016.07.081

- [11] Fagan R, McCormack DE, Dionysiou DD, Pillai SC. A review of solar and visible light active TiO₂ photocatalysis for treating bacteria, cyanotoxins and contaminants of emerging concern. Materials Science in Semiconductor Processing. 2016;42:2-14. DOI: 10.1016/j. mssp.2015.07.052
- [12] Linsebigler AL, Lu G, Yates JT. Photocatalysis on TiO₂ surfaces: Principles, mechanisms, and selected results. Chemical Reviews. 1995;95:735-758
- [13] Sclafani A, Herrmann JM. Comparison of the photoelectronic and photocatalytic activities of various anatase and rutile forms of titania in pure liquid organic phases and in aqueous solutions. The Journal of Physical Chemistry. 1996;100:13655-13661. DOI: 10.1021/jp9533584
- [14] Priecel P, Adekunle Salami H, Padilla RH, Zhong Z, Lopez-Sanchez JA. Anisotropic gold nanoparticles: Preparation and applications in catalysis. Chinese Journal of Catalysis. 2016;37:1619-1650. DOI: 10.1016/S1872-2067(16)62475-0
- [15] Daghrir R, Drogui P, Robert D. Modified TiO₂ for environmental photocatalytic applications: A review. Industrial and Engineering Chemistry Research. 2013;**52**:3581-3599. DOI: 10.1021/ie303468t
- [16] Park H, Park Y, Kim W, Choi W. Surface modification of TiO₂ photocatalyst for environmental applications. Journal of Photochemistry and Photobiology C: Photochemistry Reviews. 2013:1-20. DOI: 10.1016/j.jphotochemrev.2012.10.001
- [17] Kumar SG, Devi LG. Review on modified TiO₂ photocatalysis under UV/visible light: Selected results and related mechanisms on interfacial charge carrier transfer dynamics. Journal of Physical Chemistry A. 2011;**115**:13211-13241. DOI: 10.1021/jp204364a
- [18] Marschall R. Semiconductor composites: Strategies for enhancing charge carrier separation to improve photocatalytic activity. Advanced Functional Materials. 2014;24:2421-2440. DOI: 10.1002/adfm.201303214
- [19] Zhang Z, Yates JT. Band bending in semiconductors: Chemical and physical consequences at surfaces and interfaces. Chemical Reviews. 2012;112:5520-5551. DOI: 10.1021/ cr3000626
- [20] Primo A, Corma A, García H. Titania supported gold nanoparticles as photocatalyst. Physical Chemistry Chemical Physics. 2011;13:886-910. DOI: 10.1039/C0CP00917B
- [21] Zhang X, Chen YL, Liu R-S, Tsai DP. Plasmonic photocatalysis. Reports on Progress in Physics. 2013;76:46401. DOI: 10.1088/0034-4885/76/4/046401
- [22] Jovic V, Chen WT, Sun-Waterhouse D, Blackford MG, Idriss H, Waterhouse GIN. Effect of gold loading and TiO₂ support composition on the activity of Au/TiO₂ photocatalysts for H₂ production from ethanol-water mixtures. Journal of Catalysis. 2013;**305**:307-317. DOI: 10.1016/j.jcat.2013.05.031
- [23] Bowker M, James D, Stone P, Bennett R, Perkins N, Millard L, Greaves J, Dickinson A. Catalysis at the metal-support interface: Exemplified by the photocatalytic reforming

of methanol on Pd/TiO₂. Journal of Catalysis. 2003;**217**:427-433. DOI: 10.1016/S0021-9517(03)00074-5

- [24] Eustis S, El-Sayed MA. Why gold nanoparticles are more precious than pretty gold: Noble metal surface plasmon resonance and its enhancement of the radiative and nonradiative properties of nanocrystals of different shapes. Chemical Society Reviews. 2006;35:209-217. DOI: 10.1039/B514191E
- [25] Zhou X, Liu G, Yu J, Fan W. Surface plasmon resonance-mediated photocatalysis by noble metal-based composites under visible light. Journal of Materials Chemistry. 2012;22:21337. DOI: 10.1039/c2jm31902k
- [26] Kamat PV. Photophysical, photochemical and photocatalytic aspects of metal nanoparticles. Journal of Physical Chemistry B. 2002;106:7729-7744. DOI: 10.1021/jp0209289
- [27] Wu L, Yu JC, Fu X. Characterization and photocatalytic mechanism of nanosized CdS coupled TiO₂ nanocrystals under visible light irradiation. Journal of Molecular Catalysis A: Chemical. 2006;244:25-32. DOI: 10.1016/j.molcata.2005.08.047
- [28] Zhou P, Yu J, Jaroniec M. All-solid-state Z-scheme photocatalytic systems. Advanced Materials. 2014;26:4920-4935. DOI: 10.1002/adma.201400288
- [29] Li X, Yu J, Wageh S, Al-Ghamdi AA, Xie J. Graphene in photocatalysis: A review. Small. 2016:1-57. DOI: 10.1002/smll.201600382
- [30] Obregón S, Colón G. A ternary Er³⁺-BiVO₄/TiO₂ complex heterostructure with excellent photocatalytic performance. RSC Advances. 2014;4:6920-6926. DOI: 10.1039/c3ra46603e
- [31] Hu Y, Li D, Zheng Y, Chen W, He Y, Shao Y, Fu X, Xiao G. BiVO₄/TiO₂ nanocrystalline heterostructure: A wide spectrum responsive photocatalyst towards the highly efficient decomposition of gaseous benzene. Applied Catalysis B: Environmental. 2011;**104**:30-36. DOI: 10.1016/j.apcatb.2011.02.031
- [32] Zhang L, Tan G, Wei S, Ren H, Xia A, Luo Y. Microwave hydrothermal synthesis and photocatalytic properties of TiO₂/BiVO₄ composite photocatalysts. Ceramics International. 2013;**39**:8597-8604. DOI: 10.1016/j.ceramint.2013.03.106
- [33] Pingmuang K, Chen J, Kangwansupamonkon W, Wallace GG, Phanichphant S, Nattestad A. Composite photocatalysts containing BiVO₄ for degradation of cationic dyes. Scientific Reports. 2017;7:1-11. DOI: 10.1038/s41598-017-09514-5
- [34] Leghari SAK, Sajjad S, Chen F, Zhang J. WO₃/TiO₂ composite with morphology change via hydrothermal template-free route as an efficient visible light photocatalyst. Chemical Engineering Journal. 2011;**166**:906-915. DOI: 10.1016/j.cej.2010.11.065
- [35] Ramos-Delgado NA, Hinojosa-Reyes L, Guzman-Mar IL, Gracia-Pinilla MA, Hernández-Ramírez A. Synthesis by sol-gel of WO₃/TiO₂ for solar photocatalytic degradation of malathion pesticide. Catalysis Today. 2013;209:35-40. DOI: 10.1016/j.cattod.2012.11.011

- [36] Mou F, Xu L, Ma H, Guan J, Chen D, Wang S. Facile preparation of magnetic γ-Fe₂O₃/ TiO₂ Janus hollow bowls with efficient visible-light photocatalytic activities by asymmetric shrinkage. Nanoscale. 2012;4:4650-4657. DOI: 10.1039/c2nr30733b
- [37] Zhou W, Yin Z, Du Y, Huang X, Zeng Z, Fan Z, Liu H, Wang J, Zhang H. Synthesis of few-layer MoS₂ nanosheet-coated TiO₂ nanobelt heterostructures for enhanced photocatalytic activities. Small. 2013;9:140-147. DOI: 10.1002/smll.201201161
- [38] Serpone N, Borgarello E, Grätzel M. Visible light induced generation of hydrogen from H₂S in mixed semiconductor dispersions; improved efficiency through interparticle electron transfer. Journal of the Chemical Society, Chemical Communications. 1984;6:342-344. DOI: 10.1039/C39840000342
- [39] Yang L, Luo S, Liu R, Cai Q, Xiao Y, Liu S, Su F, Wen L. Fabrication of CdSe nanoparticles sensitized long TiO₂ nanotube arrays for photocatalytic degradation of anthracene-9-carbonxylic acid under green monochromatic light. Journal of Physical Chemistry C. 2010;**114**:4783-4789. DOI: 10.1021/jp910489h
- [40] Toyoda T, Yindeesuk W, Kamiyama K, Katayama K, Kobayashi H, Hayase S, Shen Q. The electronic structure and photoinduced electron transfer rate of CdSe quantum dots on single crystal rutile TiO₂: Dependence on the crystal orientation of the substrate. The Journal of Physical Chemistry C. 2016;120:2047-2057. DOI: 10.1021/acs.jpcc.5b09528
- [41] Yang L, Sun W, Luo S, Luo Y. White fungus-like mesoporous Bi₂S₃ ball/TiO₂ heterojunction with high photocatalytic efficiency in purifying 2,4-dichlorophenoxyacetic acid/ Cr(VI) contaminated water. Applied Catalysis B: Environmental. 2014;156-157:25-34. DOI: 10.1016/j.apcatb.2014.02.044
- [42] Ho W, Yu JC, Lin J, Yu J, Li P. Preparation and photocatalytic behavior of MoS₂ and WS₂ nanocluster sensitized TiO₂. Langmuir. 2004;20:5865-5869. DOI: 10.1021/la049838g
- [43] Jianhua L, Rong Y, Songmei L. Preparation and characterization of the TiO₂-V₂O₅ photocatalyst with visible-light activity. Rare Metals. 2006;25:636-642
- [44] Yang J, Dai J, Li J. Visible-light-induced photocatalytic reduction of Cr(VI) with coupled Bi₂O₃/TiO₂ photocatalyst and the synergistic bisphenol A oxidation. Environmental Science and Pollution Research. 2013;20:2435-2447. DOI: 10.1007/s11356-012-1131-6
- [45] Helaïli N, Bessekhouad Y, Bouguelia A, Trari M. Visible light degradation of Orange II using xCu_yO_z/TiO₂ heterojunctions. Journal of Hazardous Materials. 2009;**168**:484-492. DOI: 10.1016/j.jhazmat.2009.02.066
- [46] Bessekhouad Y, Robert D, Weber J-V. Photocatalytic activity of Cu₂O/TiO₂, Bi₂O₃/TiO₂ and ZnMn₂O₄/TiO₂ heterojunctions. Catalysis Today. 2005;**101**:315-321. DOI: 10.1016/j. cattod.2005.03.038
- [47] Yang H, Zhang K, Shi R, Tang A. Sol-gel synthesis and photocatalytic activity of CeO₂/ TiO₂ nanocomposites. Journal of the American Ceramic Society. 2007;90:1370-1374. DOI: 10.1111/j.1551-2916.2007.01540.x

- [48] Heng H, Gan Q, Meng P, Liu X. The visible-light-driven type III heterojunction H₃PW₁₂O₄₀/TiO₂-In₂S₃: A photocatalysis composite with enhanced photocatalytic activity. Journal of Alloys and Compounds. 2017;**696**:51-59. DOI: 10.1016/j.jallcom.2016.11.116
- [49] Yang H, Shi R, Zhang K, Hu Y, Tang A, Li X. Synthesis of WO₃/TiO₂ nanocomposites via sol-gel method. Journal of Alloys and Compounds. 2005;**398**:200-202. DOI: 10.1016/j. jallcom.2005.02.002
- [50] Xu H, Li G, Zhu G, Zhu K, Jin S. Enhanced photocatalytic degradation of rutile/anatase TiO₂ heterojunction nanoflowers. Catalysis Communications. 2015;62:52-56. DOI: 10.1016/j.catcom.2015.01.001
- [51] Zhu J, Wang S, Wang J, Zhang D, Li H. Highly active and durable Bi₂O₃/TiO₂ visible photocatalyst in flower-like spheres with surface-enriched Bi₂O₃ quantum dots. Applied Catalysis B: Environmental. 2011;**102**:120-125. DOI: 10.1016/j.apcatb.2010.11.032
- [52] Li N, Li Y, Li W, Ji S, Jin P. One-step hydrothermal synthesis of TiO₂@MoO₃ Core-Shell nanomaterial: Microstructure, growth mechanism, and improved photochromic property. Journal of Physical Chemistry C. 2016;**120**:3341-3349. DOI: 10.1021/acs.jpcc.5b10752
- [53] Liu L, Yang W, Sun W, Li Q, Shang JK. Creation of Cu₂O@TiO₂ composite photocatalysts with p—N heterojunctions formed on exposed Cu₂O facets, their energy band alignment study, and their enhanced photocatalytic activity under illumination with visible light. ACS Applied Materials and Interfaces. 2015;7:1465-1476. DOI: 10.1021/am505861c
- [54] Yin H, Wang X, Wang L, Nie Q, Zhang Y, Wu W. Cu₂O/TiO₂ heterostructured hollow sphere with enhanced visible light photocatalytic activity. Materials Research Bulletin. 2015;**72**:176-183. DOI: 10.1016/j.materresbull.2015.07.030
- [55] Perales-Martínez IA, Rodríguez-González V, Lee SW, Obregón S. Facile synthesis of InVO₄/TiO₂ heterojunction photocatalysts with enhanced photocatalytic properties under UV-vis irradiation. Journal of Photochemistry and Photobiology A: Chemistry. 2015;**299**:152-158. DOI: 10.1016/j.jphotochem.2014.11.021
- [56] Maeda K, Ishimaki K, Okazaki M, Kanazawa T, Lu D, Nozawa S, Kato H, Kakihana M. Cobalt oxide nanoclusters on rutile titania as bifunctional units for water oxidation catalysis and visible light absorption: Understanding the structure-sctivity relationship. ACS Applied Materials and Interfaces. 2017;9:6114-6122. DOI: 10.1021/acsami.6b15804
- [57] Zhou W, Fu H, Pan K, Tian C, Qu Y, Lu P, Sun C-C. Mesoporous TiO₂/α-Fe₂O₃: Bifunctional composites for effective elimination of arsenite contamination through simultaneous photocatalytic oxidation and adsorption. Journal of Physical Chemistry C. 2008;112:19584-19589. DOI: 10.1021/jp806594m
- [58] Peng L, Xie T, Lu Y, Fan H, Wang D. Synthesis, photoelectric properties and photocatalytic activity of the Fe₂O₃/TiO₂ heterogeneous photocatalysts. Physical Chemistry Chemical Physics. 2010;12:8033-8041. DOI: 10.1039/c002460k
- [59] Uddin MT, Babot O, Thomas L, Olivier C, Redaelli M, D'Arienzo M, Morazzoni F, Jaegermann W, Rockstroh N, Junge H, Toupance T. New insights into the photocatalytic properties of RuO₂/TiO₂ mesoporous heterostructures for hydrogen production and

organic pollutant photodecomposition. Journal of Physical Chemistry C. 2015;**119**:7006-7015. DOI: 10.1021/jp512769u

- [60] Shifu C, Lei C, Shen G, Gengyu C. The preparation of coupled WO₃/TiO₂ photocatalyst by ball milling. Powder Technology. USA. 2005;160:198-202. DOI: 10.1016/j.powtec. 2005.08.012
- [61] Yu J, Dai G, Huang B. Fabrication and characterization of visible-light-driven plasmonic photocatalyst Ag/AgCl/TiO₂ nanotube arrays. The Journal of Physical Chemistry C. 2009;113:16394-16401. DOI: 10.1021/jp905247j
- [62] Barbero N, Vione D. Why dyes should not be used to test the photocatalytic activity of semiconductor oxides. Environmental Science and Technology. 2016;50:2130-2131. DOI: 10.1021/acs.est.6b00213
- [63] Emeline AV, Ryabchuk VK, Serpone N. Dogmas and misconceptions in heterogeneous photocatalysis. Some enlightened reflections. Journal of Physical Chemistry B. 2005;109:18515-18521. DOI: 10.1021/jp0523367
- [64] Reemtsma T, Jekel M. Organic Pollutants in the Water Cycle : Properties, Occurrence, Analysis and Environmental Relevance of Polar Compounds. Wiley-VCH; 2006
- [65] Miège C, Choubert JM, Ribeiro L, Eusèbe M, Coquery M. Fate of pharmaceuticals and personal care products in wastewater treatment plants – Conception of a database and first results. Environmental Pollution. 2009;157:1721-1726. DOI: 10.1016/j.envpol.2008.11.045
- [66] Ge L, Xu M, Fang H. Synthesis and characterization of the Pd/InVO₄-TiO₂ co-doped thin films with visible light photocatalytic activities. Applied Surface Science. 2006;253:2257-2263. DOI: 10.1016/j.apsusc.2006.04.023
- [67] Yang J, Wang X, Lv X, Xu X, Mi Y, Zhao J. Preparation and photocatalytic activity of BiO_X-TiO₂ composite films (X=Cl, Br, I). Ceramics International. 2014;40:8607-8611. DOI: 10.1016/j.ceramint.2014.01.077
- [68] Monfort O, Roch T, Gregor M, Satrapinskyy L, Raptis D, Lianos P, Plesch G. Photooxidative properties of various BiVO₄/TiO₂ layered composite fi lms and study of their photocatalytic mechanism in pollutant degradation. Journal of Environmental Chemical Engineering. 2017;5:5143-5149. DOI: 10.1016/j.jece.2017.09.050
- [69] Bera S, Rawal SB, Kim HJ, Lee WI. Novel coupled structures of FeWO₄ /TiO₂ and FeWO₄ / TiO₂/CdS designed for highly efficient visible-light photocatalysis. Applied Materials & Interfaces. 2014;6:9654-9663. DOI: 10.1021/am502079x
- [70] Bessekhouad Y, Brahimi R, Hamdini F, Trari M. Cu₂S/TiO₂ heterojunction applied to visible light Orange II degradation. Journal of Photochemistry and Photobiology A: Chemistry. 2012;248:15-23. DOI: 10.1016/j.jphotochem.2012.08.013
- [71] Bian Z, Zhu J, Wang S, Cao Y, Qian X, Li H. Self-assembly of active Bi₂O₃/TiO₂ visible photocatalyst with ordered mesoporous structure and highly crystallized anatase. Journal of Physical Chemistry C. 2008;112:6258-6262. DOI: 10.1021/jp800324t

- [72] Challagulla S, Nagarjuna R, Ganesan R, Roy S. Acrylate-based polymerizable sol-gel synthesis of magnetically recoverable TiO₂ supported Fe₃O₄ for Cr(VI) photoreduction in aerobic atmosphere. ACS Sustainable Chemistry & Engineering. 2016;4:974-982. DOI: 10.1021/acssuschemeng.5b01055
- [73] Etacheri V, Michlits G, Seery MK, Hinder SJ, Pillai SC. A highly efficient TiO_{2-x} C_x nanoheterojunction photocatalyst for visible light induced antibacterial applications. ACS Applied Materials & Interfaces. 2013;5:1663-1672. DOI: 10.1021/am302676a
- [74] Kontic R, Patzke GR. Synthetic trends for BiVO₄ photocatalysts: Molybdenum substitution vs. TiO₂ and SnO₂ heterojunctions. Journal of Solid State Chemistry. 2012;189:38-48. DOI: 10.1016/j.jssc.2011.11.050
- [75] Li W, Li D, Meng S, Chen W, Fu X, Shao Y. Novel approach to enhance photosensitized degradation of rhodamine B under visible light irradiation by the Zn_xCd_{1-x}S/TiO₂ nanocomposites. Environmental Science and Technology. 2011;45:2987-2993. DOI: 10.1021/es103041f
- [76] Liu L, Yang W, Li Q, Gao S, Shang JK. Synthesis of Cu₂O nanospheres decorated with TiO₂ nanoislands, their enhanced photoactivity and stability under visible light illumination, and their post-illumination catalytic memory. ACS Applied Materials and Interfaces. 2014;6:5629-5639. DOI: 10.1021/am500131b
- [77] Zhang M, Shao C, Mu J, Zhang Z, Guo Z, Zhang P, Liu Y. One-dimensional Bi₂MoO₆/TiO₂ hierarchical heterostructures with enhanced photocatalytic activity. Crystal Engineering Communication. 2012;14:605-612. DOI: 10.1039/C1CE05974B
- [78] Liu S, Hu Q, Qiu J, Wang F, Lin W, Zhu F, Wei C, Zhou N, Ouyang G. Enhanced photocatalytic degradation of environmental pollutants under visible irradiation by a composite coating. Environmental Science and Technology. 2017;51:5137-5145. DOI: 10.1021/ acs.est.7b00350
- [79] Sood S, Mehta SK, Sinha ASK, Kansal SK. Bi₂O₃/TiO₂ heterostructures: Synthesis, characterization and their application in solar light mediated photocatalyzed degradation of an antibiotic, ofloxacin. Chemical Engineering Journal. 2016;290:45-52. DOI: 10.1016/j. cej.2016.01.017
- [80] Sun M, Chen G, Zhang Y, Wei Q, Ma Z, Du B. Efficient degradation of azo dyes over Sb2S₃/TiO₂ heterojunction under visible light irradiation. Industrial & Engineering Chemistry Research. 2012;51:2897-2903. DOI: 10.1021/ie2025882
- [81] Tang A, Jia Y, Zhang S, Yu Q, Zhang X. Synthesis, characterization and photocatalysis of AgAlO₂/TiO₂ heterojunction with sunlight irradiation. Catalysis Communications. 2014;50:1-4. DOI: 10.1016/j.catcom.2014.02.015
- [82] Wang M, Sun L, Lin Z, Cai J, Xie K, Lin C. p–n Heterojunction photoelectrodes composed of Cu₂O-loaded TiO₂ nanotube arrays with enhanced photoelectrochemical and photoelectrocatalytic activities. Energy & Environmental Science. 2013;6:1211-1220. DOI: 10.1039/c3ee24162a

- [83] Wang X, Utsumi M, Yang Y, Li D, Zhao Y, Zhang Z, Feng C, Sugiura N, Cheng JJ. Degradation of microcystin-LR by highly efficient AgBr/Ag₃PO₄/TiO₂ heterojunction photocatalyst under simulated solar light irradiation. Applied Surface Science. 2015;**325**:1-12. DOI: 10.1016/j.apsusc.2014.10.078
- [84] Xia Y, Yin L. Core–shell structured α-Fe₂O₃@TiO₂ nanocomposites with improved photocatalytic activity in the visible light region. Physical Chemistry Chemical Physics. 2013;15:18627-18634. DOI: 10.1039/c3cp53178c
- [85] Xu X, Gao Z, Cui Z, Liang Y, Li Z, Zhu S, Yang X, Ma J. Synthesis of Cu₂O octadecahedron/TiO₂ quantum dot heterojunctions with high visible light photocatalytic activity and high stability. ACS Applied Materials & Interfaces. 2016;8:91-101. DOI: 10.1021/ acsami.5b06536
- [86] Xue C, Zhang T, Ding S, Wei J, Yang G. Anchoring tailored low-index faceted BiOBr nanoplates onto TiO₂ nanorods to enhance the stability and visible-light-driven catalytic activity. ACS Applied Materials and Interfaces. 2017;9:16091-16102. DOI: 10.1021/ acsami.7b00433
- [87] Yang L, Luo S, Li Y, Xiao Y, Kang Q, Cai Q. High efficient photocatalytic degradation of p-nitrophenol on a unique Cu₂O/TiO₂ p-n heterojunction network catalyst. Environmental Science and Technology. 2010;44:7641-7646. DOI: 10.1021/es101711k
- [88] Yu C, Wei L, Chen J, Xie Y, Zhou W, Fan Q. Enhancing the photocatalytic performance of commercial TiO₂ crystals by coupling with trace narrow-band-gap Ag₂CO₃. Industrial and Engineering Chemistry Research. 2014;**53**:5759-5766. DOI: 10.1021/ie404283d

Silver Nanoparticle Incorporated Titanium Oxide for Bacterial Inactivation and Dye Degradation

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Abstract

This chapter deals with preparation and characterization of silver nanoparticles incorporated in titania or $\text{TiO}_2\text{-AgNP}$ in short and its performance study as a visible light responsive photocatalyst for bacterial inactivation and dye degradation. The preparation of $\text{TiO}_2\text{-AgNP}$ performed by several methods including sol-gel, impregnation, precipitation, and photocatalytic deposition is described. Characterizations by XRD, XPS, FTIR, DRUV, and SEM/TEM machines to confirm the formation of the metallic silver nanoparticle, as well as the shape and size, and to follow the interaction between Ag atoms and other atoms in the crystal lattice of $\text{TiO}_2\text{-AgNP}$, both under UV and visible light, are described.

Keywords: silver nanoparticle, titania, visible exposure, antibacterial activity, dye photodegradation

1. Introduction

Titanium dioxide (TiO₂) exists in three different crystal structures that are anatase, rutile, and brookite, where rutile is known as the most stable form [1]. The band gap energy of anatase, rutile, and brookite are 3.2, 3.0, 3.2 eV, respectively [1–5]. It means that they can only be activated with UV light irradiation having a wavelength (λ) of 387 nm or lower. Many studies in the area show the use of UV radiation as a photon source for both photocatalytic inactivation of microorganisms [6–11] and dye degradation [12–30].

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The titania has been employed as a photocatalyst in several photocatalytic reactions due to its high photoactivity, low cost, low toxicity and good chemical and thermal stability [1–3]. However, its large energy band gap inhibits it from being active under UV light [31–35]. The solar spectrum consists of only 4–5% UV light and around 40% visible light [31]. Therefore, the efficiency of TiO₂ as a photocatalyst under sunlight irradiation is limited.

Modification of TiO₂ to improve the photocatalytic efficiency of TiO₂ under sunlight visible irradiation is necessary. The modification by non-metal [36–51] and metal [52–83] doping on TiO₂ has been attempted. The metal doping agents introduced for TiO₂ are transition metals (Fe, Cu, Cr, Co, and Ni) [52–56] and noble metals (Ag, Au, Pd, and Pt) [57–83]. Among the noble metals, silver has received considerable interest due to its additional potential as an antibacterial agent [84]. The importance of medical applications of metallic silver [85, 86] and antibacterial activity of TiO₂ [6–11] attracts researchers to think of manufacturing silver-doped titania. There are ongoing works related with the use of Ag for possible medical devices [79], dental implants [78, 79], food packagings [80], air conditioning filters, and so on [79]. Some works focus on bacterial inactivation [34, 63] and dye waste treatment under visible light irradiation [66, 67, 81–83]. Hence, the preparation and characterization of the TiO₂-based photocatalyst and its activity are presented.

2. Preparation of TiO₂-AgNP

2.1. Sol-gel

The sol-gel method involves the interaction of titania sol with silver ion the solution, which forms a gel. The gel is heated at a low temperature to evaporate the solvent followed by calcination at high temperature [31, 35, 72, 73, 78, 80, 82, 83]. The main precursor of titania is commonly liquid titanium(IV) isopropoxide (TTiP) with a chemical formula of $Ti(OC_3H_7)_4$ [31, 35, 72, 75], but titanium n-butoxide ($Ti(OC_4H_9)_4$ [82, 83] is also potential. For silver starting material, AgNO₃ is frequently employed [31, 72, 75, 77, 80, 82, 83]; however, silver acetylacetonate is also chosen sometime [35].

Titania sol is prepared by mixing TTip solution in ethanol and water accompanied by stirring vigorously at room temperature for about 15 min. During the dissolution of TTip in the ethanol medium, an exchange of propyl group from TTip with ethyl group from the ethanol to yield titania tetra ethoxides takes places by the release of propanol. Titanium tetra ethoxide is hydrolyzed in acidic medium to form sol titanol of $Ti(OH)_4$.

The $AgNO_3$ solution is mixed with ethanol and stirred [31, 72, 75, 77, 80, 82, 83], giving the sol of silver. Finally, the silver sol is added dropwise to the titania sol with stirring, where transparent titania sol changes its viscous yellow solution. The reaction between titania sol and silver sol is commonly written as follows:

$$Ti (OH)_4 + C_2 H_5 O - Ag \rightarrow Ti (OH)_3 - Ag + C_2 H_5 OH$$
(1)

The viscous sol was heated at about 60°C to evaporate organic solvents to yield dry gel [72]. The dry gel is calcined at about 350°C to produce TiO₂-AgNP powders, according to the reaction (2):

$$4\text{Ti}(\text{OH})_3 - \text{Ag} + \text{O}_2(350^{\circ}\text{C}) \rightarrow 4\text{TiO}_2 - \text{AgNP} + 6\text{H}_2\text{O}$$
 (2)

In the preparation of TiO_2 -AgNP photocatalyst by a sol-gel method, some modifications have been done including the use of acetic acid [83], micellar medium [75], spin coating technique [82], with the purpose to improve TiO_2 -AgNP photocatalyst characteristics and performance.

2.2. Impregnation method

The synthesis of TiO_2 -AgNP by impregnation method is carried out by stirring the solution of AgNO₃ mixed with the suspension of TiO_2 in water for 24 h. The solvent is later removed by drying at 150°C followed with calcination of the product at 500°C [68]. Some modifications in the impregnation method such as the use of capping agent [74] and combustion method [63, 64] are also possible.

The modification starts with silver nanoparticles preparation in polyvinylpyrrolidone (PVP) as a capping agent. For this purpose, the AgNO₃ solution is added to methanol and is mixed with PVP. The mixture is refluxed for 3 h at 110°C to give a yellow-orange color solution. The solvent was evaporated at 55°C, and the obtained Ag nanoparticles were dispersed into ethanol and thoroughly washed with hexane and ethanol. The Ag nanoparticles are redispersed into the ethanol under sonication, and TiO₂ powder is added to the solution. This mixture is sonicated for 3 h and is dried at 60°C to remove the solvent followed temperature rise to 90°C [74].

The combustion method is carried out by heating a mixture of $AgNO_{3'}$ titanyl nitrate and glycine as fuel in the muffle furnace at 150°C for 2 h [63, 64]. The remaining solid from the combustion is supposed to be TiO₂-AgNP.

2.3. Precipitation

In the precipitation method, titanium tetra-isopropoxide and silver nitrate were used as a source of titanium and silver, respectively. Ag-doped TiO_2 nanocrystalline powder was prepared by controlled addition of TTIP to absolute ethanol with constant stirring to get a clear solution. A sufficient amount of surfactant solutions (1% CTAB +1% SDS) was added to the solution with constant stirring. The aqueous solution of silver nitrate was added to the solution. A solution of aqueous ammonia was added dropwise to the last solution under stirring with the special arrangement at room temperature until the solution pH reaches 8. After complete precipitation, the solid was washed with Millipore deionized water and acetone several times to remove excess of surfactant. The precipitate was kept under microwave irradiation for 20 min. The dried powder was ground and calcined at 300°C for 3 h in a temperature-controlled muffle furnace [68]. Following calcination, the TiO₂-AgNP was obtained.

2.4. Photocatalytic deposition

In this method, the TiO_2 powder is dispersed into ethanol and water, followed by stirring or sonicating for about 15 min to form titania sol. The AgNO₃ solution is added to the sol. The mixture is irradiated with UV lamp for a certain period of time along with constant stirring. After a certain time, the solid was separated by filtration and dried at around 300–400°C [31, 33, 67, 69–71, 73, 79, 81]. In this method, when TiO₂ photocatalyst is exposed to UV light, electrons are revealed along with the formation of OH radicals. The electrons will interact with Ag⁺ coming from AgNO₃ resulting in the reduction reaction of the Ag⁺ to form Ag⁰ metallic particles. The small particle of Ag⁰ can be inserted into the crystal lattices of TiO₂ [67] and/or deposited onto TiO₂ surface to form a small cluster.

2.5. Other methods

There are several other methods for TiO_2 -AgNP preparation, including graphene oxidation [57], radiolitic reduction by using γ -ray [61], electrolytic oxidation-reduction [62], and mirror reaction [65].

3. Characterization of TiO₂-AgNP photocatalyst

3.1. The existence of the silver species in TiO₂-AgNP

The content of Ag incorporated in the TiO_2 crystal structure prepared by sol-gel, precipitation and photodeposition can be determined by elemental analyses by X-Ray Fluorescence (XRF) [68, 75], ICP-MS [35] and atomic absorption spectrophotometry (AAS) [83]. In general, the content of Ag formed in TiO_2 -AgNP is proportional to the initial concentration of precursors of the AgNO₃ solution.

The presence of Ag in the TiO_2 -AgNP can be detected by XRD method. It can be carried out by detecting X-ray diffraction pattern evolution with the reference of native TiO_2 . The XRD pattern of TiO_2 recorded by using a CuK α source of XRD machine gives several characteristics peaks of 2 θ values at 25.091, 37.651, 48.021, 53.891, 55.071, 62.381, 68.701, 70.041 and 75.001. These peaks are confirmed with JCPD Card No. (21-1272) and are attributed to the diffraction of TiO₂ anatase. They correspond to the lattice planes (101), (004), (200), (105), (211), (204), (220), (220), and (215), respectively [67, 68, 77, 82]. In many instances, Ag is not detected in the XRD pattern. It is probably located in bulk (inside the TiO₂ crystals) [77], and/or Ag clusters smaller than 0.3 nm [66], or diffused in the TiO₂ crystal lattice [68], or well dispersed throughout the TiO₂ surface [31] (**Figure 1**).

High Ag content (more than 0.25 mol%) in TiO_2 -AgNP prepared by precipitation assisted with microwave [68] and that of by photocatalytic reduction [67] have additional diffraction peaks at 20 values of 38.011, 44.261, 64.021 and 77.361. The appearance of the peaks can be assigned to the face centered cubic lattice planes of metallic silver of (111), (200), (200) and (311) planes, respectively [67, 68]. It is evident that TiO_2 -AgNP photocatalyst with low metallic Ag content is undetectable by the XRD technique [82]. The detectable metallic Ag level

Silver Nanoparticle Incorporated Titanium Oxide for Bacterial Inactivation and Dye Degradation 335 http://dx.doi.org/10.5772/intechopen.75918



Figure 1. XRD patterns of (a) $TiO_{2'}$ (b) $TiO_{2}/Ag-0.05\%$, (c) $TiO_{2}/Ag-0.10\%$, (d) $TiO_{2}/g-0.15\%$, (e) $TiO_{2}/Ag-0.25\%$, and (f) $TiO_{2}/Ag-0.50\%$ [71].

is found to be more than 0.80 moles% [66], but 0.25 moles% or higher is also reported [68]. Depending on the concentration, the detectable metallic silver in TiO_2 -AgNP is also observed in the XRD pattern when TiO_2 -AgNP is calcined at a higher temperature (700°C) since sintering step causes Ag particles to form large aggregate [31].

The valence state of silver, as ionic Ag⁺ or metallic silver Ag⁰, in the TiO₂-AgNP photocatalyst can be distinguished by XPS. The XPS spectrum shows the characteristic Ag 3d peak that has a binding energy of 368 eV with a 6.0 eV splitting of the 3d doublet of low spin 3d^{1/2} and high spin 3d^{5/2} [33]. It confirms that the presence of metallic silver deposits on the TiO₂ [33]. It is different from the XRD data that can only provide the metallic silver in high level; the XPS gives additional proof that the metallic silvers are formed in TiO₂-AgNP at all concentration levels.

The existence of Ag in TiO_2 -AgNP can also be distinguished by temperature-programmed reduction (TPR) spectrometry technique. The profile of the TPR spectra of sol-gel TiO_2-AgNP calcined at 350°C [72] shows reduction peak at around 135°C, which suggests a reduction of Ag⁺ into Ag⁰ metallic without interacting with the support. Also, TiO₂-AgNP calcined at 500°C give spectra peak at around 350 and 500°C, probably due to Ag reduction with support material [72].

3.2. Band gap energy (Eg) and absorption edge (λ) of TiO₂-AgNP

3.2.1. Mechanism and role of Ag in TiO₂-AgNP on the absorption shift into visible light

The incorporation of Ag on TiO_2 is meant to allow the TiO_2 to be active under visible light. The photocatalytic ability of TiO_2 photocatalyst under visible is assigned by the lower band gap energy (Eg) or absorption in visible light. The band gap energy (Eg) can be determined based

on the data of the maximum absorption wavelength (λ) according to the equation Eg = 1239/ λ , where the maximum absorption wavelength is obtained from the diffuse reflectance (DR) data [67].

The DR-spectra at 200–800 nm of TiO₂ displays that the maximum absorption is seen at around 400–390 nm corresponding to 3.15-3.20 eV of the band gap energy of anatase [1–3]. Furthermore, the metallic silver loading on TiO₂ is observed to shift the maximum absorption to a longer wavelength that is about 430–574 nm [31, 66, 67, 72, 75, 81]. The DR spectra give respective band gap energy as much as 2.88-2.16 eV. The absorption wavelength or the band gap energy values allow the TiO₂-AgNP photocatalyst to be active in the visible region. The absorption shift may be resulted by the diffusion of the metallic silver into the crystal lattice of the TiO₂ structure that the silver to be dispersed or inserted between the conduction and valence bands of the host material [31, 67, 75] (**Figure 2**).

The absorption shift is found to be affected by Ag content in TiO_2 -AgNP [67, 68, 75, 81], the preparation method of TiO_2 -AgNP, and calcination temperature [72]. The shift increases with the increasing Ag amount in TiO_2 because more Ag inserted into the gap so that the gap becomes narrower than that of bare TiO_2 , shifting in the absorption wavelength to increase. Based on the preparation method, TiO_2 -AgNP photocatalyst prepared by sol-gel has a more substantial shift in the wavelength than the ones produced by the impregnation method [72]. In the sol-gel process, the silver ion (Ag⁺) having a small size interacts with the titania sol, allowing the ion to disperse into the crystal lattice of TiO_2 . Meanwhile, in the impregnation the silver introduced into the titania sol present as AgNO₃ salt is difficult to penetrate the lattice [75], giving less effect on the band gap. The final step in the TiO_2 -AgNP preparation



Figure 2. DR spectra, from the top in order representing TiO₂/Ag-0.05%, TiO₂/Ag-0.25%, and TiO₂/Ag-0.50% [71].

process is calcination at a higher temperature that is about 350–500°C. The high calcination temperature of TiO_2 -AgNP gives smaller absorption shift than the low calcination temperature [72]. With a high temperature, the silver sintering on TiO_2 may be occurred to form bigger Ag metallic cluster, which prevents it from entering the gap. The significant shift of the absorption wavelength is expected because this should promote higher photocatalyst activity in the visible region.

The diffusion of Ag into the crystal lattice of TiO_2 may enlarge its basal spacing (d) that can be confirmed by their basal spacing obtained from the XRD patterns. It is found that the presence of Ag in the TiO_2 -AgNP causes the XRD peak position of TiO_2 shifts to a low 2 θ angle. Further, the 2 θ angle position is getting lower as the Ag content increases. The 2 θ angle value is related to the basal spacing (d) of TiO_2 crystal as represented by Bragg's equation [68]:

$$n\lambda = 2 d \sin \theta \tag{3}$$

The equation describes the smaller sin θ value, the larger the d spacing. It is known that the value of d increases gradually with increase in Ag contents. The enlargement of the XRD basal spacing (d) implies that more silver diffuses into the lattice of TiO₂ [68]. As the Ag contents increasing from 0 to 0.25 mol%, the peak broadening of [101] planes gradually increases, which indicates the smaller crystallite size of Ag. The smaller size facilitates them to diffuse into the crystal lattice easily.

The insertion of the metallic silver into the TiO_2 crystal lattice may distort the structure of TiO_2 or disturb the chemical bonds of Ti-O in the solid. To better understand the effect of the Ag as a doping agent, the spectrometer data of IR is used. The FTIR spectra of both TiO₂ and TiO₂-AgNP photocatalyst illustrating several absorptions appear at various wavelengths [68, 77, 81]. A broad peak at 3448 cm⁻¹ represents O-H stretching of Ti-O-H. Also, a peak seen at 1635 cm⁻¹ is due to the OH bending mode of water adsorbed on the surface of TiO₂. The peaks at the wavelength of 540 and 678 cm⁻¹ are also observed due to Ti-O-Ti stretching and Ti-O-Ti bending, respectively [68, 75]. After loading Ag on TiO₂, the peaks at 540 and 679 cm⁻¹ shifts to 556 and 694 cm⁻¹, respectively. The shifts may be affected by the interaction between Ag and TiO₂ to form Ti-O-Ag composite and/or the insertion of Ag into host lattice of TiO₂ [68].

The XRD patterns confirm the distortion of the TiO_2 structure after doping with metallic Ag. The XRD peaks belonged to both TiO_2 and TiO_2 -AgNP seemed similar, but the peak intensity decreases after Ag loading. The intensity decreases imply the alteration of the crystallinity due to the insertion of Ag into the lattice of the TiO₂ crystal [67].

3.3. Particle size of the silver on TiO₂-AgNP

The Ag incorporation into the TiO_2 may affect several important properties including particle size and surface area. The particle size determines its surface area, where the smaller the grain size, the larger the surface area. TEM can trace the particle size of Ag in TiO_2 -AgNP. The TEM image displays that the size varied with the Ag content in the TiO_2 -AgNP [33, 67]. For the two atomic% Ag in TiO_2 -AgNP sample, Ag deposits are well dispersed on the TiO_2 particles with an average particle size of 2–4 nm. At high silver level, the formation of large Ag

particles (>100 nm) is observed in the TEM images [33, 67]. The particle size of Ag-doped TiO₂ is also directed by the preparation methods [33]. In TiO₂-AgNP prepared by the impregnation method, Ag is detected to have a larger size than that of sol-gel. In the impregnation process, AgNO₃ salt and TiO₂ are suspended in water in the TiO₂-AgNP preparation [33]. Consequently, the Ag particle is not limited by the TiO₂ structure that enables them to form a large agglomerate. Meanwhile, in the sol-gel method, TiO₂-AgNP is prepared from titania sol and Ag⁺ solution that allows them to have mutual interaction and inhibit their particle growth. As a result, it forms the small grain size (**Figure 3**).

3.4. Surface area of TiO₂-AgNP

The surface area is determined by surface area analyzer based on the BET method. In general, the surface area of TiO_2 -AgNP is controlled by the Ag content in TiO_2 -AgNP, preparation method, and the calcination temperature [33, 68, 72]. The surface area of TiO_2 -AgNP prepared by impregnation method is observed to decrease with increase in the Ag-doped TiO_2 [72]. By impregnation method, the metallic silver is formed as large agglomerate that may block the surface of the TiO_2 particle. Such surface blocking leads to the surface area to decline. In contrast, by a sol-gel method, the surface area increases with the enlargement of Ag content in TiO_2 -AgNP. The particle size of the metallic Ag is small due to the limitation of particle growth.

By the photo-deposition method, the addition of Ag at only 0.25 mol%, an appreciable increase in the specific surface area is observed [33, 68]. The surface area of TiO_2 -AgNP with Ag content smaller than 0.25 mol% is not significantly different from that of the pure TiO_2 due to the vast and thin dispersion of the Ag particles on the TiO_2 structure. Ag in TiO_2 -AgNP as much as 0.25 mol% seems to be well dispersed on the surface of the TiO_2 grain that contributes to a large surface area. The Ag loading higher than 0.25 mol% leads to the decrease in surface area that is resulted from by large silver aggregate.

The other reasons for the surface area improvement are proposed as follows [31, 68, 76]. The Ag doping with a suitable amount (ca. 2–6 mol%) promotes the phase transformation of TiO_2 from anatase to rutile since the surface area of rutile is larger than that of the anatase. The Ag-doped TiO₂ also has a depressing effect on the anatase grain growth. The average crystallite



Figure 3. The TEM images of (a) TiO₂/Ag-0.05%, (b) TiO₂/Ag-0.25%, and (c) TiO₂/Ag-0.50% [71].

size of the TiO_2 can be calculated by using the Scherrer's Equation [31]. It is observed that the TiO_2 crystallite has an average size of 15 nm, and it decreases up to 10 nm for 0.25 mol% of Ag loading [68]. It is also confirmed that the decreasing the crystallite size increases the specific surface area of the TiO, powder.

4. Activity of TiO₂-AgNP photocatalyst

The doping TiO_2 with metallic Ag is intended to activate TiO_2 -AgNP photocatalyst under visible light both for bacterial inactivation and dye photodegradation.

4.1. Bacterial inactivation

The doping TiO_2 with metallic silver to produce TiO_2 -AgNP has been investigated as a potential antibacterial agent in inactivating *Escherichia coli* [63–65, 78, 79] under visible light exposure. The TiO_2 -AgNP exposure to UV light for bacterial inactivation is also essential.

 TiO_2 -AgNP demonstrates a significant activity in the bacterial inactivation under visible light. The antibacterial performance of TiO_2 -AgNP is found to be higher than that of unmodified TiO_2 . Both TiO_2 and TiO_2 -AgNP can kill bacteria because TiO_2 provides OH radicals during UV or visible irradiation at a suitable wavelength. The OH radicals attack and destroy the bacterial wall [10, 11]. Under visible light, TiO_2 -AgNP can be activated since TiO_2 -AgNP has a low band gap energy (Eg) that matches with the visible region wavelength. Meanwhile, due to its high band gap energy (Eg), which is in the same order as UV light, TiO_2 is less active under visible light. Addition of Ag to TiO_2 also gives the excellent antibacterial agent, that is by penetrating the metallic Ag nanoparticles into the cell membrane of the bacteria [84]. There is a synergic effect of TiO_2 and Ag in inhibiting bacteria [63–65, 78, 79]. The activity of Ag in the bacteria inactivation process is examined by applying TiO_2 -AgNP in dark condition [81]. It has been postulated that silver disrupts the cell wall and affects the rapid penetration of the metallic ions into the cell where irreversible precipitation of the bacteria's DNA occurs [84].

The role of Ag in TiO_2 -AgNP in the bacterial inhibition under visible light is affected by its ability as a center of the separation of photoinduced electron and OH radicals that delay the recombination of electron and hole [34, 63–65, 78, 79]. The other role of Ag in the improving the bacterial inactivation corresponds to the electron capture that can prevent the recombination. The inhibition of the recombination creates more OH radicals, which improves the bacterial inactivation.

The Ag content in TiO_2 -AgNP is subjected to test further. Increase in Ag content leads to decline in bacterial inactivation [34, 63–65, 78, 79]. Increasing Ag in TiO_2 -AgNP can enhance the electron capture, forming anion Ag, which allows more OH radical available. The more OH radicals available, the better bacterial inactivation. However, a further increase in Ag content can block the TiO_2 surface and prevent the light absorption, producing a lower amount of OH radicals. The other possible reason is the attachment of OH radical with excess Ag anion. The depletion of OH radicals leads to the inactivation declined [64].

Comparing between the bacterial inactivation under UV and visible light with and without photocatalyst, it is similar to the UV photolysis system [63, 64]. Visible light photolysis alone is observed to play a role in microorganism inactivation. The bacterial inactivation in UV-A or visible light is observed due to the synergetic effects of radiating energy and mild heat produced during the irradiation [63]. In the presence of TiO_2 -AgNP photocatalyst, it is found the rates of inactivation were higher in the presence of UV than that of visible light.

UV light has germicidal property, and TiO_2 itself possesses higher photocatalytic activity in UV region due to its large band gap energy. On the other hand, doping with metal is mainly done to extend the absorbance of TiO_2 to the visible region. Therefore, the photocatalytic inactivation in the presence of UV light and TiO_2 : Ag catalyst is a synergetic effect of antimicrobial property of silver, the germicidal property of UV and photocatalytic activity of the TiO_2 photocatalyst [63, 64]. It should be noted that the antibacterial inactivation is dependent on several operating conditions such as visible light intensity and catalyst amount.

4.1.1. Effect of visible light intensity

Photocatalytic inactivation reactions are highly dependent on the irradiation intensity of the light source [34, 63]. The increase in the visible light intensity from 2 to 8 W.m² can enhance the bacterial inactivation over TiO_2 -AgNP photocatalysts. The observed enhancement in the inactivation is due to the increase in the number of photons produced as light intensity rise.

4.1.2. Effect of the photocatalyst dose

The addition of catalyst to the solution resulted in a better bacterial inactivation than the control experiments. At low catalyst dose (0.1 g/L), the observed inactivation was not significant because of less availability of OH radicals to target a large number of bacteria. The increase in the photocatalyst dose to 0.25 g/L shows the possibility of an increase in the number of OH radicals sufficient enough to target the microorganism number, which improves bacterial inactivation. At 0.25 g/L, the maximum inactivation shows the maximum availability of OH radicals in the solution. When the photocatalyst loading is increased above 0.25 g/L, the inactivation process becomes slow where more bacterial colonies are detected for photocatalyst loading of 0.5 and 1.0 g/L. A high amount of catalyst in the solution results in turbidity increase that blocks the radiation to reach to microorganisms and other catalyst particles (shadowing or screening effect), which leads to a low rate of inactivation. The similar effect is observed for the UV photocatalytic inactivation [63, 64].

4.1.3. Effect of pH

It is reported that the inactivation of bacteria was not influenced by changing the pH of the solution. The rate constant also remains constant for all pH range [64]. The zero point of charge (ZPC) for TiO_2 -AgNP and *E. coli* can be estimated as ZPC (TiO_2 -AgNP) = 4.0 and ZPC (*E. coli*) = 2.5, respectively. At all the pH values studied, both *E. coli* and the catalyst had a negative surface charge. Therefore, the electrostatic repulsion between bacterial cells and catalyst particles could result in the similar inactivation effect.

4.2. Dye degradation

The performance of TiO_2 -AgNP photocatalyst is investigated for dye photodegradation under visible light. Among dyes studied as examples in photodegradation test include methylene blue [31, 66], rhodamine-B (RD-B) [33], and acid read 8S [67].

4.2.1. The activity of TiO₂-AgNP photocatalyst under visible light

TiO₂-AgNP photocatalyst shows higher activity under visible light in the photodegradation of dyes than that of bare TiO₂ [33, 31]. It means that TiO₂-AgNP is also photoactive in the visible region. The energy of the visible light (2.2–3.0 eV) is near the band gap energy of TiO₂-AgNP, which is about 2.7–2.9 eV [72, 75]. The visible light is required to activate TiO₂-AgNP for the dye photodegradation. The energy of the visible light is slightly lower than the band gap of TiO₂ anatase (3.2 eV) and TiO₂ rutile (3.0 eV). The visible light is unable to excite an electron in TiO₂. Therefore, the photocatalytic performance of TiO₂ is weak.

Increasing Ag content in TiO_2 -AgNP promotes photodegradation as shown in many works. But further increase in Ag content could have a detrimental effect on the photodegradation result [31, 33, 66, 68]. The optimum Ag content in TiO_2 -AgNP is found be at about 2.5 w% [33], 0.80% mol [66], and 0.25 mol% [68].

The effect of Ag content in TiO_2 -AgNP on photocatalytic activity can be explained as follows. The appropriate amount of Ag-doped TiO_2 allows effective capture of the photoinduced electrons [31, 33, 66, 67]. The photoinduced electrons during light irradiation results in negatively charged Ag. The photoinduced electrons can be immediately transferred to oxygen atoms of TiO_2 . The electron transfer from the TiO_2 conduction band to metallic silver particles at the interface is thermodynamically favorable because the Fermi level of TiO_2 is higher than that of silver metals [31, 33]. It results in the formation of the Schottky barrier at metal-semiconductor contact region, which improves the charge separation. Accordingly, the recombination of the electron and the OH radicals can be inhibited more [33]. This condition explains the significant enhancement of the photocatalytic activity of TiO_2 -AgNP. The increase in Ag content will keep the photodegradation improve until it reaches its optimum.

At high Ag loading above its optimum level, an excess amount of negatively charged silver species are available. A significant amount of the negatively charged silver particles allows silver atoms to attract more OH radicals. However, it reduces charge separation efficiency [31, 35, 66] or raises electron-hole recombination and decrease dye photodegradation. Another possible reason is the formation of silver metallic clusters inside the TiO₂ crystal. The metal clusters give small contact surface area of the photocatalyst. The atomic Ag in TiO₂-AgNP may act as a barrier to obstruct light absorption by titania. It also prevents organic substrates from contacting the photocatalyst surface. Silver atoms may become media for electron-hole recombination [44]. As a result, they reduce photodegradation reaction.

4.2.2. The performance of TiO₂-AgNP under UV light in the dye photodegradation

The photocatalyst working under the UV light is frequently assessed for dye photodegradation such as methyl orange [68], diazo type dye of DR 23 and DB 53 [69, 70] and methylene blue [74, 82]. It is evident that in the presence of Ag, the photocatalytic performance of the TiO_2 -AgNP under UV light improves. The photocatalytic activity of TiO_2 -AgNP under the UV light is higher than that of unmodified one. The role of the Ag in the improvement of the dye photodegradation under UV light can explain similarly to the effect of Ag under visible light.

The photodegradation performance of TiO_2 -AgNP under visible light is better than under UV light. In the case of rhodamine-B degradation, the dye can be adsorbed by Ag particle in TiO_2 -AgNP. The dye adsorbed on the Ag surface can be activated by visible light because the dye absorbs the electromagnetic radiation in the range of visible light. The activated dye molecules are unstable and start to degrade. On the one hand, the lower UV light photocatalytic activity of TiO_2 -AgNP may be due to surface plasmon resonance of metallic Ag that reduces UV light excitation [66]. This unexcitability of the photocatalyst leads to the low dye photodegradation.

4.2.3. Effect of the process conditions

The dye photodegradation of dye by TiO_2 -AgNP under UV light is controlled by the level of Ag in photocatalysts and irradiation light. Also, the effectiveness of the dye photodegradation is affected by operating conditions such as photocatalyst dose, initial concentration, contact time and solution pH.

4.2.3.1. The effect of the photocatalyst dose

The dye photodegradation increases with the increase in the photocatalyst dose. The effectiveness of the photodegradation reduces when the photocatalyst dose is further increased [66–68, 81]. The maximum photodegradation is obtained by using 1 g photocatalyst/100 mL [68, 74, 81]. In other work, the use of 0.6 g photocatalyst/L is also reported [67]. Such data can be explained based on the number of active sites available for photocatalytic reactions. More active sites of the photocatalyst are available when the dose of the photocatalyst increases. However, the use of a large number of photocatalysts may cause agglomeration of the material to produce big particle size. The large particle size gives small surface area, which decreases the number of active sites on the surface [36, 38]. Another reason for the decrease in the degradation can be attributed to the increase in the turbidity of suspension due to more suspended photocatalyst solids. The light scattering by the catalyst particles leads to the blockage of photon absorption. Moreover, less OH radicals can be created [1, 2].

4.2.3.2. Effect of initial pH

In the acidic pH, the effectiveness of the dye photocatalytic degradation over TiO_2 -AgNP is found to be low. The photodegradation improves as pH increasing, but when the pH is increased further the photodegradation declines. For methyl orange photodegradation, the optimum pH is reached at 3 [68]. The dye degradation over heterogeneous photocatalyst of TiO_2 is initiated by adsorption on photocatalyst surface, leading to sequentially or simultaneously dye degradation. The effectiveness of the adsorption and degradation of dye depends on the surface charge of the catalyst and solution pH. The pH is an effective parameter to

affect the surface state [68, 74]. The amphoteric characteristics of synthesized oxides influence the surface charge of the photocatalyst. The pH of dye solution varies with the surface charge of the photocatalyst and shifts the position of redox reaction [68, 74]. Based on the amphoteric characteristics of TiO₂, the following equilibriums take place:

$$Ti - OH + H^{+} \rightleftharpoons Ti - OH_{2}^{+}$$
(4)

$$Ti - OH + OH^{-} \rightleftharpoons Ti - O^{-} + H_{2}O$$
(5)

Concerning the reactions (4) and (5), it is evident that the surface of the photocatalyst can become positively charged in acidic medium and negatively charged in alkaline medium. On the other side, methyl orange in the aqueous medium is in the anionic state that can also affect the adsorption.

At pH lower than 3, the H⁺ ions cause the dye to become positively charged. Note that the surface of the catalyst is also positive. Since both dye and photocatalyst are positively charged, it will inhibit adsorption and photodegradation. At pH 3, the dye becomes anionic, while the photocatalyst surface is still positively charged. It facilitates better electrostatic attraction between dye molecules and positively charged photocatalyst surface, which speeds up the photodegradation. At pH greater than 7, the surface of the photocatalyst has become negatively charged, which leads to electrostatic repulsion between methyl orange and photocatalyst. Therefore, it results in a decrease in the dye photodegradation efficiency [68].

Different from the anionic dye, a cationic dye such as methylene blue shows the maximum adsorption and photodegradation at neutral to basic pH. At low pH, the photodegradation may occur less efficient due to electrostatic repulsion between methylene blue molecules and photocatalyst, since both dye molecules and photocatalyst have positive charges. The electrostatic repulsion can inhibit adsorption that results in a decline in the dye degradation. In neutral pH, the dye species is positively charged, whereas photocatalyst is neutral so that they create electrostatic interaction. At higher pH, the dye is neutral, whereas the photocatalyst is in the anionic state, which facilitates efficient adsorption and photodegradation [68]. The maximum photodegradation for this dye takes place at pH 9 [74].

4.2.3.3. Effect of the initial dye concentration

It is apparent that the dye photodegradation reduces gradually when dye concentration improves [66, 75]. At low dye concentration, a few dye molecules in solution can move freely into the active surface of the photocatalyst. When the abundant active sites of the photocatalyst are available to absorb the dye, the dye photodegradation becomes efficient. High dye concentration gives more dye molecules that hinder their movement close to the photocatalyst. Therefore, the adsorption and the photodegradation decrease. For the photocatalyst, the surface has been occupied by much dye that diminishes the active sites at the surface. It leads to less dye adsorption and declines photodegradation [66, 74, 75].

4.2.3.4. Effect of the irradiation time

The UV light irradiation time can represent: (1) how long the photocatalyst contact with irradiating light, for further formation of OH radicals and (2) how long the contact between dye with OH radicals to proceed photodegradation. A general trend shows that the extension of the irradiation time enhances photodegradation, but the photodegradation stays constant or even decreases slightly for extended irradiation. Long UV light exposure produces more OH radicals, which helps the photodegradation take place more efficiently. However, further addition of irradiation time leads to surface saturation of the photocatalyst to release OH radicals [66, 75].

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References

- [1] Hoffmann MR, Martin ST, Choi W, Bahnemann DW. Chemical Reviews. 1995;95:69-96
- [2] Linsebigler AL, Guangquan LJ Jr, Yates T. Chemical Reviews. 1995;95:735-758
- [3] Nakata K, Fujishima A. Journal of Photochemistry and Photobiology C: Photochemistry Reviews. 2012;13:169-189
- [4] Fujishima A, Rao TN, Tryk DA. Journal of Photochemistry and Photobiology C. 2000;1:1-21
- [5] Mills A, O' Rourke C, Moore K. Journal of Photochemistry and Photobiology A: Chemistry. 2015;310:66-105
- [6] Caballero L, Whitehead KA, Allen NS, Verran J. Journal of Photochemistry and Photobiology A. 2009;202:92-98
- [7] Cai R, Hashimoto K, Itoh K, Kubota Y, Fujishima A. Bulletin of the Chemical Society of Japan. 1991;4:1268-1273
- [8] McCullagh C, Robertson J, Bahnemann D, Robertson P. A review. Research on Chemical Intermediates. 2007;33:359-375
- [9] Peller JR, Whitman RL, Griffith S, Harris P, Peller C, Scalzitti J. Journal of Photochemistry and Photobiology, A: Chemistry. 2007;**186**:212-217
- [10] Kiwi J, Nadtochenko V. Langmuir. 2005;21:4631-4641
- [11] Foster HA, Ditta IB, Varghese S, Steele A. Applied Microbiology and Biotechnology. 2007;90:1847-1868
- [12] Sökmen M, Özkan A. Short communication. Journal of Photochemistry and Photobiology A: Chemistry. 2002;147:77-81
- [13] Akpan UG, Hameed BH. A review. Journal of Hazardous Materials. 2009;170:520-529
- [14] Mukhlish MZB, Najnin F, Rahman MM, Uddin MJ. Journal of Scientific Research. 2013;5(2):301-314
- [15] Tayade RJ, Surolia PK, Kulkarni RG, Jasra RV. Science and Technology of Advanced Materials. 2007;8:455-462
- [16] Reza KM, Kurny ASW, Gulshan F. A review. Applied Water Science. 2017;7:1569-1578
- [17] Markovic D, Jokic B, Saponjic Z, Potkonjak B, Jovancic P, Radetic M. Clean Soil, Air, Water. 2013;41(10):1002-1009
- [18] Joseph C, Sharain-Liew YL, Bono A, Teng LY. Asian Journal of Chemistry. 2013;25(15): 8402-8406
- [19] Ahmed MA, El-Kator EE, Gharni ZH. Journal of Alloys and Compounds. 2013;553:19-29
- [20] Li R, Jia Y, Bu N, Wu J, Zhen Q. Journal of Alloys and Compounds. 2015;643:88-93
- [21] Ajmal A, Majeed I, Malik RN, Idriss H, Nadeem MA. A comparative overview. RSC Advances. 2014;4:37003-37026
- [22] Zuo R, Du G, Zhang W, Liu L, Liu Y, Mei L, Zhaohui LZ. Hindawi publishing corporation. Advances in Materials Science and Engineering. 2014:1-7
- [23] Mehra M, Sharma TR. Advances in Applied Science Research. 2012;3(2):849-853
- [24] Gautam A, Kshirsagar A, Biswas R, Banerjee S, Khann PK. RSC Advances. 2016;6:2746-2759
- [25] Giwa A, Nkeonye PO, Bello KA, Kolawole KA. Journal of Environmental Protection. 2012;3:1063-1069
- [26] Carcel RA, Andronic L, Duta A. Journal of Nanoscience and Nanotechnology. 2011; 11(10):9095-9101
- [27] Subramani AK, Byrappa K, Anand S, Lokanatha Rai KM, Ranganathaiah C, Yoshimura M. Bulletin of Materials Science. 2007;30(1):37-41
- [28] Khataee AR, Kasiri MB. Journal of Molecular Catalysis A: Chemical. 2010;328(1-2):8-26
- [29] Neppolian B, Choi HC, Sakthivel S, Arabindoo B, Murigusen V. Journal of Hazardous Materials. 2002;89(2-3):303-317
- [30] Mahadwad OK, Jasra RV, Parikh PA, Tayade RJ. Journal of Environmental Science & Engineering. 2010;52(3):181-184
- [31] Seery MK, George R, Floris P, Pillai SC. Journal of Photochemistry and Photobiology A: Chemistry. 2007;189:258-263

- [32] Pelaez M, Nolan NT, Pillai SC, Seery MK, Falaras P, Konto AG, Dunlop PSM, Hamilton JW, Byrne JA, O'shea K, Entezari MH, Dionysiou DD. Applied Catalysis B: Environmental. 2012;125:331-349
- [33] Sung-Suh HM, Choi JR, Hah HJ, Koo SM, Bae YC. Journal of Photochemistry and Photobiology A: Chemistry. 2004;163:37-44
- [34] Sontakke S, Mohan C, Modak J, Madras G. Chemical Engineering Journal. 2012; 189-190:101-107
- [35] Colmenares JC, Aramedia MA, Marinas A, Marinas JM, Ubano FJ. Applied Catalysis A: General. 2006;306:120-127
- [36] Cong Y, Zhang J, Chen F, Anpo M. Journal of Physical Chemistry C. 2007;111(19):6976-6982
- [37] Yates HM, Nolan MG, Sheel DW, Pemble ME. Journal of Photochemistry and Photobiology A: Chemistry. 2006;**179**:213-223
- [38] Cheng X, Yu X, Xing Z, Wan J. Energy Procedia. 2012;16:598-605
- [39] Cheng X, Yu X, Xing Z, Yang L. Arabian Journal of Chemistry. 2016;9:1706-1171
- [40] Mekprasart W, Pecharapa W. Energy Procedia 9th Eco-Energy and Materials Science and Engineering Symposium. 2011;9:509-514
- [41] Nassoko D, FangLi Y, Wang H, Li J-L, Li Y-Z, Yu Y. Journal of Alloys and Compounds. 2012;540:228-235
- [42] Ananpattarachai J, Kajitvichyanukul P, Seraphin S. Journal of Hazardous Materials. 2009;168(1):253-261
- [43] Zhou X, Peng F, Wang H, Yu H, Yang J. Materials Research Bulletin. 2011;46(6):840-844
- [44] Devi LG, Kavitha R. Materials Chemistry and Physics. 2014;143(3):1300-1308
- [45] Rockafellow EM, Stewart LK, Jenks WS. Applied Catalysis B: Environmental. 2009;91(1-2):554-562
- [46] Szatmáry L, Bakardjieva S, Šubrt J, Bezdičkza P, Jirkovský J, Bastl Z, Brezová V, Korenko M. Catalysis Today. 2011;161(1):23-28
- [47] Yu J, Liu S, Xiu Z, Yu W, Feng G. Journal of Alloys and Compounds. 2009;471(1-2):23-25
- [48] Lu J, Dai J, Guo M, Yu L, Lai K, Huang B. Applied Physics Letters. 2012;100:102114
- [49] Hiroshi I, Yuka W, Hashimoto Kazuhito H. Chemical Letters. 2003;32(8):772-773
- [50] Yu S, Yun HY, Kim YH, Yi J. Applied Catalysis B: Environmental. 2014;144:893-899
- [51] Yang Y, Ni D, Yao Y, Zhong Y, Ma Y, Yao J. RSC Advances. 2015;5:93635-93643
- [52] Morikawa T, Irokawa Y, Ohwaki T. Applied Catalysis A: General. 2006;314:123-127
- [53] Zhu J, Chen F, Zhang J, Chen H, Anpo M. Journal of Photochemistry and Photobiology, A: Chemistry. 2006;180(19):196-204

- [54] Siddhapara KS, Shah DV. Advances in Materials Science and Engineering. 2014;4
- [55] Khakpash N, Simchi A, Jafari T. Journal of Materials Science: Materials in Electronics. 2012;23:659-667
- [56] Yang S, Lee H. Nanoscale Research Letters. 2017;12:582
- [57] Razali MH, Ahmad-Fauzi MN, Mohamed AR, Sreekantan S. International Journal of Materials, Mechanics and Manufacturing. 2013;1(4)
- [58] Ribao P, Maria J, Rivero MJ, Ortiz I. Environmental Science and Pollution Research. 2017;24:12628-12637
- [59] Adán C, Marugán J, Obregón S, Colón G. Catalysis Today. 2015;240:93-99
- [60] Batalović K, Bundaleski N, Radaković J, Abazović N, Mitrić M, Silva RA, Savić M, Belošević-Čavor J, Rakočević Z, Rangel CM. Physical Chemistry Chemical Physics. 2017;19:7062-7071
- [61] Enachia M, Guixb M, Branistea T, Postolachea V, Ciobanua V, Ursakic V, Schmidtb OG, Tiginyanu I. Электронная обработка материалов (in English). 2015;**51**(1):3-8
- [62] Grabowska E, Remita H, Zalezka A. Physicochemical Problems of Mineral Processing. 2010;45:29-38
- [63] Maicu M, Hidalgo MC, Colón G, Navío JA. Journal of Photochemistry and Photobiology A: Chemistry. 2011;217:275-283
- [64] Sontakke S, Modak J, Madras G. Chemical Engineering Journal. 2010;165:225-233
- [65] Sontakke S, Modak J, Madras G. Applied Catalysis B: Environmental. 2011;106:453-459
- [66] Li Y, Ma M, Chen W, Li L, Zen M. Materials Chemistry and Physics. 2011;129:501-505
- [67] Li H, Cui Q, Feng MB, Wanga J, Wenga XLJ. Applied Surface Science. 2013;284:179-183
- [68] Anandan S, Sathish Kumar P, Pugazhenthiran N, Madhavan J, Maruthamuthu P. Solar Energy Materials & Solar Cells. 2008;92:929-937
- [69] Suwarnkar MB, Dhabbe RS, Kadam AN, Garadkarn KM. Ceramics International. 2014;40:5489-5496
- [70] Sobana N, Muruganadhan M, Swaminathan M. Journal of Molecular Sciences. 2006;13: 13275-13293
- [71] Sobana N, Selvam K, Swaminathan M. Separation and Purification Technology. 2008;62: 648-653
- [72] Chan SC, Barteau MA. Langmuir. 2005;21:5588-5595
- [73] Lenzi GG, Fávero CVB, Colpin LMS, Bernabe H, Baesso ML, Specchia S, Santo OAA. Desalination. 2011;270:241-247
- [74] Bo Z, Eaton RT, Gallagher JR, Canlas CP, Miller T, Notestein JM. Chemistry of Materials. 2015;27:1269-1277

- [75] Kumar R, Rashid J, Barakat MA. Colloids and Interface Science Communications. 2015;2:1-4
- [76] Koci K, Mateju K, Obalova L, Krejcikova S, Lacny Z, Placha D, Capek L. Applied Catalysis
 B: Environmetal. Review. 2010;96:239-244
- [77] Sze CC, Barteau MA. Langmuir. 2005;21:5588-5595
- [78] Demircia S, Dikicib T, Yurddaskal M, Gultekind S, Toparli M, Celik E. Applied Surface Science. 2016;390:591-601
- [79] Mei S, Wang H, Wang W, Ton L, Pan H, Ruan C, Ma Q, Yang LU, Zhang L, Cheng Y, Zhang Y, Zhao L, Chu PK. Biomaterials. 2014;35:4255-4265
- [80] Zhao L, Wang H, Huo K, Cui L, Zhang W, Ni H, Zhang Y, Wu Z, Chu PK. Biomaterials. 2011;32:5706-5716
- [81] Asghari S, Ramezani S, Ahmadipour M, Hatami M. Designed Monomers and Polymers. 2014;16(4):349-335
- [82] Wahyuni ET, Roto R, Prameswari M. Proceeding of the 15th International Conference on Environmental Science and Technology, August 31–September 2, 2017, Rhodes Island; 2017
- [83] Chang CC, Lin C-K, Chan C-C, Hsu C-S, Chen C-Y. Thin Solid Films. 2006;494:274-278
- [84] Lei XF, Xue XX, Yang H. Applied Surface Science. 2014;321:396-403
- [85] Zhou Y, Kong Y, Kundu S, Cirillo JD, Liang H. Journal of Nanobiotechnology. 2012;10:19
- [86] Ge L, Li Q, Wang M, Ouyang J, Li X, Xing MMQ. International Journal of Nanomedicine. 2014;9:2399-3407

Solar Cell and Other Applications

Controlling the Microstructure and Properties of Titanium Dioxide for Efficient Solar Cells

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Additional information is available at the end of the chapter

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Abstract

In this chapter, we review the controlling of the microstructures, the properties, and the different methods to obtain titanium dioxide and the application of these materials on solar cells. We will concentrate on the application of efficient solar cells including dye-sensitized solar cells (DSSCs). In the first section, we provide a background on energy, including its sources—photovoltaics and titanium dioxide—and the advantages of their application in solar cells. The second section outlines the different methods to obtain TiO_2 nanoparticles. The shapes of titanium dioxide are explored in the third section. In the fourth section, we discuss the use and effect of the titanium dioxide in the efficient dye-sensitized solar cells, and the last section is a summary of the current state of the art and perspectives of titanium dioxide for efficient solar cells.

Keywords: titanium dioxide, nanoparticles, solar cells, dye-sensitized solar cells, efficiency, applications

1. Introduction

The focus of this chapter is to study a general background on titanium dioxide and explain the different methods of its preparation including dry and wet chemical methods. In this section, the importance of titanium dioxide and the effect of different structural morphologies of titania are depicted with the efficiency of the solar cell applications especially dye-sensitized solar cells (DSSCs).

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1.1. Sources of energy

Energy makes change; it does things for us. The cars along the road as well as the boats over the water can be moved by energy. A cake in the oven and the ice frozen in the freezer also are been done using energy. It plays our favorite songs on the radio and lights our homes. Energy enables our bodies grow and make our minds to think. Scientists define energy as the ability to do work. Energy sources are classified into renewable and nonrenewable sources as shown in **Figure 1**.

Most of our energy is extracted from nonrenewable energy sources. Coal, petroleum, natural gas, propane, and uranium are nonrenewable energy sources. The name of nonrenewable energy sources has appeared because their supplies are limited. Petroleum, for example, was formed millions of years ago from the remains of ancient sea plants and animals. A long period of time is needed to deposit more crude oil.

Renewable energy sources include biomass, geothermal energy, hydropower, solar energy, and wind energy. They are replenished in a short time, so they are called renewable. Electricity is mainly produced from renewable energy sources. Sunlight, or solar energy, can be used directly for heating, lighting, generating electricity, and many other applications [1, 2]. Indirectly, sun's heat also creates winds, whose energy is used to generate electricity by wind turbines, which is called wind energy. Plants are grown by sunlight. Biomass is the organic matter which is composed of plants. It can be used, for example, to produce electricity and transport fuels. Furthermore, geothermal energy absorbs the Earth's internal heat and can be used for a large variety of applications such as building heating and electricity production. Ocean energy draws on energy of the ocean waves, currents, and tides which can under favorable conditions be used for the production of electricity. Global energy consumption consists of six primary sources: 44% petroleum, 26% natural gas, 25% coal, 2.5% hydroelectric power, 2.4% nuclear power, and 0.2% non-hydro renewable energy [3]. Between 1990 and 2010, worldwide consumption of petroleum, coal, and natural gas is enhanced by 22, 27, and 71%, respectively.



Figure 1. Renewable and nonrenewable energy sources. From Ref. [4]. Reprinted with permission from WordPress.

1.2. Solar energy

Solar energy develops a large variety of techniques, including photovoltaic systems, concentrating solar power, passive solar systems, solar hot water, and solar process heat [5].

Conversion of the light energy into electricity is the main use of photovoltaic solar cells and has been existing for a long time; many applications like solar panels on satellites and smaller uses as calculator or watch energy supply, which is familiar for everyone, enable them to be famous. The solar energy is instituted on the solar cell (photovoltaic) effect, which allows the conversion of light (photons) to electricity (electrons).

1.3. Photovoltaic (PV) technology

Electricity is a necessity in everyday life. The cheapest and available power plays a very crucial role in the economic development of the industrialized nations. At the beginning of the twenty-first century, more than 80% of electricity is generated by burning fossil fuels (coal, gas, and oil) [6]. Because of the limited supply of fossil fuels and the growing concerns about global warming, the use of more and more renewable energy sources in energy production is being encouraged in different parts of the world [7]. Among the various sources of renewable energy, solar energy has been considered to have great potential because of the virtually unlimited (100 KTW) supply of sunlight on the Earth [8]. The technology which harnesses the solar energy and converts it into electrical energy is called photovoltaic (PV) technology.

1.4. Titanium dioxide

The semiconductor of choice for making dye-sensitized solar cells (DSSCs) due to its good properties is titanium dioxide, TiO_2 , also known as titania. This material is a cheap and harmless water-insoluble inorganic material that is related to the family of transition metal oxide [9]. Although TiO_2 is a chemically inert substance and it does not promote chemical reactions in the absence of light, particular safety measures are needed when handling nanosized titania [10]. Moreover, TiO_2 has a strong ionic character and can be noticed as being constituted of Ti^{IV+} and O^{2-} ions. The conduction band is formed by the 3d orbital of titanium, and the valence band is obtained by the 2p orbital of oxygen. TiO_2 is commercially available and widely used in industrial applications [11].

The most common form of this oxide in nature is rutile. Another form is brookite. A third form of this oxide is anatase, which is the thermodynamically stable crystalline form at high pressure. In all of them, each titanium is surrounded by six oxygen atoms, leading to more or less distorted TiO_{6}^{2-} octahedrons. Crystal structures differ by the distortion of each octahedron and by the assembly patterns of the TiO_{6}^{2-} units [12]. For the rutile structure, each octahedron is connected with 10 neighbors (two sharing edge oxygen pairs and eight sharing corner oxygen atoms), while for the anatase and brookite structures, every moiety is in contact with eight neighbors (four sharing an edge and four sharing a corner) as shown in **Figure 2**. Three-dimensional TiO_{2} network is obtained from a mixture of corner-sharing and edge-sharing octahedral units [13].



Figure 2. Rutile, anatase, and brookite unit cells, all showing octahedral titanium coordination. Gray and red atoms correspond to Ti^{4+} and O^{2-} , respectively. Reproduced from Ref. [14] with permission from American chemical society 2010.

The most stable phase for titania is anatase below the particle size of 11 nm [15]. The structural parameters lead to differences in mass density and electronic band structure, inducing inherent properties to each polymorph. Then, it is widely confirmed that anatase is the most photoactive TiO_2 phase, although a mixture of anatase and rutile is preferred for photocatalytic applications [16].

2. Synthesis of titania nanoparticles

An exponential growth of research activities has been noticed in nanoscience and nanotechnology in the past decades [17, 18]. When the size of the material becomes smaller and smaller, down to the nanometer scale, new physical and chemical properties are obtained. Properties also change by the changing in the morphologies of the shrinking nanomaterials. One of the best features of these materials is the swimming of electrons and holes in semiconductor nanomaterials, which are first organized using the well-known quantum confinement, and the moving features owned to phonons and photons are greatly related to the size and geometry of the materials [19]. The specific surface area and surface-to-volume ratio increase dramatically as the size of a material decreases [20, 21]. Continuously, breakthroughs have been made in the preparation, modification, and applications of TiO_2 nanomaterials. Here, we focus on recent progress in the synthesis, properties, modifications, and applications of TiO_2 nanomaterials. The syntheses of TiO_2 nanomaterials, including nanoparticles, nanorods (NRs), nanowires (NWs), and nanotubes (NTs), are primarily categorized with the preparation techniques. For detailed instructions on each synthesis, the readers are referred to the corresponding literature related to the common major four preparation methods as well as the obtained shapes of titanium dioxide nanopowders.

2.1. Synthetic methods for titanium dioxide nanostructures

2.1.1. Sol-gel method

TiO₂ nanomaterials have been synthesized by the sol-gel method from hydrolysis of a titanium precursor. This process normally happened through an acid-catalyzed hydrolysis step of titanium (IV) alkoxide followed by condensation as shown in **Figure 3**. The improvement of Ti–O–Ti bonds is developed with small amount of water, low hydrolysis rates, and excess amount of

Controlling the Microstructure and Properties of Titanium Dioxide for Efficient Solar Cells 355 http://dx.doi.org/ 10.5772/intechopen.72494



Figure 3. (a) An illustration of the mechanisms of sol-gel processes: (A) acidic conditions, (B) alkaline conditions, and (C) P123-templated, containing weak alkaline conditions in this. (b) SEM images of the surface of the tubular titania membrane. Reproduced from Ref. [25] with permission from The Royal Society of Chemistry.

titanium alkoxide in the reaction content [22]. Polymeric skeletons with three-dimensional structure show close packing result from the enhancement of Ti–O–Ti chains. The Ti(OH)₄ is preferred to be obtained with high hydrolysis rates for a medium amount of water. The existence of a large quantity of Ti–OH and scanty development of three-dimensional polymeric skeletons resulted in freely packed first-order particles. Polymeric Ti–O–Ti chains are improved in the presence of a big amount of water [23]. The different sizes and shapes of highly crystalline anatase TiO₂ nanoparticles could be obtained by the polycondensation of titanium alkoxide in the presence of tetra methyl ammonium hydroxide [24].

2.1.2. Hydrothermal and solvothermal methods

Hydrothermal synthesis includes the different techniques of crystallizing substances from high-temperature aqueous solutions at high vapor pressures, whereas solvothermal method includes crystallization of materials in alcohol-based solvent such as ethanol, methanol, n-propanol, and n-butanol. The hydrothermal method has been used by many groups to obtain TiO, nanoparticles [26, 27]. For instance, hydrothermal treatment of peptized precipitates of a titanium precursor with water is considered to be a good source of TiO₂ nanoparticles [28]. The precipitate materials were fabricated by adding a 0.5 M isopropanol solution of titanium butoxide into deionized water ([H,O]/[Ti]) [29], and then they were peptized at 70°C for 1 h in the presence of tetra alkyl ammonium hydroxides (peptizer). After that, filtration and treatment have been done at 240°C for 2 h; then, the as-obtained powders were washed with deionized water and absolute ethanol and then dried at 60°C. With the same amount of peptizer, the particle size decreased with increasing alkyl chain length. The morphology of the particles is affected by the peptizers and their concentrations. In another example, TiO, nanoparticles were prepared by hydrothermal reaction of titanium alkoxide in an acidic ethanol-water solution [30]. Besides TiO, nanoparticles, TiO, nanorods have also been synthesized with the hydrothermal method [31] that obtained TiO, nanorods by treating a dilute TiCl₄ solution at 333–423 K for 12 h in the presence of acid or inorganic salts [32]. **Figure 4** illustrates the fabrication process of the titania nanorods (TNRs) film on FTO substrate via hydrothermal method as well as the SEM image of TiO, nanoparticles.

The solvothermal method has been found to be a versatile method for the synthesis of a variety of nanoparticles with narrow size distribution and disparity [33]. TiO₂ nanoparticles and nanorods with narrow size distributions can also be developed with the solvothermal method [34]. For example, in a typical synthesis from [35], the suspension of TiO₂ powder has been done by keeping 5 M NaOH water-ethanol solution at 170–200°C for 24 h in an autoclave and then cooled to room temperature naturally. After that, the obtained sample is washed with a dilute HCl aqueous solution and dried at 60°C for 12 h in air. Then, TiO₂ nanowires are obtained. The crystal morphology determination is highly dependent on the solvent used.

2.1.3. Chemical vapor deposition and physical vapor deposition methods

Materials in a vapor state are condensed to form a solid-phase material is the meaning of vapor deposition operation. These operations are basically used to form coatings to prevent the mechanical, electrical, thermal, optical, corrosion resistance, and wear resistance properties of various substrates. Lately, they have been exceedingly reconnoitered to prepare different shapes of nanomaterials. A vacuum chamber is a place where the vapor deposition process is taken place. In case where no chemical reaction happens, this operation is named physical vapor deposition (PVD); otherwise, it is named chemical vapor deposition (CVD). In CVD processes, thermal energy heats the gases in the coating chamber and drives the deposition reaction. On the other hand, plasma-enhanced chemical vapor deposition (PECVD) is a chemical vapor deposition process used to deposit thin films from a gas state (vapor) to a solid state on a substrate as shown in the schematic diagram in Figure 5. Chemical reactions are implicated in the operation, which happened following the creation of a plasma of the reacting gases. The plasma is generally obtained using radio frequency (RF) (alternating current (AC)) or direct current (DC) discharge between two electrodes, the space between which is filled with the reacting gases. Furthermore, in PVD, materials are firstly evaporated and then condensed to obtain a solid material. The primary



Figure 4. (a) Fabrication process of the TNRs film on FTO substrate via hydrothermal method. (b) SEM photograph of a TiO_2 film resulted from P25 and titanium isopropoxide ethanol solution after hydrothermal treatment at 100 °C for 12 h. Reproduced from Ref. [36, 37, 57] with permission from AIMSpress 2016 and Royal Society of Chemistry 2014.

Controlling the Microstructure and Properties of Titanium Dioxide for Efficient Solar Cells 357 http://dx.doi.org/ 10.5772/intechopen.72494



Figure 5. Schematic diagram of the plasma-enhanced chemical vapor deposition (PECVD). Reproduced from Ref. [39] with permission from IOPScience publishers.



Figure 6. TEM image of TiO_2 nanoparticles with an average size of 21 nm obtained from Evonik (Aerosil TiO_2 P-25). It consists of a mixture of 80% anastase and 20% rutile with a specific surface area of approximately 50 m2/g. Reproduced from Ref. [37, 41, 58] with permission from Springer Nature publishing 2017.

PVD methods contain thermal deposition, ion plating, ion implantation, sputtering, and laser vaporization. TiO_2 nanowire arrays have been assembled by a simple PVD method or thermal deposition [38].

2.1.4. Organic acid precursor method

The organic carboxylic acid precursor technique includes the preparation of aqueous solution of required cations and the chelation of cations in solution by addition of carboxylic acid then, raising the temperature of the solution until formation of the precursor. The precursor is calcined at low temperature. The method is also called combustion method, polymeric precursor method, and acid gel method (oxalate precursor, tartaric acid, lactic acid, and citrate precursor method). The process depends on complexation of metallic salts with aqueous solution of organic acid; the formed complex solution was evaporated at low temperature from 60 to 1000°C until viscous resin is formed; the formed polymer resin was dried and then calcined at low temperature from 200 to 1000°C for 1–4 h [40]. **Figure 6** shows TEM micrographs of titania nanopowders synthesized using organic acid precursor.

3. Shapes of titanium dioxide nanopowders for dye solar cells

Nowadays, most of the successful photovoltaic devices are assembled by semiconductor materials such as silicon (Si) [42]. In recent years, different alternatives to Si-based solar cells have become obtainable, and the large research is outstanding toward substantially decreasing the cost of electricity generation. Dye-sensitized solar cells (DSSCs) [43] are attractive alternative in comparison with others as they can be cheap, lightweight, portable, and flexible. On the other side, the attractive and extensive properties of titania (TiO₂) have led to its wide use in many industries, from traditional industries to high-technology industries [44]. The morphology and particle size of TiO₂ play critical roles in the photoelectric conversion efficiency of DSSCs [45]. For example, TiO₂ materials with different morphologies, such as nanoparticles [46], nanotubes [47], nanowires [48], and nanorods [49], have applied to fabricate the porous film electrodes. Nanostructured TiO₂ materials can be prepared by dry and wet processes as mentioned in the previous section. Because different reaction conditions, like reactants, reaction medium, temperature, and pH of solution, can be chosen in the wet processes, the crystallite size, crystal shape, and surface structure of the nanocrystals can be controlled more easily than that in the dry processes [50].

In particular, one-dimensional (1D) TiO, nanostructures, including nanorods (NRs) [49], nanowires (NWs) [48], and nanotubes (NTs) [47], have attracted large interest because of their unique microstructure and promising lineaments, like a high aspect ratio, high surface area, higher surface area/volume ratio, enhanced number of delocalized carriers, and increasing the charge transport afforded by dimensional anisotropy with the conventional properties [51]. Their remarkable properties have referred to their use in wide applications including dye-sensitized solar cells (DSSCs), photocatalysis, and photochromic devices [52]. For dyesensitized solar cell (DSSC) operation, 1D nanostructure-based photoanodes can contribute to rapid electron transport, ensuring efficient charge collection by the conducting substrate in competition with recombination. This point has promoted research on self-ordered, 1D photoanodes stretched on a substrate with enhanced electron transport properties due to their desirable features, namely, highly decreased intercrystalline contacts and a structure with a specified directionality. Kang et al. (2008) confirmed that TiO₂ nanorods (NRs) are believed to have exceptional properties and have been deemed an alternative to nanoparticles (NPs) as shown in Figure 7 [53]. Furthermore, increasing the delocalization of carriers in rods, where they can move freely throughout the length of the NRs, is expected to decrease the e^{-}/h^{+} recombination probability. However, this is partially recompensed by the traps in the



Figure 7. The TiO₂ photoanodes consisting of the NPs and NRs in the configuration of DSSCs (Kang et al., 2008). From Ref. [53]. Reprinted with permission from Royal Society of Chemistry 2016.

surface sites to guarantee more efficient charge separation [53]. Moreover, NRs can potentially enhance the charge transport in the photoanodes of DSSCs. In addition, NRs offer direct electrical pathways for photo-generated electrons and can enhance the electron transport rate, which in turn may improve the performance of DSSCs.

In the DSSC, the photoanode encompassed of oriented attachment. TiO_2 NRs showed the following two main advantages: (1) confirmation of high surface area directly proportional to the light-harvesting yield (dye uptake) resulted from the NRs synthesized from the necking of truncated NPs by recovering the low surface area of the general TiO₂ NRs and (2) fast electron transport rate and degraded charge recombination from the decreased intercrystal-line contacts between grain boundaries and specific directionality of NRs, bringing about the improved charge collection efficiency.

4. The architecture of the dye-sensitized solar cell (DSSC)

The architecture of a dye-sensitized solar cell (DSSC) is discussed in **Figure 8**. The DSSC consists of a dye-covered, nanoporous TiO_2 (titanium dioxide) layer and an electrolyte founded in between two glass substrates. Front and back electrodes are decorated with a transparent conducting oxide (TCO). Fluorine doped tin oxide (SnO₂: F), FTO, is the most widely known. The FTO at the back electrode is covered with few nanometers of atomic layers of platinum (Pt), which enhance the formation of electrons through the redox reaction with the electrolyte. The front electrode is covered firstly with thin layer of TiO_2 as a blocking layer which is responsible to prevent the holes from reaching the anode and then coated with a nanocrystalline TiO_2 layer with an average particle size of 5–20 nm. Considering a layer thickness of 10 µm, the resulting effective surface is about 1000 times larger than the dense compact TiO_2 layer. Three modifications of TiO_2 exist: rutile, anatase, and brookite. In the DSSC preferably only the anatase modification is used [54].

Subsequently, a monolayer of dye molecules (scattering layer) is adsorbed on the surface of the TiO_2 . The huge nanoporous surface allows for an adsorption of a sufficiently huge number of dye molecules for efficient light harvesting. The most widespread dye molecule employed in DSSC is usually a ruthenium (Ru) metal-organic complex, the so-called N719 [56]. The spectral absorption of the dye lies between 300 nm and 800 nm. Sufficient adsorption of the dye to the TiO_2 is critical and is obtained by the two carboxylic groups of the ligand (L = 2,2'-bipyridyl-4,4'-dicarboxylic acid) of the RuL₂ (NCS)₂. Finally, a liquid redox electrolyte is inserted between the two electrodes.



Figure 8. Schematic diagram of a solar cell sensitized by dye. The nanoporous semiconductor (TiO_2) and the redox electrolyte are founded between two substrates, covered with fluorinated tin oxide (FTO). The TiO₂ is filled with a dye, and the cathode is covered with a platinum layer. From Ref. [55]. Reprinted with permission from Springer Nature 2003.

4.1. How does the DSSC work?

When the solar light is irradiated, the dye sensitized it, and the electron excited from the valence band (VB) to the conduction band (CB) of the dye leaving a hole in the valence band. After that, the electron moves from the valence band of the dye to the valence band of the TiO_2 nanoparticles which facilitate the swimming of the electrons to the FTO anode substrate and then to the Pt cathode to generate electricity. On the other hand, the redox reaction occurs in the iodine electrolyte to facilitate the formation of the electron to fill the hole founded in the valence band of the dye to regenerate the electron in the cell, and the process occurs continuously.

4.2. Uses of titanium dioxide in DSSC

 TiO_2 is used for DSSCs for the following key properties: (i) is a suitable band that adjusts for electron injection from most commercial dyes, (ii) has a high surface area which is suitable for higher dye loading, and (iii) has high electronic mobility for photo-generated electron collection.

Nowadays, many groups and results mentioned that TiO_2 is the best available choice compared to other metal oxide semiconductors such as ZnO, $SnO_{2'}$ and so on due to the internal network structure which is important to achieve high charge collection efficiency and more electron transportation. These features enable a good electrode while fabricating a typical DSSC device.

5. Summary and perspectives

Since many years, titanium dioxide nanomaterials have been highly discussed because of their application in solar to electricity conversion for their matching with modern technologies. The persistent permeation in the synthesis and modifications of titanium dioxide nanomaterials has imparted novel properties and applications in the photovoltaic field with enhanced performance. Aside from that, recently improved devices depend on a novel concept that have largely expanded the application range of titanium dioxide and also put forwarded new requirements for titanium dioxide properties. In this chapter, the major advances of applying titanium dioxide nanomaterials to photovoltaics have been discussed, including the dye-sensitized solar cells. These steady progresses have demonstrated that TiO, nanomaterials play an important role in the search for efficient and low-cost photovoltaic technologies. The charge transfer process in these photovoltaic devices is nearly correlating with the features of titanium dioxide nanomaterials as well as the titanium dioxide interface. The unique physical and chemical properties of titanium dioxide nanomaterials can be controlled through modulation of nanocrystal structure, size, shape, and organization. Furthermore, the properties of titanium dioxide interface can be amended through the interaction between TiO₂ and the surrounding elements, including light harvesters, charge transport materials, additives, as well as interfacial modifiers. Moreover, many efforts have been done to develop large-scale preparation technique for high-quality, low-cost titanium dioxide nanomaterials and transformative technology. In order to realize the marketing economically of solar panels with wide application prospect, many studies have been considered. It is believed that future research efforts on new materials and key interfaces will make the titania-based solar cells as a new PV energy source.

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References

- Iychettira KK, Hakvoort RA, Linares P, de Jeu R. Towards a comprehensive policy for electricity from renewable energy: Designing for social welfare. Applied Energy. 2017;187:228-242
- [2] de Souza JS, De Andrade LOM, Müller AV, Polo AS. Nanomaterials for solar energy conversion: dye-sensitized solar cells based on ruthenium (II) Tris-heteroleptic compounds or natural dyes. Nanoenergy. 2018:69-106. https://doi.org/10.1007/978-3-319-62800-4_2

- [3] Kriegler E, Bauer N, Popp A, Humpenöder F, Leimbach M, Strefler J, Baumstark L, Bodirsky BL, Hilaire J, Klein D. Fossil-fueled development (SSP5): An energy and resource intensive scenario for the 21st century. Global Environmental Change. 2017;42:297-315
- [4] http://greenplanetethics.com/wordpress/renewable-and-non-renewable-energy-sourcesexplained/
- [5] Soon-HC. Thermal type seawater desalination with barometric vacuum and solar energy. 2017;141:1332-1349
- [6] DeCotis PA. Market-pricing idiosyncrasies present a twenty-first-century grid challenge. Natural Gas & Electricity. 2016;**32**:27-28
- [7] Lamnatou C, Chemisana D. Concentrating solar systems: Life Cycle Assessment (LCA) and environmental issues. Renewable and Sustainable Energy Reviews. 2017;78:916-932
- [8] Elseman AM, Rashad MM, Hassan AM. Easily attainable, efficient solar cell with mass yield of nanorod single-crystalline organo-metal halide perovskite based on a ball milling technique. ACS Sustainable Chemistry & Engineering. 2016;4:4875-4886
- Bonelli B, Esposito S, Freyria FS. Mesoporous titania: Synthesis, properties and comparison with non-porous Titania. Titanium Dioxide. 2017:119-141. DOI: 10.5772/ intechopen.68884
- [10] Vranic S, Gosens I, Jacobsen NR, Jensen KA, Bokkers B, Kermanizadeh A, Stone V, Baeza-Squiban A, Cassee FR, Tran L. Impact of serum as a dispersion agent for in vitro and in vivo toxicological assessments of TiO₂ nanoparticles. Archives of Toxicology. 2017; 91:353-363
- [11] Sterchele S, Bortolus M, Biasi P, Boström D, Mikkola J-P, Salmi T. Is selective hydrogenation of molecular oxygen to H₂O₂ affected by strong metal–support interactions on Pd/TiO₂ catalysts? A case study using commercially available TiO₂. Comptes Rendus Chimie. 2016;19:1011-1020
- [12] Luo B, Tang H, Cheng Z, Ji Y, Cui X, Shi Y, Wang B. Detecting the photoactivity of anatase TiO₂ (001)-(1× 4) surface by formaldehyde. Journal of Physical Chemistry C. 2017; 121:17289-172962017
- [13] Baldini E, Chiodo L, Dominguez A, Palummo M, Moser S, Yazdi-Rizi M, Auböck G, Mallett BP, Berger H, Magrez A. Strongly bound excitons in anatase TiO₂ single crystals and nanoparticles. Nature Communications. 2017;8:13. DOI: 10.1038/s41467-017-00016-6
- [14] Dambournet D, Belharouak I, Amine K. Chem. Mater. 2010;22(3):1173-1179
- [15] Satoh N, Nakashima T, Yamamoto K. Metastability of anatase: Size dependent and irreversible anatase-rutile phase transition in atomic-level precise titania. Scientific Reports. 2013;3:1959
- [16] Cao L, Chen D, Wu W-Q, Tan JZ, Caruso RA. Monodisperse anatase titania microspheres with high-thermal stability and large pore size (~80 nm) as efficient photocatalysts. Journal of Materials Chemistry A. 2017;5:3645-3654

- [17] Cogan NM, Liu C, Qiu F, Burke R, Krauss TD. Ultrafast dynamics of colloidal semiconductor nanocrystals relevant to solar fuels production. SPIE Defense+ Security. 2017 101930B-101930B-11
- [18] Rashad M, Shalan A, Lira-Cantu M, Abdel-Mottaleb M. Synthesis and characterization of mesoporous anatase TiO₂ nanostructures via organic acid precursor process for dyesensitized solar cells applications. Journal of Industrial and Engineering Chemistry. 2013;19:2052-2059
- [19] Liu XY, Chen H, Peng JH, Zhang JX. One-pot synthesis of close-packed titanium dioxides on graphene oxides. Ceramics International. 2016;42:11478-11481
- [20] Shalan AE, Narra S, Oshikiri T, Ueno K, Shi X, Wu H-P, Elshanawany MM, Diau EW-G, Misawa H. Optimization of a compact layer of TiO₂ via atomic-layer deposition for highperformance perovskite solar cells. Sustainable Energy & Fuels. 2017;1:1533-1540
- [21] Shalan A, Rasly M, Rashad M. Organic acid precursor synthesis and environmental photocatalysis applications of mesoporous anatase TiO₂ doped with different transition metal ions. Journal of Materials Science: Materials in Electronics. 2014;25:3141-3146
- [22] Rashad M, Elsayed E, Al-Kotb M, Shalan A. The structural, optical, magnetic and photocatalytic properties of transition metal ions doped TiO₂ nanoparticles. Journal of Alloys and Compounds. 2013;581:71-78
- [23] Mombrú D, Romero M, Faccio R, Mombrú AW. Microstructure evolution, thermal stability and fractal behavior of water vapor flow assisted in situ growth poly (vinylcarbazole)titania quantum dots nanocomposites. Journal of Physics and Chemistry of Solids. 2017; 111:199-206
- [24] Di Noto V, Boaretto N, Negro E, Bettiol M, Bassetto F. Hybrid membranes containing titanium dioxide doped with fluorine, Google Patents. 2017
- [25] Xueping C, Wenheng J, Weihong X, Yiqun F, Yan K, Junhang D. Fabrication of a visiblelight response mesoporous TiO₂ membrane with superior water permeability via a weak alkaline sol-gel process. Chemical Communications. 2011;47:3457-3459
- [26] Elgh B, Yuan N, Cho HS, Magerl D, Philipp M, Roth SV, Yoon KB, Müller-Buschbaum P, Terasaki O, Palmqvist AE. Controlling morphology, mesoporosity, crystallinity, and photocatalytic activity of ordered mesoporous TiO₂ films prepared at low temperature. APL Materials. 2014;**2**:113313
- [27] Cargnello M, Gordon TR, Murray CB. Solution-phase synthesis of titanium dioxide nanoparticles and nanocrystals. Chemical Reviews. 2014;114:9319-9345
- [28] Li L, Zhang P, Wang W-M, Lin H, Zerdoum AB, Geiger SJ, Liu Y, Xiao N, Zou Y, Ogbuu O. Foldable and cytocompatible sol-gel TiO, photonics. Scientific Reports. 2015;5:13832
- [29] Rezaee M, Mousavi Khoie SM. Mechanically induced polymorphic phase transformation in nanocrystalline TiO₂ powder. Journal of Alloys and Compounds. 2010;507:484-488
- [30] Krumdieck S, Gorthy R, Gardecka AJ, Lee D, Miya SS, Talwar SD, Polson MI, Bishop C. Characterization of photocatalytic, wetting and optical properties of TiO₂ thin films and

demonstration of uniform coating on a 3-D surface in the mass transport controlled regime. Surface and Coatings Technology. 2016;**326**:402-410

- [31] Jiang W, He X, Liu H, Yin L, Shi Y, Ding Y. Digital selective fabrication of micro/nanocomposite structured TiO₂ nanorod arrays by laser direct writing. Journal of Micromechanics and Microengineering. 2014;24:115005
- [32] Wang X, Li Z, Shi J, Yu Y. One-dimensional titanium dioxide nanomaterials: Nanowires, nanorods, and nanobelts. Chemical Reviews. 2014;114:9346-9384
- [33] Wang P, Zhang Y, Su L, Gao W, Zhang B, Chu H, Wang Y, Zhao J, William WY. Photoelectrochemical properties of CdS/CdSe sensitized TiO₂ nanocable arrays. Electrochimica Acta. 2015;165:110-115
- [34] Wang X, Zhuang J, Peng Q, Li YD. A simple chemical technique can be used to create a large family of high-quality nanocrystals. Nature. 2005;**437**:121-124
- [35] Wen B, Liu C, Liu Y. Depositional characteristics of metal coating on single-crystal TiO₂ nanowires. The Journal of Physical Chemistry. B. 2005;109:12372-12375
- [36] Pham Van V, Le Van H, Cao Minh T. The directed preparation of TiO₂ nanotubes film on FTO substrate via hydrothermal method for gas sensing application. AIMS Materials Science. 2016;3:460-469
- [37] Abazari R, Mahjoub RA, Sanati S. RSC Adv. 2014;4:56406-56414
- [38] Shalan AE, Rashad MM, Yu Y, Lira-Cantu M, Abdel-Mottaleb MSA. Controlling the microstructure and properties of titania nanopowders for high efficiency dye sensitized solar cells. Electrochimica Acta. 2013;89:469-478
- [39] Baghgar M, Abdi Y, Arzi E. Fabrication of low-pressure field ionization gas sensor using bent carbon nanotubes. Journal of Physics D: Applied Physics. 2009;42:135502
- [40] Mohamed RM, Rashad MM, Haraz FA, Sigmund W. Structure and magnetic properties of nanocrystalline cobalt ferrite powders synthesized using organic acid precursor method. Journal of Magnetism and Magnetic Materials. 2010;322:205
- [41] Mohamed MS, Torabi A, Paulose M, Kumar DS, Varghese OK. Scientific Reports. 2017;7: 1-11. Article number: 41844
- [42] Green MA, Emery K, Hishikawa Y, Warta W. Solar cell efficiency tables (version 31). Progress in Photovoltaics. 2008;16:61-67
- [43] Bartelt AF, Schütz R, Strothkämper C, Schaff J, Janzen S, Reisch P, Kastl I, Ziwritsch M, Eichberger R, Fuhrmann G. Efficient electron injection from acyloin-anchored semi-squarylium dyes into colloidal TiO₂ films for organic dye-sensitized solar cells. The Journal of Physical Chemistry C. 2014;118:6612-6623

- [44] Ali K, Khan SA, Jafri MM. Effect of double layer (SiO₂/TiO₂) anti-reflective coating on silicon solar cells. International Journal of Electrochemical Science. 2014;9:7865-7874
- [45] Gonzalez-Valls I, Lira-Cantu M. Dye sensitized solar cells based on vertically-aligned ZnO nanorods: Effect of UV light on power conversion efficiency and lifetime. Energy & Environmental Science. 2010;**3**:789-795
- [46] Freitag M, Teuscher J, Saygili Y, Zhang X, Giordano F, Liska P, Hua J, Zakeeruddin SM, Moser J-E, Grätzel M. Dye-sensitized solar cells for efficient power generation under ambient lighting. Nature Photonics. 2017;11:372-378
- [47] Gonzalez GL, Irene Gonzalez V, Monica Lira C, Angel Barrancoa Agustin R, Gonzalez E. Aligned TiO₂ nanocolumnar layers prepared by PVD-GLAD for transparent dye sensitized solar cells. Energy & Environmental Science. 2011;4:3426
- [48] Mehmood U, Malaibari Z, Rabani FA, Rehman AU, Ahmad SHA, Atieh MA, Kamal MS. Photovoltaic improvement and charge recombination reduction by aluminum oxide impregnated MWCNTs/TiO₂ based photoanode for dye-sensitized solar cells. Electrochimica Acta. 2016;203:162-170
- [49] Rajamanickam G, Narendhiran S, Muthu SP, Mukhopadhyay S, Perumalsamy R. Hydrothermally derived nanoporous titanium dioxide nanorods/nanoparticles and their influence in dye-sensitized solar cell as a photoanode. Chemical Physics Letters. 2017;689:19-25
- [50] Wang X, Karanjit S, Zhang L, Fong H, Qiao Q, Zhu Z. Transient photocurrent and photovoltage studies on charge transport in dye sensitized solar cells made from the composites of TiO₂ nanofibers and nanoparticles. Applied Physics Letters. 2011;98:082114
- [51] Yang Z, Xu T, Ito Y, Welp U. Enhanced electron transport in dye-sensitized solar cells using short ZnO nanotips on a rough metal anode. Journal of Physical Chemistry C. 2009;113:20521-20526
- [52] Subramaniam MR, Kumaresan D, Jothi S, JD MG, Watson TM. Reduced graphene oxide wrapped hierarchical TiO₂ nanorod composites for improved charge collection efficiency and carrier lifetime in dye sensitized solar cells. Applied Surface Science. 2017; 428:439-447
- [53] Hsieh M-Y, Lai F-I, Chen W-C, Hsieh M-C, Hu H-Y, Yu P, Kuo H-C, Kuo S-Y. Nanoscale. 2016;8:5478-5487
- [54] Shalan AE, Elseman AM, Rasly M, Moharam MM, Lira-Cantu M, Rashad MM. Concordantly fabricated heterojunction ZnO–TiO₂ nanocomposite electrodes via a coprecipitation method for efficient stable quasi-solid-state dye-sensitized solar cells. RSC Advances. 2015;5:103095-103104
- [55] Durrant JR, Haque SA. Solar cells: A solid compromise. Nature Materials. 2003;2:362-363

- [56] Lies S. Visible light photocatalysis of radical cation Diels–Alder cycloadditions: Preparation of Tris (2,2'-bipyrazyl) ruthenium(II) Bis (tetrakis(3,5-bis (trifluoromethyl)phenyl)borate). Organic Syntheses. 2016;**93**:178-199
- [57] Oekermann T, Zhang D, Yoshida T, Minoura H. Journal of Physical Chemistry B. 2004; 108:2227-2235
- [58] Wilke T, Schneider M, Kleinermanns K. Open Journal of Physical Chemistry. 2013;3(2): 97-102. DOI: 10.4236/ojpc.2013.32012

One-Dimensional Titanium Dioxide and Its Application for Photovoltaic Devices

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Abstract

One-dimensional (1D) TiO, nanostructures (e.g., nanotubes, nanobelts, nanowires, and nanorods) have been considered to be very attractive candidates for various applications including photocatalytic degradation of pollutants, photocatalytic CO₂ reduction into energy fuels, water splitting, solar cells, supercapacitors, and lithium-ion batteries. More importantly, the dimensionality associated with zero-dimensional TiO₂ nanostructures gives unique physical properties, including a high aspect ratio structure, chemical stability, excellent electronic or ionic charge transfer, and a specific interface effect. This chapter elaborates on crystal structure and properties, preparation techniques, strategies for improving photocatalytic activity of 1D-TiO₂ nanostructure and its applications. Amongst all preparation techniques, the influence of experimental parameters on morphologies of 1D-TiO, nanostructure using hydro/solvothermal method is extensively explained. Furthermore, some critical engineering strategies to enhance the properties of 1D-TiO, nanostructures like increasing the surface area, extending the light absorption, and efficient separation of electrons/holes that advantage their potential applications are described. Moreover, a brief summary of their environmental and energy applications is provided.

Keywords: TiO₂, photocatalyst, one dimensional, hydrothermal, nanorod, nanobelts

1. Introduction

The wide applications of titanium dioxide, such as pigments, sunscreen, paints, and various commercialize applications correspond to its profound optical refractive ability, chemical stability, and low toxicity. Furthermore, TiO_2 has been extensively investigated as one of the most promising materials in photovoltaic devices, photocatalysis, photodegradation,

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energy storage, and electrochromic devices. This is being established when the photoelectrolysis of water into H_2 and O_2 was reported under UV irradiation of the solar spectrum over the surface of TiO₂ photoelectrode in the photoelectrochemical (PEC) cell by Fujishima and Honda. In recent years, 1D-TiO₂ nanostructures have been significantly studied due to its distinctive advantages with regard to less charge carrier recombination rate and unique physical and chemical properties [1, 2]. In general, 1D nanostructures are well-known for their high aspect ratio in which at least one of its dimensions should be in the range of 1–100 nm regardless of their shapes such as rod, wire, belt or tube. The properties of one-dimensional single crystalline Ti-O-based nanomaterials are comparable with titania nanoparticles not only inherit almost all typical features of the nanoparticles, but also illustrate some new properties and improved performance in specific area [1]. It can afford direct transport pathways for charge carriers, decouple the direction for light absorption, and charge carrier transportation. Moreover, 1D semiconductor nanostructures are able to facilitate the light absorption and scattering, which is beneficial for photocatalytic reactions.

However, wide applications of 1D-TiO₂ nanostructures are diminished due to absorption of small portion of solar spectrum, relatively low specific surface area, and presence of single phase that pose certain limitations for it performance [3]. Several published research works have illustrated that well designed 1D-TiO₂ nanostructures play a significant role to overcome the above-mentioned problem, preserve the intrinsic characteristics of TiO₂, and finally the material with some new properties. In recent years, breakthroughs have continually been made in the preparation, modification, and applications of 1D-TiO₂ nanomaterials. In this chapter, we would like to address the crystal structure of TiO₂ and various synthesis process of 1D-TiO₂ nanostructured materials. Then, we will look into some critical structure engineering strategies that give 1D-TiO₂ nanostructured materials excellent properties for various applications.

2. Crystal structure and properties of 1D-TiO, nanostructure

TiO₂ is typically the *n*-type photocatalyst due to oxygen deficiency. Anatase (tetragonal, a = b = 3.782 Å, c = 9.502 Å), rutile (tetragonal, a = b = 4.584 Å, c = 2.953 Å), and brookite (rhombohedral, a = 5.436 Å, b = 9.166 Å, c = 5.135 Å) are three different crystalline polymorphs of TiO₂ [4]. **Figure 1a–c** shows that all these phases are constructed by connecting Ti–O octahedrons through a variable number of shared corners, and/or faces.

Figure 1a reveals that tetragonal structure of anatase is the result of corner (vertices) sharing octahedron which form (001) planes. In rutile structure, sharing edges of octahedrons at (001) planes give the tetragonal structure as shown in **Figure 1b**. While an orthorhombic structure of Brookite is the result of sharing both edges and corners of octahedrons [5, 6]. Rutile is the most stable crystal phase of TiO₂ while anatase is a metastable phase, which can be transformed to thermodynamically stable rutile over calcination temperature exceeding ~600°C [7, 8].



Figure 1. Crystalline structures of titanium dioxide (a) anatase, (b) rutile, and (c) brookite [5].

It is worth to mention, amongst all three different phases of TiO_{γ} , anatase is well-known phase for better photocatalytic performance in various applications, including photocatalytic degradation of organic dye molecules, photocatalytic water splitting and dye-sensitized solar cells compared to other phases [9, 10]. The photocatalytic reaction usually accelerates when a semiconductor interacts with light with enough energy (or a certain wavelength). Two simultaneously reactions occur, including oxidation of dissociative adsorbed H₂O by photogenerated holes and reduction of an electron acceptor by photoexcited electrons. In the photocatalysis process, light energy greater than the bandgap energy is required to transfer photoexcited electrons to the conduction band of semiconductors. Figure 2 shows that the absorption of photons with enough energy ($\lambda \leq 390$ nm for anatase TiO₂) transfer photoexcited electron to the conduction band (\bar{e}_{cx}) and leave a positive hole behind in the valence band (h_{vx}^{+}) [4, 11]. Many parameters such as size, specific surface area, pore volume, pore structure, crystalline phase, and the exposed surface facets can significantly influence the photocatalytic performance of TiO, [2, 10]. It is well known that the photocatalytic applications of TiO, are based on the nanoscale materials due to the quantum confinement effects in nanoparticles. Therefore, this effect could change the electron and hole transport behavior and shifts the electronic band structures [7, 12]. However, they also show unavoidable disadvantages such as fast recombination rate of electron and holes, slow charge carriers transfer and high recycling cost [3]. It is noteworthy to mention that effective charge separation can be considered as the most important factor to determine the photocatalytic activities. Construction of one-dimensional nanostructure of TiO₂ photocatalyst like nanowire, nanorod, and nanotube also facilitates charge transportation and promotes charge separation efficiency [1]. The one-dimensional titanium oxide with a large surface area can be used as catalytic carrier and be beneficial in absorbing degradation products [13].



Figure 2. The principle of photocatalytic degradation over TiO, photocatalyst [5].

3. Synthesis of 1D-TiO, nanostructures

Several methods such as hydrothermal, vapor deposition, sol-gel, and electrospinning, etc. were applied to synthesis various morphologies of $1D-TiO_2$ nanostructures like nanotubes, nanorods, nanowires, nanobelts, nanosheets and nanofiber. In this section, we provide the comprehensive information related to hydrothermal method, which is widely used for manufacturing of small particles in the ceramic industry using aqueous or non-aqueous solution.

3.1. Hydrothermal

Hydrothermal is one of the most common methods to synthesis 1D-TiO₂ nanostructure due to simple setup, facile operation, and desirable results. Ever since Kasuga et al. [12] in 1988 showed the first evidence that oxide nanotubes can be obtained easily via chemical treatment, without the need for molds for replication or templates, much research has been carried out on the formation of 1D-TiO₂ nanostructures. In a typical hydrothermal synthesis, TiO_2 or its precursors are dissolved in a concentrated aqueous acidic or alkaline solution and is implemented stainless steel at elevated temperature and pressures [13]. In the former method, the reactants are usually titanium salts with hydrochloric acid and the reaction normally leads to the formation of TiO_2 nanorods. In the latter method, the reactants are TiO_2 nanoparticles and sodium hydroxide solution, which dissolution–recrystallization is always involved in this process and the products include nanotubes, nanowires, and nanobelts. **Figure 3** shows the various morphology of synthesized 1D-TiO₂ nanostructure with hydrothermal method [13–16].



Figure 3. Various morphologies of hydrothermally synthesized $1D-TiO_2$ nanostructures: (a) nanotube, (b) nanorods, (c) nanobelts, (d) nanowires, and (e) nanosheets.

Although the synthesis process seems simple, the preparation parameters including the choice of TiO₂ precursors, the hydrothermal condition (temperature, the concentration of reactants and hydrothermal duration), and post washing procedures play important role in the crystal structures and physicochemical properties of 1D-TiO, nanostructures [17]. The choice of initial raw materials such as anatase, rutile, brookite, and amorphous TiO₂ may affect the morphology of the resultant 1D-TiO, nanostructures but no systematic data is available. Yuan and Su [18] reported the effect of various TiO, precursors on the morphology of produced 1D-TiO₂ nanostructures. Crystalline anatase or rutile or commercial P-25 as the raw materials formed titanium oxide nanotubes with diameter 10 nm in the range of reaction temperature of 100–160°C as illustrated in Figure 4a [18]. In addition, the surface area of product also affected by raw materials as surface areas of the produced nanotubes from commercial P-25 powder was higher than lab-made anatase TiO₂. It noteworthy to mention that no nanotubes were identified when amorphous TiO, powders were the precursor with similar hydrothermal treatment in the presence of NaOH. Figure 4b shows that the product morphology was non-tubular needle-shaped fibers morphology in the presence of NaOH with concentration of 5–15 mol/l at the hydrothermal temperature range of 100–160°C. In addition, Nian et al. [19] synthesized anatase TiO, nanorods with a specific crystal-elongation direction through hydrothermal treatment of titanate nanotube suspensions under an acidic environment in the absence of surfactants or templates. They suggested that the transformation of the tube to rode is a result of local shrinkage of the tube walls to form anatase crystallites and the subsequent oriented attachment of the crystallites. Furthermore, the hydrothermal temperature strongly controls the morphologies of products. In addition, the increasing of hydrothermal temperature improves yield, length, and degree of crystallinity of nanotubes.



Figure 4. Synthesis of various morphologies of one-dimensional TiO_2 (a) nanotube and (b) nanofiber with crystalline anatase or rutile, amorphous TiO_2 , respectively, and (c) effect of increasing hydrothermal temperature on transfer morphology to nanoribbons [18].

The yield of nanotubes increased with the hydrothermal temperature when the temperature was in the range of 100-150°C. The experimental results showed that hydrothermal treatment at below 100°C is not effective to transfer TiO, particles and a large amount of residual TiO₂ particles can be found in the product. In another perspective, increasing temperature could facilitate unidirectional crystal growth, leading to different morphologies of 1D-TiO, nanostructures. As Yuan et al. reported that crystalline or amorphous TiO, powder mainly was transferred to nanoribbons with very high yields (almost 100%) when hydrothermal temperature was in the range of 180-250°C with the NaOH concentration of 5-15 mol/l as shown in Figure 4c [18]. Moreover, the hydrothermal treatment duration has a strong effect on the morphological structure of the synthesized product; it also plays a major rule in the conversion of the nanotube structure into nanoribbons as reported by Elsanousi et al. [20]. Figure 5 shows the effect of hydrothermal treatment duration (5–72 h) at the fixed temperature of 180°C on the morphology of the titanate nanotubes and nanoribbons. The hollow nanotubes were found out with an outer diameter of about 10 nm at treatment duration of 5 and 20 h. While further treatment duration up to 72 h was caused bundles of nanoribbons with widths ranging from 50 to 500 nm and lengths up to several tens of micrometers. Additionally, the experimental results illustrate that there are critical conditions depending on both the treatment duration and varying temperatures (120–195°C), possibly due to a critical pressure, which is needed to be reached so that the transformation process takes place. The concentration and type of alkaline solution also play an important role in the hydrothermal process. The increasing concentration of NaOH can accelerate the hydrothermal reaction owing to the enhancement of Ti (IV) dissolution and exfoliation rates of the precursors. High yield of nanotubes with the maximum surface area of $350 \text{ m}^2/\text{g}$ can be synthesized with the NaOH concentration between 10 and 15 mol/l. The yield of nanotubes is very low when the NaOH concentration is lower than 5 M or as high as 20 M [18]. Bavykin et al. [21] investigated the influence of the binary NaOH/KOH aqueous mixture used in the hydrothermal process on the morphology of 1D-TiO, nanostructures. All observed nanostructures, including nanosheets, nanotubes, nanofibers, and nanoparticles, have been mapped over a wide



Figure 5. SEM images of the nanotubes and nanoribbons synthesized hydrothermally at 180°C for different durations: (a) 5, (b) 15, (c) 22, (d) 48, and (e and f) 72 h [20].

range of compositions (from pure NaOH to pure KOH) and temperatures (from 50 to 110°C). The hydrothermal process is a cost-effective method with good dispersibility and high purity illustrating the great potential for formation of 1D-TiO₂ nanostructures. However, we cannot ignore its limitations, which diminish its wide applications. For instance, slow reaction kinetics result in long reaction, limited length of the nanotubes, and non-uniformed nanotube for large-scale application.

The coupling hydrothermal treatment with microwave heating, ultrasonication and a rotating autoclave on the reaction mixture can reduce the shortcomings of hydrothermal technique [17, 22].

3.2. Solvothermal method

Solvothermal method facilitates the synthesis of nanometer-sized crystalline TiO_2 powder at relatively low temperatures. Solvothermal reactions are similar to hydrothermal method while a non-aqueous solvent reacts under conditions of high pressure and mild temperature. This method shows promise for developing nanotechnologies. Organic solvents during solvothermal synthesis control the properties of products, corresponding to the structure. The various physical and chemical properties of selected solvent such as reactivity, the polarity, coordinating ability of the solvent, etc. affect the morphology and the crystallization of the final products. Furthermore, the influence of other reaction parameters such as temperature, stirring conditions, and co-solvent (water-ethanol, water-ethylene glycol) on the morphologies of the synthesized nanostructures (nanotubes, nanorods, nanowires, and nanoribbons), as well as their growth mechanism, have been explored [23]. Chen et al. [24] reported the



Figure 6. SEM images of various TiO_2 morphologies synthesized by solvothermal method: (a) nanosheets, (b) nanobelts, and (c) nanorods.

preparation of a single-layer polycrystalline anatase TiO_2 (SLP TiO_2) nanosheets **Figure 6a** with a porous structure through a simple solvothermal method by employing, rod-like titanyl sulfate, as the starting material, in the presence of glycerol, followed by a calcination process.

The structure and morphology were found to be dependent on the experimental conditions such as solvothermal reaction time, morphology of titanyl sulfate, and solvent type. Que et al. [25] successfully synthesized the nitrogen-fluorine co-doped TiO_2 nanobelts (**Figure 6b**) with anatase phase structure by the solvothermal method, which employs amorphous titania microspheres as the precursor. Results demonstrate a significantly enhanced photocatalytic degradation of methyl orange compared to commercial TiO_2 . Zhao and his co-workers [26] reported the synthesis of TiO_2 nanorod arrays (TNRs) directly on FTO glass (**Figure 6c**) through the solvothermal method, and thermal treatments. The results show that the crystal structure does not change due to thermal treatment. However, the surface morphology appears to change significantly from a thin amorphous layer to tiny crystallite spheres. All of these changes lead to a 39% improvement in the photoelectric conversion efficiency for the nanorod-based photoanode in dye-sensitized solar cells (DSSCs). These findings might be useful in photoelectrical applications of the solvothermal method.

3.3. Other synthesis method

Sol-gel method is another solution-based growth technique, offering several major advantages for mass production of nanomaterials including low-cost, simple processing, and good scalability. This technique is typically conducted through two steps; sol preparation, including mixing the precursors such as metal organic compounds or inorganic metal salts through vigorous stirring to complete hydrolysis and polymerization reaction and gel preparation by removing solvent and converting the sol to a three-dimensional network [27]. This technique is mainly useful for synthesizing oxide ceramic nanomaterials from hydrolyzing titanium precursors. Through sol-gel process, TiO_2 NPs can be aligned following their crystal orientations and form NWs. For example, Rodríguez-Reyes et al. prepared nanocrystalline TiO_2 wires (**Figure 7a–c**) by the sol-gel method, using titanium isopropoxide (TIP) and acetic acid as a TiO_2 sol modifier in alcohol solvent showed to be a successful synthesis route of Ti–O–Ti inorganic network with controlled properties [28].



Figure 7. HR-SEM images of TiO, calcined at different temperatures (a) 400°C, (b) 500°C, and (c) 600°C [28].



Figure 8. (a) Schematic diagram of the cold wall MOCVD aperture and (b) SEM images of vertically aligned and densely packed TiO, NRs grown on sapphire (100) substrate.

The apparent 1-D morphology of TiO_2 -related nanowires was thermally stable from 400 to 600°C, showing a similar diameter (about 76 nm); however, crystallite size increases with respect to temperature from 13 to 75 nm.

Vapor deposition method has been developed to high degree of crystallinity 1D-TiO₂ nanostructures (usually single crystal TiO₂) and it can be classified in chemical vapor deposition (CVD) and physical vapor deposition (PVD) [27]. Chen et al. [29] grown well-aligned densely-packed rutile TiO₂ nanorod via metal-organic chemical vapor deposition (MOCVD) (**Figure 8a**), using titanium-tetraisopropoxide (TTIP, Ti(OC₃H₇)₄) as a source reagent at a deposition temperature of 550°C and under an oxygen pressure of 1.5 and 5 mbar, respectively. The rutile TiO₂ nanorods (**Figure 8b**) were grown with a very high density and exhibited uniform height. However, this method requires expensive equipment and the cost is too high for mass production.

In addition, nanofibers in different forms, such as core-shell hollow and porous nanofibers are produced with electrospinning method as one of the most conventional methods [30]. These structures of nanofibers can be utilized for new applications such as ultra-filtration, fuel cells, membranes, tissue engineering, catalysis and hydrogen storage. Electrospinning provides



Figure 9. SEM image of TiO₂/PVP nanofibers (a) before calcination and (b) after calcination process at 500°C during 3 h [30].

a straightforward electrohydrodynamical mechanism to produce fibers with diameters less than 100 nm, even up to 5 nm. Under the influence of an electric field, a pendant droplet of the polymer solution at the spinneret is deformed into a conical shape. The post heat treatment is usually needed to remove the solvent and solidify the fiber structures. The viscosity, conductivity, and applied solvents, as well as the conformation and molecular weight of the polymer limit the electrospun ability of a polymer solution. Some polymers are not spinnable because of limited solubility in a proper solvent for electrospinning, having proper polar characteristics [31]. In addition, electrospinning is an efficient method for mass production however; the high resistance caused by the polycrystalline characteristics of the product nanofibers limits its applications. Figure 9 shows that synthesized anatase nanofibers using electrospinning technique by Li and Xia [30]. They injected ethanol solution including poly(vinyl pyrrolidone) (PVP) and titanium tetraisopropoxide through a needle under a strong electrical field. The final product was the composite nanofibers with lengths up to several centimeters, consisting of PVP and amorphous TiO, and followed by calcination process at 500°C. The average diameter of nanofibers was varied from 20 to 200 nm owing to changing a number of parameters like ratio between PVP and titanium tetraisopropoxide, their concentrations in the alcohol solution, the strength of the electric field, and the feeding rate of the precursor solution.

4. Strategies for improving TiO, nanostructured photoactivity

As mentioned in the previous sections, $1D-TiO_2$ has a wide range of applications, however in this book chapter, we intend to address only the photocatalytic applications including photocatalytic degradation and photocatalytic solar hydrogen production. Nanostructure materials need to meet some requirements for photocatalytic application; (i) should possess a sufficiently large active surface area, (ii) have a broad light absorption band to utilize the full range of solar spectrum, and (iii) should be an effective charge carrier separation to transfer more electron and hole to the interface of the electrode/electrolyte. Nevertheless, there is no single material, which can match all above criteria [1, 6, 32, 33]. Here, we reviewed the developed strategies on bandgap engineering of titania to extend light absorption into visible light through doping metal and non-metal ions and compositing with another semiconductor for synergic absorption and charge separation for enhanced utilization of solar energy [34].

4.1. Doping with metal and non-metal ions

Incorporation selective doping of metal ion into 1D-TiO, nanostructured materials has been proven an efficient route to improve visible light absorption with hindered charge carrier recombination rate. The presence of transition metal ion in the structure of 1D-TiO, nanostructured materials increases the formation of Ti³⁺ ions, leading to improve photocatalytic activity, owing to the existence of more oxygen defects, which facilitate the efficient adsorption of oxygen on the titania surface. In addition, the substitution of metal ions into the TiO, induces visible light absorption because of introducing intraband state close to the CB or VB edge and charge transfer transition between the **d** electrons of the dopant and the CB (or VB) of TiO, nanostructures [34, 35]. Wang et al. [36] investigated the effect of Fe, Mn and Co as dopants on the photoelectrochemical cell performance of TiO, nanorods. The maximum photocurrent density of 2.92 mA/cm² at 0.25 V vs. Ag/AgCl for Fe/TiO₂, which is five times higher than that of undoped TiO, confirmed the presence of Fe into TiO, is the most favorable metal to improve the photocatalytic activity of TiO, compared to others. Figure 10a shows that the photocurrent density of Fe-TiO, is as high as 0.96 mA/cm² at 0.25 V vs. Ag/AgCl under visible light illumination (>420 nm). Incident-photon-to-current-conversion (IPCE) efficiency (up to 18%) measurements reveal that the Fe-TiO, nanorod sample significantly improves the photoresponse not only in the UV region but also in the visible light region, as illustrated in Figure 10b.



Figure 10. (a) Photocurrent density vs. applied potential curves of four nanorod photoanodes under visible light illumination >420 nm and (b) IPCE spectra of nanorod photoanodes measured at an applied bias of 0.6 V (vs. RHE) in 1 M KOH solution [36].

Moreover, doping non-metal atoms such as nitrogen, sulfur carbon, boron and iodine can extend the absorbance to the visible region and improve the stability of materials through the simple and effective method [37]. For instance, $\text{TiO}_2/\text{graphene}$ composites were synthesized by Xing et al. [38] through hydrothermal method by decorating Ti^{3+} self-doped TiO_2 nanorods on boron-doped graphene sheets, in which NaBH₄ acted as reducing agent and sources of boron dopant on graphene. The produced TiO_2 nanorods had the length of 200 nm with exposed (100) and (010) facets as shown in **Figure 11a**.

The loading of TiO₂ nanorods on graphene sheets was characterized by TEM (**Figure 11b**), and confirmed TiO₂ nanoparticles were covalent bonded to GO, forming a composite favoring the





Figure 11. (a) FESEM of TiO₂ nanorods, (b) TEM images of TiO₂/GR composite, and (c) schematic diagram of the charge transfer of TiO₂-x/GR composite [38].

separation of electron-hole pairs (**Figure 11c**). All of the composites tested exhibited improved photocatalytic activities as measured by the degradation of methylene blue and phenol under visible light irradiation. This better photocatalytic activity was attributed to the synergistic effect between Ti³⁺ self-doped TiO, and boron-doped graphene.

4.2. Coupling TiO, with semiconductors

The fabrication, design, and tailoring of coupling other semiconductors like CdS, Cu₂O, CdSe, $WO_{3'}$ etc. with 1D-TiO₂ nanostructures to achieve better charge carrier separation in a light energy conversion system have received significant attentions. The charge transfer from one semiconductor to another with suitable band edge positions is thermodynamically favorable to increase the lifetime of the charge carriers thus promoting the interfacial charge transfer and catalytic efficiency [34, 39]. Zhu et al. [39] deposited CdS on TiO₂ nanotube arrays (TNTAs) by successive ionic layer adsorption and reaction (SILAR) method for visible-light-driven hydrogen production and organic compound degradation. CdS has narrow bandgap (~2.40 eV) and relatively high visible absorption coefficient of CdS enables its highly desirable use in solar applications. Coupling CdS with TiO₂ can hamper electron-hole recombination that dominating the charge separation. **Figure 10** shows the schematic diagram of charge transfer in CdS-TNTAs photocatalyst for visible-light photocatalysis. Therefore, this charge transfer can accelerate the separation of charge carriers and enhance the visible-light response and photocatalytic activity for H₂ generation and Rh B degradation of CdS-TNTAs.

5. Applications of 1D-TiO, nanostructures

 TiO_2 nanostructured materials are widely used as photocatalysts due to its high oxidation and reduction ability. 1D-TiO₂ nanostructures have been paid much attention to photocatalytic degradation of pollutants, photocatalytic CO₂ reduction into energy fuels, photocatalytic water splitting, solar cells, supercapacitors and lithium batteries. This section is dedicated to the application of 1D-TiO₂ nanostructures in photocatalytic water splitting and dye sensitized solar cells (**Figure 12**).

5.1. Dye sensitized solar cell

The first sensitization of large bandgap energy toward the visible region was reported in 1972 with ZnO semiconductor with the photoconversion efficiency of 1–2.5%. Gratzel et al. reported a breakthrough in the efficiency over 7% in 1991 using large surface area nano-crystalline TiO_2 thin film, sensitizing with ruthenium complex. They explained that high surface area of TiO_2 helps to better absorb and attach dye on the surface of TiO_2 thin film [40, 41]. **Figure 13a** and **b** displays a schematic presentation of DSSC and its operation principle. It includes nano-crystalline TiO_2 thin film as a working electrode (WE) or photoanode with a monolayer of sensitizer in contact with iodide/tri-iodide redox electrolyte, which is sandwiched by second conductive glass covered with platinum as a counter electrode (CE). The most efficient DSSC had the highly mesoporous of anatase phase of TiO_2 which was coated on the surface of FTO (F-doped tin oxide) glass substrate with thickness 5–20 µm and covered



Figure 12. SEM image and schematic diagram of charge transfer in CdS-TNTAs photocatalyst for visible-light photocatalysis [39].

by a monolayer of sensitizer. To overcome the drawback of TiO_2 nanoparticles, a $1D-TiO_2$ nanostructure is often applied as photoanode to enhance electron transfer ability. **Figure 14a** shows a novel TiO_2 nanoparticles and TiO_2 nanotube (TNP/TNA) multilayer photoelectrode via a layer-by-layer assembly process to improve the DSSC performance as reported by Yang et al. [42]. The fabricated DSSC with multilayer photoelectrode has higher efficiency than the single-layer or bare DSSCs. The TNP/TNA four-layer photoelectrode provided a large surface area for dye adsorption with the highest photocurrent density (**Figure 14b**) and maximum photoconversion efficiency of 7.22% because of effective electron transport.

5.2. Photocatalytic solar hydrogen production

Energy dense fossil fuels are non-renewable source and the most coveted fuel that have ever been discovered, burning fossil fuels release such significant amount of greenhouse gases in



Figure 13. (a) Schematic diagram and (b) principle of operation and energy level of DSSC.
One-Dimensional Titanium Dioxide and Its Application for Photovoltaic Devices 381 http://dx.doi.org/10.5772/intechopen.72976



Figure 14. (a) Structure of multilayer DSSC and (b) I-V curves of DSSC with single to five-layer photoelectrodes [42].

the atmosphere as major threats to the environment and human health. Hydrogen has been established as a clean energy carrier in many applications such as automotive, domestic heating, aircrafts and stationary power generation. Utilizing solar energy to split water into H₂ and O₂ in photoelectrochemical (PEC) cell is in fact one of the most promising technologies for hydrogen production. It would be interesting to combine solar energy and water in PEC cell to produce truly renewable and low environmental impact fuel on both large and small scale. A photocatalyst is the core of this system with some requirements like an optimal bandgap energy approximately 2 eV and a sufficient negative CB position [6]. Up to date, there has not been found any photocatalyst that meets all requirements for hydrogen production in the PEC cell. Amongst different metal oxide photocatalysts, TiO₂ is an attractive n-type photocatalyst in terms of hydrogen production regardless of its limitations [43, 44]. The vertically oriented 1D-TiO₂ nanostructure are promising materials for photocatalytic solar hydrogen production due to their impressive vectorial 1D-channel pathways for fast electron transport in the axial direction. Shinde et al. [45] synthesized nanocomposite heterojunction photoanode involving



Figure 15. Surface FESEM images of (a) annealed TiO_2NT photoanode and CdS-NF/TiO₂-NT photoanodes prepared with different annealing conditions: (b) as-grown CdS on as-grown TiO₂ NT array, (c) as-grown CdS on annealed $TiO_2 NT$ array, (d) annealed CdS on annealed $TiO_2 NT$ array, and (e) the schematic of charge transfer mechanism in heterojunction of CdS NFs and TiO₂ NT array [45].

CdS nanoflowers (NFs) and one-dimensional TiO_2 nanotube (TNT) arrays. An anodization method was employed for fabrication of TiO_2 nanotube (TNT) arrays and CdS NFs was decorated on the surface of TNT using hydrothermal method as shown in **Figure 15a–d**. As-grown CdS-NF/TiO₂-NT array photoanode exhibited a 5.5-fold photocurrent enhancement in a poly-sulfide electrolyte compared to the pristine TiO_2 NT photoanode. Annealing of TiO_2 NTs as well as CdS NFs led to further improvement in the photocurrent owing to greater crystal-linity, significantly higher visible light photon absorption and improved interface properties between CdS and TiO_2 . The better photocatalytic performance of CdS-NF/TiO₂-NT was attributed to effective absorption of the visible light photons, leading to the photo-generation of electron-hole pairs and greater charge carrier separation as shown in **Figure 15e**.

6. Conclusion

Over recent decades, the tremendous efforts have been paid to develop TiO_2 nanomaterials and large amount of information provided on their synthesis, modification, and applications. The one-dimensional TiO_2 nanostructures have been comprehensively studied due to its distinctive advantages with regard to less charge carrier recombination rates and unique physical and chemical properties. In this chapter, we first explain the structural features of the three TiO_2 polymorphs that have been seen in TiO_2 nanostructures. Then, the various synthesis processes of one-dimensional TiO_2 nanostructures were discussed. Hydro/solvothermal method and the effect of the experimental parameters on the formation of various morphologies and properties of 1D- TiO_2 nanostructures were thoroughly reviewed. In addition, we studied some strategies on bandgap engineering of titania to improve optical properties and charge carrier separation and transfer to the surface of photocatalyst. Finally, the applications of 1D- TiO_2 nanostructures in photocatalytic water splitting and dye-sensitized solar cells have been reported with regard to their specific structure and properties. Therefore, these data favorable for further investigation on the development of sustainable environmental remediation and energy technologies based the photocatalytic process by driving solar light as renewable source of energy.

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References

- [1] Tian J, Zhao Z, Kumar A, Boughton RI, Liu H. Recent progress in design, synthesis, and applications of one-dimensional TiO₂ nanostructured surface heterostructures: A review. Chemical Society Reviews. 2014;43(20):6920-6937. DOI: 10.1039/C4CS00180J
- [2] Nakata K, Fujishima A. TiO₂ photocatalysis: Design and applications. Journal of Photochemistry and Photobiology C: Photochemistry Reviews. 2012;13(3):169-189. DOI: 10. 1016/j.jphotochemrev.2012.06.001
- [3] Ge M, Cao C, Huang J, Li S, Chen Z, Zhang KQ, Al-Deyab SS, Lai Y. A review of onedimensional TiO₂ nanostructured materials for environmental and energy applications. Journal of Materials Chemistry A. 2016;4(18):6772-6801. DOI: 10.1039/C5TA09323F
- [4] Bashiri R, Mohamed NM, Kait CF, Sufian S, Khatani M. Enhancing photoelectrochemical hydrogen production over Cu and Ni doped titania thin film: Effect of calcination duration. Journal of Environmental Chemical Engineering. 2017;5(4):3207-3214. DOI: 10.1016/j.jece.2017.06.027
- [5] Pelaez M, Nolan NT, Pillai SC, Seery MK, Falaras P, Kontos AG, Dunlop PSM, Hamilton JWJ, Byrne JA, O'Shea K, Entezari MH, Dionysiou DD. A review on the visible light active titanium dioxide photocatalysts for environmental applications. Applied Catalysis B: Environmental. 2012;125:331-349. DOI: 10.1016/j.apcatb.2012.05.036
- [6] Bashiri R, Mohamed NM, Kait CF. Advancement of sol-gel-prepared TiO₂ photocatalyst. In: Chandra U, editor. Recent Applications in Sol-Gel Synthesis. Rijeka: InTech; 2017. pp. 151-167
- Bashiri R, Mohamed NM, Kait CF, Sufian S. Hydrogen production from water photosplitting using Cu/TiO₂ nanoparticles: Effect of hydrolysis rate and reaction medium. International Journal of Hydrogen Energy. 2015;4(18):6021-6037. DOI: 10.1016/j.ijhydene. 2015.03.019
- [8] Samsudin MFR, Sufian S, Mohamed NM, Bashiri R, Wolfe F, Ramli RM. Enhancement of hydrogen production over screen-printed TiO₂/BiVO₄ thin film in the photoelectrochemical cells. Materials Letters. 2018;**211**(Supplement C):13-16. DOI: 10.1016/j. matlet.2017.09.013
- [9] Yang S, Huang N, Jin YM, Zhang HQ, Su YH, Yang HG. Crystal shape engineering of anatase TiO₂ and its biomedical applications. CrystEngComm. 2015;17(35):6617-6631. DOI: 10.1039/C5CE00804B
- [10] Bashiri R, Mohamed NM, Kait CF, Sufian S, Kakooei S, Khatani M, Gholami Z. Optimization hydrogen production over visible light-driven titania-supported bimetallic photocatalyst from water photosplitting in tandem photoelectrochemical cell. Renewable Energy. 2016;99:960-970. DOI: 10.1016/j.renene.2016.07.079
- [11] Liu J, Yu X, Liu Q, Liu R, Shang X, Zhang S, Li W, Zheng W, Zhang G, Cao H, Gu Z. Surface-phase junctions of branched TiO₂ nanorod arrays for efficient photoelectrochemical water splitting. Applied Catalysis B: Environmental. 2014;158-159:296-300. DOI: 10.1016/j.apcatb.2014.04.032

- [12] Kasuga T, Hiramatsu M, Hoson A, Sekino T, Niihara K. Formation of titanium oxide nanotube. Langmuir. 1998;14(12):3160-3163. DOI: 10.1021/la9713816
- [13] Liu N, Chen X, Zhang J, Schwank JW. A review on TiO₂-based nanotubes synthesized via hydrothermal method: Formation mechanism, structure modification, and photocatalytic applications. Catalysis Today. 2014;225(Supplement C):34-51. DOI: 10.1016/j. cattod.2013.10.090
- [14] Chen J, Yang HB, Miao J, Wang H-Y, Liu B. Thermodynamically driven one-dimensional evolution of anatase TiO₂ nanorods: One-step hydrothermal synthesis for emerging intrinsic superiority of dimensionality. Journal of the American Chemical Society. 2014;136(43):15310-15318. DOI: 10.1021/ja5080568
- [15] Zhou W, Du G, Hu P, Li G, Wang D, Liu H, Wang J, Boughton RI, Liu D, Jiang H. Nanoheterostructures on TiO₂ nanobelts achieved by acid hydrothermal method with enhanced photocatalytic and gas sensitive performance. Journal of Materials Chemistry. 2011;**21**(22):7937-7945. DOI: 10.1039/C1JM10588D
- [16] Zhang X, Li D, Wan J, Yu X. Hydrothermal synthesis of TiO₂ nanosheets photoelectrocatalyst on Ti mesh for degradation of norfloxacin: Influence of pickling agents. Materials Science in Semiconductor Processing. 2016;43(Supplement C):47-54. DOI: 10.1016/j.mssp. 2015.11.020
- [17] Zhou W, Liu H, Boughton RI, Du G, Lin J, Wang J, Liu D. One-dimensional single-crystalline Ti-O based nanostructures: Properties, synthesis, modifications and applications. Journal of Materials Chemistry. 2010;20(29):5993-6008. DOI: 10.1039/B927224K
- [18] Yuan Z-Y, Su B-L. Titanium oxide nanotubes, nanofibers and nanowires. Colloids and Surfaces A: Physicochemical and Engineering Aspects. 2004;241(1):173-183. DOI: 10.1016/j.colsurfa.2004.04.030
- [19] Nian J-N, Teng H. Hydrothermal synthesis of single-crystalline anatase TiO₂ nanorods with nanotubes as the precursor. The Journal of Physical Chemistry B. 2006;110(9): 4193-4198
- [20] Elsanousi A, Elssfah EM, Zhang J, Lin J, Song HS, Tang C. Hydrothermal treatment duration effect on the transformation of titanate nanotubes into nanoribbons. The Journal of Physical Chemistry C. 2007;111(39):14353-14357. DOI: 10.1021/jp074566m
- [21] Bavykin DV, Kulak AN, Walsh FC. Metastable nature of titanate nanotubes in an alkaline environment. Crystal Growth & Design. 2010;10(10):4421-4427. DOI: 10.1021/ cg100529y
- [22] Ge M, Li Q, Cao C, Huang J, Li S, Zhang S, Chen Z, Zhang K, Al-Deyab SS, Lai Y. Onedimensional TiO₂ nanotube photocatalysts for solar water splitting. Advanced Science. 2017;4(1):1600152. DOI: 10.1002/advs.201600152
- [23] Nam CT, Falconer JL, Duc LM, Yang W-D. Morphology, structure and adsorption of titanate nanotubes prepared using a solvothermal method. Materials Research Bulletin. 2014;51(Supplement C):49-55. DOI: 10.1016/j.materresbull.2013.11.036

- [24] Chen Y, Tian G, Ren Z, Tian C, Pan K, Zhou W, Fu H. Solvothermal synthesis, characterization, and formation mechanism of a single-layer anatase TiO₂ nanosheet with a porous structure. European Journal of Inorganic Chemistry. 2011;2011(5):754-760. DOI: 10.1002/ejic.201000999
- [25] He Z, Que W, Chen J, Yin X, He Y, Ren J. Photocatalytic degradation of methyl orange over nitrogen–fluorine codoped TiO₂ nanobelts prepared by solvothermal synthesis. ACS Applied Materials & Interfaces. 2012;4(12):6816-6826. DOI: 10.1021/am3019965
- [26] Zhao J, Yao J, Zhang Y, Guli M, Xiao L. Effect of thermal treatment on TiO₂ nanorod electrodes prepared by the solvothermal method for dye-sensitized solar cells: Surface reconfiguration and improved electron transport. Journal of Power Sources. 2014;255:16-23. DOI: 10.1016/j.jpowsour.2013.12.127
- [27] Wang X, Li Z, Shi J, Yu Y. One-Dimensional Titanium Dioxide Nanomaterials: Nanowires, Nanorods, and Nanobelts. Vol. 1142014
- [28] Rodríguez-Reyes M, Dorantes-Rosales HJ. A simple route to obtain TiO₂ nanowires by the sol-gel method. Journal of Sol-Gel Science and Technology. 2011;59(3):658. DOI: 10.1007/s10971-011-2541-5
- [29] Chen CA, Chen YM, Korotcov A, Huang YS, Tsai DS, Tiong KK. Growth and characterization of well-aligned densely-packed rutile TiO₂ nanocrystals on sapphire substrates via metal–organic chemical vapor deposition. Nanotechnology. 2008;19(7):075611
- [30] Li D, Xia Y. Fabrication of titania nanofibers by electrospinning. Nano Letters. 2003; 3(4):555-560. DOI: 10.1021/nl0340390
- [31] Khajavi R, Abbasipour M. Electrospinning as a versatile method for fabricating coreshell, hollow and porous nanofibers. Scientia Iranica. 2012;19(6):2029-2034. DOI: 10.1016/j. scient.2012.10.037
- [32] Bashiri R, Mohamed NM, Fai Kait C, Sufian S. Influence of hydrolysis rate on properties of nanosized TiO₂ synthesized via sol-gel hydrothermal. In: Advanced Materials Research. Trans Tech Publ.; 2015
- [33] Norani MM, Bashiri R, Chong FK, Sufian S, Kakooei S. Photoelectrochemical behavior of bimetallic Cu–Ni and monometallic Cu, Ni doped TiO₂ for hydrogen production. International Journal of Hydrogen Energy. 2015;40(40):14031-14038. DOI: 10.1016/j. ijhydene.2015.07.064
- [34] Kumar SG, Devi LG. Review on modified TiO₂ photocatalysis under UV/visible light: Selected results and related mechanisms on interfacial charge carrier transfer dynamics. The Journal of Physical Chemistry A. 2011;115(46):13211-13241. DOI: 10.1021/jp204364a
- [35] Bashiri R, Mohamed NM, Kait CF, Sufian S, Khatani M, Hanaei H. Effect of preparation parameters on optical properties of Cu and Ni doped TiO₂ photocatalyst. Procedia Engineering. 2016;148:151-157. DOI: 10.1016/j.proeng.2016.06.506
- [36] Wang C, Chen Z, Jin H, Cao C, Li J, Mi Z. Enhancing visible-light photoelectrochemical water splitting through transition-metal doped TiO₂ nanorod arrays. Journal of Materials Chemistry A. 2014;2(42):17820-17827. DOI: 10.1039/C4TA04254A

- [37] Szkoda M, Siuzdak K, Lisowska-Oleksiak A. Non-metal doped TiO₂ nanotube arrays for high efficiency photocatalytic decomposition of organic species in water. Physica E: Low-Dimensional Systems and Nanostructures. 2016;84(Supplement C):141-145. DOI: 10.1016/j.physe.2016.06.004
- [38] Xing M, Li X, Zhang J. Synergistic effect on the visible light activity of Ti³⁺ doped TiO₂ nanorods/boron doped graphene composite. Scientific Reports. 2014;4:5493 https:// www.nature.com/articles/srep05493#supplementary-information
- [39] Zhu Y, Wang Y, Chen Z, Qin L, Yang L, Zhu L, Tang P, Gao T, Huang Y, Sha Z, Tang G. Visible light induced photocatalysis on CdS quantum dots decorated TiO₂ nanotube arrays. Applied Catalysis A: General. 2015;498(Supplement C):159-166. DOI: 10.1016/j. apcata.2015.03.035
- [40] Baraton M-I. Nano-TiO₂ for solar cells and photocatalytic water splitting: Scientific and technological challenges for commercialization. The Open Nanoscience Journal. 2011;5(1):64-77
- [41] Boercker JE. Synthesis of Titanium Dioxide and Zinc Oxide Nanowires for Excitonic Solar Cells. Faculty of the Graduate School; 2009. p. 204
- [42] Yang JH, Kim KH, Bark CW, Choi HW. The effect of dye-sensitized solar cell based on the composite layer by anodic TiO₂ nanotubes. Nanoscale Research Letters. 2014;9(1):671. DOI: 10.1186/1556-276x-9-671
- [43] Naseri N, Kim H, Choi W, Moshfegh AZ. Optimal Ag concentration for H₂ production via Ag:TiO₂ nanocomposite thin film photoanode. International Journal of Hydrogen Energy. 2012;37(4):3056-3065. DOI: 10.1016/j.ijhydene.2011.11.041
- [44] Sreethawong T, Laehsalee S, Chavadej S. Comparative investigation of mesoporous- and non-mesoporous-assembled TiO₂ nanocrystals for photocatalytic H₂ production over N-doped TiO₂ under visible light irradiation. International Journal of Hydrogen Energy. 2008;**33**(21):5947-5957. DOI: 10.1016/j.ijhydene.2008.08.007
- [45] Shinde PS, Park JW, Mahadik MA, Ryu J, Park JH, Yi Y-J, Jang JS. Fabrication of efficient CdS nanoflowers-decorated TiO₂ nanotubes array heterojunction photoanode by a novel synthetic approach for solar hydrogen production. International Journal of Hydrogen Energy. 2016;41(46):21078-21087. DOI: 10.1016/j.ijhydene.2016.08.205

Titanium Dioxide Modifications for Energy Conversion: Learnings from Dye-Sensitized Solar Cells

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Abstract

During the last two and half decade modifying anatase TiO_2 has appreciably enhanced our understanding and application of this semiconducting, non-toxic material. In the domain of DSCs, the main focus has been to achieve band adjustment to facilitate electron injection from anchored dyes, and high electronic mobility for photo-generated electron collection. In retrospection, there is a dire need to assimilate and summarize the findings of these studies to further catalyze the research, better understanding and comparison of the structure–property relationships in modifying TiO_2 efficiently for crucial photocatalytic, electrochemical and nanostructured applications. This chapter aims at categorizing the typical approaches used to modify TiO_2 in the domain of DSCs such as through TiO_2 paste additives, TiO_2 doping, metal oxides inclusion, dye solution co-adsorbing additives, post staining surface treatment additives and electrolyte additives. A summary of the consequences of these modifications on electron injection, charge extraction, electronic mobility, conduction band shift and surface states has been presented. This chapter is expected to hugely benefit the researchers employing TiO_2 in energy, catalysis and battery applications.

Keywords: modification, co-adsorption, surface treatment, recombination, electron lifetime, electronic mobility, photovoltage

1. Introduction

Global energy demand is expected to increase from 18 TW in 2013 to 50 TW in 2050, along with corresponding increase in CO_2 emissions due to inevitable increase in population and industrialization in the developing world [1, 2]. So far, most of the energy (~80%) have been derived from fossil fuels, which is not sustainable and detrimental to the environment [2]. Thus,

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sustainable and fossil-free pathways for producing clean energy and fuels such as conversion of sunlight to electricity and molecules in atmosphere, e.g., water, CO₂ and nitrogen, to H₂, hydrocarbons and ammonia respectively are highly required [3-8]. In this regard, dependence on renewable energy sources such as solar, wind and hydroelectric has been strategically deployed from last few decades with reasonable effect [5, 7]. Among all the renewable energy sources, solar energy is the most potent and exploitable source [9]. However, in order to achieve large scale, cost effective, carbon neutral supply of energy from sun; capture, conversion and storage of energy should be highly efficient and cost effective [6, 9]. In this regard, photovoltaics (PVs) are playing a substantial role in harnessing the sun energy mainly dominated by silicon based solar cells at present. However, manufacturing of silicon PVs require high temperature (>1600°C for silicon melting) and ultra-pure materials, thus adding to the manufacturing complexity and cost [10]. Additionally, the scarcity of silver, a common electrode material greatly limits to meet the future terawatt challenge. This have motivated researchers around the globe to develop strategies for solar energy conversion based on abundant, non-toxic, easy to process, commercially viable and cost effective systems. In this regard solar PVs prepared from mesoscopic metal oxides such as (TiO₂, ZnO, SnO₂, etc.) and organic light absorbing materials could meet the criteria as a suitable alternative, provided high efficiency can be realized. Metal oxide serves as an electron acceptor and facilitates the transport of electrons, along with being a scaffold for the adsorption of light harvesting constituents in many cases [11, 12]. Out of different metal oxides, mesoscopic (10-50 nm size pores) titanium dioxide (TiO₂) by far has been the most widely studied and employed owing to ease process-ability, chemical stability, high surface area, low cost and non-toxic nature. [12–15] Out of the four naturally occurring polymorphs of TiO₂, anatase (tetragonal), rutile (tetragonal), brookite (orthorhombic), and TiO₂ (monoclinic), anatase is preferred for PV's applications because of higher conduction band energy and slower recombination rate of charge carriers [16–18].

In terms of mesoscopic-TiO₂ based solar cells, dye-sensitized solar cells (DSCs) are the most widely studied with recent surge in research for perovskite solar cells [12, 19, 20]. The discussion in the remaining chapter will be with the reference to DSCs employing TiO₂ as electron accepting and transport layer. The seminal report of 1991 on TiO₂ based DSCs by Grätzel and O' Regan has garnered more than 26,500 citations (November 2017) highlighting the plethora of knowledge generated and wide spread interest of scientific community [11]. It should be noted that nanocrystalline morphology which goes through necking as the result of sintering and lead to mesoscopic film of TiO_2 is essential for the efficient operation of the DSCs, since a monolayer of sensitizer on flat metal oxide surface only absorb small portion of incident light [13]. Realization of this important nanostructure requirement aspect enhanced the adsorption and subsequent light harvesting in DSCs by molecular sensitizers or dyes more than 1000 time [13]. This enabled DSCs only system where charge generation (sensitizer) and transport (semiconductor) is performed by separate components. [14] DSCs are attractive compared to other photovoltaic technologies in terms of economic advantage, tunability of color, can be built on rigid and flexible substrates, made of benign materials such as TiO_2 and metal free organic dyes, offer sustained efficiency for indoor applications, and perform independently of the angle of incidence [11, 12, 21–24]. Current, DSC record power conversion efficiency (PCE) up to 14.3% has been demonstrated by judicious choice of co-sensitizing organic photosensitizers having strong binding to TiO_2 and broad absorption, post staining surface capping and tailored solution based redox shuttle and electrolyte additives [25]. However, for further improvement in PCE (1) sensitizers with efficient conversion of absorbed photons to electrons (400–900 nm), particularly beyond 650 nm (2) redox shuttles with photovoltage output greater than 1.2 V (3) minimized recombinations and over potential losses and (4) optimized tandem devices are highly required [26–29].

The standard components of a typical DSC embodiment are (1) FTO (fluorine doped tin oxide) deposited on glass substrate (2) mesoscopic TiO_2 film (3) sensitizer, organic or metal complex anchored to TiO_2 (4) mediator, to regenerate the dye (5) counter electrode with platinum (pt) to reduce the mediator (Figure 1). Upon illumination the sensitizer gets photo-excited and injects an electron in the conduction band (CB) of TiO₂ thus generating an electric potential difference. This injected electron then diffuses through the mesoporous TiO_2 where it is extracted to outer circuit at photoanode. Meanwhile the oxidized sensitizer is regenerated by the redox mediator, whereas the extracted electron travels through the load to the counter electrode, which then transfers electron to the mediator. At the interface boundary, back electron transfer to the oxidized dye and recombination with the electrolyte has been known the most drastic events which lower the performance along with inefficient light absorption beyond 650 nm [13, 14]. On the same note before printing the mesoporous TiO_2 film a compact TiO_2 layer (mostly from aqueous TiCl₄ solution) is deposited on the FTO glass which prevents the short circuiting of the device, improves adhesion of TiO₂ nanoparticles and minimizes the direct contact of electrolyte with FTO [30-32]. In terms of characterization of DSCs, two important measurements are short photocurrent-density (J_{sc}) and open circuit voltage (V_{oc}) curve also known as



Figure 1. Operational principle of DSCs.

J-V curve and incident photon to current conversion efficiency (IPCE) or EQE (external quantum efficiency). IPCE depicts the photocurrent density response of the device at monochromatic wavelength and depends on the same parameters as J_{sc} [33].

J-V curve is measured by scanning the voltage across the device from 0 to higher voltage (forward bias) or higher to zero voltage (reverse bias) either with a source meter or a potentiostat. Power conversion efficiency (PCE) of the cells, the main performance metric is then calculated according to the equation, PCE = $(J_{sc}V_{oc} FF)/I_0$, where *FF* is the fill factor which is simply the measure of the squareness of the *J-V* curve, and depicts the electrochemical losses in the device with value between 0 and 1 (normally between 0.65 and 0.75 for DSCs) [34]. I₀ is the power input for the incident irradiation which is normally 1 sun (100 mW/cm²). A high performing DSC should behave an ideal diode with infinite shunt resistance and minimum series resistance which will lead to higher *FF* and PCE ultimately [13]. Briefly, $J_{sc} \alpha$ LHE. φ_{inj} . φ_{reg} . η_{coll} , where LHE is light harvesting efficiency of sensitizer on given thickness of TiO₂, φ_{inj} and φ_{reg} are the quantum yield of electron injection and dye regeneration and η_{coll} is the charge collection efficiency [12].

In **Figure 2**, thermodynamic requirements for electron injection (up to 300 mV) and dye regeneration (100–500 mV) overpotential has been shown. Dotted lines highlight the unwanted recombination reactions with redox shuttle (10^{-2} sec) and oxidized sensitizer (10^{-4} sec) also known as "dark current" [12, 35, 36]. Kinetically, electron injection happens in 100 s of pico seconds and vary with sensitizer, with usual ms to μ s range of recombination with electrolyte and oxidized dye, respectively. [24] Tuning of electrochemical properties of sensitizers (Ru (II), organic, and porphyrin) with optimized geometry offering higher light absorption and minimum aggregation and redox shuttles (iodide/triiodide, cobalt and copper) has been widely studied for DSCs with the aim of minimum overpotential loss, broad absorption and higher PCE [37–40]. Interested readers are encouraged to consult the more detailed reviews on design principles of sensitizers and redox shuttles for DSCs [21, 33, 40–43].



Figure 2. Energy level diagram, overpotential requirements and typical time constants.

 J_{sc} can be increased by molecular engineering of the sensitizer, with ideal ground and excited state energetics, high molar absorptivity, and aggregation less anchoring on TiO₂ [12]. V_{oc} is the energy difference between the TiO₂ fermi level and the redox potential of the mediator and depends on the electron density in TiO₂. Higher V_{oc} can be achieved by minimization of the dark current, increase in electron injection, negative (upward) shift in the energy of the conduction band, positive (downward) shift in the energy of the redox shuttle and series connection of devices [35, 44]. Both V_{oc} and *FF* are hugely related to recombination reactions (dark current) and can be substantially influenced by modification of TiO₂ in the presence of additives *vide infra*. Along with *J*-*V* and IPCE measurements, electrochemical impedance spectroscopy (EIS) and small modulation photovoltage transient measurements have been widely employed to fully characterize the devices. Readers are kindly referred to the previously published reviews to learn about these powerful techniques to characterize interface and charge transfer properties [45–48].

In terms of achieving higher efficiency by modification of TiO_2 the main objective is to minimize the recombination losses by blocking the TiO_2 surface, increase in electron injection by manipulation of TiO_2 CB, aid in better orientation, structure and geometry of the dyes on TiO_2 and suppression of dye aggregation and stacking. This enhancement of DSCs devoid of dye and electrolyte designing and arduous manipulations of their molecular structures can be achieved by (1) TiO_2 paste additions (2) dye solution co-adsorbing additives (3) post staining surface treatment additives and (4) electrolyte additives (**Figure 3**). This chapter is now further divided into sections as shown in **Figure 3**. to integrate and analyze the most successful strategies, their role in enhancing DSCs performance, similarities among different approaches and discussion of proposed mechanisms.

It is crucial to highlight that just like dyes for DSCs most of the additives will require an anchoring group for immobilization on TiO_2 , other than plasmonic nanoparticles and composite of TiO_2 NPs (Section 1, which become the intrinsic part of TiO_2 NPs after sintering also termed as "hard modification"). The most widely used anchoring groups are same as dyes, e.g., carboxylic acid, phosphonic/phosphinic acid, pyridine, and most recently siloxanes. Though multitude of anchoring modes such as covalent attachment, hydrogen bonding, electrostatic interaction, van der Waals interaction and physical entrapment has been proposed [49]. It is important to notice that these anchoring systems should also facilitate the electron transfer. Additionally, due to structural complexity of the interface environment several models are used to elucidate the anchoring. For physical characterization of interface Fourier



Figure 3. Summary layout for TiO₂ modification approaches.

transform infrared spectroscopy (FT-IR) and photoelectron spectroscopy (PES) are mainly employed [50]. However for anchoring on TiO_2 for the well-known carboxylic acid, (similarly anchoring phosphonic/phosphinic acid, siloxane, etc.) (**Figure 4**) covalent interaction can only offer the strongest coupling for stable anchoring with ester type bonds or metal complexation for pyridine additives [51]. For an in depth analysis of anchoring mode and surface adsorption for different anchoring groups, readers are kindly referred to reviews published previously [49, 51].

For efficient light harvesting different kinds of TiO₂ pastes (active layer for dye anchoring with scattering or reflective layer on top of it) are used for achieving specific features such as iodide/ triiodide systems mainly employ 18–20 nm size NPs based formulations, whereas for larger size redox shuttles such as cobalt and copper based systems 28–31 nm size NPs are employed [52, 53]. This selectivity comes from the mass-transport related limitations of outer sphere based redox shuttles (cobalt and copper) which is mitigated by the larger pore size of bigger NP size based TiO₂ films [54]. On top of active layer, 4–5 μ m thick scattering or reflective layer is printing with NPs size of >100 nm, to back scatter light into the cell.

1.1. Scope

Though synthesis and preparation of TiO₂ paste for film formation has historical importance, however, at this stage more than 95% of the studies employ a commercially available TiO₂ paste which is developed after years of research and employ patented methods [53, 55]. However, design of morphologically new structures, and development of efficient synthesis routes for anatase TiO₂ is an active area to achieve higher loading, better charge transport, and minimum recombinations losses [18]. For this chapter please be referred to commercially available TiO₂ (transparent 18–20 nm from Dyesol or Solaronix, or 30–31 from Dyesol or Dyenamo nm particle size for active layer and > 100 nm size for scattering layer from Dyesol, Solaronix and Dyenamo) for improvement [56–58]. With ready to use TiO₂ paste in hand, its light absorption properties can be enhanced by simple mixing in systematic way with silver



Figure 4. Depiction of anchoring mode of general additives for TiO₂ modifications.

and gold nanoparticles (Section 1). Additionally, different types of TiO₂ geometries such as nanotubes (NTs) and hollow spheres can be mixed with nanoparticles (NPs) to achieve higher loading (Section 1.2 and 1.3). An important class of additives to modify and enhance the interface properties of TiO₂ is the addition of electronically insulating molecules with anchoring groups (Section 2). Quite recently, simple surface treatment by chemical bath method on dye anchored TiO₂ (stained) films has been explored with impressive enhancements, such strategies are discussed in Section 3. Historically, most widely studied approach in regard to enhancement of DSCs and modification of TiO₂ is the introduction of new electrolyte additives including solvent, surface and recombination blocking pyridines and different anchoring groups, which are discussed in Section 4. At the end an overall perspective on the state of DSCs and the role of learnings to other fields is analyzed.

2. TiO₂ paste modifications

Integration of subwavelength plasmonic nanostructures and morphologically varied mesoporous films of TiO2 have been widely explored for enhancing DSCs performance. Hard modification of TiO2, such as sintering step is required at high temperature (500 0C) to activate the functionality are discussed below.

2.1. Plasmonic enhancement of DSCs

Plasmonic enhancement or light entrapment in DSCs by means of the plasmonic resonance of metal nanostructures has been a topic of intense research in the last decade. Since the first report in 2000 of metal nanostructured mediated enhancements in DSCs, many successful studies has been published outlining the role of size, shape and composition of metal nanoparticles on DSCs performance and working mechanisms [59–61]. Metal nanostructures capable of surface plasmon such as Au and Ag has been systematically introduced with TiO₂ NPs. Such as these nanoparticles can be designed and integrated in TiO₂ NPs in a way to offer light entrapment from visible to NIR region [62].

In plasmonic materials the coupling of incident photons to conduction band electrons upon excitation give rise to collective oscillations of electrons defined as *localized surface plasmon resonances* (LSPR) [63, 64]. By the engineering of plasmonic nanostructure's geometry, dimensions and composition LSPR's radiative (hot electron transfer, plasmon resonant energy transfer) and non-radiative (far-field scattering >50 nm size, near field coupling 3–50 nm size) processes can be tailored (**Figure 5**) [55, 56]. Out of four processes summarized in **Figure 5** far-field scattering and near field coupling are easily observed for DSCs such as by improvement in IPCE, whereas role of hot electron transfer and PRET to improve DSCs is thus far poorly explored [62]. Detailed discussion of each process and its implications for DSCs are beyond the scope of this chapter [62, 65].

In radiative effects metal nanostructure acts as a secondary light source and in non-radiative effects absorbed energy is subsequently transferred to neighboring semiconductor NPs (**Figure 5**).



Figure 5. Summary of radiative (a) and (b) and non-radiative LSPR-based processes and their features, modified from reference [62], with permission from the Royal Society of Chemistry.

For LSPR based enhancement of DSCs the size of the metal nanoparticles plays huge role. Such as at 5 nm regime of metal nanostructure non-radiative processes are dominant, near field coupling for 45 nm size regime and far field scattering for 120 nm size metal nanostructures [62]. In terms of application, some reports evidence the beneficial effect of topical presence of plasmonic nanoparticles on TiO_2 film, however, homogenous integration of plasmonic nanoparticles throughout active layer have proven more efficient, particularly in enhancing photocurrent response of devices (**Figure 6**) [67, 68].

The highest PCE achieved through plasmonic enhancements so far (2013) is 10.8% which is 30% higher (8.3% PCE) than the control device employing **N719** sensitizer by Belcher et al.. with 0.01–0.32% core shell particles mixed with regular TiO₂ [61]. In this study, oxide-metal-oxide multiple core-shell nanostructured spheres were blended with already available photoactive materials to achieve balanced light harvesting in panchromatic fashion. Kamat et al.. in a pioneering work (2012) identified the plasmonic and charging effect based on the composition of Au@SiO₂ and Au@TiO₂, leading to achieve a higher photocurrent and photovoltage with overall PCE of 10.2 and 9.7%, respectively [60]. Au nanoparticles of 5 nm size were used in the core with shell as passivation layer of either SiO₂ or TiO₂ and mixed with Solaronix T/SP paste in 0.7 wt%. Wang et al in 2013, in a unique study employed the organic sensitizer **FNE29** and I^-/I_3^- , along with TiO₂ inlaid 2 nm sized Au nanoparticles resulting in 10.1% PCE improved from 5.5% PCE (84% increase) [66]. Au nano colloid in 0–0.8 wt% ratio

Titanium Dioxide Modifications for Energy Conversion: Learnings from Dye-Sensitized Solar Cells 395 http://dx.doi.org/10.5772/intechopen.74565



Figure 6. Effect of ~2 nm sized inlaid Au NPs with different wt% in TiO_2 paste on IPCE, adopted from Ref. [66], with permission from the Royal Society of Chemistry.

was blended with TiO_2 paste to constitute the active layer (**Figure 6**). With most prominent current report, DSCs employing organic dye (**FNE29**) compared to Ru (II) dyes for plasmonic enhanced DSCs are rare. With the survey of reports published so far it is clear that though plasmonics has led to increased device efficiencies however, reports lack (1) application of nonprecious metal plasmonics for enhanced DSCs such as Al, graphene and semiconducting nanocrystal plasmonics (2) application of metal nanoparticles in conjunction with high photovoltage redox shuttles such as Co (III/II) or Cu (II/I) and organic sensitizers (3) long term stability studies particularly against redox shuttles for corrosion and chemical resistance of plasmonic DSCs [69–74].

2.2. Morphological investigation on TiO₂

NP based mesoporous TiO_2 shows excellent features for DSCs however it suffers from low electrical conductivity and charge recombination losses [75–78]. Additionally, enhanced light scattering and dye adsorption can be achieved by modifying the shape of NPs or mixing nanotubes, nanowires, nanospheres, and hollow TiO_2 [58, 77–81]. On the same note, 2D and 3D structures of TiO_2 such as nanoribbons, nanodisks, nanoleaves, nanoflowers, nanorods, hedgehog nanostructure and dendritic hollow structures have also be explored for DSCs [82–87]. The studies focused on the morphological modification of TiO_2 have demonstrated marginal increase in DSC performance with scattered results, however, due to structural complexity and reproducibility issues such investigations has not resulted in wide spread application for DSCs [76]. For details please refer to the cited work.

2.3. Metals and metal oxides for TiO₂ modifications

Doping or intentional addition of impurities while synthesis of TiO_2 can have substantial effect on band structure and surface states which dictate charge transport and dye/ TiO_2 interface in DSCs [88]. The purpose of doping is to achieve higher conductivity and minimized recombinations. In the regime of DSCs, doping has been studied with metals (lithium, magnesium or calcium), metalloids (boron, silicon, germanium, antimony), non-metals (carbon, nitrogen, sulfur, fluorine and iodine), transition metals, post transition metals and lanthanides. For a detailed analysis on choosing the dopant and its effects interested readers are referred to previously published review on the topic [88]. These dopants are generally added during the synthesis stage and require subsequent sintering step to be integrated as the part of crystalline structure of TiO_2 (hard modification).

Additionally, to enhance the interface properties of DSCs at TiO₂/dye/electrolyte for efficient charge transfer wide bandgap and electronically insulating metal oxides has been widely studied [75, 89]. Wide band gap metal oxides such as ZnO, Nb₂O₅, and WO₃ and electronically insulating oxides such as SrO, Al₂O₃, ZrO₂ and SiO₂ are known to form barrier layer at the interface which impedes back electron transfer at the interface boundary thus lowering recombination losses [90]. Most recently, MgO have been studied for TiO₂ modification during synthesis, leading to negative shift of up to 200 mV of TiO₂ owing to its more basic nature [91, 92]. An alternative approach is to surface treat the TiO₂ film with Mg⁺² precursor such as (Mg (OC₂H₅) or Mg (NO₃)₂) followed by high temperature sintering, however, concentration control becomes very critical for final performance [90, 93, 94]. Albeit, these studies report higher V_{oc} for DSCs employing Mg⁺² and reduced recombination losses. However, negatively shifted conduction band can also lower the electron injection if the sensitizer-excited state potential gets very close to CB energy. Interested readers are referred to relevant reviews for in-depth analysis of such modifications [75, 89].

3. Dye solution co-adsorbing additives

"Soft modification," simple rinse and dry to alter TiO₂/dye/electrolyte interface favorably is to add additives along with the dye adsorption solution known as "co-adsorbents" [95–98]. These additives are also known as de-aggregating agents which aid in favorable dye orientation on TiO₂ and increased electron injection through minimization of dye–dye intermolecular charge transfer and π - π stacking [99]. These mainly insulating additives are known to occupy the vacant spaces among dye molecules which prevents the diffusion of oxidized redox species (e.g., I₃⁻) to TiO₂ (**Figure 7**) [100, 101]. This approach has been widely explored for DSCs since the first report in 1993, though such modifications of TiO₂ surface were already explored by Miayasak et al. in 1978 [95, 96]. These co-adsorbents are amphiphilic in nature and consists of an anchoring group (**Figure 4**) such as carboxylic or phoshonic/phosphinic moiety and a long alkyl chain or three dimensional aromatic and alkyl components acting as a buffer between TiO₂ and electrolyte. These co-additives can be divided based on the chemical identity of anchoring group and their influence on the interface can be best studied through EIS and Titanium Dioxide Modifications for Energy Conversion: Learnings from Dye-Sensitized Solar Cells 397 http://dx.doi.org/10.5772/intechopen.74565



Figure 7. Illustration of dye on TiO_2 surface with (right) and without co-additive, I_3^- is the oxidized redox component.



Figure 8. Representative co-additives.

electron lifetime measurements. Since aggregation is a common phenomenon for mostly planar organic sensitizer including phthalocyanine and porphyrin, the effect of co-additives on aggregation can be studied by simple current dynamic measurements at different light intensities [102, 103].

3.1. Carboxylic acid based anchoring co-additives

Since the first report on deoxycholic acid (DCA) and chenodeoxycholic acid (CDCA, **Figure 8**) in 1993 by Grätzel et al. in ethanolic dye solution along with the sensitizers, CDCA has become the most widely used co-additive [96]. CDCA adsorption for pre-stained and post stained TiO₂ films was found less effective in terms of enhancing J_{sc} and V_{oc} [104]. Generally, the optimum concentration of CDCA in the dye solution depends on the nature of the dye and study of several concentrations (such as 2, 10, 20, and 40 times, etc., of the dye) is a normal routine [105, 106]. It should be kept in mind that excess of CDCA or any other co-adsorbent can adversely affect the dye loading as well. Under optimum conditions, CDCA is generally known to positively (downward) shift the conduction band of TiO₂, increasing electron injection along with lower recombination losses thus enhancing both J_{sc} and V_{oc} . It should be noted that CDCA mainly serves the role of de-aggregating agent for organic, porphyrin and phthalocyanine

sensitizers and a recombination blocking agent for Ru (II) sensitizers since latter dyes do not aggregate on TiO₂ [102]. In a recent study for ladder-like carbazole donor and cyanoacrylic acid (CA) anchor based D-A- π -A type dye, CDCA resulted in up to 9% enhancement in PCE when co-adsorbed with the dye [107]. Concentration of CDCA was 5 mM compared to 0.3 mM of the dye. The effect for the presence of CDCA was analyzed through EIS measurements which confirmed higher recombination resistance leading to 8% increase in J_{sc} and 2% increase in V_{oc} for most efficient dye in the series (C1). In a similar study for an organic phenothiazine based dye (P2), effect of different concentrations of CDCA was studied in detail [106]. CDCA concentration of 10 mM was found to result in optimum improvement in DSCs performance compared to 0.3 mM concentration of the dye.

Figure 8 shows the CDCA alternatives such as pivalic acid (PVA), 3,4,5-Tris(dodecyloxy) benzoic acid (DOBA) and EG1 (an amidoamine dendritic molecule) [108–110]. PVA in a comparative study approach showed enhanced electron lifetime and negative shift in the conduction band of TiO₂. This lead to 53 mV increase in V_{oc} and 8% increase in PCE. Adsorption of PVA before staining was found to be more effective, compared to co-adsorption with the dye. In an example with ss-DSCs (solid state-DSCs), DOBA and **Z907** sensitizer resulted in negative shift of the TiO₂ CB, decreased charge recombination, higher hydrophilicity and enhanced PCE as evidenced by EIS, and IMVS (intensity modulated photovoltage decay spectroscopy) measurements. In another example, strategically designed amidoamine-dendron based molecules (EG0–2) were studied as the co-additives and compared with CDCA. This study showed that superior surface blocking, higher electron injection, minimized intermolecular energy transfer and higher PCE can be tailored with increasing size of the dendritic molecules. In spite of co-additives examples (**Figure 8**), CDCA is mostly widely employed co-additive to modify the interface on TiO₂, however, it should be employed with caution particularly in terms of its co-adsorbing concentration.

3.2. Phosphonic/phosphinic acid anchoring and zwitterion-based co-additives

Co-additives with phosphorous containing anchoring groups are generally believed to anchor strongly compared to carboxylic acid anchors. First example of such an additive was appeared in 2003 by Zakeerudin et al. when 1-decyl phosphonic acid (DPA, **Figure 9**) was used with a **Z-907** (a benchmark hydrophobic dye historically popular for stable devices) [111]. It was claimed as the first example of stable DSCs under heat stress and continuous illumination,



Figure 9. Representative additives.

with 7% increase in PCE due to DPA (4:1 dye/co-additive concentration was employed). Later on in a unique example octydecyl phosphonic acid (OPA) was also characterized for **Z-907** and cobalt redox shuttle [112].

OPA (18C) was found more effective in blocking recombination compared to DPA (10C) because of longer alkyl chain with overall 20% increase in PCE (8.4% versus 7% no OPA, **Figure 10**) with 18:1 (dye:OPA) concentration ratio. This is one of the highest efficiency reported so far for a Ru (II) dye containing NCS with cobalt redox shuttles, owing to inherently higher recombination losses [113–115].

In this class of co-additives, dineohexyl phosphinic acid (DINHOP, **Figure 11**) is known as an efficient molecular insulator to electronically passivate the oxide junctions such as TiO₂, even outperforming CDCA in some comparative studies *vide infra* [105, 116]. DINHOP particularly benefits from the three dimensional orientation leading to better surface coverage [116]. Increase in PCE of 9% was realized for **Z-907** and DINHOP with 1:1 dye concentration (PCE 7.9% versus 7.24%).

In a comparative study for different small molecules (**Figure 9** containing phenylphosphonic acid (PPA), diphenylphosphinic acid (DPPA), phosphoric acid triethyl ester (PATEE), and phosphoric acid tributylester (PATBE) were employed as co-adsorbents [117]. It was found that alkyl chains performed better than the aromatic containing co-additives with ~12% enhancement in device PCE with **N719** sensitizer. The observed effect was established by EIS measurements (Nyquist plot), showing larger semicircle for high performing PATBE, pointing



Figure 10. Effect of OPA on Z907 performance, taken from Ref. [66], with permission from The Royal Society of Chemistry.



Figure 11. Co-additives employed in the comparative study.

to higher recombination resistance as the result of co-additive pretreatment of TiO_2 film before dipping in dye solution.

4-guanidino butyric acid (GBA, **Figure 8**) was first time employed in 2005 by Grätzel group with a Ru (II) sensitizer **K19** [118]. In that detailed study, cyclic voltammetry was employed to determine the density of states (DOS), EIS to analyze interface charge transfer properties and photovoltage decay measurements for the effect of GAB on electron life time and capacitance of TiO₂. GBA was found to have similar kind of effect as t-butyl pyridine on TiO₂ conduction band with negative shift in the quasi-fermi level of TiO₂. Additionally, increase in V_{oc} did not come as the result of decreased J_{sc} , thus leading to higher overall PCE (~9% increase with 1:1 concentration with the dye). In 2009, same group studied and compared GBA and 4-aminobutyric acid (ABA) for solid state DSCs and additives effect on long term stability (**Figure 11**) [101]. GBA outperformed ABA with about 37% increase in PCE compared to 16% decrease with ABA at 1:1 concentration. This was caused presumably due to more effective barrier formation to recombination and upward shift in the conduction band of TiO₂ by GBA. Enhancement in device performance due to GBA was caused by 15% increase (113 mV) in V_{oc} and 18.5% increase in J_{sc} . GBA was also found to enhance the long term stability.

In a recent study based on **C106** dye, Chandiran et al. studied four different additives (**Figure 11**) for their potential effect on the TiO_2 interface and device performance with different concentrations [105]. For **C106**, 4-guanidino butyric acid (GBA) resulted in 11% PCE, compared to 10.8% with CDCA at 0.5:1 (dye:CDCA) ratio compared to 6:1 for GBA (dye: GBA). In the same study, dineohexyl phosphinic acid (DINHOP) also showed slightly better results compared to CDCA (11% versus 10.8%), whereas dodecyl phosphonic acid (DPA) at 6:1 ratio marginally improved to 9.7% PCE. The device PCE without additives was reported to be 10.6%.

3.3. Dual function dyes as co-additives

An interesting approach to achieve multiple functionality such as light absorption and aggregation/recombination blocking at TiO_2 surface is to employ small molecule organic light absorbing dyes along with main dye [119–122]. Few successful example of such yellow to orange dyes which can be termed as co-sensitizers and co-additives are shown in **Figure 12**. In a detailed study in 2011, it was shown that Y-shaped molecules such as **HC-A**, can

Titanium Dioxide Modifications for Energy Conversion: Learnings from Dye-Sensitized Solar Cells 401 http://dx.doi.org/10.5772/intechopen.74565



Figure 12. Small molecule co-sensitizing dyes as co-additives to modify TiO₂.

potentially play multiple roles when co-adsorbed along with another organic dye (NKX2677) [119, 120]. IPCE confirmed the increased photocurrent response, EIS was used to rationalize the higher V_{oc} due to increased electron lifetime, and transient absorption studies showed the carbazole cation formation favorable for hole conduction. In a detailed study on similar lines with different molecules (HC3–5, Figure 12), black dye (BD) was optimized from 10.3% PCE to 11.3% for BD + HC-5, with 1:1 dye solution concentration [121]. As the result of cosensitization, **BD** + **HC-5** mainly realized enhancement in I_{sc} (8.5%). It should be noted that CDA (chenodeoxycholic acid) as a co-adsorbent was also added in 100 times excess in this study. In a recent study, similar effects were claimed with LD03 and LD04 when co-sensitized along with N719. N719 + LD04 showed highest enhancement of PCE from 7.896% to 8.955% (13.4% increase) due to better light harvesting, decrease in aggregation and higher electron recombination resistance [122]. BPHA (2-(4-butoxyphenyl)-N-hydroxyacetamide), Figure 12), was recently applied for chemical modification of TiO₂ before dye adsorption [123]. Though BPHA, was found to lower the adsorbed dye concentration, however, faster regeneration was reasoned for improved device performance (10-20%). Co-sensitizing approach of adsorbing multiple dyes on TiO_2 for enhanced light harvestings works on the same principles, in addition to order of staining, and dyes ratio, etc., interested readers are referred to the cited work [124–126].

4. Post-staining surface treatment additives

To minimize the non-productive electron recombination pathways at the interface, chemical bath surface treatment of stained or dyed TiO_2 is a very effective approach (soft modification). Such that the highest reported efficiency DSCs (12–14.3%), applied the most extensive surface treatments known (**Figure 13**) [25, 53, 127, 128]. It should be noted that post staining surface treatment additive need to be inert towards the sensitizer, i.e., it should not impede light harvesting and detach it from the surface of TiO_2 . Surface treatment is less complex than co-additive approach and offer better control on treatment parameters such as concentration,



Figure 13. Post staining surface treatment example "alkyl-thicket" layer formation, adopted from Ref. [127], with permission from The Royal Society of Chemistry.

dipping time, etc. Below section highlights the most successful strategies categorized on the basis of anchoring groups.

4.1. Carboxylic/phosphonic acid anchoring additives

Similar to dyes and co-adsorbing additives carboxylic/phosphonic acid anchoring groups are widely applied for surface treatment additives as well (**Figure 14**). Effect of long alkyl chain on enhancing electron lifetime in TiO₂ was already known in conjunction with DSC sensitizers [129–131]. However, Hanaya et al. popularized the concept of "alkyl thicket" as an insulating barrier layer to block unwanted electron recombinations at TiO₂. As the result, overall device PCE increased impressively ~20% (9.44–11.3%), with increase in J_{sc} from 15.1 to 15.8 mA/cm² and increase in V_{oc} from 0.826 to 0.958 V (16% increase). It is interesting to note, the presence of long alkyl chains was not found to impede the charge transfer and diffusion with potentially favorable effect on long term stability as well [47]. These additives are usually applied in a hierarchical (stepwise) way with dipping in 0.1 M conc. (empirical) solution with the longest chain additives followed by small chain additives which can penetrate well in smaller cavities. In a very interesting study, a multifunctional methoxy-terminated oligomeric poly(ethylene glycol) (PEG) chain containing a carboxylic acid at one chain end (Mw - 2000) (*m*-PEG-succinic acid, **Figure 14**) is employed for post staining surface treatment [132]. The presence of electron rich oxygen atoms in *m*-PEG was claimed to favorably co-ordinate with vacant sites on TiO₂

 Titanium Dioxide Modifications for Energy Conversion: Learnings from Dye-Sensitized Solar Cells
 403

 http://dx.doi.org/10.5772/intechopen.74565
 403



Figure 14. Additives used to modify TiO₂ in post-staining fashion.



Figure 15. Alkoxysilyl-based alkyl chain additives to modify TiO_2 .

and worked collegially with common electrolyte additives such as Li⁺, and tBP (4-ter butylpyridine). Increase in electron lifetime, decrease in dark current, and entrapment of Li⁺ resulted in both J_{sc} and V_{oc} enhancements.

4.2. Alkoxysilyl-based anchoring additives

In addition to "alkyl thicket" barrier layer for modifying TiO_2 surface, Hanaya et al. also introduced and studied the silanol-based sensitizer and additives for TiO_2 anchoring (**Figures 13** and **15**). It was found that titano-siloxane bonds are stronger and are more resistant to detachment from TiO_2 compared to carboxylic acid anchors [127, 133]. However, it should be noted, other groups reported on the synthetic challenges related to the inclusion of siloxanes for DSC sensitizers [134].

An interesting and effective evolution is the replacement of hydrocarbon chain by fluorocarbon chain while keeping alkoxysilyl anchoring groups the same (**Figure 16**) [135–138]. In the regime of organic PV's (OPVs) fluorinated alkyl chains has been effectively employed to result in surface segregated monolayer to achieve better charge transfer, polymer alignment and



Figure 16. Alkoxysilyl and fluorocarbon based additives to modify TiO2.

direction of dipole moment at the interface [139–141]. For TiO_2 modification, detailed studies focused on unrevealing the impressive effect of fluorinated alkyl chains evidenced, enhanced electron lifetime in TiO_2 , de-aggregating behavior for organic dyes, negative (upward) conduction band shift of TiO_2 with metal complex dye, hydrophobicity and overall PCE enhancements presumably due to fluorinated self-assembled monolayer formation (FSAM) [53, 94, 142–145]. Interestingly, in one study, cationically charged TMEA-TMOS (**Figure 15**) outperformed C16 based alkyl chain analog when used with Ru (II) dye and cobalt redox shuttle. Detailed studies on unrevealing the structure–property relationship of such fluorocarbon chains for modifying TiO_2 are rare in literature at this stage.

5. Electrolyte additives

Electrolyte is an integral component of DSCs, and its composition has huge effect on performance, and long term stability. It consist of redox active species such as iodide/triiodide, Co (III)/Co(II), Fc (I)/Fc (0), and Cu (II)/Cu(I), etc., and certain additives which are known to adsorb on TiO₂ surface such as lithium cation (Li⁺), 4-ter butylpyridine (4-tBP) and guanidium thiocyanate (GuNCS) and others as shown in **Table 1** [160–162]. Source of Li⁺ is mostly LiI for iodide/triiodide mediator and LiTFI or LiClO₄ for cobalt and copper based redox shuttles. Two widely studied redox systems for DSCs are iodide/triiodide and Co(III)/Co(II) with most recent as Cu(II)/Cu(I) [160–162]. Iodide/triiodide redox shuttle has been the favorable choice historically, but it results in lower photovoltage due to higher (less positive) redox potential, higher dye regeneration overpotenial due to complex two step chemistry and corrosion of the DSCs components [160]. On the other hand, one electron redox shuttles such as cobalt and copper offer higher photovoltage, tunability, and less dye regeneration overpotential making them Titanium Dioxide Modifications for Energy Conversion: Learnings from Dye-Sensitized Solar Cells 405 http://dx.doi.org/10.5772/intechopen.74565

| No. | Additive | Conc. (M) | Electrolyte/dye | CB effect | Electron lifetime | Jsc | V_{oc} | PCE |
|-----|---------------------------------------|-----------|-----------------|-----------|-------------------|------|----------|------|
| 1. | Li ⁺ [146] | 0.05-0.5 | I/Co | Down | Inc. | Inc. | Dec. | Inc. |
| 2 | CDCA [147] | 0.1 | Co/Ru (II) | Inc. | Inc. | Inc. | Inc. | Inc. |
| 3 | Li ₂ CO ₃ [148] | 0.0025 | I/Ru (II) | Up | Inc. | Inc. | Inc. | Inc. |
| 4 | K ₂ CO ₃ [148] | 0.05 | I/Ru (II) | Up | Inc. | Inc. | Inc. | Inc. |
| 5 | GuNCS [149] | 0.1 | Ι | Down | Dec. | Inc. | Dec. | Inc. |
| 6 | GuNO ₃ [150] | 0.1 | Ι | Up | Inc. | Inc. | Inc. | Inc. |
| 7 | S [151] | 1 | I/Ru (II) | Down | Dec. | Inc. | Dec. | Inc. |
| 8 | N [152, 153] | 0.25–0.5 | I/Co | Up | Inc. | Dec. | Inc. | Inc. |
| 9 | N-(154-156] | 0.5 | I/Ru (II) | Up | Inc. | Dec. | Inc. | Dec. |
| 10 | -SiN[157] | 0.5 | Со | Up | Inc. | Dec. | Inc. | Inc. |
| 11 | | 0.1 | Co | Up | Inc. | Inc. | Inc. | Inc. |
| | | | | | | | | |
| 12 | L /[159] | 0.5 | I/Ru (II) | Up | Inc. | Dec. | Inc. | Inc. |
| | | | | | | | | |
| 13 | [159] | 0.5 | I/Ru (II) | Up | Inc. | Dec. | Inc. | Dec. |
| | | | | | | | | |

Up = upward shift, Down = downward shift, Inc. = increase, and Dec. = decrease.

popular for recent studies [52, 163]. For iodide/triiodide most commonly employed additives are Li⁺, GuNCS and 4-tBP, whereas one electron redox shuttles mainly employ Li⁺ and 4-tBP only. Generally speaking, cationic additives charge the TiO₂ surface positively thus lowering the conduction band (**Table 1**, entry 1) [56, 146]. Electron rich or nitrogen containing additives on the other hand charge the TiO₂ surface negatively or increase electron density thus raising the conduction band, blocking the recombination and resulting in higher V_{oc} . An important factor is the concentration which is commonly optimized empirically such as for Li₂CO₃, GuNO₃, etc., additives [148, 150]. Electrolyte additives and their known effect in terms of TiO₂ modification and subsequent DSC device parameters are shown in **Table 1**.

Table 1. Summarizing the effect of electrolyte additives effect on TiO₂ and DSC parameters.

Since NCS containing Ru (II) sensitizers are incompatible with cobalt, inclusion of CDCA (Table 1, entry 2) substantially lowered the recombination losses and increased the PCE from 1.9 to 5.7% [147]. An interesting study, was the inclusion of Li₂CO₃ and K₂CO₃ (Table 1, entries 3 and 4) as a source of Li⁺, where former outperformed latter [148]. Li₂CO₃ enhanced the device performance (6.5–7.6%) without lowering V_{ocr} presumably due to formation of carbonate layer on TiO₂, as evidenced by FT-IR. In a comparative study, GuNO₃ showed overall better performance compared to well-known GuNCS, without negative effect on V_{oc} [150]. It was supported by the favorable effect of NO_3^- on TiO₂ CB (upward shift), which was not observed for NCS⁻ without affecting diffusion negatively. Thiophene (Table 1, entry 7) when added in 1 M concentration had Li⁺ like effect to enhance the J_{sc} [151]. 4-tBP (**Table 1**, entries 8–10) and its derivatives such as methyl pyridine, pyrimidine, pyrazole, triazole, thiazole and quinolone has been extensively explored by Arakawa et al. [154, 164-167]. Out of these, 4-trimethylsilylpyridine (Table 1, entry 10), have particularly shown better overall performance due to its bulkiness to block recombination reaction at interface, and better electron donating ability without negatively effecting the electron injection [157]. In a recent study, tris(4-methoxyphenyl)amine (TPAA, Table 1 entry 11) as an electron donor was explored by Boschloo et al. [158].

The inclusion of TPAA in cobalt electrolyte particularly blocked the recombination with oxidized sensitizer which lead to 26% increase in the DSC performance. 2-ethylimidazole and benzimidazole (**Table 1**, entries 12 and 13) due to labile proton and lone pairs on electron were expected to be good coordinating candidates to modify TiO_2 as studied by Wei et al. [159]. Benzimidazole and 2-ehtylimidazole were found to perform best when employed in the molar ratio of 9.5/0.5 respectively (7.93% PCE compared to 6.8%). These additives showed pyridine type effect in modifying TiO_2 . To this point, only few reports are available on the long term stability effect of these additives on TiO_2 properties and DSC device performance [168, 169].

In this chapter, DSC electrolyte additives are discussed with respect to liquid based systems, whereas liquid in these electrolytes eventually has to be replaced for long term stability either by solid or semi-solid (gel type) systems. Reader are kindly referred to the published literature for semisolid gel type electrolyte which generally apply similar additives and offer better long term stability [162, 170–172].

6. Summary

In summary, this chapter aimed at recognizing and highlighting various approaches to modify TiO_2 material based on the studies focusing on dye-sensitized solar cells. The emphasis was to identify the most successful examples and to rationalize their effect in enhancing electronic mobility, charge carrier generation and diffusion, conduction band shift, surface passivation, light harvesting, long term stability and ease of application. In general, TiO_2 modification can be categorized into hard modification and soft modification. Hard modification involves the addition of moieties such as plasmonic nanostructures, metal oxides, and morphological variations during synthesis such as a high temperature sintering (400–500°C) step is required

to achieve required functionality. On the other hand, soft modification (simple rinse and dry) post sintering surface treatment with additives, co-adsorbents, and electrolyte additives is rather simple to apply. With the discussion and literature provided in the chapter we hope the state of knowledge learned from dye-sensitized solar cells will benefit the scientific community to expand on the functionality of TiO_2 as it is being applied and explored in the fields of energy storage (batteries, super capacitors), photocatalysis, PVs, and sensors.

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References

- Joya KS, Joya YF, Ocakoglu K, van de Krol R. Water-splitting catalysis and solar fuel devices: Artificial leaves on the move. Angewandte Chemie, International Edition. 2013; 52(40):10426-10437
- [2] Outlook WE. World energy outlook 2015. International Energy Agency. 2015
- [3] Colton W. The Outlook for Energy: A View to 2040. Exxon Mobil Corporation; 2011
- [4] Olah GA. Beyond oil and gas: The methanol economy. Angewandte Chemie, International Edition. 2005;44(18):2636-2639
- [5] Chu S, Majumdar A. Opportunities and challenges for a sustainable energy future. Nature. 2012;488(7411):294-303
- [6] Turner JA. Sustainable hydrogen production. Science. 2004;305(5686):972-974
- [7] Joya KS, Morlanes N, Maloney E, Rodionov V, Takanabe K. Immobilization of a molecular cobalt electrocatalyst by hydrophobic interaction with a hematite photoanode for highly stable oxygen evolution. Chemical Communications. 2015;51(70):13481-13484
- [8] Ocakoglu K, Joya KS, Harputlu E, Tarnowska A, Gryko DT. A nanoscale bio-inspired lightharvesting system developed from self-assembled alkyl-functionalized metallochlorin nano-aggregates. Nanoscale. 2014;6(16):9625-9631

- [9] Lewis NS, Nocera DG. Powering the planet: Chemical challenges in solar energy utilization. Proceedings of the National Academy of Sciences. 2006;103(43):15729-15735
- [10] Feltrin A, Freundlich A. Material considerations for terawatt level deployment of photovoltaics. Renewable Energy. 2008;33(2):180-185
- [11] O'Regan B, Grätzel M. A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO₂ films. Nature. 1991;353(6346):737-740
- [12] Hagfeldt A, Boschloo G, Sun L, Kloo L, Pettersson H. Dye-sensitized solar cells. Chemical Reviews. 2010;110(11):6595-6663
- [13] Gratzel M. Photoelectrochemical cells. Nature. 2001;414(6861):338-344
- [14] Grätzel M. Recent advances in sensitized mesoscopic solar cells. Accounts of Chemical Research. 2009;42(11):1788-1798
- [15] Kalyanasundaram K. Dye-sensitized Solar Cells. Boca Raton, Fla.; London: CRC; Taylor & Francis [distributor]; 2009
- [16] Kavan L, Grätzel M, Gilbert SE, Klemenz C, Scheel HJ. Electrochemical and photoelectrochemical investigation of single-crystal anatase. Journal of the American Chemical Society. 1996;118(28):6716-6723
- [17] Carp O, Huisman CL, Reller A. Photoinduced reactivity of titanium dioxide. Progress in Solid State Chemistry. 2004;32(1):33-177
- [18] Dambournet D, Belharouak I, Amine K. Tailored preparation methods of TiO₂ anatase, rutile, brookite: Mechanism of formation and electrochemical properties. Chemistry of Materials. 2010;22(3):1173-1179
- [19] Yang WS, Noh JH, Jeon NJ, Kim YC, Ryu S, Seo J, et al. High-performance photovoltaic perovskite layers fabricated through intramolecular exchange. Science. 2015
- [20] Gratzel M. The light and shade of perovskite solar cells. Nature Materials. 2014;13(9): 838-842
- [21] Mishra A, Fischer MKR, Bäuerle P. Metal-free organic dyes for dye-sensitized solar cells: from structure: Property relationships to design rules. Angewandte Chemie, International Edition. 2009;48(14):2474-2499
- [22] Zhang S, Yang X, Numata Y, Han L. Highly efficient dye-sensitized solar cells: Progress and future challenges. Energy & Environmental Science. 2013;6(5):1443-1464
- [23] Ahmad S, Guillen E, Kavan L, Gratzel M, Nazeeruddin MK. Metal free sensitizer and catalyst for dye sensitized solar cells. Energy & Environmental Science. 2013;6(12):3439-3466
- [24] Ardo S, Meyer GJ. Photodriven heterogeneous charge transfer with transition-metal compounds anchored to TiO₂ semiconductor surfaces. Chemical Society Reviews. 2009; 38(1):115-164

- [25] Kakiage K, Aoyama Y, Yano T, Oya K, Fujisawa J-i, Hanaya M. Highly-efficient dyesensitized solar cells with collaborative sensitization by silyl-anchor and carboxy-anchor dyes. Chemical Communications. 2015;51(88):15894-15897
- [26] Li J-Y, Chen C-Y, Ho W-C, Chen S-H, Wu C-G. Unsymmetrical squaraines incorporating quinoline for near infrared responsive dye-sensitized solar cells. Organic Letters. 2012; 14(21):5420-5423
- [27] Liyanage NP, Yella A, Nazeeruddin M, Grätzel M, Delcamp JH. Thieno[3,4-b]pyrazine as an electron deficient π -bridge in D-A- π -A DSCs. ACS Applied Materials & Interfaces. 2016;8(8):5376-5384
- [28] Lu X, Zhou G, Wang H, Feng Q, Wang ZS. Near infrared thieno[3,4-b]pyrazine sensitizers for efficient quasi-solid-state dye-sensitized solar cells. Physical Chemistry Chemical Physics (PCCP). 2012;14(14):4802-4809
- [29] Wu J, Li G, Zhang L, Zhou G, Wang Z-S. Energy level engineering of thieno[3,4-b] pyrazine based organic sensitizers for quasi-solid-state dye-sensitized solar cells. Journal of Materials Chemistry A. 2016;4(9):3342-3355
- [30] Ito S, Murakami TN, Comte P, Liska P, Grätzel C, Nazeeruddin MK, et al. Fabrication of thin film dye sensitized solar cells with solar to electric power conversion efficiency over 10%. 6th International Conference on Coatings on Glass and Plastics (ICCG6). Advanced Coatings for Large-Area or High-Volume Products. 2008;516(14):4613-4619
- [31] Yella A, Mathew S, Aghazada S, Comte P, Gratzel M, Nazeeruddin MK. Dye-sensitized solar cells using cobalt electrolytes: The influence of porosity and pore size to achieve high-efficiency. Journal of Materials Chemistry C. 2017;5(11):2833-2843
- [32] Cheema H, Ogbose L, El-Shafei A. Structure–property relationships: Steric effect in ancillary ligand and how it influences photocurrent and photovoltage in dye-sensitized solar cells. Dyes and Pigments. 2015;113(0):151-159
- [33] Yum J-H, Baranoff E, Wenger S, Nazeeruddin MK, Grätzel M. Panchromatic engineering for dye-sensitized solar cells. Energy & Environmental Science. 2011;4(3):842-857
- [34] Pazoki M, Cappel UB, Johansson EMJ, Hagfeldt A, Boschloo G. Characterization techniques for dye-sensitized solar cells. Energy & Environmental Science. 2017;10(3):672-709
- [35] Ning Z, Fu Y, Tian H. Improvement of dye-sensitized solar cells: What we know and what we need to know. Energy & Environmental Science. 2010;3(9):1170-1181
- [36] Hardin BE, Snaith HJ, McGehee MD. The renaissance of dye-sensitized solar cells. Nature Photonics. 2012;6(3):162-169
- [37] Cheema H, Islam A, Han L, El-Shafei A. Monodentate pyrazole as a replacement of labile NCS for Ru (II) photosensitizers: Minimum electron injection free energy for dyesensitized solar cells. Dyes and Pigments. 2015;120:93-98

- [38] Cheema H, Islam A, Han L, Gautam B, Younts R, Gundogdu K, et al. Influence of mono versus bis-electron-donor ancillary ligands in heteroleptic Ru(ii) bipyridyl complexes on electron injection from the first excited singlet and triplet states in dye-sensitized solar cells. Journal of Materials Chemistry A. 2014;2(34):14228-14235
- [39] Liyanage NP, Cheema H, Baumann AR, Zylstra AR, Delcamp JH. Effect of donor strength and bulk on thieno[3,4-b]-pyrazine-based panchromatic dyes in dye-sensitized solar cells. ChemSusChem. 2017;10:2635-2641
- [40] Brogdon P, Cheema H, Delcamp JH. Low-recombination thieno[3,4-b]thiophene-based photosensitizers for dye-sensitized solar cells with panchromatic photoresponses. ChemSusChem. 2017;10(18):3624-3631
- [41] Brogdon P, Cheema H, Delcamp JH. NIR absorbing metal-free organic, porphyrin, and phthalocyanine dyes for panchromatic DSCs. ChemSusChem.n/a-n/a
- [42] Wu Y, Zhu W. Organic sensitizers from D-π-A to D-A-π-A: Effect of the internal electron-withdrawing units on molecular absorption, energy levels and photovoltaic performances. Chemical Society Reviews. 2013;42(5):2039-2058
- [43] Wu Y, Zhu WH, Zakeeruddin SM, Gratzel M. Insight into D-A-π-A structured sensitizers: A promising route to highly efficient and stable dye-sensitized solar cells. ACS Applied Materials & Interfaces. 2015;7(18):9307
- [44] Ito S, Dharmadasa IM, Tolan GJ, Roberts JS, Hill G, Miura H, et al. High-voltage (1.8 V) tandem solar cell system using a GaAs/AlXGa(1–X)As graded solar cell and dye-sensitised solar cells with organic dyes having different absorption spectra. Solar Energy. 2011;85(6):1220-1225
- [45] Fabregat-Santiago F, Bisquert J, Garcia-Belmonte G, Boschloo G, Hagfeldt A. Influence of electrolyte in transport and recombination in dye-sensitized solar cells studied by impedance spectroscopy. International Conference on Physics, Chemistry and Engineering. 2005;87(1–4):117-131
- [46] Koide N, Islam A, Chiba Y, Han L. Improvement of efficiency of dye-sensitized solar cells based on analysis of equivalent circuit. Journal of Photochemistry and Photobiology A: Chemistry; Proceedings of 7th AIST International Symposium on Photoreaction Control and Photofunctional Materials 7th AIST International Symposium on Photoreaction Control and Photofunctional Materials. 2006;182(3):296-305
- [47] Cheema H, Islam A, Younts R, Gautam B, Bedja I, Gupta RK, et al. More stable and more efficient alternatives of Z-907: Carbazole-based amphiphilic Ru(ii) sensitizers for dye-sensitized solar cells. Physical Chemistry Chemical Physics. 2014;16(48):27078-27087
- [48] Barnes PRF, Miettunen K, Li X, Anderson AY, Bessho T, Grätzel M, et al. Interpretation of optoelectronic transient and charge extraction measurements in dye-sensitized solar cells. Advanced Materials. 2013;25(13):1881-1922

- [49] Zhang L, Cole JM. Anchoring groups for dye-sensitized solar cells. ACS Applied Materials & Interfaces. 2015;7:3427-3455
- [50] Deacon GB, Phillips RJ. Relationships between the carbon-oxygen stretching frequencies of carboxylato complexes and the type of carboxylate coordination. Coordination Chemistry Reviews. 1980;33(3):227-250
- [51] Kalyanasundaram K, Grätzel M. Applications of functionalized transition metal complexes in photonic and optoelectronic devices. Coordination Chemistry Reviews. 1998; 177(1):347-414
- [52] Freitag M, Teuscher J, Saygili Y, Zhang X, Giordano F, Liska P, et al. Dye-sensitized solar cells for efficient power generation under ambient lighting. Nature Photonics. 2017; 11(6):372-378
- [53] Cheema H, Rodrigues RR, Delcamp JH. Sequential series multijunction dye-sensitized solar cells (SSM-DSCs): 4.7 volts from a single illuminated area. Energy & Environmental Science. 2017;10(8):1764-1769
- [54] Feldt SM, Gibson EA, Gabrielsson E, Sun L, Boschloo G, Hagfeldt A. Design of organic dyes and cobalt polypyridine redox mediators for high-efficiency dye-sensitized solar cells. Journal of the American Chemical Society. 2010;132(46):16714-16724
- [55] Fakharuddin A, Jose R, Brown TM, Fabregat-Santiago F, Bisquert J. A perspective on the production of dye-sensitized solar modules. Energy & Environmental Science. 2014; 7(12):3952-3981
- [56] Bai Y, Mora-Seró I, De Angelis F, Bisquert J, Wang P. Titanium dioxide nanomaterials for photovoltaic applications. Chemical Reviews. 2014;114(19):10095-10130
- [57] Li Z-Q, Chen W-C, Guo F-L, Mo L-E, Hu L-H, Dai S-Y. Mesoporous TiO(2) yolk-shell microspheres for dye-sensitized solar cells with a high efficiency exceeding 11%. Scientific Reports. 2015;5:14178
- [58] Li Z-Q, Ding Y, Mo L-E, Hu L-H, Wu J-H, Dai S-Y. Fine tuning of nanocrystal and pore sizes of TiO₂ submicrospheres toward high performance dye-sensitized solar cells. ACS Applied Materials & Interfaces. 2015;7(40):22277-22283
- [59] Wen C, Ishikawa K, Kishima M, Yamada K. Effects of silver particles on the photovoltaic properties of dye-sensitized TiO₂ thin films. Solar Energy Materials and Solar Cells. 2000;61(4):339-351
- [60] Choi H, Chen WT, Kamat PV. Know thy nano neighbor. Plasmonic versus electron charging effects of metal nanoparticles in dye-sensitized solar cells. ACS Nano. 2012; 6(5):4418-4427
- [61] Dang X, Qi J, Klug MT, Chen P-Y, Yun DS, Fang NX, et al. Tunable localized surface plasmon-enabled broadband light-harvesting enhancement for high-efficiency panchromatic dye-sensitized solar cells. Nano Letters. 2013;13(2):637-642

- [62] Erwin WR, Zarick HF, Talbert EM, Bardhan R. Light trapping in mesoporous solar cells with plasmonic nanostructures. Energy & Environmental Science. 2016;9(5):1577-1601
- [63] Maier SA. Plasmonics: Fundamentals and Applications. Springer Science & Business Media; 2007
- [64] Novotny L, Van Hulst N. Antennas for light. Nature Photonics. 2011;5(2):83-90
- [65] Xu Q, Liu F, Meng W, Huang Y. Plasmonic core-shell metal-organic nanoparticles enhanced dye-sensitized solar cells. Optics Express. 2012;20(S6):A898-A907
- [66] Li Y, Wang H, Feng Q, Zhou G, Wang Z-S. Gold nanoparticles inlaid TiO₂ photoanodes: A superior candidate for high-efficiency dye-sensitized solar cells. Energy & Environmental Science. 2013;6(7):2156-2165
- [67] Adhyaksa GWP, Baek S-W, Lee GI, Lee DK, Lee J-Y, Kang JK. Coupled near- and farfield scattering in silver nanoparticles for high-efficiency, stable, and thin plasmonic dyesensitized solar cells. ChemSusChem. 2014;7(9):2461-2468
- [68] Zheng D, Pang X, Wang M, He Y, Lin C, Lin Z. Unconventional route to hairy plasmonic/semiconductor core/shell nanoparticles with precisely controlled dimensions and their use in solar energy conversion. Chemistry of Materials. 2015;27(15):5271-5278
- [69] Liu M, Yin X, Ulin-Avila E, Geng B, Zentgraf T, Ju L, et al. A graphene-based broadband optical modulator. Nature. 2011;474(7349):64
- [70] Akimov YA, Koh W. Resonant and nonresonant plasmonic nanoparticle enhancement for thin-film silicon solar cells. Nanotechnology. 2010;21(23):235201
- [71] Chen X, Jia B, Zhang Y, Gu M. Exceeding the limit of plasmonic light trapping in textured screen-printed solar cells using Al nanoparticles and wrinkle-like graphene sheets. Light: Science and Applications. 2013;**2**(8):e92
- [72] Hwang E, Sarma SD. Dielectric function, screening, and plasmons in two-dimensional graphene. Physical Review B. 2007;75(20):205418
- [73] Comin A, Manna L. New materials for tunable plasmonic colloidal nanocrystals. Chemical Society Reviews. 2014;43(11):3957-3975
- [74] Liu X, Swihart MT. Heavily-doped colloidal semiconductor and metal oxide nanocrystals: An emerging new class of plasmonic nanomaterials. Chemical Society Reviews. 2014;43(11):3908-3920
- [75] Jose R, Thavasi V, Ramakrishna S. Metal oxides for dye-sensitized solar cells. Journal of the American Ceramic Society. 2009;92(2):289-301
- [76] Shakeel Ahmad M, Pandey AK, Abd Rahim N. Advancements in the development of TiO₂ photoanodes and its fabrication methods for dye sensitized solar cell (DSSC) applications. A review. Renewable and Sustainable Energy Reviews. 2017;77(Supplement C):89-108

- [77] Feng X, Zhu K, Frank AJ, Grimes CA, Mallouk TE. Rapid charge transport in dyesensitized solar cells made from vertically aligned single-crystal rutile TiO₂ nanowires. Angewandte Chemie. 2012;**124**(11):2781-2784
- [78] Feng X, Shankar K, Varghese OK, Paulose M, Latempa TJ, Grimes CA. Vertically aligned single crystal TiO₂ nanowire arrays grown directly on transparent conducting oxide coated glass: Synthesis details and applications. Nano Letters. 2008;8(11):3781-3786
- [79] Fattakhova-Rohlfing D, Zaleska A, Bein T. Three-dimensional titanium dioxide nanomaterials. Chemical Reviews. 2014;**114**(19):9487-9558
- [80] Mor GK, Varghese OK, Paulose M, Shankar K, Grimes CA. A review on highly ordered, vertically oriented TiO₂ nanotube arrays: Fabrication, material properties, and solar energy applications. Solar Energy Materials and Solar Cells. 2006;90(14):2011-2075
- [81] Zhou Q, Fang Z, Li J, Wang M. Applications of TiO₂ nanotube arrays in environmental and energy fields: A review. Microporous and Mesoporous Materials. 2015;202(Supplement C):22-35
- [82] Lin J, Peng Y, Pascoe AR, Huang F, Cheng Y-B, Heo Y-U, et al. A bi-layer TiO₂ photoanode for highly durable, flexible dye-sensitized solar cells. Journal of Materials Chemistry A. 2015;3(8):4679-4686
- [83] Lee CS, Kim JK, Lim JY, Kim JH. One-step process for the synthesis and deposition of anatase, two-dimensional, disk-shaped TiO₂ for dye-sensitized solar cells. ACS Applied Materials & Interfaces. 2014;6(23):20842-20850
- [84] Deepak TG, Anjusree GS, Pai KRN, Subash D, Nair SV, Nair AS. Cabbage leaf-shaped two-dimensional TiO₂ mesostructures for efficient dye-sensitized solar cells. RSC Advances. 2014;4(51):27084-27090
- [85] Oh J-K, Lee J-K, Kim H-S, Han S-B, Park K-W. TiO₂ branched nanostructure electrodes synthesized by seeding method for dye-sensitized solar cells. Chemistry of Materials. 2010;22(3):1114-1118
- [86] Roh DK, Chi WS, Jeon H, Kim SJ, Kim JH. High efficiency solid-state dye-sensitized solar cells assembled with hierarchical anatase pine tree-like TiO₂ nanotubes. Advanced Functional Materials. 2014;24(3):379-386
- [87] Kim H-B, Kim H, Lee WI, Jang D-J. Hierarchical mesoporous anatase TiO₂ nanostructures with efficient photocatalytic and photovoltaic performances. Journal of Materials Chemistry A. 2015;3(18):9714-9721
- [88] Roose B, Pathak S, Steiner U. Doping of TiO₂ for sensitized solar cells. Chemical Society Reviews. 2015;44(22):8326-8349
- [89] Lee J-J, Rahman MM, Sarker S, Nath ND, Ahammad AS, Lee JK. Metal oxides and their composites for the photoelectrode of dye sensitized solar cells. In: Advances in Composite Materials for Medicine and Nanotechnology. Rijeka: InTech; 2011

- [90] Peng T, Fan K, Zhao D, Chen J. Enhanced energy conversion efficiency of Mg²⁺-modified mesoporous TiO₂ nanoparticles electrodes for dye-sensitized solar cells. The Journal of Physical Chemistry C. 2010;114(50):22346-22351
- [91] Kakiage K, Osada H, Aoyama Y, Yano T, Oya K, Iwamoto S, et al. Achievement of over 1.4 V photovoltage in a dye-sensitized solar cell by the application of a silyl-anchor coumarin dye. Scientific Reports. 2016;6:35888
- [92] Kakiage K, Tokutome T, Iwamoto S, Kyomen T, Hanaya M. Fabrication of a dyesensitized solar cell containing a Mg-doped TiO₂ electrode and a Br³⁻/Br⁻ redox mediator with a high open-circuit photovoltage of 1.21 V. Chemical Communications. 2013; 49(2):179-180
- [93] Zhang C, Chen S, Mo L, Huang Y, Tian H, Hu L, et al. Charge recombination and bandedge shift in the dye-sensitized Mg²⁺-doped TiO₂ solar cells. The Journal of Physical Chemistry C. 2011;115(33):16418-16424
- [94] Cheema H, Delcamp JH. Harnessing photovoltage: Effects of film thickness, TiO₂ nanoparticle size, MgO and surface capping with DSCs. ACS Applied Materials & Interfaces. 2017;9(3):3050-3059
- [95] Miyasaka T, Watanabe T, Fujishima A, Honda K. Light energy conversion with chlorophyll monolayer electrodes. In vitro electrochemical simulation of photosynthetic primary processes. Journal of the American Chemical Society. 1978;100(21):6657-6665
- [96] Kay A, Graetzel M. Artificial photosynthesis. 1. Photosensitization of titania solar cells with chlorophyll derivatives and related natural porphyrins. The Journal of Physical Chemistry. 1993;97(23):6272-6277
- [97] Ogunsolu OO, Murphy IA, Wang JC, Das A, Hanson K. Energy and electron transfer cascade in self-assembled bilayer dye-sensitized solar cells. ACS Applied Materials & Interfaces. 2016;8(42):28633-28640
- [98] Manthou VS, Pefkianakis EK, Falaras P, Vougioukalakis GC. Co-adsorbents: A key component in efficient and robust dye-sensitized solar cells. ChemSusChem. 2015;8(4): 588-599
- [99] Delcamp JH, Shi Y, Yum JH, Sajoto T, Dell'Orto E, Barlow S, et al. The role of π-bridges in high-efficiency DSCs based on unsymmetrical squaraines. Chemistry - A European Journal. 2013;19:1819-1827
- [100] Reynal A, Palomares E. Increasing the performance of cis-dithiocyanato (4, 4'-dicarboxy-2, 2'-bipyridine)(1, 10-phenanthroline) ruthenium (ii) based DSC using citric acid as co-adsorbant. Energy & Environmental Science. 2009;2(10):1078-1081
- [101] Wang M, Grätzel C, Moon S-J, Humphry-Baker R, Rossier-Iten N, Zakeeruddin SM, et al. Surface design in solid-state dye sensitized solar cells: effects of zwitterionic coadsorbents on photovoltaic performance. Advanced Functional Materials. 2009;19(13): 2163-2172

- [102] Peddapuram A, Cheema H, Adams RE, Schmehl RH, Delcamp JH. A stable panchromatic green dual acceptor, dual donor organic dye for dye-sensitized solar cells. The Journal of Physical Chemistry C. 2017;121(16):8770-8780
- [103] Cheema H, Peddapuram A, Adams RE, McNamara L, Hunt LA, Le N, et al. Molecular engineering of near infrared absorbing thienopyrazine double donor double acceptor organic dyes for dye-sensitized solar cells. The Journal of Organic Chemistry. 2017
- [104] Neale NR, Kopidakis N, Van DL, GrÃtzel M, Frank AJ. Effect of a coadsorbent on the performance of dye-sensitized TiO₂ solar cells: Shielding versus band-edge movement. The Journal of Physical Chemistry B. 2005;109(49):23183-23189
- [105] Chandiran AK, Zakeeruddin SM, Humphry-Baker R, Nazeeruddin MK, Grätzel M, Sauvage F. Investigation on the interface modification of TiO₂ surfaces by functional co-adsorbents for high-efficiency dye-sensitized solar cells. Chemphyschem. 2017;18(19):2724-2731
- [106] Li J, Wu W, Yang J, Tang J, Long Y, Hua J. Effect of chenodeoxycholic acid (CDCA) additive on phenothiazine dyes sensitized photovoltaic performance. Science China: Chemistry. 2011;54(4):699-706
- [107] Zheng L, Cao Q, Wang J, Chai Z, Cai G, Ma Z, et al. Novel D-A-π-A-type organic dyes containing a ladderlike dithienocyclopentacarbazole donor for effective dye-sensitized solar cells. ACS Omega. 2017;2(10):7048-7056
- [108] Li X, Lin H, Zakeeruddin SM, Grätzel M, Li J. Interface modification of dye-sensitized solar cells with pivalic acid to enhance the open-circuit voltage. Chemistry Letters. 2009; 38(4):322-323
- [109] Kwon YS, Song IY, Lim J, Park S-H, Siva A, Park Y-C, et al. Reduced charge recombination by the formation of an interlayer using a novel dendron coadsorbent in solid-state dye-sensitized solar cells. RSC Advances. 2012;2(8):3467-3472
- [110] Xu J, Wu H, Jia X, Kafafy H, Zou D. Amidoamine dendron-based co-adsorbents: Improved performance in dye-sensitized solar cells. Journal of Materials Chemistry A. 2013;1(46):14524-14531
- [111] Wang P, Zakeeruddin SM, Humphry-Baker R, Moser JE, Grätzel M. Molecular-scale interface engineering of TiO₂ nanocrystals: Improve the efficiency and stability of dyesensitized solar cells. Advanced Materials. 2003;15(24):2101-2104
- [112] Liu Y, Jennings JR, Wang X, Wang Q. Significant performance improvement in dyesensitized solar cells employing cobalt(iii/ii) tris-bipyridyl redox mediators by cografting alkyl phosphonic acids with a ruthenium sensitizer. Physical Chemistry Chemical Physics. 2013;15(17):6170-6174
- [113] Liu Y, Jennings JR, Huang Y, Wang Q, Zakeeruddin SM, Grätzel M. Cobalt redox mediators for ruthenium-based dye-sensitized solar cells: A combined impedance spectroscopy and near-IR transmittance study. The Journal of Physical Chemistry C. 2011; 115(38):18847-18855

- [114] Wu K-L, Huckaba AJ, Clifford JN, Yang Y-W, Yella A, Palomares E, et al. Molecularly engineered Ru(II) sensitizers compatible with cobalt(II/III) redox mediators for dyesensitized solar cells. Inorganic Chemistry. 2016;55(15):7388-7395
- [115] Omata K, Kuwahara S, Katayama K, Qing S, Toyoda T, Lee K-M, et al. The cause for the low efficiency of dye sensitized solar cells with a combination of ruthenium dyes and cobalt redox. Physical Chemistry Chemical Physics. 2015;17(15):10170-10175
- [116] Wang M, Li X, Lin H, Pechy P, Zakeeruddin SM, Gratzel M. Passivation of nanocrystalline TiO₂ junctions by surface adsorbed phosphinate amphiphiles enhances the photovoltaic performance of dye sensitized solar cells. Dalton Transactions. 2009;(45):10015-10020
- [117] Shen H, Li X, Li J, Wang W, Lin H. Effect of proton numbers of phosphate-based coadsorbents on the photovoltaic performance of dye-sensitized solar cells. Electrochimica Acta. 2013;97(Supplement C):160-166
- [118] Zhang Z, Zakeeruddin SM, O'Regan BC, Humphry-Baker R, Grätzel M. Influence of 4guanidinobutyric acid as coadsorbent in reducing recombination in dye-sensitized solar cells. The Journal of Physical Chemistry B. 2005;109(46):21818-21824
- [119] Song BJ, Song HM, Choi IT, Kim SK, Seo KD, Kang MS, et al. A desirable holeconducting coadsorbent for highly efficient dye-sensitized solar cells through an organic redox cascade strategy. Chemistry - A European Journal. 2011;17(40):11115-11121
- [120] Choi IT, Ju MJ, Kang SH, Kang MS, You BS, Hong JY, et al. Structural effect of carbazolebased coadsorbents on the photovoltaic performance of organic dye-sensitized solar cells. Journal of Materials Chemistry A. 2013;1(32):9114-9121
- [121] Zhang S, Islam A, Yang X, Qin C, Zhang K, Numata Y, et al. Improvement of spectral response by co-sensitizers for high efficiency dye-sensitized solar cells. Journal of Materials Chemistry A. 2013;1(15):4812-4819
- [122] Luo J, Wan Z, Jia C, Wang Y, Wu X. A co-sensitized approach to efficiently fill the absorption valley, avoid dye aggregation and reduce the charge recombination. Electrochimica Acta. 2016;215:506-514
- [123] Aung SH, Hao Y, Oo TZ, Boschloo G. 2-(4-butoxyphenyl)-N-hydroxyacetamide: An efficient preadsorber for dye-sensitized solar cells. ACS Omega. 2017;2(5):1820-1825
- [124] Yum JH, Holcombe TW, Kim Y, Yoon J, Rakstys K, Nazeeruddin MK, et al. Towards high-performance DPP-based sensitizers for DSC applications. Chemical Communications. 2012;48:10727-10729
- [125] Pei K, Wu Y, Li H, Geng Z, Tian H, Zhu WH. Cosensitization of D-A-pi-A quinoxaline organic dye: Efficiently filling the absorption valley with high photovoltaic efficiency. ACS Applied Materials & Interfaces. 2015;7(9):5296-5304
- [126] Babu DD, Elsherbiny D, Cheema H, El-Shafei A, Adhikari AV. Highly efficient panchromatic dye-sensitized solar cells: Synergistic interaction of ruthenium sensitizer with
novel co-sensitizers carrying different acceptor units. Dyes and Pigments. 2016;**132**:316-328

- [127] Kakiage K, Aoyama Y, Yano T, Otsuka T, Kyomen T, Unno M, et al. An achievement of over 12 percent efficiency in an organic dye-sensitized solar cell. Chemical Communications. 2014;50(48):6379-6381
- [128] Kakiage K, Aoyama Y, Yano T, Oya K, Kyomen T, Hanaya M. Fabrication of a highperformance dye-sensitized solar cell with 12.8% conversion efficiency using organic silyl-anchor dyes. Chemical Communications. 2015;51(29):6315-6317
- [129] Cao Y, Cai N, Wang Y, Li R, Yuan Y, Wang P. Modulating the assembly of organic dye molecules on titania nanocrystals via alkyl chain elongation for efficient mesoscopic cobalt solar cells. Physical Chemistry Chemical Physics. 2012;14(23):8282-8286
- [130] Zhang M, Zhang J, Fan Y, Yang L, Wang Y, Li R, et al. Judicious selection of a pinhole defect filler to generally enhance the performance of organic dye-sensitized solar cells. Energy & Environmental Science. 2013;6(10):2939-2943
- [131] Kroeze JE, Hirata N, Koops S, Nazeeruddin MK, Schmidt-Mende L, Grätzel M, et al. Alkyl chain barriers for kinetic optimization in dye-sensitized solar cells. Journal of the American Chemical Society. 2006;128(50):16376-16383
- [132] Lee Y-G, Park S, Cho W, Son T, Sudhagar P, Jung JH, et al. Effective passivation of nanostructured TiO2 interfaces with PEG-based oligomeric coadsorbents to improve the performance of dye-sensitized solar cells. The Journal of Physical Chemistry C. 2012;116(11):6770-6777
- [133] Unno M, Kakiage K, Yamamura M, Kogure T, Kyomen T, Hanaya M. Silanol dyes for solar cells: higher efficiency and significant durability. Applied Organometallic Chemistry. 2010;24(3):247-250
- [134] Sobuś J, Gierczyk B, Burdziński G, Jancelewicz M, Polanski E, Hagfeldt A, et al. Factors affecting the performance of champion silyl-anchor carbazole dye revealed in the femtosecond to second studies of complete ADEKA-1 sensitized solar cells. Chemistry - A European Journal. 2016;22(44):15807-15818
- [135] Gregg BA, Fo P, Ferrere S, Fields CL. Interfacial recombination processes in dyesensitized solar cells and methods to passivate the interfaces. The Journal of Physical Chemistry B. 2001;105(7):1422-1429
- [136] Feldt SM, Cappel UB, Johansson EMJ, Boschloo G, Hagfeldt A. Characterization of surface passivation by poly(methylsiloxane) for dye-sensitized solar cells employing the ferrocene redox couple. The Journal of Physical Chemistry C. 2010;114(23):10551-10558
- [137] Spivack J, Siclovan O, Gasaway S, Williams E, Yakimov A, Gui J. Improved efficiency of dye sensitized solar cells by treatment of the dyed titania electrode with alkyl(trialkoxy) silanes. Solar Energy Materials & Solar Cells. 2006;90(9):1296-1307

- [138] Morris AJ, Meyer GJ. TiO₂ surface functionalization to control the density of states. The Journal of Physical Chemistry C. 2008;112(46):18224-18231
- [139] Geng Y, Wei Q, Hashimoto K, Tajima K. Dipole layer formation by surface segregation of regioregular poly(3-alkylthiophene) with alternating alkyl/semifluoroalkyl side chains. Chemistry of Materials. 2011;23(18):4257-4263
- [140] Tada A, Geng Y, Wei Q, Hashimoto K, Tajima K. Tailoring organic heterojunction interfaces in bilayer polymer photovoltaic devices. Nature Materials. 2011;**10**:450
- [141] Ma J, Hashimoto K, Koganezawa T, Tajima K. End-on orientation of semiconducting polymers in thin films induced by surface segregation of fluoroalkyl chains. Journal of the American Chemical Society. 2013;135(26):9644-9647
- [142] Carli S, Casarin L, Caramori S, Boaretto R, Busatto E, Argazzi R, et al. A viable surface passivation approach to improve efficiency in cobalt based dye sensitized solar cells. Polyhedron. 2014;82:173-180
- [143] Sewvandi GA, Tao Z, Kusunose T, Tanaka Y, Nakanishi S, Feng Q. Modification of TiO₂ electrode with organic silane interposed layer for high-performance of dye-sensitized solar cells. ACS Applied Materials & Interfaces. 2014;6(8):5818-5826
- [144] Wooh S, Kim T-Y, Song D, Lee Y-G, Lee TK, Bergmann VW, et al. Surface modification of TiO₂ photoanodes with fluorinated self-assembled monolayers for highly efficient dyesensitized solar cells. ACS Applied Materials & Interfaces. 2015;7(46):25741-25747
- [145] Matsui M, Mizutani T, Manseki K, Kubota Y, Kubo S, Tomoda H, et al. Effects of alkyl-, polyfluoroalkyl-, and perfluoroalkyl carboxylic acids on the performance of D205 in dye-sensitized solar cells. Journal of Photochemistry and Photobiology, A: Chemistry. 2017;348(Supplement C):134-138
- [146] Jennings JR, Wang Q. Influence of lithium ion concentration on Electron injection, transport, and recombination in dye-sensitized solar cells. The Journal of Physical Chemistry C. 2010;114(3):1715-1724
- [147] Konstantakou M, Falaras P, Stergiopoulos T. Blocking recombination in Ru(II) complexsensitized solar cells by incorporating co-adsorbents as additives in the Co(II)/(III)-based redox electrolytes. Polyhedron. 2014;82:109-115
- [148] Zhang J, Zaban A. Efficiency enhancement in dye-sensitized solar cells by in situ passivation of the sensitized nanoporous electrode with Li₂CO₃. Electrochimica Acta. 2008; 53(18):5670-5674
- [149] Kopidakis N, Neale NR, Frank AJ. Effect of an adsorbent on recombination and bandedge movement in dye-sensitized TiO₂ solar cells: Evidence for surface passivation. The Journal of Physical Chemistry B. 2006;110(25):12485-12489
- [150] Nath NCD, Jun Y, Lee J-J. Guanidine nitrate (GuNO₃) as an efficient additive in the electrolyte of dye-sensitized solar cells. Electrochimica Acta. 2016;201(Supplement C): 151-157

- [151] Afrooz M, Dehghani H. Significant improvement of photocurrent in dye-sensitized solar cells by incorporation thiophene into electrolyte as an inexpensive and efficient additive. Organic Electronics. 2016;29:57-65
- [152] Boschloo G, Häggman L, Hagfeldt A. Quantification of the effect of 4-tert-butylpyridine addition to I-/I3- redox electrolytes in dye-sensitized nanostructured TiO2 solar cells. The Journal of Physical Chemistry B. 2006;110(26):13144-13150
- [153] Nakade S, Kanzaki T, Kubo W, Kitamura T, Wada Y, Yanagida S. Role of electrolytes on charge recombination in dye-sensitized TiO₂ solar cell (1): The case of solar cells using the I-/I3- redox couple. The Journal of Physical Chemistry B. 2005;109(8):3480-3487
- [154] Kusama H, Arakawa H. Influence of alkylaminopyridine additives in electrolytes on dye-sensitized solar cell performance. Solar Energy Materials & Solar Cells. 2004;81(1): 87-99
- [155] Sun Z, Zhang R-K, Xie H-H, Wang H, Liang M, Xue S. Nonideal charge recombination and conduction band edge shifts in dye-sensitized solar cells based on adsorbent doped poly(ethylene oxide) electrolytes. The Journal of Physical Chemistry C. 2013;117(9):4364-4373
- [156] Koh TM, Li H, Nonomura K, Mathews N, Hagfeldt A, Gratzel M, et al. Photovoltage enhancement from cyanobiphenyl liquid crystals and 4-tert-butylpyridine in co(ii/iii) mediated dye-sensitized solar cells. Chemical Communications. 2013;49(80):9101-9103
- [157] Kakiage K, Tsukahara T, Kyomen T, Unno M, Hanaya M. Significant improvement of photovoltaic performance of dye-sensitized solar cells by using 4-Trimethylsilylpyridine as organic additive to electrolyte solution. Chemistry Letters. 2012;41(9):895-896
- [158] Hao Y, Yang W, Zhang L, Jiang R, Mijangos E, Saygili Y, et al. A small electron donor in cobalt complex electrolyte significantly improves efficiency in dye-sensitized solar cells. Nature Communications. 2016;7:13934
- [159] Sun X, Li Y, Mao H, Dou J, Wei M. Towards a high open-circuit voltage by co-additives in electrolyte for high-efficiency dye-sensitized solar cells. Journal of Power Sources. 2017;359:142-146
- [160] Boschloo G, Hagfeldt A. Characteristics of the iodide/Triiodide redox mediator in dyesensitized solar cells. Accounts of Chemical Research. 2009;42(11):1819-1826
- [161] Cong J, Yang X, Kloo L, Sun L. Iodine/iodide-free redox shuttles for liquid electrolytebased dye-sensitized solar cells. Energy & Environmental Science. 2012;5(11):9180-9194
- [162] Wu J, Lan Z, Lin J, Huang M, Huang Y, Fan L, et al. Electrolytes in dye-sensitized solar cells. Chemical Reviews. 2015;115(5):2136-2173
- [163] Saygili Y, Söderberg M, Pellet N, Giordano F, Cao Y, Muñoz-García AB, et al. Copper Bipyridyl Redox Mediators for Dye-Sensitized Solar Cells with High Photovoltage. Journal of the American Chemical Society. 2016;138(45):15087-15096

- [164] Kusama H, Arakawa H. Influence of benzimidazole additives in electrolytic solution on dye-sensitized solar cell performance. Journal of Photochemistry and Photobiology, A: Chemistry. 2004;162(2–3):441-448
- [165] Kusama H, Arakawa H. Influence of pyrimidine additives in electrolytic solution on dye-sensitized solar cell performance. Journal of Photochemistry and Photobiology, A: Chemistry. 2003;160(3):171-179
- [166] Kusama H, Arakawa H. Influence of quinoline derivatives in I–/I3– redox electrolyte solution on the performance of Ru(II)-dye-sensitized nanocrystalline TiO₂ solar cell. Journal of Photochemistry and Photobiology, A: Chemistry. 2004;165(1–3):157-163
- [167] Yin X, Tan W, Zhang J, Lin Y, Xiao X, Zhou X, et al. Synthesis of pyridine derivatives and their influence as additives on the photocurrent of dye-sensitized solar cells. Journal of Applied Electrochemistry. 2009;39(1):147-154
- [168] Gao J, Yang W, Pazoki M, Boschloo G, Kloo L. Cation-dependent photostability of Co(II/ III)-mediated dye-sensitized solar cells. The Journal of Physical Chemistry C. 2015; 119(44):24704-24713
- [169] Gao J, Bhagavathi Achari M, Kloo L. Long-term stability for cobalt-based dye-sensitized solar cells obtained by electrolyte optimization. Chemical Communications. 2014;50(47): 6249-6251
- [170] Suzuki K, Yamaguchi M, Kumagai M, Tanabe N, Yanagida S. Dye-sensitized solar cells with ionic gel electrolytes prepared from imidazolium salts and agarose. Comptes Rendus Chimie. 2006;9(5):611-616
- [171] Ileperuma O. Gel polymer electrolytes for dye sensitised solar cells: A review. Materials Technology. 2013;28(1–2):65-70
- [172] De Gregorio GL, Agosta R, Giannuzzi R, Martina F, De Marco L, Manca M, et al. Highly stable gel electrolytes for dye solar cells based on chemically engineered polymethacrylic hosts. Chemical Communications. 2012;48(25):3109-3111

TiO₂ Applications as a Function of Controlled Surface Treatment

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Additional information is available at the end of the chapter

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Abstract

For the end use, the structure and morphology of the coated film are very important since they determine the final properties of the resultant material. The effect of coatings largely depends on their composition and method of application, which may give porous or dense coatings. To achieve uniform coatings on dispersed TiO, particles, various compounds were deposited one after another under specific conditions by the wet chemical deposition method starting from rutile TiO₂, produced by the sulfate method in Cinkarna Celje. With the synthesis of composite particles consisting of a core TiO, particle coated with a functional shell with dimensions in the nano scale, we prepared advanced materials, where the shell protects the particles from undesirable interactions with the environment and improves surface reactive properties of the dispersed particles to meet special requirements. The morphology of surface-treated TiO, particles has been identified directly using electron microscopy, while the degree of functionalization by various hydroxides was determined using X-ray fluorescence spectrometer (XRF). In addition, zeta potential (ZP) measurements have been utilized to determine the electrochemical properties of resultant particles. The precipitation of hydroxides on the TiO, surface resulted in the shift of the isoelectric point (IEP). UV-Vis spectroscopy has been used for determining light scattering efficiency. In addition to internal characterization, light fastness of durable grade intended for the application in laminates has been tested by the end user.

Keywords: TiO₂, pigment, surface treatment

1. Introduction

Titanium dioxide (TiO_2) is used in a variety of applications, all of which have different sets of performance requirements. As a result, the pigments designed for the various applications

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are different. Variations in crystal structure (anatase/rutile), inorganic coating and organic treatments provide a wide range of titanium dioxide grades, each with different properties.

Generally, the properties of a pigment are determined by the particle size distribution of the base pigment, the chemical composition and the morphology of the surface treatment. The morphology of the treatment layers can, in turn, have an effect on the final properties of the pigment.

 TiO_2 pigments are generally coated to improve their performance in many end-use applications. Thus, the pH, temperature, reagents, order of addition and other factors can affect product characteristics. Optimum treatment conditions need to be determined after the surface treatment chemicals have been selected [1].

There are differences between grades, partially based on the fact that TiO_2 particle surfaces may be modified differently with inorganic and organic post treatments. With regard to colloidal chemistry, a TiO_2 with an Al_2O_3 surface treatment behaves completely different from one having a SiO_2 surface treatment [2]. Both of these, again, are different from a pure, untreated TiO_2 , which has its IEP at pH values between 4.5 and 6.5.

Surface treatment of TiO_2 particles by colorless inorganic compounds of low solubility affects dispersibility of the pigments in the matrix and weather resistance and lightfastness of the pigmented organic matrix [3].

These treatments are most commonly precipitated in layers. However, some of the components can be co-precipitated to alter the pigment characteristics [1]. There are many works regarding this subject in literature [4–14].

Inorganic surface treatment influences optical performance of the pigment approximately in proportion to the decrease in the TiO_2 content. Surface coatings prevent direct contact between the binder matrix and the reactive surface of the TiO_2 . The treatment process also affects dispersibility of the pigment, and therefore a compromise often has to be made. High weather resistance and good dispersibility of the pigment in the binder or matrix are usually desired. These effects are controlled by using different coating densities and porosities. In addition, organic substances can be added during the final milling of the dried pigment [3].

Several types of treatment are known:

- Deposition from the gas phase by hydrolysis or decomposition of volatile substances.
- Addition of oxides, hydroxides or substances that can be absorbed onto the surface during pigment grinding, which results in partial coating of the pigment surface.
- Precipitation of the coating from aqueous solution onto the suspended TiO₂ particles by batch processes in stirred tanks starting from various compounds, which are deposited one after another under specific conditions. The most common are oxides, oxide hydrates, silicates and/or phosphates of titanium, zirconium, silicon and aluminum.

Typical groups of inorganic coatings are as follows:

- 1. Pigments with dense surface coatings for paints or plastic made by
 - Homogeneous precipitation of SiO₂ with precise control of temperature, pH and precipitation rate.

- After-treatment with Zr, Ti, Al and Si compounds.
- After-treatment with merely 1–3% of alumina [15–18].
- **2.** Pigments with porous coating for use in emulsion paints obtained by simple treatment with Ti, Al and Si compounds, giving a silica content of 10% and a TiO_2 content of 80–85%.
- **3.** Lightfast pigments with dense surface coatings for the paper laminate industry that have a highly stabilized lattice and a surface coating based on silicates or phosphates of titanium, zirconium and aluminum: cca. 90% TiO₂.

For coloring of plastics, usually smaller TiO_2 particles are used with typically less than 3% of inorganic coating (TiO₂ typically >95%).

Before micronizing the pigment in a jet-mill and sometimes also before drying, the pigment surface is further modified by adding organic substances to improve dispersibility and facilitate further processing. The nature of the compounds used depends on the intended use of the pigment [3].

1.1. About TiO,

1.1.1. Pigment properties

Scattering power, hiding power (tinting strength), brightness, mass tone (or color), gloss formation, gloss haze, dispersibility, lightfastness and weather resistance are the most important pigment properties of TiO_2 pigments; these properties are a function of chemical purity, lattice stabilization, primary particle size, particle size distribution and the coating.

 TiO_2 's theoretical optimum particle size is between 0.2 and 0.3 µm, but the pigment obtained is considerably larger mainly because of the formation of agglomerates while handling during the manufacturing process. The presence of agglomerates affects hiding power, tinting strength and other end-use properties of the coating. The graph in **Figure 1** illustrates the effect of TiO_2 's dispersion states vs. particle size distribution on pigment properties. A well-dispersed system helps to develop coatings with improved optical properties, hiding power, tinting strength and gloss.

1.1.2. Uses of TiO,

Titanium dioxide pigment (TiO_2) is an important material used in many applications due to its opacity, high chemical stability, excellent whiteness and brightness. It is required in applications such as the following:

- paints and coatings
- printing inks
- plastics
- paper



Figure 1. TiO, dispersion states as a function of particle size distribution.

1.1.3. Stability towards light and weather

When subjected to intense radiation or weathering, systems with incorporated TiO_2 show color or structural changes. Yellowing, chalking and loss of gloss occur due to photocatalytic activity of TiO_2 . Formation of extremely reactive radicals (.OH, HO₂.), that cause deterioration of the coating matrix can be suppressed by doping or coating the surface of the pigment [3, 19–21].

1.2. About surface treatment

1.2.1. Silica

Rutile TiO_2 particles must be coated with protective layers of SiO_2 and Al_2O_3 through wet chemistry processes in order to decrease their photoactivity, increase weather durability and increase dispersibility in certain media [4, 22–24]. The morphology of the SiO_2 coating layers on the surface of TiO_2 powders can be controlled by adjusting the reaction temperature, pH value of the reaction solution and the SiO_2 loading [4].

Depending on the silica precipitation conditions, very disparate pigment characteristics could be produced. "Fluffy" coating, which provides better spacing and optical efficiency, increases oil absorption and decreases gloss forms at acidic or neutral pH [1]. An example of a "fluffy" coating composed of submicroscopic particles joined together in a gel-like structure is presented in **Figure 2**.

During slow deposition at basic pH, silica can also be formed as a dense, glassy shell that encapsulates the particle and provides the highest durability available. Durability of the silica layer and the amount of energy needed to develop gloss are proportional to the amount of silica in the layer [1]. A dense, glass-like coating is shown in **Figure 3**. Coating is a few nm thick, encapsulating the entire surface of the pigment.

Island-like SiO₂ coating layers can be formed on a TiO₂ surface when the reaction temperature, the pH value and the mole ratio of Na₂SiO₃ to TiO₂ are low. Continuous and uniform SiO₂ coating layers form in an alkaline pH ranging from 9 to 10. The thickness of the coating



Figure 2. Silica surface treatment as a fluffy layer.

layer increases with the increase of the mole ratio of Na_2SiO_3 to TiO_2 . The SiO₂ coating layers are anchored onto the TiO_2 surface by the Ti–O–Si bonding. Dispersibility of the SiO₂-coated TiO₂ powders is affected by the morphology of the SiO₂ coating [4].

1.2.2. Coating process of the SiO, layer

Isoelectric point (IEP) of rutile TiO_2 is usually located around pH 3.5 [24, 25]. The rutile TiO_2 surface is negatively charged under conditions where the pH value of the reaction solution is greater or equal to 7. Under conditions where pH values of the reaction solutions are in the range 7–8, Na₂SiO₃ rapidly hydrolyzes to form a large number of siliceous micelles. The resultant siliceous micelles anchor on the surface of TiO₂ powders via Ti–O–Si bonding to obtain island-like coating layers.

The hydrolysis rate of Na_2SiO_3 should be lowered by increasing the pH value to 9–10. This results in the formation of small-sized or less aggregated siliceous micelles. Small-sized micelles anchor on the surface of TiO₂ powders initially via Ti–O–Si bonding. Later, the micelles present in the solution and the anchored micelles condense via Si–O–Si bonding resulting in the formation of continuous and uniform coating layers. Over pH 10.5, silicon



Figure 3. Silica surface treatment as a dense, glass-like layer.

species exist as single silicate anions, or less aggregated siliceous micelles with very small particle size, which should be more negatively charged. The single silicate anions and the highly negatively charged siliceous micelles do not react with the negatively charged TiO_2 surface due to the strong electrostatic repulsion. Therefore, no SiO_2 coating layers forms on the TiO_2 surface at this high pH value.

Raising the temperature of the reaction affects the covering extent and causes the formation of a dense SiO, coating layer on the surface of the rutile TiO, powder.

1.2.3. Alumina

Hydrous aluminum oxide is probably the most common treatment agent of TiO_2 pigments. Various reagents can be used for deposition, e.g., sodium aluminate, which reacts with acid (see **Figure 4**), or aluminum sulfate, which reacts with base (see **Figure 5**).

Alumina can also be deposited from a combination of sodium aluminate and aluminum sulfate, which neutralize each other (**Figure 6**).

Irrespective of the reagent used, under controlled conditions of surface treatment, a thin, even layer, which entirely encapsulate the surface of TiO₂ is formed.

1.2.4. Coating process of the Al₂O₃ layer

By coating the surface of TiO_2 uniformly with alumina, coated particles behave in some ways similar to pure alumina. Alumina coating increase the amount of -OH groups on particle surface and consequently improve dispersibility of particles in aqueous solution and provide more active sites for further organic modification [24].

The level of alumina depends on the gloss, tint strength and opacity needed in the pigment. Low alumina levels yield better gloss but lower tint strength compared with higher levels [10].

The morphology of the alumina layer depends on the deposition conditions. Aluminum oxide and hydrous alumina have many different structures, which can give many different properties to coated particles. Formation of aluminum layers as a function of the suspension's pH is



Figure 4. Sodium aluminate as a source of aluminum hydroxide.



Figure 5. Aluminum sulfate as a source of aluminum hydroxide.

presented in **Figure 7**. From literature, we know that the structure of the alumina layer on TiO₂ pigment varies with the pH, i.e., the alumina tends to deposit as a pseudoboehmite in basic solutions. Alumina deposits in an amorphous form in the acid solutions. The transition pH is temperature-sensitive and tends to shift to lower pH at higher temperature [1].

Parameters such as temperature, pH, coating reagent concentration, core particle concentration and particle surface characteristics significantly affect precipitation coating process [26]. Hydrolysis polymerization, a precipitation process of the coating reagent as well as the coating morphology is influenced by pH and temperature. At high pH values, hydrolysis of Al³⁺ is accelerated and more multinuclear OH—Al species are formed compared to the situation at low pH [27]. The number of Al³⁺ ions depends on pH and Al³⁺ concentration, while the structure of the OH—Al species depends on the process conditions, e.g., concentration of Al³⁺, temperature and stirring strength [28]. pH also affects the protonation and deprotonation reactions on the core particle surface [29].

Condensation between OH–Al species and –OH groups on the TiO₂ particle surface occurs when the OH–Al species collide with TiO₂ particles through random collisions. Formation of



Figure 6. Sodium aluminate and aluminum sulfate as a source of aluminum hydroxide.



Figure 7. Formation of aluminum layers as a function of the suspension's pH.

Ti–OvAl bond formed via condensation of –OH groups from TiO₂ surface and OH–Al species is presented in **Figure 8**.

When the pH is higher than the isoelectric point, the TiO₂ particles carry negative charge [11]. The number of –OH groups on the particle surface that could provide protons is large; the surface is easy to provide protons, which facilitated the condensation between the OH–Al species and the –OH groups on the particle surface. In such a case, heterogeneous precipitation is



Figure 8. At pH higher than the IEP, the number of –OH groups on the particle surface that could provide protons is large and the condensation with the OH–Al species easily occurs [13].

preferred. Since a large amount of –OH groups on the particle surface could provide protons at higher pH, there were many OH–Al species that condense with the –OH groups on the particle surface; neighboring condensed OH–Al species easy condense each other, forming a continuous film coating, as shown in **Figure 9**.

When the pH is lower than the IEP, the number of –OH groups on the particle surface that could provide protons is small and condensation with the OH-Al species hardly occurs; here, homogeneous nucleation or the dotted layer is preferred (**Figure 10**).

At high pH, the OH—Al species are large, having a certain shape, and their sedimentation leads to a loose floccule or flake-like layer (**Figure 11**).

The layer morphology mainly depends on the sedimentation speed and the directed growth speed of the OH—Al species [30]. When the temperature is in the middle range, the sedimentation speed and the directed growth speed of the OH—Al species are about the same. At increased temperature, the directed growth speed of the OH—Al species dominates the precipitation



Figure 9. TEM image of a continuous film aluminum hydroxide coating.



Figure 10. Image of TiO₂ particles with dotted alumina layer.



Figure 11. TEM image provides an excellent view of the shell covering of a crystalline core of TiO_2 with a loose floccule or flake-like layer.

process regardless of the pH and size of the OH—Al species, which results in a directed growth [10]. Layer morphology changes from uniform and continuous film to loose floccules.

Temperature has a significant effect on the direction and growth speed of the OH–Al species in gel precipitation or coating, while also affecting the self-assembly of the OH–Al species in the aging process. Under high pH conditions, the OH–Al species form a large particle size, which facilitates the formation of boehmite Al(OH)₃ gels or a floccule/flake coating. Amorphous Al(OH)₃ gel forms only under conditions when the precipitation and aging proceed at a low temperature and pH; it can be converted to boehmite under high pH or temperature conditions.

However, boehmite gel cannot be converted to the amorphous form when the pH and temperature are low in the aging process [10].

2. TiO₂ grades

2.1. Highly coated TiO, grades

There is a special route for improving TiO_2 light scattering efficiency that is closely related to targeted spacing—the encapsulation of the TiO_2 particles by a thick, porous material. This coating material, which in practice is aluminosilicates, needs to be thick enough to effectively prevent close contact of the TiO_2 portion of these pigments and highly porous because a solid coating would unnecessarily dilute the TiO_2 content of the pigment. Even with high porosity, these coatings dilute the weight percent of TiO_2 in the pigment to roughly 80%.

It is important to manage the process under controlled conditions. **Figures 12** and **13** indicate differences between two highly coated $\text{TiO}_{2'}$ produced under controlled and uncontrolled conditions. Surface of $\text{TiO}_{2'}$ coated under appropriate conditions is uniform with coatings covering the entire surface of the particles (**Figure 13**). Increased SiO₂ loading up to 10 wt.% resulted in thicker layers. Coating TiO₂ particles under neutral conditions yields fluffy coatings with coating thickness up to 50 nm. Pigment particles are separated from each other, showing no agglomeration.

On the contrary, uncontrolled coating process yielded incomplete coatings (**Figure 12**). Homogeneous coating was not attained and some particles were not coated with the silica layer.



Figure 12. Highly surface treated TiO₂ (uncontrolled conditions).



Figure 13. Highly surface treated TiO₂ (controlled conditions).

2.1.1. Particle size distribution

The particle size relevant for inorganic pigments stretch between several tens of nanometers for transparent pigment types to approximately 2 μ m. For practical applications, it is desirable to determine not only the mean particle size but also the whole distribution [3].

The distribution of highly surface-treated TiO_2 in a controlled process indicates narrow particle size distribution, while an uncontrolled process yields material with broad particle size

distribution. Different populations are evident, meaning that the sample consists of many small and many over-sized particles (**Figure 14**).

Surface modification treatment in the suspension brings a significant shift in the pattern toward the higher particle diameter region due to high hydroxide loadings of silica and alumina imparted on the TiO_2 surface. The higher degree of surface modification and greater tendency for particle agglomeration can be attributed for the higher average particle diameter.

If we take into account only the mean particle sizes, we can conclude that we have two very similar samples. But, if we look at the whole distribution, it is obvious that the samples consist of very different populations. With this, we confirmed the fact that it is significant to determine not only the mean particle size but also the whole distribution.

After the grinding operation, particle size distribution again shifted to the lower particle diameter region. The sample produced by an uncontrolled process again contain over-sized particles (**Figure 15**).

2.1.2. Optical density

The problem with particle size distribution measurements is that the data cannot be directly related to the scattering power without using a theoretical model. An optical density test has been developed to provide a direct measure of the actual pigment scattering potential, which can then be used to evaluate performance in end-use applications [31–33].

A lab-dispersed sample in water is accurately diluted and analyzed for its total light transmission *T*. We have used the 'DuPont optical density', which is defined as $-\log(\text{total } T)/\text{concentration}$ and defines the scattering potential of the pigment. Compared to standard end-use tests of scattering power such as tint strength, optical density (OD) measurement offers the advantage of faster turn-around and improved precision with standard deviations less than 0.5% of the mean value.

The optical density was determined by UV-Vis spectrophotometer. To determine the optical density, 1 L of the diluted suspension of pigment particles TiO_2 in ethanol (c $TiO_2 = 30$ mg/L) was prepared. During the analysis, the suspension was subjected to ultrasound stirring. The



Figure 14. Particle size distribution of highly coated TiO_2 in slurry after controlled (narrow curve) and uncontrolled (wider curve) surface treatment.



Figure 15. Particle size distribution of micronized highly coated TiO_2 after controlled (narrow curve) and uncontrolled (wider curve) surface treatment.

optical density method determines the optical properties of the particles. This method determines the dispersibility or degree of particles agglomeration.

The results of the optical density determination indicated the differences between particles coated under different process conditions, controlled and uncontrolled (**Figure 16**). The light scattering highly depends on the particle size and the distribution of the size and degree of agglomeration of the material. Agglomeration always reduces the effectiveness of pigment light scattering. With the results obtained, we gained information about the light scattering efficiency, which is most likely a consequence of the particle size distribution and the degree of dispersion. Differences in dispersion between differently coated particles are the result of a different particle size distribution, the degree of milling step and the controlled coating mode, where the particle surface was completely coated with a layer of hydroxide. Surface treatment is important in determination of the physical properties of the particle surface and thus, affects the dispersion in a particular medium. The quality of surface treatment defines how the pigment will perform when incorporated into a particular medium. Light scattering efficiency (LSE) will depend on how well the pigment will be dispersed. Differently agglomerated particles should exhibit different OD value.

Results of the OD method indicate that coating the surface in a controlled manner resulted in particles with higher LSE (gray curve) in comparison with the particles coated under



Figure 16. Light scattering efficiency of TiO, particles coated under controlled and uncontrolled process conditions.

uncontrolled conditions (black curve). Consequently, differences in undertone for both samples were evident.

Smaller particles ($\leq 0.2 \mu m$) scatter the light of the short wavelength more strongly; therefore, they have a slightly blue undertone, while the larger particles scatter the light of a longer wavelength, i.e., they have a yellow undertone.

2.2. Weather resistant grades

Due to the light absorption in the near UV, electrons are hoisted from the energy level of the valence band of TiO_2 into that of the conductive band, thus leaving a positively charged hole in the valence band. The separated electron-hole pair is called an 'exciton'. The generation of excitons is the cause for the light induced semiconductor properties of TiO_2 . The photoactivity of TiO_2 is generally not preferred, since the excitons can have an oxidizing influence on its surroundings and, for example, destroy a polymer matrix in which it is embedded. Therefore, the TiO_2 pigment industry takes some efforts to diminish the photoactivity of TiO_2 . On the other hand, this property is utilized purposefully in TiO_2 photocatalysts [2].

From experience, anatase pigments are generally much less photo- and weather-resistant than rutile pigments [2]. Since a durable pigment is in demand, a heavy dense silica treatment is used. In addition, alumina has been chosen as the final layer over the silica treatment. Examples of surface treatment for weather resistant grades are presented in **Figures 17** and **18**. **Figure 17** presents the dense silica-alumina coating while **Figure 18** presents the dense silica-zirconia-alumina coating, covering the entire surface of TiO₂ particles.

Due to the fact that anatase is more photocatalytically active in the crystalline form than rutile, we selected material with the highest level of rutile crystalline structure as a base material. The level of rutile crystalline structure was determined before surface treatment using XRD (see **Table 1**).

Weather resistant grades can be produced by various surface treatments. We decided on two different versions, depending on the final applications. The structure of the coatings is presented in **Table 2**.



Figure 17. Dense silica-alumina coating.



Figure 18. Special Al-Si-Zr surface treatment.

| Sample | R [%] |
|----------------------------|-------|
| TiO ₂ —Al—Si | 99.7 |
| TiO ₂ -Al-Si-Zr | 99.8 |

Table 1. Level of rutile crystalline structure in TiO₂.

| Sample | SiO ₂ [%] | A ₁₂ O ₃ [%] | ZrO ₂ [%] |
|----------------------------|----------------------|------------------------------------|----------------------|
| TiO ₂ —Al—Si | 3.6 | 3.1 | - |
| TiO ₂ –Al–Si–Zr | 3.4 | 2.1 | 0.39 |

Table 2. Metal oxides determination.

2.3. TiO₂ for applications in printing inks

2.3.1. Gloss effect

Gloss is a visual impression gained when light is reflected at a surface in a preferential direction. The gloss of a coating system is determined by a number of factors. Pigments can influence the gloss of a coating through their concentration, particle size distribution and degree of dispersion in the binder system [34].

A conventional, high quality TiO_2 pigment has a mean particle diameter (weight average) of approximately 0.3 µm. The particle size distribution should not exceed the 1 µm limit in order to be useful for high gloss coatings [2].

Only those pigment particles lying directly below the surface of the coating are involved in this process. The higher the concentration of pigment, the greater the number of gloss-reducing particles and lower the gloss [34].

2.3.2. Rheology

An ink with required rheological properties can be successfully applied to the image on a plate, transferred correctly to the stock and finally, retain its form as a print. Each printing technique has specific requirements. For opacity, it is important to select pigment and pigment volume concentrations that play a role on opacity, gloss and whiteness, but also on the rheology of the ink. Different pigment grades have different medium absorption. As a consequence, the rheology of the ink at the time of application will be affected. Many ingredients, apart from TiO₂ pigments, will affect the final rheology of the ink. It is important to note that formulation of inks calls for much practical experience and skill.

It is vital to incorporate TiO_2 pigment into the printing ink medium in a way that maximum dispersion is achieved. In the case of a poor dispersion stability even viscosity could be affected.

2.3.3. Solubility parameters and dispersion

From the economical point of view, the best dispersion state of TiO_2 should be obtained in the shortest time and with minimum expenditure of energy.

Inorganic and organic surface treatments of TiO_2 could be optimized in order to maximize pigment affinity with both binder and solvents. This results in pigments with better dispersion and stabilization in a wide range of printing ink formulations, i.e., improved opacity, gloss and color [35].

The end-user of printing inks has the skill to select a range product (TiO₂ grade); the best suited grade for a particular purpose.

Optical properties of the pigment are defined by the particle size distribution, while the applicative properties are determined by the surface treatment. By implementation of more intensive milling, we prepared a slurry of more dispersed TiO₂ particles. The prepared TiO₂ slurry has been used for further surface treatment. Our goal was to keep the particles separated from each other through the whole process.

The influence of milling and coating process on optical properties are presented in **Table 3**. In order to improve the applicable properties, it is important to coat TiO₂ particles under



Figure 19. Alumina surface-treated TiO₂ intended for printing inks applications.

| Sample | Gloss | Scattering |
|------------------------|-------|------------|
| Poorly milled material | 24.4 | 97.4 |
| More intense milling | 40.5 | 104.1 |

Table 3. Influence of milling and coating process on optical properties.

controlled conditions (*T*, pH, precursor dosing rate). Under such conditions, the alumina surface-treated particles are separated from each other; coating is uniform and dense, covering the entire surface of the particle (**Figure 19**). Such particles exhibit excellent optical properties, as demonstrated in **Table 3**. In the case where the process of surface treatment started from suspension with more dispersed or deagglomerated particles (intense milling), higher gloss was obtained for the system with incorporated TiO₂.

2.3.4. Optical density

A layer of alumina oxide layer can increase the amount of -OH groups on the particle surface, which can improve the dispersibility of the particles and provide more active sites for further organic modification; this was evidenced from the results obtained by OD method. TiO₂ particles surface-treated under controlled conditions exhibit significantly higher light scattering efficiency due to complete aluminum layer coating the entire TiO₂ surface. Lower LSE was determined for TiO₂ particles with incomplete coatings, produced under uncontrolled conditions (**Figure 20**).

Printing ink with incorporated TiO_2 particles with incomplete coatings was highly viscous. For printing inks production approximately 10% more solvent was needed. Since the viscosity



Figure 20. Light scattering efficiency (LSE) for pigmentary TiO, with complete and incomplete coatings.

of the dispersion and the type of optical properties (especially the undertone and gloss) are strongly dependent on the degree of particulate dispersion, we can conclude that in controlled surface treatment, we obtained more dispersed particles.

2.4. TiO₂ applications in paper laminates

As already mentioned before, TiO_2 is a semi-conducting material and show some intrinsic photocatalytic activity. During weathering, interaction of UV light with TiO_2 occurs resulting in the formation of free electrons and electron-holes in the crystal lattice. These radicals react easily with neighboring organic molecules and, result in degradation of the medium [36–38].

The interaction of UV light with TiO_2 particles results in the formation of Ti^{3+} centers that are violet-colored species. For that reason, discoloration (greying) of the exposed area might be observed. This is usually described in terms of the lightfastness [37].

Generally, commercial TiO_2 grades are surface-treated with hydrated compounds of aluminum, silicon and zirconium [39–42]. Silica contributes to durability, while zirconia improves gloss and durability. Alumina is usually used as a final layer to increase dispersion stability. Sometimes, special surface treatment, for example, with aluminum phosphate is required to provide high lightfastness in applications such as decorative papers [43]. Scanning transmission electron microscopy (STEM) image of TiO_2 , surface treated with aluminum phosphate is presented in **Figure 21**.

2.4.1. Lightfastness

The lightfast properties of printing inks can be defined as the amount of resistance to fade or color change of a printed surface when exposed to daylight (or an artificial light source) over a set period of time.

For determination of lightfastness of prints, Blue Wool Scale is utilized. According to this method, samples are exposed to a standard xenon light in appropriate equipment.



Figure 21. STEM image of TiO₂ with aluminum phosphate coating.

The lightfastness is indicated by the grades on the Blue Wool Scale: BWS 1 = poor, BWS 2 = low, BWS 3 = average, BWS 4 = rather good, BWS 5 = good, BWS 6 = very good, BWS 7 = extremely good, BWS 8 = excellent.

 TiO_2 with aluminum phosphate coating successfully underwent testing by the end-user with grades 4/5 on the Gray Scale (grades 1–5) and with grade > 6 on the Blue Wool Scale; we met the requirements of the user.

2.4.2. Electrochemical properties determination

IEP of pure TiO₂ particles is about pH 4. Modifying the pigment surface with inorganic layers of, for example, $Al_2O_{3'}$ SiO_{2'}, $ZrO_{2'}$ phosphates changes the IEPs [2]. Whereas, for example, Al_2O_3 (IEP = 9) and $Al(OH)_3$ species (IEP is about 6.8) shifts the IEP to higher pH values, other substances normally tend to reduce the IEP to lower pH values (IEP of SiO₂ = 2, IEP of ZrO_2 = 4). Phosphates, used for surface treatment form acidic groups on the surface of particles, which are acidic and becomes a potential determinant [2, 14].

In **Figure 22**, the zeta potential as a function of pH for untreated and surface-treated TiO_2 pigments are presented. IEP of pure TiO_2 particles is about 4 and according to literature [2], IEP of aluminum surface-treated TiO_2 is 8.65, which is close to the values determined for Al_2O_3 . IEP of Si surface-treated TiO_2 shifted to pH 2.5, close to IEP characteristic for SiO_2 . Complete alumina layers contributed to shift IEP to higher pH values (pH 8.6), which proves a successful surface treatment, since the IEP value of surface-treated samples lies close to the IEP value characteristic for alumina. The results are in agreement with literature. Multi-layered surface treatments, alumina in combination with silica and phosphate, shifted IEP to lower pH. IEP values for all samples are presented in **Table 4**. The uniformity and the properties of hydroxide coatings influenced the surface properties of the pigment particles because the coated particles show similar surface characteristic, such as surface charge and surface active sites or groups, as the coating material.



Figure 22. Zeta potential as a function of pH.

| Sample | IEP |
|-------------------------|------|
| TiO ₂ | 4.1 |
| TiO ₂ –Si | 2.5 |
| TiO ₂ –Al | 8.65 |
| TiO ₂ –Si–Al | 7.3 |
| TiO ₂ —Al—P | 6.3 |

Table 4. IEPs for untreated and surface-treated TiO₂ particles.

3. Conclusions

Surface treatment of TiO_2 particles is one of the most important steps in the production of TiO_2 pigment. It is a delicate and complex process. Process parameters such as pH and temperature have to be carefully controlled, as this is essential to ensure the formation of uniform oxide coatings and achieving the desired useful features. Surface-treated TiO_2 particles were prepared starting from various precursors by the chemical liquid deposition method. Uniform hydroxide layers formed on the surfaces of the TiO_2 particles under mild hydrolysis rate of, for example, sodium aluminate, aluminum sulfate or sodium silicate in gel precipitation and aging. The morphology of the layers was significantly affected by the temperature and pH value of the reaction solution. Formation of thin and uniform hydroxide layers influenced optical and electrochemical properties. Surface-treated particles altered their electrokinetic behavior in a way similar to the coating material, suggesting formation of a complete hydroxide layer on the TiO_2 surface. We can conclude that inappropriate pH conditions can lead to undesirable phases of hydroxides or to an incomplete layer. By applying a dense silica layer of colorless alumina phosphate, photoactivity of TiO_2 pigments was successfully suppressed.

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References

 Tyler F. Tailoring TiO₂ treatment chemistry to achieve desired performance properties. Paint & Layers Industry. 2000;**32**:16-32

- [2] Winkler J. Titanium Dioxide. Vincentz: Hannover; 2003
- [3] In: Buxbaum G, Pfaff G, editors. Industrial Inorganic Pigments. 3rd ed. Weinheim: Wiley-VCH; 2005
- [4] Liu Y, Ge C, Ren M, Yin H, Wang A, Zhang D, Liu C, Chen J, Feng H, Yao H, Jiang T, editors. Effects of coating parameters on the morphology of SiO₂-coated TiO₂ and the pigmentary properties. Applied Surface Science. 2008;254:2809-2819
- [5] Liu Y, Zhang Y, Ge C, Yin H, Wang A, Ren M, Feng H, Chen J, Jiang T, Yu L. Evolution mechanism of alumina coating layer on rutile TiO₂ powders and the pigmentary properties. Applied Surface Science. 2009;255:7427-7433
- [6] Zhang Y, Liu Y, Ge C, Yin H, Ren M, Wang A, Jiang T, Yu L. Evolution mechanism of alumina nanofilms on rutile TiO₂ starting from sodium metaaluminate and the pigmentary properties. Powder Technology. 2009;**192**:171-177
- [7] Zhang Y, Yin H, Wang A, Ren M, Gu Z, Liu Y, Shen Y, Yu L, Jiang T. Deposition and characterization of binary Al₂O₃/SiO₂ coating layers on the surfaces of rutile TiO₂ and the pigmentary properties. Applied Surface Science. 2010;257:1351-1360
- [8] Zhang Y, Yin H, Wang A, Liu C, Yu L, Jiang T, Hang Y. Evolution of zirconia coating layer on rutile TiO₂ surface and the pigmentary property. Journal of Physics and Chemistry of Solids. 2010;71:1458-1466
- [9] Wu HX, Wang TJ, Duan JL, Jin Y. Effects of SO₄²⁻ on the heterogeneous precipitation coating of hydrous alumina on TiO₂ particles in an aqueous process. Industrial and Engineering Chemistry Research. 2007;46:3590-3594
- [10] Wu HX, Wang TJ, Jin Y. Morphology "phase diagram" of the hydrous alumina coating on TiO₂ particles during aqueous precipitation. Industrial and Engineering Chemistry Research. 2006;45:5274-5278
- [11] Wu HX, Wang TJ, Jin Y. Film-coating process of hydrated alumina on TiO₂ particles, Industrial and Engineering Chemistry Research. 2006;45:1337-1342
- [12] Veronovski N, Lešnik M, Verhovšek D. Surface treatment optimization of pigmentary TiO₂ from an industrial aspect. JCT Research. 2014;**11**:255-264
- [13] Veronovski N, Lesnik M, Verhovšek D. Alumina surface treated pigmentary titanium dioxide with suppressed photoactivity. LifeScience Global. 2014;1:51-58
- [14] Veronovski N. Alumina surface treated TiO₂—From process to application. Journal of Surface Science and Technology. 2015;2-1:6-12
- [15] Jeer RK. DuPont. US 2885366; 1956
- [16] Evans AW, Shon C. Tioxide Group Ltd. GB 1008652; 1961
- [17] Rechmann H, Vial F, Weber H. Kronos Titangesellschaft Mbh. DE 1208438; 1960
- [18] Moody JR, Lederer G. British Titanium Products. DE 146712; 1965

- [19] Brugger K, Jehle N. In: Congress FATIPEC XII (EREC); Paris. 1976. p. 15
- [20] Volz HG, Kampf G, Fitzky HG, Klaeren A. The chemical nature of chalking in the presence of titanium dioxide pigments. Photodegradation and Photostabilization of Coatings. In: ACS Symposium Series. 151; 1981 p. 163
- [21] Volz HG, Kampf G, Fitzky HG. Surface reactions on titanium dioxide pigments in paint films during weathering. In: Progress in Organic Coatings. 1974;2-3:223-235
- [22] Powell QH, Fotou GP, Kodas TT, Anderson B. Coating of TiO₂ with metal oxides by gasphase reactions. Journal of Aerosol Science. 1995;26:557-558
- [23] Atou Y, Suzuki H, Kimura Y, Sato T, Tanigaki T, Saito Y, Kaito C. Novel method for the preparation of silicon oxide layer on TiO₂ particle and dynamic behavior of silicon oxide layer on TiO₂ particle. Physica E. 2003;**16**:179-189
- [24] Lin YL, Wang TJ, Jin Y. Surface characteristics of hydrous silica coated TiO₂ particles. Powder Technology. 2002;**123**:194-198
- [25] Yin H, Wada Y, Kitamura T, Kambe S, Murasawa S, Mori H, Sakata T, Yanagida S. Journal of Materials Chemistry. 2001;11:1694-1703
- [26] He YX. Ceramic composites through solution precipitation coating [thesis]. Berkeley, CA: University of California; 1998
- [27] Lu XQ, Chen ZL, Yang XH. Spectroscopic study of aluminum speciation in removing humic substances by Al coagulation. Water Research. 1999;33:3271
- [28] Bi SP, Wang CY, Cao Q, Zhang CH. Studies on the mechanism of hydrolysis and polymerization of aluminum salts in aqueous solution: Correlations between the "core-links" model and "cage-like" keggin-Al₁₃ model. Coordination Chemistry Reviews. 2004;248:441
- [29] Tomba'cz E, Libor Z, Ille's E, Majzik A, Klumpp E. The role of reactive surface sites and complexation by humic acids in the interaction of clay mineral and iron oxide particles. Organic Geochemistry. 2004;35:257
- [30] Shen Z, Zhao ZG, Wang GT. Colloid and Surface Chemistry. Beijing, China: Chemistry Industry Press; 2004
- [31] Shedding light on white. European Coatings Journal. Vincentz Network 06/200
- [32] US Patent 6,040,913, March 21; 2000
- [33] US Patent 6,236,460, May 22; 2001
- [34] Brock T, Groteklaesm, Mischke P. European Coating Handbook. 2nd revised ed. Hannover, Germany: Vincentz Network; p. 120
- [35] Efficient use of TiO₂ in white printing inks. Tioxide Group. Available from: http://www. tio2.net [Accessed: 2017-11-02]
- [36] Diebold MP. The causes and prevention of titanium dioxide induced photo-degradation of paints. Part I: Theoretical considerations and durability. Surface Coatings International. 1995;6:250-256

- [37] Woditsch P, Westerhaus A. Industrial Inorganic Pigments. 3rd ed. New York: VCH Weinheim; 1993
- [38] Li X, Cubbage JW, Tetzlaff TA, Jenks WS. Photocatalytic degradation of 4-chlorophenol.
 1. The hydroquinone pathway. The Journal of Organic Chemistry. 1999;64:8509-8524
- [39] Decolibus RL. TiO₂ pigment coated with porous alumina/silica and dense silica. US Patent No. 3928057 assigned to Wilmington, DE: E.I. Du Pont de Nemours & Company; 1975
- [40] Thomas DC. Process of treating titanium dioxide pigments. US Patent No. 3876442 assigned to Oklahoma City, OK: Kerr-McGee Chemical Co.; 1975
- [41] Jacobson HW. Alumina coated TiO₂. US Patent No. 4416699; 1983
- [42] Tuomo L. Process of coating titanium dioxide pigments. US Patent No. 5165995 assigned to Helsinki, FI: KemiraOy; 1992
- [43] George J, Gireesh VS, Ninan G, Krishnan Nair S. Modification of TiO₂ surface for improved light fastness. International Journal of Industrial Chemistry. 2015;6-3:133-141

Nanostructured Titanium Dioxide for Functional Coatings

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Additional information is available at the end of the chapter

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Abstract

Synthesis routes to nanostructured titanium dioxides (spherical nanoparticles, nanotubes, mesostructure) have been studied. Their potential applications in various fields based on coating technology have been explored, i.e., dye-sensitized solar cells (using ruthenium sensitizer and some results of natural dyes), photocatalysts for self-cleaning films (TiO_2 on textiles), antibacterial coating for multifunctional textiles (TiO_2-SiO_2 on cotton), and recent result on antifouling coating on wood. The synthesis/preparation procedures were developed to obtain green protocols based on combined techniques of hydro- or solvo-thermal (templated, seeded, deposition), sol–gel (templated, room temperature, dip coating), and solvent-casting techniques. Discussion on the properties and synthesis mechanism is presented. It will be shown that sonication has important role to shorten the preparation of nanotube titania and has been proposed as one green synthesis route. The changing of morphology of titanium dioxide has presented unexpected results to the shifting of photoactivity into visible irradiation.

Keywords: nanostructure, TiO_2 , solar cells, photocatalyst, functional textile, antibacterial

1. Introduction

Titanium dioxide (TiO_2) , so-called titania, has shown excellent properties for functional coating materials. As a semiconductor, it functions as photoactive materials. Designing the morphology down to the scale of nanometer, which is called nanostructured, results in some new properties to be envisaged. Synthesis routes are designed to achieve the desired properties

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for certain applications. A high-surface-area titania is beneficial as photoanode in photoelectrochemical solar cells to obtain efficient light harvesting due to the characteristics of dyemonolayer adsorption. However, high surface area is not enough for efficient photoanodes. The titania must also have high crystallinity of the photoactive phase, which is mostly anatase crystalline phase. The presence of microporosity is not favorable for the dye adsorption, hindering efficient dye adsorption. Previous studies have shown that there is a compromise between high surface areas with porosity and crystallinity of the anatase phase [1–3]. For multifunctional textiles, amorphous titania is favored due to strong adherence to the surface of the cellulose-based fabrics [4] compared to the crystalline phase of titania. Interestingly, 1D-nanostructured titania, such as nanorods or nanotubes, has shown notable photocatalytic activity under the visible light irradiation.

Here, synthesis route to obtain high-surface-area titania with full domain of anatase phase will be presented and discussed. Some results for the application of the resulted mesostructured titania for dye-sensitized solar cells (DSSC) will be included. Secondly, applications to functional coating for textile and wood are also deliberated by considering photocatalytic and hydrophilic/hydrophobic mechanism. Combining nanostructured titania and silica resulted in excellent antibacterial coatings. Recent results of nanorod titania and silica as antifouling coating on wood are presented.

2. Synthesis routes to nanostructured titanium dioxides (mesostructure spherical nanoparticles, nanotubes)

Firstly, mesostructured titania as photoanodes for photoelectrochemical solar cells that are famously called dye-sensitized solar cells (DSSC) is discussed. Hydrothermal-seeded protocol is offered as a recommended synthesis route to achieve the targeted photoactivity. Secondly, one-dimensional nanostructured titania is proposed for the photoanodes. Nanotube titania was synthesized through templated-hydrothermal method and has shown improved photoactivity than that of nanoparticles. Sonication is proposed to shorten the synthesis time to prepare nanotube titania.

2.1. Hydrothermal-seeded synthesis of mesostructured titania

Synthesis of nanostructured titanium dioxides has been greatly explored and discussed. The hydrothermal-seeded synthesis route was inspired by a similar approach in preparing mesoporous aluminosilicates containing zeolite framework [5–8]. The auto-assembly zeolite seed concept was applied by creating anatase seeds to the synthesis of mesoporous titania. Basically, there are three main steps in the synthesis route, namely, anatase seed preparation, hydrothermal self-assembly, and template removal. Anatase phase was chosen as the nanocrystal seed due to its highest photocatalytic activity among other crystalline phases of titania. Instead, some studies showed that it is easy to obtain such phase at low temperature and short-time synthesis [9, 10]. Anatase is also well known as a kinetically favored crystalline phase of titania for most synthesis routes. In this study, the anatase seeds prepared via neutral

and acidic route (**Figure 1**) are discussed. Hydrothermal interaction between block-copolymer surfactant and the anatase seeds is illustrated. Results on the adsorption of Ru-"black dye" onto selected powders are included.

The preparation of anatase seed is aimed at obtaining nanocrystals with less than 5 nm size, as the thickest wall obtained for mesoporous titania so far does not exceed 5 nm [11]. Hydrothermal technique was proposed to be the technique of choice to prepare the anatase seeds, due to its simplicity and its good reproducibility [9]. The resultant materials were then examined either by XRD or TEM for the presence of the anatase nanocrystals.

Two main routes of the seed preparation, as displayed in **Figure 1**, were proposed. It comprises the hydrothermal hydrolysis and condensation of titanium precursor at a neutral and an acidic condition. A mixture of ethanol in water was used as the hydrolysis media. Ethanol was introduced as a cosolvent to slightly slow down the hydrolysis and condensation rates. It was also chosen to obtain higher oxide content from the hydrolytic condensation of titanium (IV) tetraisopropoxide compared to the process using its parent alcohol [12]. Then, in the second route, acid is introduced to further retard the condensation [13, 14] and obtain clear solution seeds. **Figures 2** and **3** show the dark- and bright-field TEM images of the resulted anatase seeds resulted from neutral and acidic solution, respectively.

The seed suspensions were obtained after 4 h hydrothermal treatment at 80°C. The brightand dark-field TEM images of this seed as well as its selected area electron diffraction (SAED) pattern are presented in **Figure 2**. Diffuse ring SAED pattern indicates the formation of a very small polycrystalline material, which has been indexed as the anatase crystal phase of titania [1]. The presence of bright spots all over the sample region shows the uniform distribution of these crystal phases, while the magnified image in the dark-field TEM image presents the observed lattice strain from [101] anatase phase. Based on the TEM image, the crystal size is around 5 nm as designed. However, the seed solution was a milky solution. Anatase seeds obtained from neutral hydrothermal route can be recovered as a very light powder.



Figure 1. Flow diagram of the approach used in anatase seed preparation via hydrothermal technique.

The acidic route was proposed in order to obtain an ideal clear seed solution containing the desired crystalline phase as applied in zeolitic-aluminosilicate synthesis. Previous study has proven the importance of introducing acid to stabilize colloidal particles resulted during hydrolysis-condensation reaction and obtaining transparent solution [12, 15]. Variation on the acid concentration can be altered to obtain fewer amounts of HCl for such purpose. HCl is also known to accelerate the anatase nucleation [10], which will be beneficial for hydrothermal process at low temperature. Since the seed is a clear solution, TEM was used to examine the crystal size and phase by using dark-field/bright-field images at the same area and selected area electron diffraction, respectively.

Figure 3 displays the bright- and dark-field TEM images of anatase seed resulted from the acidic route with molar ratio precursor composition of 1TTIP:26.10EtOH:34.06H,O:1.25HC



Figure 2. Bright-field TEM image with the respective SAED pattern (left) and the dark-field (right) [1] TEM image of anatase seed solution prepared hydrothermally at 80°C for 4 h and neutral condition.



Figure 3. Bright-field TEM image with the respective SAED pattern (left) and the dark-field (right) TEM image of anatase seed solution prepared hydrothermally in acidic solution at 80°C for 4 h.

1. The bright spots observed in the dark-field images confirm the formation of nanocrystals. From **Figures 2** and **3**, it can be seen that the presence of acidic strength resulted in smaller crystalline phase, which are averaged at 2.05 nm. As a result of such small crystallites, the SAED of the seed from acidic route (indexed as an anatase phase) is more diffuse compared to that of the anatase seed obtained from neutral route. The seed solution is hazy. Those two anatase seeds were then proceeded into step 2 hydrothermal synthesis which is mesoporous titania synthesis.

Table 1 lists the textural parameters of the resulted titania powders synthesized at various condition of hydrothermal temperature and time, while **Figure 4** displays the N₂ adsorption–desorption isotherms as well as the corresponding pore size distribution (BJH model desorption branch) of calcined mesoporous titania obtained from hydrothermal interaction between neutral route-derived anatase seed and neutral aqueous surfactant solution. The second step of hydrothermal synthesis involved block copolymer, P123 as the pore template [1, 2]. **Figure 5** shows the N₂ adsorption–desorption isotherms as well as the corresponding pore size distribution (BJH model desorption branch) of calcined mesoporous titania obtained from hydrothermal interaction between neutral route-derived neutral aqueous surfactant solution.

From **Table 1** and **Figure 4**, it can be seen that the time alternation at given temperature does not change significantly the isotherm type, as well as the surface area and pore diameter. Type IV isotherm of typical mesoporous materials with well-defined hysteresis loops was obtained. However, the pore size distribution is much broadened at shorter (5 h) or longer (48 h) hydrothermal treatment, more likely due to insufficient interaction or disrupted interaction, respectively, between anatase seed and block copolymer micelles. On the other hand, effect of hydrothermal temperature is much pronounced on surface area, pore size, and pore volume as demonstrated in **Table 1** and **Figure 5**. Type IV isotherms with hysteresis loop corresponding to the ordered mesopore filling are evidenced. The relative pressure of pore filling increases with hydrothermal temperature. Thus, an increase of pore size and a decrease in the surface area with the hydrothermal temperature are observed. Pore size broadening is

| 101.00 100.90 | 0.26 | 7.86 |
|------------------|---|---|
| 100.90 | 0.04 | |
| | 0.24 | 7.83 |
| 106.00 | 0.23 | 7.72 |
| 110.40 | 0.27 | 7.89 |
| 152.30 | 0.29 | 6.19 |
| 106.00 | 0.23 | 7.72 |
| 98.70 | 0.24 | 7.90 |
| | 106.00 110.40 152.30 106.00 98.70 | 106.00 0.23 110.40 0.27 152.30 0.29 106.00 0.23 98.70 0.24 |

¹TTIP:P123:EtOH:H₂O = 1:0.034:10.55:431.6 (molar ratio precursor composition).

Table 1. Textural parameters of mesoporous titania resulted from neutral route anatase seed and neutral aqueous surfactant.



Figure 4. N_2 adsorption–desorption isotherms (A) and pore size distribution (B) of mesoporous titania synthesized from neutral anatase seed and neutral surfactant solution at various hydrothermal times at 100°C after calcination at 400°C.



Figure 5. N_2 adsorption–desorption isotherms and pore size distribution of mesoporous titania synthesized from neutral anatase seed and neutral surfactant solution at various hydrothermal temperatures for 20 h after calcination at 400°C.

prominent at 150°C hydrothermal treatment, which is likely due to phase separation of the block copolymer template at temperature higher than its *cloud point* (85°C for P123 in aqueous neutral solution) [16, 17]. At higher temperature than its *cloud point*, micelle-micelle interaction is getting more prominent as water becomes less effective solvent for the polyethylene oxide (PEO) chains, resulting in strong micelle-micelle aggregation. Therefore the micelle aggregate size is getting bigger, directing the formation of larger pores. The interaction is illustrated in **Figure 6**.



Figure 6. Illustration of micelle-stabilized anatase seed aggregation mechanism during hydrothermal treatment.

At 80°C hydrothermal treatment, the low-angle XRD peak (data not shown) appears as a shoulder around 1.5° 2 θ , indicating less order mesopore structuration as implied by the presence of broad hysteresis loop in its N₂ adsorption–desorption isotherm as well. Higher hydrothermal temperature results in broad low-angle XRD peak, indicating possible mesopore distribution broadening. This fact is also evidenced by its pore size distribution obtained using N₂ adsorption–desorption analysis.

On the other hand, anatase seed undergoes transformation into rutile crystalline phase at 150° C (data not shown). The high temperature results in rapid crystallization owing to a favored dissolution precipitation mechanism [10], which allows the fast transformation from anatase to rutile crystalline phase. It has been shown that anatase seed treated hydrothermally with aqueous block copolymer solution at 100°C for 20 h exhibits highest porosity with ordered mesopores and full anatase crystalline domain [1]. The TEM images of the resulted powder can be found elsewhere [1].

From the TEM images, it is clear that block copolymer functions to aid pore organization without showing template mechanism as usually observed in micelle-templated silica or metal oxide using the same nonionic surfactant [11, 16–19]. The possible mechanism is assumed to be an aggregation mechanism over block copolymer-steric stabilized-anatase seed particles. $EO_{20}PO_{70}EO_{20}$ is known to form spherical micelles, with the dense cores consisting of dehydrated PO blocks and hydrated EO blocks at the micellar surface (coronas), at critical micellar concentration (cmc) of 0.03 wt% at 25°C in water [20, 21].

The micelles are attached to the anatase seed via their protruded-EO chains in such a way covering the anatase surface, creating steric stabilization to the anatase seeds. Such interaction is likely driven by a surface charge potential between the micelles and anatase seeds. Control over pore formation and crystalline growth is attained by a corona of block copolymer micelles formed around anatase seed particles as illustrated in **Figure 6**. The subsequent

removal of the block copolymer leads to interstitial pore arrangements resulting in the formation of uniform and well-controlled mesopores.

Table 2 tabulates the textural porosity of the resultant powders derived from hydrothermal interaction between acidic route anatase seeds with neutral aqueous surfactant. Subjecting acidic route anatase seed for longer hydrothermal treatment with acidic aqueous surfactant results in different effects to the porosity of the resultant calcined powders. Larger pores are created, while they present type IV isotherm with type H2 hysteresis loops (**Figure 7**). As predicted, prolonged hydrothermal treatment induces the formation of wide pore size distribution (**Figure 7** and **Table 2**). The crystalline phase is assigned as the anatase titania. Our study for higher acidity of the anatase seed resulted in a mixture of crystalline phase of anatase and rutile titania (data not shown).

Figure 8 shows the UV–Visible spectra of the Ru-"black dye" solution before and after overnight adsorption using the respective mesoporous titania powder synthesized hydro-thermally from anatase seeds, as the adsorbents. Porosity characteristics of the samples are summarized in **Table 3**. It is clear that the powders resulted from anatase seed hydrothermal synthesis demonstrates significant adsorption of Ru-"black dye." Correlating the adsorption

| Sample ¹ | S _{BET} (m ² /g,STP) | $V_{p} (cm^{3} g^{-1})$ | Pore diameter (nm) |
|---------------------------|--|-------------------------|--------------------|
| Hydrothermal 100°C, 40 h | 156.70 | 0.46 | 9.70 |
| Hydrothermal 100°C, 65 h | 152.00 | 0.44 | 9.72 |
| Hydrothermal 100°C, 90 h | 127.30 | 0.47 | 12.52 |
| Hydrothermal 100°C, 190 h | 128.80 | 0.44 | 9.71 |

Table 2. Textural parameters of mesoporous titania resulted from acidic route anatase seed and neutral aqueous surfactant.



Figure 7. (A) N_2 adsorption–desorption isotherms and (B) pore size distribution of mesoporous titania synthesized at various hydrothermal times from acidic route anatase seeds' neutral aqueous surfactant.
capability with textural properties of the powders, large pore samples perform higher ability to adsorb the dye molecules. Therefore, it is confirmed that the presence of large pore with appreciable porosity is favorable for dye adsorption to sensitize titania photoanode in photoelectrochemical solar cells. The optimum peaks of the dye solution after adsorption have shifted to higher wavelengths due to possible dye oxidation during the measurement. The discussion on the DSSC performance will be on Section 3. Based on the textural properties and the resulted crystalline phase of anatase titania, mesostructured titania from hydrothermal-seeded synthesis are suitable for photoanodes of DSSC.

2.2. Hydrothermal synthesis of 1D nanostructured titania

The needs to get high surface area for DSSC and also photocatalysis encourage the search to utilize 1D-nanostructured titania, such as nanotube, nanorods, and/or nanofibers. Interest to the



Figure 8. Absorbance of ruthenium-"black dye" after various hydrothermal-derived mesoporous titania powder adsorption. A commercial titania Degussa P25 was used as comparison.

| Sample | Pore volume (cc/g) | Dp (nm) BJH _d | S _{BET} (m²/g) | Isotherm/hysteresis loop type | Dye adsorbed (%) |
|---------------|-----------------------|-----------------------------|-------------------------|-------------------------------|------------------|
| NSNS-1 | 0.48 | 9.66, 60.60 | 146.50 | II–IV/H1–H2 | 61.20 |
| NSAS-1 | 0.54 | 12.61 | 118.70 | IV/H2 | 81.28 |
| P25 (Degussa) | 0.10 | 74.2 | 55.74 | Ш | >99.00 |

NS = neutral anatase seed, NSNS = neutral anatase seed + neutral surfactant, NSAS = neutral anatase seed + acidic surfactant, NSNS-1 = 1.25 g P123/40 mL H,O, NSAS-1 = 3.2 g P123/(40 mL H,O + 4 mL HCl₂).

Table 3. Ru-"black dye" adsorption onto selected calcined mesostructured titania along with their corresponding textural properties.

structure is mostly due to the surface area. Nanotube with open-ended tube structure may have surface area of ~400 m²/g [22]. Nanorods or nanofibers may only have 50 m²/g [23]. Therefore, the synthesis then is focused at obtaining titania nanotubes. Titania nanotubes can be achieved via alkaline hydrothermal method which is the most promising method, because of its simplicity and high reproducibility. Excess concentrated alkaline of 10 M NaOH is commonly used as the hydrothermal medium at low temperature of 110–150°C for 24 h to obtain sodium titanate nanotube. Washing with dilute acid and heating may lead the sodium titanate to transform into anatase crystalline phase via the formation of hydrogen titanate and TiO₂(B) [23].

Using excessive amount of highly concentrated and corrosive base such as NaOH is not environmentally benign. This encourages several researches to alternate and study the effect of alkaline alteration. A vapor pressure by using $NH_3(aq)$ during the hydrothermal is one of the quests [24]. However, bundles of nanotubes could only be formed by the presence of KOH. It was found that only KOH and NaOH are the contributing alkaline medium for nanotube formation. The spherical titania will not transform into nanotube by the presence of LiOH₂ or NH_3 . Successful route without NaOH(aq) in the solvent was proposed by Liu et al. [25] involving titania foil covered with NaOH as the titania source. They proposed scrolling mechanism induced by NH_3 vapor pressure to transform titania nanosheets into nanotubes. NaOH was needed to make the titania nanosheets. Steps for the transformation of TiO₂ to nanotubular titanate can be summarized as follows: first, the dissolution of the TiO₂ sources, at the same time, to the growth of layered nanosheets of sodium trititanates. Secondly, nanosheets are curving and then wrapping into nanotubes [23].

The as synthesized products from hydrothermal method were titania with titanate crystalline phases, which were sodium trititanate or hydrogen trititanate, as depicted in **Figure 9** (right). These phases are not favored for the DSSC, due to its low photocatalytic activity [26]. Later, efforts to induce the anatase phase formation by acid washing and calcination are introduced. Care must be taken for using the acid, since too acidic medium exceeding the pH of 3 may ruin the tube structure [27, 28]. By applying calcination, the anatase crystalline phase starts to form at 200°C and complete at 500°C [29]. High temperature may lead to breaking up of nanotube structure [30]. Therefore, the optimum conditions for acid washing and calcination temperature are needed to obtain anatase TiO₂ with nanotube morphology.

In this research, the way to alter or reduce the amount of NaOH in the alkaline hydrothermal method was sought, by using NH₃ as the solvent combined by NaOH, at high concentration level for both solutions. Then, posttreatments, in particular the acid washing and calcination temperature, were introduced. The synthesis protocol for these nanotubes can be found elsewhere [31]. **Figure 9** shows the TEM images of the resulted titania synthesized using NaOH with (Na-Ti-DW) and without acid washing (Na-Ti-H), as well as using a mixed solution of NH₃ and NaOH (1:3 molar ratio) with acid washing.

The TEM images (**Figure 9** left) show nanotube structure without the presence of other structures, such as nanorods or nanoparticles. Images of TEM show dispersed TiO_2 nanotubes with diameter around 3–5 nm and outer diameter of 8–12 nm. Nanotube lengths are ranging from 80 to 400 nm. The selected area electron diffraction (SAED) was taken to define the crystal-linity of a certain area in the sample (**Figure 9** right). Sample Na-Ti-DW exhibits diffuse ring

Nanostructured Titanium Dioxide for Functional Coatings 455 http://dx.doi.org/10.5772/intechopen.74555



Figure 9. Bright-field TEM images of sample (left), the corresponding SAED pattern (middle) of (A) Na-Ti-DW, (B) Na-Ti-H, and (C) 3:1 NaNH₄-Ti-H and XRD patterns (right) of Na-Ti-DW and Na-Ti-H.

pattern and low-intensity diffraction, which identifies the contributions of amorphous material instead of polycrystalline materials. It has diffraction at crystal plane [011], [300], and [204] that belong to sodium trititanate phase. To ensure the materials crystallinity, XRD pattern was also taken to obtain the contributing crystalline phase of the sample. The XRD results show that the crystalline phase of sample Na-Ti-DW has strong peaks at $2\theta \approx 10.5^\circ$, 24° , 28° , 43° , and 48° similar to the XRD pattern by Sikhwivhilu et al. [24], with distinct peak at $2\theta \approx 10^\circ$ and low-intensity peaks at $2\theta \approx 24^\circ$, 28° , and 48° . It is indicated that the as synthesized product has the similar crystalline phase, which is predominantly titanate phase. It is confirmed as sodium trititanate (PDF 31–1329). The sample Na-Ti-DW also bears amorphous, signified from the bland feature at around $2\theta \approx 30^\circ$ and 60° , and anatase (PDF 21–1272) phase, identified from reflections at ~ 24° (d₁₀₁) and 60° (d₂₀₀). For Na-Ti-H, the XRD pattern shows the diminishing peaks of sodium trititanate phase. It is found that the synthesis of nanotubes with water washing treatment (Na-Ti-DW) exhibits titanate nanotube, while with dilute acid (Na-Ti-H), it produces anatase crystalline phase. Diffraction at $2\theta \approx 24^{\circ}$ is probably due to the shifts from peak at 25° of anatase (101) and titanate (011). Peak shifts are preferred due to the formation of nanotubes, which put strains on the bonding in sample. The corresponding Raman spectra published elsewhere [31] support the formation of anatase phase after acid washing.

The morphological structure for sample 3:1 NaNH₃-Ti-H (**Figure 9C**) with 3:1 base ratio (NaOH:NH₃) was found to be similar with Na-Ti-H, as mostly all of the morphology of titania were open-ended nanotubes. The nanotubes are highly distributed (separated from each other), showing that the bundles of titania did not form. Yet a few nanosheets are visible in the image, confirming that the morphological changes did not perfectly occur. High amount of NH₃ leads to the transformation from nanotubes into nanosheets and later to spherical structures [31]. Thus, nanotube preparation can be sought at NH₃ ratio to NaOH of 1:3. Alteration to only using NH₃ as the alkaline results in the formation of spherical nanoparticle titania with anatase crystalline phase [31].

Short-time synthesis of titania nanotube was proposed by applying mechanical or sonicationassisted stirring prior hydrothermal. The effect of various stirring times and hydrothermal treatments on the crystalline phases and morphology of the resulted titania has been studied [32]. It has been shown that the nanotube titania can be obtained after 5 h hydrothermal treatment at 150°C. The XRD patterns of the resulted powders showed the existence of a mixture of anatase and titanate crystalline phases with increased intensity of [200] as the stirring time increasing. At the longest stirring time, the existence of TiO₂ (B) was observed. Raman spectra have also confirmed the existence of both anatase and titanate crystalline phases. The high textural coefficient for [200] (TC₂₀₀) has indicated oriented growth of one-dimensional anatase along [200]. All powders resulted at various stirring time were nanotubes, as confirmed by transmission electron microscope (TEM).

The next section will discuss the application of titanium dioxide for photoelectrochemical solar cells (DSSC) and multifunctional coatings for textiles and woods.

3. Titania as the photoanode for dye-sensitized solar cells

The dye-sensitized solar cell consists of three main components, namely, a working electrode, a counter electrode, and an electrolyte. The current most efficient cells of 10.4% [33] used a nanostructured titanium dioxide film on a transparent conducting glass (TCO) as a working electrode, a platinized conducting glass as the counter electrode and I_3 pairs as the electrolyte solution. In this section, performance of the mesoporous titania electrodes as photoanodes in DSSCs is presented. Some results using natural dyes as the photosensitizers will also be discussed.

Since the anatase crystalline phase seems to be preferred for this DSSC, attempts to incorporate the neutral route hydrothermal powder into a DSSC were carried out. A one-coat slip-cast electrode was assembled with sputtered and thermally platinized counter electrodes. **Figure 10** shows the I-V curves of these DSSCs using ruthenium "N3" as the sensitizer by using different



Figure 10. I-V curves of mesoporous titania derived from neutral hydrothermal route using different platinization methods for counter electrodes: (A) light current and (B) the corresponding dark current curves [1].

counter electrodes. It is observed that the thermally platinized counter electrode gave better DSSC performance with increased open-circuit voltage (V_{oc}) and short-circuit current (I_{sc}). The increased variables enhanced the cell efficiency to about 5%. This improvement can be attributed to the high surface area of platinum in thermally platinized counter electrode that will act as an efficient catalyst for iodine reduction [8]. The redox electrolyte shuttles the electron from the site of regeneration on the sensitized titania working electrode to the counter electrode to complete the electron cycle. During this process, the iodine must be reduced back to iodide at minimum energy loss on the counter electrode. However, the fill factor of this cell is much lower than that assembled with a sputtered Pt counter electrode. This may be caused by the loss of some scattered light, which may enhance the electron generation throughout the titania film. The possible recombination rate for this thermally platinized cell is slightly lower than that of the sputtered Pt counter electrode. Thus, it is expected to compromise the losses. In addition, this type of counter electrode produced a transparent DSSC. Illumination can be performed in both sides of the sandwiched cells that cannot be done by using sputtered Pt counter electrode.

Comparing the performance of acid treated-acid route photoanode with neutral route, a higher efficiency was achieved for the latter photoanode [1]. High open-circuit voltage and short-circuit current are responsible for this performance, which may be caused by the presence of the full anatase domain characteristic of the powder precursor as previously demonstrated (Section 1).

Table 4 shows the solar cell parameters of various titania photoanodes and natural dyes as sensitizers. Results on natural dyes as the sensitizers are not as high as the cells using ruthenium complex. Dried fruit of *joho*, bark of *tingi*, and *tegeran* were commonly used as dyes for traditional *Batik* clothes in Indonesia. The cells with *joho* and *tegeran* dyes have shown appreciable generated photovoltage and photocurrent compared to *tingi*. Both *joho* and *tegeran* dyes

| Sample | V _{oc} (mV) | J _{SC} (mA/cm ²) | Fill factor (FF, %) | η (%) |
|---|-------------------------|---------------------------------------|------------------------|-------|
| Neutral route meso-Ti-sputtered Pt counter electrode* | 688 | 7.60 | 68.14 | 3.56 |
| Neutral route meso-Ti-thermal platinized counter electrode* | 717 | 12.12 | 58.11 | 5.05 |
| Acid treated-acid route meso-Ti-thermal platinized counter electrode* | 666 | 11.24 | 62.40 | 4.67 |
| Joho (<i>Terminalia bellirica(gaertn)roxb</i>)** | 100 | 1.60 | 31.00 | 0.19 |
| Tingi (Ceriops tagal)** | 70 | 0.80 | 21.00 | 0.05 |
| Tegeran (Maclura cochinensis)** | 100 | 1.60 | 38.00 | 0.24 |
| Bixin extract (<i>Bixa orellana</i> L.) and nanotube TiO_2 60 min stirring prior hydrothermal ^{***} | 310 | 3.10 | 44.08 | 1.48 |
| Bixin extract (Bixa orellana L.) and commercial titania electrode*** | 749 | 8.50 | 28.29 | 0.42 |
| Sargassum mclurei Setchell** | 60 | 0.30 | 25.00 | 0.09 |
| Hypnea esperi Bory**` | 55 | 1.30 | 31.00 | 0.44 |

^{*}Testing done at photovoltaic testing facility in Physics Department, University of Queensland, Brisbane, Australia, across a 0.025 cm² active area DSSC under illumination of 100 mW/cm² power source equal to AM1.5 Direct Sun, sensitizer ruthenium N3 dye.

"Active area TiO = P25 0.25 cm²; P_{input} = 25.6 mW/cm², Au counter electrode, testing done in Physics Department, Universitas Gadjah Mada, Yogyakarta, Indonesia.

***Testing done in Universitas Negeri Sebelas Maret, Surakarta, Indonesia.

Table 4. Solar cell parameters of various titania photoanodes and natural dyes as sensitizers.

have absorption spectra indicating reasonable composition of red-shift absorption maxima and blueshift absorption edges, while *tingi* dye has slightly low red-shift and blueshift contribution (data not shown). Upon adsorption on a TiO₂ layer, the absorption spectra of the three *Batik* dyes are all broadened forward to red side compared with their respective spectra in ethanol solution. These indicate sensitizing effect of natural *Batik* dyes on TiO₂ films [34, 35]. The small red-shift of the absorption maxima suggests the absence of the formation of *J*-like aggregates which was predicted to lower the photocurrent efficiency in DSSC [36]. Thus, the natural *Batik* dyes used are predicted mostly in the monomer form. However, the absorption edges were shifted with the large blueshift of 85–165 nm, which may be induced by the formation of *H*-aggregates. In contrast with *J*-aggregates, the formation of *H*-aggregates supports efficient ability of the dyes for sensitization [36]. Low sensitization effect may occur owing to self-quenching of the dyes in the *J*-like aggregate form.

Results on Bixin extract of achiote (*Bixa orellana* L.) seed as sensitizer has shown relatively higher efficiency sensitizer than the *Batik* dyes. It also confirms that nanotube titania performs better than commercial titania which has nanoparticle structure. Whereas algae's dyes (the latter two) have comparable performance as *Batik* dyes and bixin of around 0.1-0.5%. Large difference in photocurrent density of the two cells rather than in photovoltage suggests that the solar cell performance of the cells is influenced by the efficiency of the electron injection from the sensitizers into TiO_2 [1]. High photocurrent resulted from efficient electron injection of the pigments into the conduction band of TiO_2 owing to the effective attachment of the pigment molecules on the TiO_2 surface.

4. Titania as active component for multifunctional coatings

Crystalline TiO, (titanium dioxide), anatase, is widely known as material having excellent photocatalytic properties. Anatase coatings have also been prepared by a number of deposition techniques, such as sputtering, spray pyrolysis [37], and sol-gel processing [38]. The film formations are aimed at finding more flexible application in electronic devices, optical coatings, instrument hard coatings, and decorative parts. They are also generating different functionalities by engineering the surface, saving the energy consumption in production, and minimalizing the use of toxic materials since the quantity used is limited only to the surface and/or thin film layer. Thus, the film formation is an environmentally benign material technology and fits well to the current global trend of sustainable chemistry concept. However, sol-gel methods usually require a heating process at relatively high temperatures above 400°C to obtain sufficient crystallinity [39]. Thus, anatase coatings on organic substrates and incorporation of organic molecules into the coatings were not directly achieved using these techniques. TiO, layers on organic substrates are mostly amorphous, while the photoactivity of amorphous phase of TiO, has been less studied and explored. In this section, self-cleaning titania coating on textile will be discussed, as well as antibacterial functional. Recent results on coating of titania on wood as antifouling agent will also be explored.

Self-cleaning and antibacterial coatings on textile. This study aims at preparing amorphous and crystalline TiO_2 coating on cotton fabrics and examining the discoloration of organic materials modeled by turmeric extract stain on the cotton textile coated with those TiO_2 . Turmeric extract obtained from rhizomes of *Curcuma longa* is one of the main pigments produced in Brazil [10]. Besides the yellow pigment for food, this plant is widely used as a seasoning for Asian food including Indonesian food. Mature rhizomes are ground to give an aromatic yellow powder, employed as the coloring ingredient in curry powder. With the growing demand for natural colors, the use of turmeric is likely to increase. Therefore, turmeric extract stain is used as the model stain for self-cleaning action. It is also reported that amorphous TiO_2 coating on cotton fabrics has self-cleaning action similar to the crystalline TiO_2 coating but lower activity. The use of TiO_2 -loaded flexible substrates will possibly allow their application for the photodegradation of micelles, oils, solvents, sooth, and aromatic and aliphatic hydrocarbons under daylight.

The white cotton textiles were purchased from local market after examining the burning characteristic of cotton fibers. Pure cotton fibers gave only black gray ash after burning. Turmeric powders were also obtained from local market. All the reagents are of analytical grade and used without further purification. Titanium (IV) tetraisopropoxide (TTIP 97%, Aldrich) and TiO₂ powder of P25 (Degussa) were used as titanium sources. TiO₂ P25 was a gift from Degussa Germany. The pre-cleaned cotton fabrics were dipped into the Ti suspension and withdrawn vertically at the rate of 20 cm/min. The coating was repeated one, five, and fifteen times before dried naturally and cured at 100°C for 15 min. The cured coated cotton fabrics were then rinsed with distilled water in ultrasonic washer to wash out the unbonded TiO₂ for 5 min and dried at room temperature [40]. **Figure 11** displays the XRD patterns of amorphous and crystalline TiO₂-coated cotton fabrics. From Figure 11 (left), it is evident that coating by employing hydrolyzed TTIP sols results in no observable crystalline TiO, diffraction peaks. The observed peaks were corresponding to the cellulose fibers of the cotton fabrics [41]. XRD pattern of xerogels obtained from drying the sol precursor used for coating displays very broad peaks around 2θ of ~25°, suggesting that TiO, layers on the surface of cotton fabrics predominantly consisted of amorphous titania. After curing, the diffraction peaks of the coated cotton fabrics have decreased. It is presumably due to the sintering of both cellulose fibers and TiO, layers. The XRD patterns in Figure 11 (right) shows that TiO, P25 coating resulted in crystalline peaks of anatase (A) TiO, at diffraction angle ~25° and rutile (R) TiO, at ~27°. This is in accordance with the fact known that TiO, P25 powder consists of 80% anatase and 20% rutile crystalline phases [42]. Similar to Figure 11 (left), the bulk of the XRD peaks originated from cotton, as cotton is the underlying substrate. As the thickness of the coating layers increased, which resulted from multiple coatings, both anatase and rutile peaks are getting more intense. These results are comparable to the work of Qi et al. [41], who has observed that anatase peaks are intensifying due to increased crystalline nature of the corresponding sol precursors. It is also observed that the thicker the TiO_2 coating, the weaker the cotton. This may be attributed to titania coatings on cotton which shield the X-ray beam, therefore weakening the intensities of the peaks of cotton coated with titania [41, 43]. The structure and morphology of TiO, layers on cotton fabrics were investigated by using scanning electron microscopy (SEM) as depicted in Figure 4.

SEM images (**Figure 12**) of the coatings on cotton fabrics show that the surface structures of the two titania-coated cotton fabrics look similar. The surface structure of these titania-coated cotton fibers shows that a thick uniform layer has been formed. The low-resolution image



Figure 11. The XRD patterns of samples (left): (a) pristine cotton fabrics, (b) cotton fabrics coated with amorphous TiO_2 from 0.2 M Ti precursor, and (c) cotton fabrics coated with amorphous TiO_2 from 0.2 M Ti sol precursor after curing at 120°C for 1 h. P25-coated (right): (a) 1×, (b) 5×, and (c) 15× coatings with curing.

of the pristine cotton fibers (**Figure 12a**) has shown no such uniform layers on the surface. **Figure 12b and c** has also confirmed TiO_2 layers covering the surface of cotton fibers. This type of coating is similar as obtained by Qi et al. [41] for TiO_2 and for chitosan coating on textiles [44, 45]. However, the formation of interconnected layers over the fibers as observed for thicker coating of chitosan on textiles [45] was not observed for this TiO_2 coating suggesting bigger particle size of the coating materials. It is supposed that smaller particles have more tendencies to form polymeric-like network due to smaller solvation spheres.

The self-cleaning effect of TiO_2 -coated white cotton fabrics was evaluated by the decomposition of turmeric extract stains in ethanolic solution under UV light irradiation. **Figure 13** displays the self-cleaning performance of amorphous (a)- and crystalline (b)-coated cotton fabrics under (light) and without (dark) UV illumination.

It is clear that the TiO_2 P25-coated cotton fabrics which have crystalline nature of TiO_2 layers demonstrate higher photoactivity than the amorphous. The mechanism of decomposition of colorant molecules on titania under UV irradiation is widely known suggesting the generation



Figure 12. The SEM images of (a) pristine cotton fabrics, (b) cotton fabrics coated by amorphous TiO_2 from 0.1 M Ti precursor, and (c) cotton fabrics coated by amorphous TiO₂ from 0.2 M Ti precursor.



Figure 13. Self-cleaning action at alternated Ti loading of (a) amorphous TiO₂-coated cotton fabrics and (b) crystalline TiO₂-coated cotton fabrics.

of highly oxidative radicals on the TiO_2 surface when light below 400 nm is applied on the TiO_2 photocatalyst surface [42, 46]. **Figure 14** shows the color difference of the self-cleaning action on the coated and uncoated cotton.

The 15 times coating of TiO_2 P25-coated cotton fabrics have the highest self-cleaning action which is considered to be attributed to the highest anatase crystallinity as demonstrated by its sharpest anatase peaks with greatest intensities from the XRD studies in **Figure 12**. From these self-cleaning testing, it is worth noting that the amorphous coating has demonstrated significant photocatalytic activity toward turmeric stain discoloration reaching almost 80% discoloration. The mechanism behind this is still unclear and needed further investigation.

Antibacterial coatings on textile. To enhance crystallization of amorphous titania coating on textiles, exposure of the coated cotton to water vapor for certain times was performed. Introduction of silica on titania coating was also done to enhance the mechanical strength of the coated titania on fabrics [47]. This section will discuss antibacterial properties of the coated cotton with TiO_2 -SiO₂ against bacteria *E. coli* by counting the bacteria before and after testing using colony counter technique. The XRD patterns of the vapor treated coated cotton are shown in **Figure 15a**, and the antibacterial test results are in **Figure 15b**.

Based on the XRD patterns (**Figure 15a**), diffraction peaks of crystalline cellulose as the major component of the cotton fabrics are prominent, with the highest at $2\theta \sim 23$ of d_{002} [4]. It can be seen that the higher the amount of Ti, the peak intensity tends to decrease. A very small hump was observed at sample with Ti:Si 3:1, indicating the presence of anatase titania. It also appears that the peak intensity decreases as increasing the Ti content showing the thick coating of Si-Ti on the cotton fiber. The antibacterial activities of the coated cottons are comparable to the commercial antibacterial cloth, which is Ag-coated. It is worth to note that the coated cotton without exposure to water vapor has almost similar inhibition compared to the ones that have been exposed. This supports the photoactivity of amorphous titania and the fact that the antibacterial coating is active even without UV irradiation.

Antifouling coatings on wood. Fouling has been a big problem for infrastructure in the sea. Algae, mollusks including zebra mussels and barnacles, wood boring worms, and also critters like to make the hull their home and can seriously affect the performance of a boat. The current antifouling agents are mostly based on organo-tin, which is highly toxic; therefore



Figure 14. Discoloration of coated cotton before UV illumination: (a) amorphous titania, (c) 1 time coating, and (e) 15 times coating of P25 titania; and after UV illumination: (b) amorphous titania, (d) 1 time coating, and (f) 15 times coating of P25 titania.

coating of nanorod-TiO₂ and SiO₂ on wood is proposed. The antifouling mechanism is expected from combined effect of surface hydrophobicity and photocatalysis. Nanorod morphology is expected to build the surface roughness as well as photoactive agent [48]. The silica will provide sturdy coating formulation in the acrylic-based paints. **Figure 16** shows our prompt results on antifouling test of the coated woods in the sea water. Clean surface of wood was achieved for the coated wood, both by TiO₂-nanorod and TiO₂-nanorod-SiO₂. More quantitative data and elaboration on mechanism are on progress [49].



Figure 15. (a) XRD patterns of cotton fabrics coated by Ti:Si (A) 0:1, (B) 1:0, and (C) 2:1; (b) antibacterial test of commercial antibacterial cloth and cotton fabrics coated with silica-titania with Ti:Si 3:1 which are exposed and not exposed to water vapor.



Figure 16. Antifouling test in the sea water: (a) uncoated wood, (b) TiO_2 -nanorod-coated wood, and (c) TiO_2 -nanorod/SiO_2-coated wood.

5. Concluding remarks

It has been shown that hydrothermal-seeded technique offered excellent method to obtain mesostructured titanium dioxide with large porosity and full anatase domain ideal as photoanodes on photoelectrochemical solar cell. Designing the morphology of titanium dioxide into 1D titania such as nanotube has also resulted in improved solar photoconversion due to enhanced surface area. Alteration of morphology into nanotube also has induced photoactivity to be visible-responsive photocatalyst. Mechanical mixing prior hydrothermal synthesis provided the way to shorten the preparation of nanotube titania to the shortest time as long as 5 h.

By applying dip coating and sol–gel precursor preparation of titanium, amorphous and nanocrystalline anatase/rutile coatings have been successfully deposited on cotton fabrics at near room temperature. Both coated fabrics have shown significant self-cleaning action toward decoloration of turmeric extract stains reaching almost full decoloration under UV illumination for the crystalline TiO_2 -coated cotton fabrics. The higher the crystallinity of anatase TiO_2 , the higher the degree of the photodecoloration. Our study also revealed that amorphous TiO_2 coating has demonstrated about 80% photodecoloration and about 60% antibacterial inhibition against *E. coli*. Excellent coatings of TiO_2 nanorod on wood have provided antifouling activity by testing in sea water. More studies on characterization and mechanism are being underway.

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References

- Kartini I, Menzies D, Blake D, da Costa JCD, Meredith P, Riches JD, Lu GQ. Hydrothermal seeded synthesis of mesoporous titania for application in dye-sensitised solar cells (DSSCs). Journal of Materials Chemistry. 2004;14:2917-2921
- [2] Kartini I, Meredith P, Da Costa JCD, Lu GQ. A novel route to the synthesis of mesoporous titania with full anatase nanocrystalline domains. Journal of Sol-Gel Science and Technology. 2004;31:185-189
- [3] Meredith P, Powell BJ, Riesz J, Vogel R, Blake D, Kartini I, Will G, Subianto S. Broadband Photon-Harvesting Biomolecules for Photovoltaics. In Artificial Photosynthesis. Weinheim: Wiley-VCH; 2005
- [4] Kartini I, Ilmi I, Kunarti ES, Kamariah. Wash fastness improvement of malachite greendyed cotton fabrics coated with nanosol composites of silica-Titania. Bulletin of Materials Science. 2014;37(6):1419-1426
- [5] Zhang Z, Han Y, Xiao FS, Qiu S, Zhu LWR, Yu Y, Zhang Z, Zou B, Wang Y, Sun H, Zhao D, Wei Y. Mesoporous aluminosilicates with ordered hexagonal structure, strong acidity, and extraordinary hydrothermal stability at high temperatures. Journal of the American Chemical Society. 2001;123(21):5014-5021
- [6] Liu Y, Zhang W, Pinnavaia TJ. Steam-stable MSU-S aluminosilicate mesostructures assembled from zeolite ZSM-5 and zeolite beta seeds. Angewandte Chemie International Edition. 2001;40(7):1255-1258
- [7] Pinnavaia TJ, Pauly TR, Kim S-S. Process for the preparation of hybrid mesoporous molecular sieve silicas from amine surfactants. Studies in Surface Science and Catalysis. 2001;135(Zeolites and Mesoporous Materials at the Dawn of the 21st Century):1337-1344
- [8] Liu J, Zhang X, Han Y, Xiao F-S. Direct observation of nanorange ordered microporosity within mesoporous molecular sieves. Chemistry of Materials. 2002;**14**(6):2536-2540
- [9] Wang YQ, Ying JY. Sol-gel synthesis and hydrothermal processing of anatase and rutile titania nanocrystals. Chemistry of Materials. 1999;**11**:3113-3120
- [10] Yanagisawa K, Ovenstone J. Crystallization of anatase from amorphous titania using the hydrothermal technique: Effect of starting material and temperature. The Journal of Physical Chemistry. B. 1999;103:7781-7787
- [11] Yang PD, Zhao DY, Margolese DI, Chmelka BF, Stucky GD. Block copolymer templating syntheses of mesoporous metal oxides with large ordering lengths and semicrystalline framework. Chemistry of Materials. 1999;11(10):2813-2826
- [12] Yoldas BE. Hydrolysis of titanium alkoxide and effects of hydrolytic polycondensation parameters. Journal of Materials Science. 1986;21:1087-1092

- [13] Bradley DC, Mehrotra RC, Gaur DP. Metal Alkoxides. London: Academic Press Inc.; 1978
- [14] Brinker CJ, Scherer GW. Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing. San Diego: Academic Press Ltd.; 1990
- [15] Bosc F, Ayral A, Albouy P, Guizard C. A simple route for low-temperature synthesis of mesoporous and nanocrystalline anatase thin films. Chemistry of Materials. 2003;15:2463
- [16] Yang PD, Zhao DY, Margolese DI, Chmelka BF, Stucky GD. Generalized syntheses of large-pore mesoporous metal oxides with semicrystalline frameworks. Nature. 1998;396(6707):152-155
- [17] Alberius PCA, Frindell KL, Hayward RC, Kramer EJ, Stucky GD, Chmelka BF. General predictive syntheses of cubic, hexagonal, and lamellar silica and titania mesostructured thin films. Chemistry of Materials. 2002;**14**(8):3284-3294
- [18] Zhao D, Huo Q, Feng J, Chmelka BF, Stucky GD. Nonionic triblock and star diblock copolymer and oligomeric surfactant syntheses of highly ordered, hydrothermally stable, mesoporous silica structures. Journal of the American Chemical Society. 1998;120(24):6024-6036
- [19] Kleitz F, Choi SH, Ryoo R. Cubic Ia3d large mesoporous silica: Synthesis and replication to platinum nanowires, carbon nanorods and carbon nanotubes. Chemical Communications. 2003;17:2136-2137
- [20] Wanka G, Hoffmann H, Ulbricht W. Phase diagrams and aggregation behavior of poly (ox yethy1ene)-poly (oxypropylene)-poly(oxyethylene) triblock copolymers in aqueous solutions. Macromolecules. 1994;27:4145-4159
- [21] Su Y-l, Wang J, Liu H-Z. FTIR spectroscopic investigation of effects of temperature and concentration on PEO-PPO-PEO block copolymer properties in aqueous solutions. Macromolecules. 2002;35:6426-6461
- [22] Kasuga T, Hiramatsu M, Hoson A, Sekino T, Niihara K. Formation of titanium oxide nanotube. Langmuir. 1998;14(12):3160-3163
- [23] Bavykin DV, Walsh FC. Titanate and Titania Nanotubes. Cambridge: RSC; 2010
- [24] Sikhwivhilu LM, Sinha Ray S, Coville NJ. Influence of bases on hydrothermal synthesis of titanate nanostructures. Applied Physics A: Materials Science and Processing. 2009;94(4):963-973
- [25] Liu P, Zhang H, Liu H, Wang Y, Yao X, Zhu G, Zhang S, Zhao H. A facile vapor-phase hydrothermal method for direct growth of titanate nanotubes on a titanium substrate via a distinctive nanosheet roll-up mechanism. Journal of the American Chemical Society. 2011;133(47):19032-19035
- [26] Bach U, Lupo D, Comte P, Moser JE, Weissortel F, Salbeck J, Spreitzer H, Gratzel M. Solid-state dye-sensitized mesoporous TiO₂ solar cells with high photon-to-electron conversion efficiencies. Nature. 1998;395:583-585

- [27] Stone JL. Photovoltaics: Unlimited electrical energy from the sun. Physics Today. 1993;46(9):22
- [28] Nazeeruddin MK, Kay A, Rodicio I, Humphry-Baker R, Muller E, Liska P, Vlachopoulos N, Gratzel M. Conversion of light to electricity by cis-X2Bis(2,2'-bipyridil-4,4'-dicarboxylate)ruthenium(II) charge-transfer sensitizers (X=Cl-, Br-, I-, CN-, and SCN-) on nanocrystalline TiO₂ electrodes. Journal of the American Chemical Society. 1993;115:6382-6390
- [29] Gratzel M. Perspectives for dye-sensitized nanocrystalline solar cells. Progress in Photovoltaics: Research and Applications. 2000;8:171-185
- [30] Morgado E, de Abreu MAS, Moure GT, Marinkovic BA, Jardim PM, Araujo AS. Effects of thermal treatment of nanostructured trititanates on their crystallographic and textural properties. Materials Research Bulletin. 2007;42(9):1748-1760
- [31] Turki A, Kochkar H, Guillard C, Berhault G, Ghorbel A. Effect of Na content and thermal treatment of titanate nanotubes on the photocatalytic degradation of formic acid. Applied Catalysis B: Environmental. 2013;138-139:401-415
- [32] Kartini I, Khairani IY, Mustofa S, Santosa SJ, Wang L. The effect of alkaline ratios of NaOH to NH₃ on the formation of nanostructured titania. Materials Science Forum. 2017;886:42-47
- [33] Kartini I, Jannah INA, Amalia FR, Mustofa S, Kunarti ES, Swasono RT. Short-time synthesis of titania nanotubes: The effect of pre-mixing prior hydrothermal. Indonesian Journal of Chemistry. 2018. Submitted
- [34] Nazeeruddin MK, Pechy P, Renouard T, Zakeeruddin SM, Humphry-Baker R, Comte P, Liska P, Cevey L, Costa E, Shklover V, Spiccia L, Deacon GB, Bignozzi CA, Gratzel M. Engineering of efficient panchromatic sensitizers for nanocrystalline TiO₂-based solar cells. Journal of the American Chemical Society. 2001;**123**:1613-1624
- [35] Yao Q-H, Meng F-S, Li F-Y, Tian H, Huang C-H. Photoelectric conversion properties of four novel carboxylated hemicyanine dyes on TiO₂ electrode. Journal of Materials Chemistry. 2003;13:1048-1053
- [36] Dai Q, Rabani J. Photosensitization of nanocrystalline TiO₂ films by anthocyanin dyes. Journal of Photochemistry and Photobiology A: Chemistry. 2002;148:17-48
- [37] Sayama K, Tsukagoshi S, Mori T, Hara K, Ohga Y, Shinpou A, Abe Y, Suga S, Arakawa H. Efficient sensitization of nanocrystalline TiO₂ films with cyanine and merocyanine organic dyes. Solar Energy Materials and Solar Cells. 2003;80:47-71
- [38] Yanagi H, Ohoka Y, Hishiki T, Ajito K, Fujishima A. Characterization of dye-doped TiO₂ films prepared by spray-pyrolysis. Applied Surface Science. 1997;113-114:426-431
- [39] Yoko T, Yuasa A, Kamiya K, Sakka S. Sol-Gel-Derived TiO₂ Film Semiconductor Electrode for Photocleavage of Water: Preparation and Effects of Postheating Treatment on the Photoelectrochemical Behavior. Journal of the Electrochemical Society. 1991;138: 2279-2285

- [40] Manzan ACM, Toniolo FS, Bredow E, Povh NP. Extraction of Essential Oil and Pigments from Curcuma longa [L.] by Steam Distillation and Extraction with Volatile Solvents. Journal of Agricultural and Food Chemistry. 2003;51(23):6802-6807
- [41] Vainio U. Report Series in Physics: HU-P-D145. Finlandia: Helsinki University Printing House; 2007
- [42] Qi K, Daoud WA, Xin JH, Mak CL, Tanga W, Cheung WP. Self-cleaning cotton. Journal of Materials Chemistry. 2006;16:4567-4574
- [43] Hoffmann MR, Martin SM, Choi W, Bahnemann DW. Environmental Applications of Semiconductor Photocatalysis. Chemical Reviews. 1995;95:69-96
- [44] Bozzi A, Yuranova T, Kiwi J. Self-cleaning of wool-polyamide and polyester textiles by TiO2-rutile modification under daylight irradiation at ambient temperature. Journal of Photochemistry and Photobiology A: Chemistry. 2005;172:27-34
- [45] Ye W, Leung MF, Xin J, Kwong TL, Lee DKL, Li P. Novel core-shell particles with poly(nbutyl acrylate) cores and chitosan shells as an antibacterial coating for textiles. Polymer. 2005;46:10538-10543
- [46] Kartini I, Andriani LK. Functionalization of textiles by chitosan coating. In: Proceeding of 14th Regional Symposium on Chemical Engineering 2007; AM33, 4-5th December 2007; Yogyakarta-Indonesia: Chemical Engineering Department, Gadjah Mada University. 2007. ISBN 978-979-16978-0-4
- [47] Linsebigler AL, Lu C, Yates JT. Photocatalysis on TiO₂ Surfaces: Principles, Mechanisms, and Selected Results. Chemical Reviews. 1999;95:735-758
- [48] Hayakawa S, Liu JF, dan Tsuru K. Wet deposition of titania-apatite in cotton fibrils. Journal of Sol-Gel Science and Technology. 2006;40:253-258
- [49] Wahyuni S, Kunarti ES, Swasono RT, Kartini I. Study on the properties and photoactivity of TiO₂(nanorod)-SiO₂ synthesized by sonication technique. Oriental Journal of Chemistry. 2017;33:249-257

Titanium Dioxide Nanotube Arrays for Biomedical Implant Materials and Nanomedicine Applications

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Abstract

Nanotechnology has become a research hotspot to explore functional nanodevices and design materials compatible with nanoscale topography. Recently, titanium dioxide nanotube arrays (TNA) have garnered considerable interest as biomedical implant materials and nanomedicine applications (such as nanotherapeutics, nanodiagnostics and nanobiosensors). In bio-implants studies, the properties of TNA nanostructures could modulate diverse cellular processes, such as cell adhesion, migration, proliferation, and differentiation. Furthermore, this unique structure of TNA provides larger surface area and energy to regulate positive cellular interactions toward the mechanosensitivity activities. As for an advanced medical application, the TNA—biomolecular interactions knowledge are critical for further characterization of nanomaterial particularly in nanotherapeutic manipulation. Knowledge of these aspects will create opportunities for better understanding which may help researchers to develop better nanomaterial products to be used in medicine and health-line services.

Keywords: titanium dioxide nanotube arrays, titania, titanium dioxides nanomaterial, biomaterial, nanomedicine, nanotherapeutic manipulation

1. Nano-properties of titanium dioxide nanotube arrays

Titanium dioxide (TiO_2) nanotube arrays are also referred to as titania nanotube arrays (TNA). Nanotubes layered by anodization in particular, have garnered considerable interest in the enhancement of orthopedic procedures due to their inherent high quality and cost-effectiveness [1, 2]. The anodization process produces continuous and vertically aligned TiO₂ nanotubes structure in an array form on the titanium (Ti) alloy surface as shown in **Figure 1**.

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Figure 1. TNA nanomatrix observation by field emission scanning electron microscopy. (A) The surface modification by anodization produced nanotubular structure of TiO_2 layer (TNA) in vertical view and (B) nanoporous structure from top view; the formation of well-aligned nanotubular structure (nanotubes). The nanotubes were linked to each other and ripple marks occurred at the sidewalls.

Several researchers have investigated a range of parameters associated with the physical and element properties of TNA. The physical parameters involve different crystal structures, nanotubes diameter and length, as well as surface roughness. The element contents are the core compositions of TNA. The effect of different parameters could solely or communally modulate diverse cellular responses of the cells adhesion, migration, proliferation and differentiation [3, 4].

Interaction of these parameters may also result in the wettability factors of cellular interaction and biocompatibility [5]. Hence, these parameters need to be optimized before performing a detailed study of the material. This might also help in gaining an understanding of the cell-nanostructure interactions and designing novel regenerative biomaterials that could favor-ably modulate cellular responses to enhance the tissue regeneration [6–8].

The Ti surface readily reacts with oxygen upon contact and results in three titanium oxide crystalline phases such as rutile, brookite and anatase. These phases may also be responsible for the material biological properties [9]. Anatase phase is metastable and exhibit stronger interactions between metal and support, which would be advantageous for medical application [10]. Anatase phase shows better absorption properties of hydroxyl-OH- and phosphate- PO_4^{3+} than rutile titania in simulated body fluid which could favor bonelike apatite component to be deposited [9]. The deposition of bone-like apatite component is crucial in mediating a positive osseointegration, the interaction of implant surface with surrounding bone tissues [11, 12].

Therefore, anatase crystal phase TNA has become a major interest in medical research. A study by Yu et al. [13] reported that anatase TNA could yield an optimal biological response for cell adhesion, spreading, proliferation and differentiation. TNA with 100 nm diameter have been suggested to provide similar characteristic as the natural bone topography comprising nanophase hydroxyapatite (100 nm size regime) in the collagen matrix [14, 15].

2. Potential application of TNA in biomedical implants

Biomaterials are the core needs in diverse medical areas such as for the orthopedic, dental, cardiovascular, and craniofacial implants [59–64]. In the past, Ti or Ti alloys were commonly used as biomaterial implants [16]. Besides having great mechanical properties and excellent corrosion resistance, titanium possesses a good biocompatibility, which related to the behavior and function of nontoxic materials in living systems [17, 18].

This metal surface is known to be cytocompatible, which refers to the ability to bind with biomolecules and supported cellular attachment (adhesion), growth and proliferation [11, 19–22]. Conventionally, Ti alloys have a thin layer of titania also known as titanium oxide (TiO₂) on the surface. This naturally occurring oxide of titanium (Ti⁴⁺) resulted from the reduction–oxidation action of surrounding oxygen (O_2^{4-}) and water (H_2O) [23]. This oxidized layer of Ti is known to be bioactive which makes it possible to establish direct contact with bone cells and promote the formation of apatite (major component of bone tissue) [24].

To meet the expectation of successful biomedical implants, there is a critical need in reducing the post-operation healing time and safe placement of implants have become a major concern. This is because the human body has minimum time to react to osseointegration before the body starts rejecting the implants. The currently available implants possess these limitations. For instance, at the early stage of implantation of Ti implant materials into human body, the material surface cannot bind directly to living bone due to biologically inert metallic surface properties [25]. Hence, the healing period takes a longer time and sometimes the surface gets encapsulated over the time [26]. This attributes to poor osseointegration, leading to aseptic loosening of the implant, development of fibrous tissue (at interface of implant-bone), micromotion (at interface of bone implant) and/or wear debris formation (wear particles of bone implant interface) and further delamination (or fracture) between bone and implant material [26, 27].

The surface of implant materials plays a vital role in controlling osseointegration to decrease healing time; in this regard, scholars aim to improve or alter the biocompatibility of Ti implant surface for long-term clinical use [16]. Current studies focus on the potential of titania with a three-dimensional (3-D) microporous or nanoporous structure to enhance the formability of apatite (bone component) and the adherence speed of osteoblastic cells compared with that of a dense titania layer [28–30]. The nanometric scaled surface modification has shown to be critical for the tissue acceptance and cell survival.

Notably, the proposed TNA structure has adaptive features which are required to successfully improve cell interaction with the implant materials. The continuous and vertically aligned TNA topography demonstrates extremely larger surface area than the flat titanium surface and has been assumed to overcome current clinical implants limitations [31]. Moreover, this improved bioactive layer of inward growth TiO_2 nanotubes on Ti provides good adherence of the nanotube layer to the titanium metal which eventually rectifies the problems of existing ceramic coatings arising from weak interfacial bonding [28]. Besides that, TNA topography may provide similar characteristic as a natural bone topography (pore size/diameter ~ 60–100 nm) that might improve the interference of bone cells response [15].

Furthermore, the unique structure of TNA exhibit surface area that is three times higher than that of flat titanium, creating additional spaces for cell interaction particularly at the cell extracellular matrix level; this structure may also address the limitations of existing clinical implants [14, 21, 32, 33]. Moreover, the improved bioactive layer of the oxide nanotube structures on Ti allows the nanotube layer to adhere to the titanium metal (metastable), leading to stronger interfacial bonding that that of existing ceramic coatings [34]. These nanostructure properties can increase the surface energy and improve interactions with various proteins (such as vitronectin and fibronectin), resulting in enhanced specific cell adhesion and osseointegration [13, 35–38]. Yu et al. [13] reported that anatase TNA elicits optimal biological responses for cell adhesion, spreading, proliferation, and differentiation. Furthermore, the surfaces of these nanostructures can effectively reduce inflammatory responses compared with surfaces of conventional implants [39–41]. Therefore, the proposed TNA structure possesses adaptive features that can successfully improve cell interaction with the implant materials and may potentially enhance osseointegration [42–44].

2.1. Examples of biomedical implants

An orthopedic implant is a medical device built from metallic alloys such as Ti which is used to replace a missing joint or bone or to support a damaged bone. It may consist of a single type or comprise modular parts of biomaterial. For example, bone plates and bone screws used in spinal fusion surgery and fixation of fractured bone part. Meanwhile, the hip and knee replacements are medically termed as artificial joints or prostheses used to treat various type of arthritis affecting these joints, which are common health complaints in elderly patients. Besides, the bone implants are also used to treat the bone damaged from accident or cancer or musculoskeletal diseases [30].

Dental implant is an artificial tooth root made of Ti used to place into the jaw and hold a dental prosthesis as replacement for tooth or bridge. This technique was invented in 1952 by a Swedish orthopedic surgeon named Per-Ingvar Brånemark [45]. The implant is considered the standard in replacement of missing teeth due to periodontal diseases, injuries, or some other reasons [46]. Dental implants are divided into three types, namely, the osseointegrated, mini-implant for orthodontic anchorage, and zygomatic [47]. Besides, another important implant used in dental application is the titanium mesh membrane. This barrier implant membrane surface provides great mechanical properties for Guided Bone Regeneration (GBR) treatment to assist the new bone formation [48].

Cardiovascular implants use Ti metals for the replacement of heart valves (pacemaker cases and defibrillators), endovascular stents, and stent-graft combinations. These implants help to overcome cardiovascular diseases which physically damage the heart, resulting in loss of cardiac function. The types of implants are classified as temporary internal, temporary external and permanent internal devices. One of the demands is stents which include the bare metal stents, drug-eluting stent, and bioabsorbable stents [49]. Craniofacial implants are important in the application of craniofacial prostheses or also known as an epistheses. Epistheses may be used to repair or improve absence of facial structures due to malformation present at birth, operations that involve treatment for cancer, or trauma. The osseointegrated titanium implant is one of the common types of implants used in epistheses [45].

Further development and improvement on the implant is required for complete compatibility with the area of implantation, for shorter surgical duration and improved cosmesis [30, 50].

3. Potential application of TNA in nanomedicine

The application of nanotechnology in medicine has led to a new concept termed as nanomedicine. Nanosized materials exhibit extraordinary functional characteristics due to their unique dimension properties. This nanomaterial technology could lead to advances in medical therapies various diseases, especially cancers. TNA might improve efficiency of an existing therapies and diagnostic methods. In addition, this it could also reduce the total medical care expenses. The further prospect of TNA will be discussed in this section especially for nanotherapeutics, nanodiagnostics, and nanobiosensors applications [42].

3.1. Nanotherapeutics: Nanomedicine in therapy

3.1.1. Nanodrug delivery agents

New nanoengineering approaches allow target drug delivery, improve drug solubility, increase therapeutic index, extend drug half-life, and decrease drug immunogenicity. Nanotherapeutics enables the delivery of drugs to specific cells by using nanostructured materials [51]. This property overcomes the limitations of systemic drug administration and may potentially revolutionize treatment of numerous diseases [52].

3.1.2. Nanomatrix therapeutic induction

The inner volume of TiO_2 nanotubes can be also filled with chemicals and biomolecules, such as enzymes or proteins. Subsequently, TNA could be applied into new drug-releasing implants for emerging therapies for localized drug delivery [53, 54]. Whereby, the TNA topology can be coated with inflammation-reducing drugs, such as dexamethasone, by using simple physical adsorption or deposition of the drug by magnetic stimuli-responsive drug delivery system as described in **Figure 2**. This technology may act together radiation therapy and even stem cell transplant for an intensification therapy which also known as consolidation or postremission therapy.

3.1.3. Nano-immunomodulatory agents

Nanomaterial technology allows the development of new immunomodulatory agents, which are either immunologically active components or immunosuppressive agents. This nanostructured material could effectively surpass vaccination, adjuvants, and other immunomodulatory drug treatments. Besides, this unique surface structure could act together with an immunosuppressive agent to therapeutically prevent damage to immune response toward unsuccessful transplant in allergic or even localized autoimmune reaction. Hence, this technology could improve the clinical outcomes of treatments for a range of infectious and noninfectious diseases [55].



Figure 2. TNA nanomatrix as therapeutics system. (A) The system composes TNA structures created on a Ti surface, (B) loaded with drug-encapsulated polymer micelles at the top acting as drug-carriers and magnet nanoparticles (MNs) at the bottom of the nanotubes. A magnetic stimulated release of drug-carriers was achieved by activating magnetic nanoparticles loaded at the bottom of the nanotubes. (C) The drug may move from a region of high concentration to one of lower concentration via passive diffusion activity. (D) The stimuli-release concept is based on applying a magnetic field to induce the movement of magnetic particles from the bottom and force the release polymer micelles out from the TNA.

3.1.4. Nano-antibacterial agents

Bacterial infection of in-dwelling medical devices could be controlled by the technology of TNA nanomatrix surface coated with infection-reducing drugs, such as penicillin and streptomycin (**Figure 3**). Traditional antibiotic treatment is limited in solving the bacterial infection problem. Kulkarni et al. [58] discovered that the use of nanotubes with large diameter (30–100 nm) might reduce the growth of bacteria, such as *Staphylococcus aureus* and *Staphylococcus epidermidis*, compared with the smaller size of nanotube (20 nm).

3.1.5. Nano-blood-contacting agents

Adsorption of blood proteins is the immediate primary outcome observed at the implantliquid interface [55]. TNA able to increase the formation of fibrin network by transforming



Figure 3. TNA as nano-antibacterial agent. (A) The TNA could be aligned on any medical device surface (substrate) and may act as antimicrobial chemotherapy agent. (B) The bactericidal antibiotics such as *Penicillin and Streptomycin* can be coated at TNA cylindrical inner surface. (C) This antibacterial surface will inhibit and avoid bacteria grow, thus may reduce the bacteria infection risk from the system.

fibrinogen to fibrin and reduce clotting time also forming dense fibrin network (**Figure 4**). Moreover, TNA elicited low monocyte activation and cytokine secretion. The adsorption of biomaterial and blood able to evaluate by using a micro-BCA assay and X-ray photoelectron spectroscopy (XPS) [56].

3.2. Nanodiagnostics

Nanobiotechnology and molecular diagnosis are emerging concepts in nanodiagnostics for development of personalized medicine or cancer therapy. With the advances in nanotechnology, biomarkers can be refined using nanomaterials, which provide high volume/surface ratio and multifunctionality. Diagnostic information is obtained based on pharmacogenetics, pharmacogenomics, pharmacoproteomics, and environmental factors influencing responses to therapy. This approach provides effective and progressive personalized treatment, which is tailored directly from the genetic makeup of an individual, thereby preventing unwanted side-effects [57].

3.3. Nano-biosensors

Biosensors are analytical devices used to detect biological analytes, such as biomolecules (protein, lipid, DNA, and RNA), and biological cells (blood cell, virus, and microorganism). These devices present wide applications, including for detection of infectious organisms and



Figure 4. TNA as nano-blood-contacting agent. The TNA topology could enhance increase the protein adsorption of blood serum, adhesion and activation of platelets (fibrin and fibrinogen) and kinetics of whole blood coagulation. Thus, the TNA surface may provide interconnecting between the biological substances for providential blood-related implants.

molecular detection of biomarkers for disease diagnosis. Biosensors consist of physicochemical transducers (electrochemical, mass, optical, and thermal) and biological analytes as a molecular recognition system. The sensitivity of biosensors depends on the properties of the transducers and the bio-recognition element. Nanostructured transducers with TNA could be used as diagnostic tools with increased sensitivity, specificity, and reliability for medical applications [42].

4. Molecular cross-talks between TNA and molecular stability

The nanometric scaled topography of biomedical products plays a decisive role in the surrounding tissue acceptance, cellular stability and cell survival [59–64]. It is important to understand nanomaterials-molecular interactions at different cellular mechanisms in order to predict the safety of nanomaterials application and their long-term effects. The study of molecular signaling pathways could help to explain the cell fate activity when it interacts with this nanomaterial. A study by Arcelli et al. [9] has found that Ti with various surface textures on osteoblast cells is able to regulate the expression of genes that are linked to osteoblast differentiation and bone regeneration such as TIMP1, PTN, and RUNX1 whether directly or indirectly. The indirect mechanism has been found through cell communication (PLCG2 and EPHA7), cellular proliferation, differentiation (MSX1), cycle regulation (RASSF2 and WDR26) and cell adhesion (TNC, TNXB, ZFHX1B and TRPM7).

Furthermore, material surface textures interaction may trigger various cellular mechanisms such as tissue remodeling (reorganization or restoration of existing tissues), organization of extracellular matrix and protein development, arrangement and disassembly activities (biogenesis), bone remodeling (bone matrix, reabsorption minerals and bone development), morphogenesis of anatomical structure and macromolecule complex assembly of biological process. Most of material surface textures such as nanorough/nanomaterials interactions are predicted from functional analysis using bioinformatics software such as gene ontology (GO) analysis [64]. However, precise laboratory work needs to be done in accordance with these mechanisms and the knowledge of designing safe nano-biomedical products from molecular genetic aspects.

The nanomaterial technology could lead to advances in medical therapies for a variety of diseases, especially cancer. Indeed, nanotechnology may have a great impact in medicine and healthline. However, little is known about the impact of nanotechnology on human health and also on the environment especially in terms of new mechanisms associated with nanotoxicology [4, 65]. Nanomaterial toxicological profile requires the analysis of different endpoints and cellular mechanisms. Numerous studies have indicated that some nanoparticles reveal traces of toxicity in biological systems [66]. This has led to an interest in the area of nanotoxicology, which examines the possible toxicity of nanomaterial products for advanced medical applications. These research issues have underlined the need for toxicogenomic studies which govern the examination of toxicology, genomics, proteomics and metabolomics of human cells interaction with targeted nanomaterial product. The need of molecular biology study on nanomaterial product is important in the development of specific strategies treatment especially in nanotherapeutic manipulation.

5. Conclusion

Nanotechnology in biomedical field focuses on improving the existing therapies and diagnostic methods. The aim of developments in this area is to improve the available practice efficiency and reusability, thus saving the total medical cost. Presently, TNA nanostructure provides a promising approach for the advanced biomedical implant and nanomedicine applications. Furthermore, TNA opens up the possible tie-up in nanotherapeutics, nanodiagnostics and nano-biosensors. Further research must be conducted to explore nanomaterialbiomolecular interactions in order to develop novel or improved biomaterials products for medicine and health-line services.

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References

[1] Fadl-allah S, Quahtany M, El-Shenawy N. Surface modification of titanium plate with anodic oxidation and its application in bone growth. Journal of Biomaterials and Nanobiotechnology. 2013;04(01):74-83. DOI: 10.4236/jbnb.2013.41010

- [2] Guehennec L, Soueidan A, Layrolle P, Amouriq Y. Surface treatments of titanium dental implants for rapid osseointegration. Dental Materials. 2007;23:844-854
- [3] He J, Zhou W, Zhou X, Zhong X, Zhang X, Wan P, et al. The anatase phase of nanotopography titania plays an important role on osteoblast cell morphology and proliferation. Journal of Materials Science: Materials in Medicine. 2008;19(11):3465-3472. DOI: 10.1007/ s10856-008-3505-3
- [4] Salata O. Applications of nanoparticles in biology and medicine. Journal of Nanobiotechnology. 2004;**2**:1-6. DOI: 10.1186/1477-3155-2-3
- [5] do Nascimento GM, Olivera R, Pradie NA, PRG L, Worfel PR, Martinez GR, Mascio P, Dresselhaus MS, Corio P. Single-wall carbon nanotubes modified with organic dyes: Synthesis characterization and potential cytotoxic effects. Journal of Photochemistry and Photobiology A: Chemistry. 2010;211:99-107. DOI: 10.1016/j.jphotochem.2010.01.0199
- [6] Tan AW, Murphy BP, Akhbar SA. Review of titania nanotubes: Fabrication and cellular response. Ceramics International. 2012;**38**:4421-4435. DOI: 10.1016/j.ceramint.2012.03.002
- [7] Webster T, Ejiofor J. Increased osteoblast adhesion on nanophase metals: Ti, Ti6Al4V, and CoCrMo. Biomaterials. 2004;**25**(19):4731-4739. DOI: 10.1016/j.biomaterials.2003.12.002
- [8] Uchida M, Kim H, Kokubo T, Fujibayashi S, Nakamura T. Structural dependence of apatite formation on titania gels in a simulated body fluid. Journal of Biomedical Materials Research. 2002;64A(1):164-170. DOI: 10.1002/jbm.a.10414
- [9] Arcelli D, Palmieri A, Pezzetti F, Brunelli G, Zollino I, Carinci F. Genetic effects of a titanium surface on osteoblasts: A meta-analysis. Journal of Oral Science. 2007;49(4):299-309. DOI: 10.2334/josnusd.49.299
- [10] Pozio A, Palmieri A, Girardi A, Cura, F, Carinci F. Titanium nanotubes activate genes related to bone formation *in vitro*. Dental Research Journal. 2012;9(Suppl 2):S164
- [11] Xu J, Liu L, Munroe P, Xie ZH. Promoting bone-like apatite formation on titanium alloys through nanocrystalline tantalum nitride coatings. Journal of Materials Chemistry B. 2015;3:4082-4094
- [12] Jiao Y. Effect of hydrolysis pretreatment on the formation of bone-like apatite on poly(Llactide) by mineralization in simulated body fluids. Journal of Bioactive and Compatible. 2007;22(5):492-507. DOI: 10.1177/088391150708216
- [13] Yu W, Jiang X, Zhang F, Xu L. The effect of anatase TiO₂ nanotube layers on MC3T3-E1 preosteoblast adhesion, proliferation, and differentiation. Journal of Biomedical Materials Research Part A. 2010;94:1001-1332. DOI: 10.1002/jbm.a.32687. http://onlinelibrary.wiley.com/doi/10.1002/jbm.a.32687/pdf
- [14] Jäger M, Zilkens C, Zanger K, Krauspe R. Significance of Nano- and Microtopography for cell-surface interactions in orthopaedic implants. Journal of Biomedicine and Biotechnology. 2007;2007:1-19. DOI: 10.1155/2007/69036
- [15] Puleo D, Nanci A. Understanding and controlling the bone–implant interface. Biomaterials. 1999;20(23-24):2311-2321. DOI: 10.1016/s0142-9612 (99)00160-x

- [16] Ajeel SA, Ali AM, Karm Z. Titanium oxide nanotubes arrays used in implant material. UPB Scientific Bulletin Series B. 2014;76:95-104
- [17] Sidambe AT. Biocompatibility of advanced manufactured titanium implants–A review. Materials. 2014;7:8168-8188. DOI: 10.3390/ma7128168
- [18] Gepreel MA, Niinomi M. Biocompatibility of Ti-alloys for long-term implantation. Journal of the Mechanical Behavior of Biomedical Materials. 2013;20:407-415
- [19] Roshasnorlyza H, Srimala S, Rabiatul Basria SMNM, Yusof A, Ishak M. Study of TiO₂ nanotubes as an implant application. AIP Conference Proceedings. 2016;1704:040009. DOI: 10.1063/1.4940096
- [20] Saharudin K, Sreekantan S, Aziz S, Hazan R, Lai C, Mydin R, Mat I. Surface modification and bioactivity of anodic Ti6Al4V alloy. Journal of Nanoscience and Nanotechnology. 2012;13(3):1696-1705. DOI: 10.1166/jnn.2013.7115
- [21] Lindahl C, Engqvist H, Xia W. Influence of surface treatments on the bioactivity of Ti. ISRN Biomaterials. 2013;2013:13. Article ID: 205601
- [22] Mikulewicz M, Chojnacka K. Cytocompanility of medical biomaterials containing nickel by Osterblasts: A sytematic literature review. Biological Trace Element Research. 2011;142(3):865-889
- [23] Idrus MHM. Anodic oxidation of titanium in sulphuric acid (H₂SO₄) for biomedical application. Masters thesis, Universiti Tun Hussein Onn Malaysia; 2013
- [24] Von Wilmowsky C, Bauer S, Lutz R, Meisel M, Neukam F, Toyoshima T, et al. *In vivo* evaluation of anodic TiO₂ nanotubes: An experimental study in the pig. Journal of Biomedical Materials Research Part B: Applied Biomaterials. 2009;89B(1):165-171. DOI: 10.1002/jbm.b.31201
- [25] Lee S, Yang D, Yeo S, An H, Ryoo K, Park K. The cytocompatibility and osseointegration of the Ti implants with XPEED ® surfaces. Clinical Oral Implants Research. 2011;23(11):1283-1289. DOI: 10.1111/j.1600-0501.2011.02304.x
- [26] Swami N, Cui Z, Nair LS. Titania nanotubes: Novel nanostructures for improved osseointegration. Journal of Heat Transfer. 2011;133(3):034002
- [27] Herrmann H, Bar H, Kreplak L, Strelkov SV, Aebi U. Intermediate filaments: From cell architecture to nanomechanics. Nature Reviews. Molecular Cell Biology. 2007;8(7):562-573. http://www.ncbi.nlm.nih.gov/pubmed/17551517(November 7, 2014)
- [28] Zhou H, Lee J. Nanoscale hydroxyapatite particles for bone tissue engineering. Acta Biomaterialia. 2011;7(7):2769-2781. DOI: 10.1016/j.actbio.2011.03.019
- [29] Oh S, Brammer KS, Li YSJ, Teng D, Engler AJ, Chien S, Jin S. Stem cell fate dictated solely by altered nanotube dimension. Proceedings of the National Academy of Sciences of the United States of America. 2009;106(7):2130-2135. http://www.ncbi.nlm.nih.gov/ pubmed/19179282

- [30] Wilson W, Poh CK. Titanium alloys in orthopaedics. In: Sieniawski J, editor. Titanium Alloys - Advances in Properties Control. Rijeka: InTech; 2013. DOI: 10.5772/55353. https:// www.intechopen.com/books/titanium-alloys-advances-in-properties-control/titaniumalloys-in-orthopaedics
- [31] Oh S, Brammer, KS, Moon KS, Bae JM, Jin S. Influence of sterilization methods on cell behavior and functionality of osteoblasts cultured on TiO₂ nanotubes. Materials Science and Engineering: C. 2011;31(5):873-879
- [32] Oh S, Daraio C, Chen LH, Pisanic TR, Finones RR, Jin S. Significantly accelerated osteoblast cell growth on aligned TiO₂ nanotubes. Journal of Biomedical Materials Research. Part A. 2006;**78**(1):97-103
- [33] Bariana M, Dwivedi P, Ranjitkar S, Kaidonis JA, Losic D, Anderson PJ. Biological response of human suture mesenchymal cells to Titania nanotube-based implants for advanced craniosynostosis therapy. Colloids and Surfaces B: Biointerfaces. 2017;**150**:59-67
- [34] Sakamoto N, Saito N, Han X, Ohashi T, Sato M. Effect of spatial gradient in fluid shear stress on morphological changes in endothelial cells in response to flow. Biochemical and Biophysical Research Communications. 2010;395(2):264-269. DOI: 10.1016/j.bbrc. 2010.04.002
- [35] Fujibayashi S, Neo M, Kim H, Kokubo T, Nakamura T. Osteoinduction of bioactive titanium metal. KEM. 2004;25(3):953-956. DOI: 10.4028/www.scientific.net/kem.254-256.953
- [36] Bigerelle M, Anselme K. Statistical correlation between cell adhesion and proliferation on biocompatible metallic materials. Journal of Biomedical Materials Research. 2004;72A(1):36-46. DOI: 10.1002/jbm.a.30212
- [37] Brammer K, Oh S, Gallagher J, Jin S. Enhanced cellular mobility guided by TiO₂ nanotube surfaces. Nano Letters. 2008;8(3):786-793. DOI: 10.1021/nl072572
- [38] Raimondo T, Puckett S, Webster TJ. Greater osteoblast and endothelial cell adhesion on nanostructured polyethylene and titanium. International Journal of Nanomedicine. 2010;5:647-652. http://www.pubmedcentral.nih.gov/articlerender.fcgi?artid=2939710&t ool=pmcentrez&rendertype=abstract (October 30, 2014)
- [39] Yang H, Qin X, Tian A, Zhang D, Xue X, Wu A. Nano size effects of TiO₂ nanotube array on the glioma cells behavior. International Journal of Molecular Sciences. 2013;14:244-254. DOI: 10.3390/ijms14010244
- [40] Taylor E, Webster T. Reducing infections through nanotechnology and nanoparticles. International Journal of Nanomedicine. 2011;6:1463. DOI: 10.2147/ijn.s22021
- [41] Zhang L, Webster TJ. Nanotechnology and nanomaterials: Promises for improved tissue regeneration. NanoToday. 2009;4:66-80. DOI: 10.1016/j.nantod.2008.10.014
- [42] Hamlekan A, Takoudis C, Sukotjo C, Mathew T, Mathew M, Virdi A, Shahbazian-Yassar R, Shokuhfar T. Recent progress toward surface modification of bone/dental implants with titanium and zirconia dioxide nanotubes fabrication of TiO₂ nanotubes. Journal of Nanotechnology and Smart Materials. 2014;1(301):1-14

- [43] Teng FY, Ko CL, Kuo HN, Hu JJ, Lin JH, Lou CW, Hung CC, Wang YL, Cheng CY, Chen WC. A comparison of epithelial cells, fibroblasts, and osteoblasts in dental implant titanium topographies. Bioinorganic Chemistry and Applications. 2012;2012
- [44] Hazan R, Sreekantan S, Mydin RBS, Abdullah Y, Mat I. Study of TiO₂ nanotubes as an implant application. Vol. 1704. In: Mohamed AA, Idris FM, Hasan AB, Hamzah Z, editors. No. 1, p. 040009. AIP Conference Proceedings. AIP Publishing; 2016, January
- [45] Federspil PA. Implant-retained craniofacial prostheses for facial defects. GMS Current Topics in Otorhinolaryngology, Head and Neck Surgery, 8, Doc03. 2009. http://doi.org/10.3205/ cto000055
- [46] Lavenus S, Louarn G, Layrolle P. Nanotechnology and dental implants. International Journal of Biomaterials. 2010;2010:9. Article ID: 915327. http://dx.doi.org/10.1155/ 2010/915327
- [47] Elias CN, Lima JHC, Valiev R, Meyers M. Biomedical applications of titanium and its alloy. Journal of the Minerals, Metals and Materials Society. 2008;60(March):46-49
- [48] Rakhmatia Y, Ayukawa Y, Furuhashi A, Koyano K. Current barrier membranes: Titanium mesh and other membranes for guided bone regeneration in dental applications. Journal of Prosthodontic Research. 2013;57(1):3-14. DOI: 10.1016/j.jpor.2012.12.001
- [49] Jaganathan S, Supriyanto E, Murugesan S, Balaji A, Asokan M. Biomaterials in cardiovascular research: Applications and clinical implications. BioMed Research International. 2014;2014:1-11. DOI: 10.1155/2014/459465
- [50] Chauhan N, Moin S. Indian aspects of drug information resources and impact of drug information centre on community. Journal of Advanced Pharmaceutical Technology & Research. 2013;4(2):215-222
- [51] Webster T, Puckett S, Raimondo T. Greater osteoblast and endothelial cell adhesion on nanostructured polyethylene and titanium. International Journal of Nanomedicine. 2010;5:647-652. DOI: 10.2147/ijn.s13047
- [52] Yang W, Xi X, Shen X, Liu P, Hu Y, Cai K. Titania nanotubes dimensions-dependent protein adsorption and its effect on the growth of osteoblast. Journal of Biomedical Materials Research Part A. 2013;102(10):3598-3608. DOI: 10.1002/jbm.a.35021
- [53] Wang Q, Huang JY, Li HQ, Zhao AZJ, Wang Y, Zhang KQ, et al. Recent advances on smart TiO₂ nanotube platforms for sustainable drug delivery applications. International Journal of Nanomedicine. 2017;**12**:151
- [54] Wang Q, Huang JY, Li HQ, Chen Z, Zhao AZJ, Wang Y, et al. TiO₂ nanotube platforms for smart drug delivery: A review. International Journal of Nanomedicine. 2016;11:4819
- [55] Kulkarni M, Mazare A, Schmuki P, Iglič A. Biomaterial surface modification of titanium and titanium alloys for medical applications. Nanomedicine. 2014:111-136
- [56] Smith BS, Yoriya S, Grissom L, Grimes CA, Popat KC. Hemocompatibility of titania nanotube arrays. Journal of Biomedical Materials Research Part A. 2010;95(2):350-360

- [57] Alharbi KK, Al-sheikh Y. Role and implications of nanodiagnostics in the changing trends of clinical diagnosis. Saudi Journal of Biological Sciences. 2014;21(2):109-117. DOI: 10.1016/j.sjbs.2013.11.001
- [58] SMN Mydin RB, Sreekantan S, Hazan R, Farid Wajidi MF, Mat I. Cellular homeostasis and antioxidant response in epithelial HT29 cells on titania nanotube arrays surface. Oxidative Medicine and Cellular Longevity. 2017;2017:10. Article ID: 3708048. https:// doi.org/10.1155/2017/3708048
- [59] Saharudin KA, Sreekantan S, Aziz SNQAA, Hazan R, Lai CW, Mydin RBS, Mat I. Surface modification and bioactivity of anodic Ti6Al4V alloy. Journal of Nanoscience and Nanotechnology. 2013;13(3):1696-1705
- [60] Gulati K, Maher S, Findlay DM, Losic D. Titania nanotubes for orchestrating osteogenesis at the bone–implant interface. Nanomedicine. 2016;**11**(14):1847-1864
- [61] Yu WQ, Zhang YL, Jiang XQ, Zhang FQ. In vitro behavior of MC3T3-E1 preosteoblast with different annealing temperature titania nanotubes. Oral Diseases. 2010;16(7):624-630
- [62] Mydin RBSMN, Farid Wajidi MF, Hazan R, Sreekantan S. Nano-biointerface of titania nanotube arrays surface influence epithelial HT29 cells response. Transactions on Science and Technology. 2017;4(3-3):348-353
- [63] RBSMN Mydin. Cellular and molecular impacts of titania nanotube arrays interaction with human colorectal cancer cell lines HT-29, human osteosarcoma cell lines SAOS-2 and human dermal fibroblast cell lines HDF-A [thesis]. Malaysia: Universiti Sains Malaysia; 2016
- [64] Zijno A, De Angelis I, De Berardis B, Andreoli C, Russo M, Pietraforte D. Different mechanisms are involved in oxidative DNA damage and genotoxicity induction by ZnO and TiO₂ nanoparticles in human colon carcinoma cells. Toxicology *In Vitro*. 2015;29(7):1503-1512. DOI: 10.1016/j.tiv.2015.06.009
- [65] Biazar E, Majdi A, Zafari M, Avar M, Aminifard S, Zaeifi D, et al. Nanotoxicology and nanoparticle safety in biomedical designs. International Journal of Nanomedicine. 2011;6:1117. DOI: 10.2147/ijn.s16603
- [66] Magdolenova Z, Collins A, Kumar A, Dhawan A, Stone V, Dusinska M. Mechanisms of genotoxicity. A review of *in vitro* and *in vivo* studies with engineered nanoparticles. Nanotoxicology. 2014;8(3):233-278. DOI: 10.3109/17435390.2013.773464

Investigation of Optical Properties and Radiation Stability of TiO₂ Powders before and after Modification by Nanopowders of Various Oxides

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Abstract

The titanium dioxide powders are widely used as a pigment for coatings and paints, the important characteristics of which are reflectivity and stability to irradiation. The results of investigations of the optical properties and radiation stability of titanium dioxide powders before and after high-temperature modification with nanopowders are presented in this chapter. The diffuse reflection spectra of various titanium dioxide powders in the UV, visible, and near-IR ranges, and their change during irradiation by electrons with 30 keV energy and a different fluence in vacuum in situ were investigated: (1) TiO₂ powders with particle size in the range 60–240 nm; (2) Microsized TiO₂ powder (240 nm) modified by Al₂O₃, ZrO₂, SiO₂, TiO₂, ZnO, MgO nanoparticles with grain size from 30 up to 60 nm; (3) Microsized TiO₂ powder (260 nm) modified by SiO_2 with the grain size of 12–14 nm at the temperature of 150, 400, and 800°C. The reduction in reflectivity in entire spectrum with decrease in grain sizes of TiO₂ nanopowders was established. Nanopowder with the grain size of 80 nm possesses the highest stability to irradiation. It was shown that the average grain size and specific surface of introduced nanoparticles effect noticeably on the radiation stability increase of titanium dioxide powders modified with nanoparticles of various oxides. The micro-sized TiO₂ powder heating at temperature of 800°C is the factor which positively influences on the radiation stability.

Keywords: titanium dioxide, nanoparticles, optical properties, radiation stability, modification, irradiation, defects

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1. Introduction

The titanium dioxide powders are widely used in many branches of industry. They are utilized as effective photocatalyst [1–3], pigments of thermal control, and anti-reflective coatings of spacecraft [4, 5]. In recent years, the investigations of possibility of their usage as solar photoconverters are conducted [6, 7]. But they have found the largest application as household paints [8].

Such fields of the use imply a work in conditions of an action of charged particle fluxes, UV, and visible radiations. The absorption centers, caused by cation and anion defect sublattices, are formed due to these radiations. That is why the method development of an increase in radiation stability of titanium dioxide powders is a relevant problem.

Theoretical and experimental studies revealed [9–14] that the modification with nanopowders is sufficiently effective way to increase the radiation stability because they possess large specific surface and work as a "sink" for gathering electronic excitations formed during irradiation. However, the modification by nanopowders can lead to a deterioration of initial optical properties that can be induced by large absorption of native point defects in the UV and visible ranges and by absorption of chemosorbed gases in near-infrared (IR) range of spectrum. The modification is associated with high temperature heating of powders, an effect of which on optical properties and radiation stability is studied poorly.

An influence of the modification by nanopowders on photo- and radiation stability of reflective powders is discussed in [9–14]. There are no data about an effect of modification conditions (temperature and heating time, type, and concentration of nanopowders) on the optical properties of materials and their stability to an impact of ionizing radiations.

In the present chapter, the data obtained by the authors regarding optical properties and radiation stability of titanium dioxide powders before and after modification with nanoparticles of various oxides are considered. The radiation stability of titanium dioxide powders of different sizes and different types of crystal structures is considered. The results of investigations of the rutile titanium dioxide powder modification by nanoparticles of oxide compounds at the temperature of 800°C as well as the studies of an effect of the anatase titanium dioxide powder modification by SiO₂ nanoparticles with large specific surface at the temperatures of 150, 400, and 800°C are presented.

2. Experimental

For modification by various nanoparticles, the rutile TiO_2 powders with the average particle size of 240 nm and specific surface of 8 m²/g were used. The anatase TiO_2 powders with the average particle size of 260 nm and specific surface of 7 m²/g were used for modification with SiO_2 nanoparticles (average particle size 12–14 nm). The TiO_2 powder was mixed with oxide nanoparticles in a ratio 100:7, the distilled water was added, and it was evaporated at the temperature of 150°C for 6 hours. Then, the mixture was heated in an oven for 2 hours at 400 or 800°C. After heating, the mixture was grinded in agate mortar and was pressed into metal substrates with 28 mm diameter and 2 mm height. The prepared samples were mounted in

space environment simulator "Spektr" [15]. Since the sample interaction with atmospheric oxygen after irradiation can lead to "bleaching" – a decrease in concentration of formed absorption centers of oxide reflective powders, the diffuse reflection spectra (ρ_{λ}) were registered in vacuum (*in situ*) after irradiation with accelerated electrons (E = 30 keV, $\varphi = 1 \cdot 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$, F = (0.5, 1, and 2) × 10¹⁶ cm⁻², T = 300 K, P = 10⁻⁶ torr). The radiation stability was evaluated with using the difference spectra and the change in integral absorption coefficient of solar radiation (a_s), which is computed from diffuse reflection spectra according to the following expression:

$$a_{s} = 1 - R_{s} = 1 - \frac{\int_{\lambda_{1}}^{\lambda_{2}} \rho_{\lambda} I_{\lambda} d\lambda}{\int_{\lambda_{1}}^{\lambda_{2}} I_{\lambda} d\lambda} = 1 - \frac{\sum_{i=1}^{n} \rho_{\lambda}}{n},$$
(1)

where ρ_{λ} —spectral reflectivity; I_{λ} —solar radiation intensity; $\lambda_1 \div \lambda_2$ —Sun spectrum range (the Sun radiates 98% of total energy in the range of 0.2 ÷ 2.5 µm); n—the number of equienergy ranges of the solar spectrum [16].

Changes in absorption coefficient a_s were defined from subtraction its values before (a_{s0}) and after ($a_{s,irr}$) irradiation of powders by accelerated electrons:

$$\Delta a_{\rm s} = a_{\rm s, irr} - a_{\rm s0} \tag{2}$$

3. Optical properties and radiation stability of micro and nanopowders of titanium dioxide before modification

The study objects were the TiO₂ submicron sized powders of industry production with an average particle size of 240 nm (m-240), as well as nanopowders with an average particle size of 60 (n-60), 80 (n-80), and 160 (n-160) nm. The specific surface of m-240, n-160, n-80, and n-60 powders was 8.0, 13, 16, and 28 m²/g, respectively [17].

The m-240 powder possessed rutile lattice, and the nanopowders were the mixture of anatase and rutile. The ratio of these phases changed with the change in particle size. With a decrease in particle size from 160 down to 80 and 60 nm, the concentration of rutile changed from 50 down to 33.9 and 98.7 mass%, the anatase concentration was 49.8, 66.1, and 1.3 mass%.

The largest value of the reflection coefficient (ρ_0) was registered in $\rho_{\lambda 0}$ spectra of micropowder m-240. The nanopowders n-160, n-80, and n-60 follow in order of its decrease (**Figure 1**).

The absolute values of the reflection coefficient on the various regions of the spectrum reduce with decreasing powder particle sizes. Its largest values are registered in the range from 500 to 1200 nm. The reflection coefficient reduces in more short-wavelength ($\lambda < 500$ nm) and more long-wavelength ($\lambda > 1200$ nm) ranges. The more is the decrease, the less is the size particles of powders. In the short-wavelength region, the decrease in the reflection coefficient is sharp with pronounced outlines of the absorption bands, and in the long-wavelength region, the decry is



Figure 1. The diffuse reflection spectra of TiO₂ powders measured in vacuum (in situ).

smooth. The more is the reflection coefficient, the less is the specific surface of the powders in the range of values $8-13 \text{ m}^2/\text{g}$.

Such a character of the difference in the reflection coefficient on the various regions of the spectrum allows to believe that its reduction is determined by a variety of factors. For their identification, the difference diffuse reflection spectra were obtained by means of subtraction from 100% value of ρ in ρ_{E0} spectra, which depend on energy:

$$\Delta \boldsymbol{\rho}_{\mathrm{E0}} = (100 - \boldsymbol{\rho}_{\mathrm{E0}}) \tag{3}$$

Such spectra (**Figure 2**) are the absorption spectra of powders before modification. They indicate which absorption bands define a decrease in reflection coefficient. Qualitatively, all spectra are similar. They consist of three regions. First region from absorption edge up to 2.5 eV is characterized by several absorption bands. These bands are encased in integral contour, which is defined by native point defects of titanium dioxide. The intensity of this band in the maximum is 15, 33, 38, and 60%. It is inversely proportional to particle sizes of powders m-240, n-160, n-80, and n-60.

The second region is characterized by an absence of relationship between $\Delta \rho$ and energy. Its length depends on grain size of powders: the less is the grain size, the shorter is the region. The second region of m-240 powder is in the range of 3-1 eV, n-60 powder—in the range of 2.25–1.5 eV, which has an absorption by Ti_i', O_i', V_O', and Ti_i'' defects. There is a dependence of $\Delta \rho$ values on particle size of powders: the less is the particle size, the larger is the absorption coefficient. Since nanoparticles possess the large specific surface, the concentration of native lattice defects on their surface is higher than in micropowders, and consequently, the larger concentration of interstitial titanium ions (Ti_i^X) will be in the nanoparticles.
Investigation of Optical Properties and Radiation Stability of TiO₂ Powders before and after... 489 http://dx.doi.org/10.5772/intechopen.74073



Figure 2. The absorption spectra of the TiO₂ powders before modification: $1 - Ti_i$; $2 - O_i$, $3 - V_O$; $4 - Ti_i$, $5 - Ti_i$, $6 - V_O$, $7 - O_i$, $8 - Ti_i$, $9 - V_{Ti}$, $10 - V_{Ti}$, $11 - V_O^X$, 12 - 0.69 eV, 13 – free carriers of charge.

The third region in the vicinity above 1.5 eV is determined by increasing values of absorption coefficient with an increase in energy. The slope of these absorption contours is different for various powders: with reducing particle size, the slope increases. In the near-IR range, the absorption of semiconductors is defined by free electrons, which is described by a power law of absorption coefficient from wavelength:

$$\Delta \rho = \eta \lambda^n \tag{4}$$

The power function is defined by free electron transitions between levels in the conductance band. That is why, the exponent can be a measure of free electron concentration [18]. The calculations showed that with the decrease in particle sizes of powders the exponent n increases (**Table 1**). It means that the concentration of free electrons increases with decreasing grain sizes or increasing specific surface.

Thus, the reflection coefficient of initial powders is determined by native point defects and free electrons. The less is the particle sizes of powders, the larger is the concentration of native point defects on the surface and the concentration of free electrons. The particle size defines a value of the reflection coefficient on the first and third regions of the reflection spectra. The

| Average particle size of the powders, nm | 60 | 80 | 160 | 240 |
|--|------|------|------|------|
| n | 1.67 | 1.53 | 1.48 | 0.85 |

Table 1. The dependence of exponent n on the particle sizes of TiO₂ powders.

joint influence of absorption coefficient of point defects and free electrons determines the reflection coefficient in the second region: the larger is the $\Delta \rho$ on the first and third regions, the larger is its value in the second region and the less the size of this region.

Qualitatively, the change in diffuse reflection spectra obtained after irradiation ($\Delta \rho_F$) is the same for all powders (**Figure 3**). They are absorption spectra induced by accelerated electron exposure. The spectra include the bands in the visible range with the maximum at 2.9 eV and wide unstructured band in the near-IR range with maximums at 1 eV.

The $\Delta \rho_{\text{Ea}}$ spectra of powders n–60 significantly differ from m–240, n–160, and n–80, where three regions can be distinguished with qualitatively difference of absorption coefficient. The first region is characterized by the presence of absorption bands in UV and visible ranges. The second one has absorption in the range of 2–1.5 eV. The third one is in the range above 1.5 eV with absorption peak in the range of 1–0.7 eV.

In order to understand the origin of bands and to conduct an analysis of nanoparticle size effect on absorption center accumulation, the $\Delta \rho_{\rm E}$ spectra were decomposed on elementary bands [19–23]. The function of decomposition consists of 80% of Gaussian and 20% of Lorentzian functions [24]. From decomposition of the induced irradiation spectra on absorption spectra, it follows that during electron exposure in m–240, n–160, n–80, and n–60 titanium dioxide



Figure 3. The change in diffuse reflection spectra of titanium dioxide powders m-240 (A), n-160 (B), n-80 (C), and n-60 (D) after electron irradiation with fluence of 0.5 (1), 1 (2), and $2 \cdot 10^{16}$ (3) cm⁻² and after residual vacuum exposure (4). $1-Ti_i$, $2-O_i$, $3-V_O$, $4-Ti_i$, $5-Ti_i$, $6-V_O$, $7-O_i$, $8-Ti_i$, $9-V_{Ti}$, $10-V_{Ti}$, $11-V_O$, $11-V_O$, 12-0.69 eV.

| Fluence, 10 ¹⁶ cm ⁻² | m-240 | n-160 | n-80 | n-60 |
|--|-------|-------|-------|-------|
| F _{0.5} | 46 | 30 | 32.22 | 51.5 |
| F ₁ | 51.77 | 39.28 | 42.76 | 56.43 |
| F ₂ | 56.40 | 43.56 | 46.99 | 62 |

Table 2. The dependence of integral area of absorption bands in the spectra of TiO₂ powders on electron fluence.

powders, the negatively charged defects V_{Ti} ^{····}, V_{Ti} ^{···}, and V_O ^X are formed, mostly, in the near-IR range, and then positively charged defects Ti_i ^{···}, V_O ^{··}, O_i ^{··}, Ti_i ^{····} in the visible and Ti_i [·], O_i [·], V_O [·], and Ti_i ^{···} in the UV ranges are formed.

The analysis of the integral area of the bands during a variety of fluences of electron exposure with energy of 30 keV shows (**Table 2**) that the highest radiation stability belongs to powders with 80–160 nm particle size and the powders with 60 nm particle size possess the lowest radiation stability. Advantageously, the difference is due to a greater concentration of defects V_{Ti} , V_{Ti} , and V_O^X , as well as due to Ti_i , and V_O , formed defects, which lead to absorption band generation close to 2.17 eV in difference diffuse reflection spectra. The similar band is registered in the spectrum of n–80 nanopowder, but its intensity is significantly less than n–60.

Elementary processes leading to formation and accumulation of such defects are described by reactions given below, where the following designations were accepted: Ti_{Ti}^{X} , O_{O}^{X} , $(Ti_{Ti}^{X})^{*}$, $(O_{O}^{X})^{*}$ -titanium and oxygen atoms and ions in points of lattice; (H')*, H', (e')*, e'-accelerated and thermolyzed proton and electron, correspondingly; Ti_{i}^{*} , Ti_{i}^{*} , Ti_{i}^{*} , Ti_{i}^{*} , V_{Ti}^{*} , V_{Oi}^{*} , V_{O}^{*} , V_{Oi}^{*} -interstitial ions and vacancies of titanium and oxygen in various charge states; and h'-hole. The impact of accelerated electrons leads to interstitial titanium and oxygen generation and corresponding vacancies due to ionizing displacement mechanisms, electrical repulsion from the same charged ions placed close to each other, or the displacement of neighboring simultaneously ionized atoms by the following reactions:

$$\mathrm{Ti}_{\mathrm{Ti}}X + O_{O}^{X} + (e')^{*} \to V_{\mathrm{Ti}}^{''''} + \mathrm{Ti}_{i}^{''''} + O_{O}^{X} + e' \leftrightarrow V_{\mathrm{Ti}}^{'''''} + \mathrm{Ti}_{i}^{''''} + O_{O}^{X}$$
(5)

$$V_{\text{Ti}}^{''''} + \text{Ti}_{i}^{'''} \leftrightarrow V_{\text{Ti}}^{'''} + \text{Ti}_{i}^{''} \leftrightarrow V_{\text{Ti}}^{''} + \text{Ti}_{i}^{'}$$
(6)

$$\operatorname{Ti}_{\mathrm{Ti}}^{X} + O_{O}^{X} + (e')^{*} \to \operatorname{Ti}_{\mathrm{Ti}}^{X} + V_{O}^{\cdot \cdot} + O_{i}^{''} + e' \leftrightarrow \operatorname{Ti}_{\mathrm{Ti}}^{X} + V_{O}^{\cdot} + O_{i}^{''}$$
(7)

$$V_{O}' + O_{i}^{''} \leftrightarrow V_{O}^{X} + O_{i}^{'} \tag{8}$$

4. Optical properties and radiation stability of titanium dioxide powders after heating and modification with nanoparticles

4.1. Reflection spectra of modified powders

The rutile titanium dioxide pigment (m-240) was used for investigation of an influence of nanoparticle type of various oxide compounds on diffuse reflection spectra of modified TiO₂ powder and their changes after accelerated electron irradiation [25]. The average grain size of

nanoparticles was, nm: Al₂O₃-30, ZrO₂-30, ZnO-50, MgO-60, SiO₂-55, and TiO₂-60. The specific surface area of the powders was equal to m^2/g : Al₂O₃-49, ZrO₂-25, ZnO-20, MgO-26, SiO₂-60, and TiO₂-26. All nanopowders possess a crystalline structure except the SiO₂ powder, which was amorphous.

Modification effects on ρ_{λ} spectra are shown in **Figure 4**. In the range of 440 nm, the reflectivity of heated and modified powders increases by 2–3% (**Figure 5**). An exception is a powder modified with n-ZnO, the ρ value of which reduces by 2–4%. In the range of 580 nm, the reflectivity increases for powders doped by n-MgO and n-TiO₂ only. For other modified powders, the reflectivity does not change noticeably, for the powder doped with ZnO nanoparticles—it decreases as well.

The ρ value of powders modified with n-TiO₂ and n-SiO₂ increases noticeably in the near-IR range at 850 nm. For other modified and heated powders, the ρ changes insignificantly. The increase in ρ is detected in the spectra of powders modified with n-MgO, n-ZrO₂, n-ZnO, and n-SiO₂ at 1200 nm. The largest increase is 4%. The increase in ρ in the range of 1800 nm is observed at both heating and modification by all nanopowders. The largest value, equaled to 4.7%, belongs to powder modified with n-ZnO.

The change in ρ_{λ} spectra of powders at heating and high-temperature modification can be because of the distinction between the reflection coefficient of nanoparticles and the reflection coefficient of micropowder. This distinction is determined by large value of nanoparticle scattering coefficient in comparison to micro-sized particles and will appear, mainly, in the visible range of spectra.



Figure 4. The diffuse reflection spectra of heated at 150 and 800° C unmodified TiO₂ powder and modified with nanoparticles of various oxide compounds in quantity of 7 mass% at 800° C.

Investigation of Optical Properties and Radiation Stability of TiO₂ Powders before and after... 493 http://dx.doi.org/10.5772/intechopen.74073



Figure 5. The value of reflection coefficient of unmodified TiO_2 powders and modified with nanoparticle of various oxide compounds.

Another reason of the reflection coefficient distinction is desorption of gases molecules from the surface at heating, the main component of which is OH-groups and molecules of water [24, 26]. The desorption leads to a reduction of absorption band intensity in the near-IR range at 1240, 1420, 1950, and 2250 nm [27–29].

An oxygen chemisorption, simultaneously with desorption, on the freed bonds on the surface and oxygen diffusion into the bulk of powder grains occur at heating in atmosphere. This leads to a decrease in the concentration of native point defects, to a decrease in the intensity of the absorption bands, and to an increase in the reflection coefficient in the regions where the bands are located.

4.2. Radiation stability of modified powders

Radiation stability was estimated from the difference diffuse reflection spectra ($\Delta \rho_{\lambda}$), in which two parts can be distinguished, determined by the absorption bands. In the visible range the bands at 420–580 nm are registered, in the near-IR range at 850–1200 nm (**Figure 6**). The position of maximums changes depending on type of nanopowder. Two bands appear in some spectra and one band in others. Based on types and number of absorption bands in these ranges of TiO₂ absorption spectra, it can be assumed that these integral contours include a large number of elementary bands. The $\Delta \rho$ values in these regions are different: for some powders, they are approximately the same; for others, the intensity of the band in the near-IR region is substantially larger.

Judging by the $\Delta \rho_{\lambda}$ values, it can be concluded that the largest changes occur during irradiation in the visible range in the powder heated at 150°C and in the powders modified with n-MgO and n-ZnO. The changes in ρ_{λ} spectra reach 27% after exposure.



Figure 6. The $\Delta \rho$ values of heated and modified TiO₂ powders by nanoparticles of different oxide compounds for various wavelengths.

The radiation stability of TiO₂ powders modified by all types of nanoparticles is higher compared to unmodified powder but heated at 150°C. A reduction in $\Delta\rho$ values of modified powders is registered in entire range of $\Delta\rho_{\lambda}$ spectra (**Figure 6**). The effectiveness of modification ($\Delta\rho_{150}/\Delta\rho_{mod}$) reaches almost two times in the visible range. In the near-IR range, it is even larger and reaches more than six times. The best result in the visible range corresponds to n-ZrO₂ modification, in the near-IR range–n-SiO₂.

Radiation stability in the visible region of the spectrum of TiO_2 powder heated at 800°C is the same or even higher in comparison to the modified powders. Only the modification with n-ZrO₂ gives, although not significant, an increase in radiation stability compared to the heated powder. Modification with n-SiO₂ nanopowder results in a slight decrease and the modification with n-MgO, n-ZnO, n-Al₂O₃, and n-TiO₂ to a noticeable decrease in radiation stability in comparison to the heated powder.

In the near-IR region, the modification with some nanopowders has a significant effect on the radiation stability. The largest effect was obtained using $n-SiO_2$ and $n-ZrO_2$. Then, mixtures with $n-Al_2O_3$ and $n-TiO_2$ follow. The least effect from the modification was obtained using n-MgO and n-ZnO.

With respect to the aggregate values of $\Delta \rho$ in the visible and near-IR regions of the spectrum, the series of the largest effect at modifying with nanoparticles is as follows: $1-SiO_2$, $2-ZrO_2$, $3-Al_2O_3$, $4-TiO_2$, 5-MgO, and 6-ZnO. The largest effect in increasing the radiation stability of micropowders of titanium dioxide is obtained by modifying with n-SiO₂ and n-ZrO₂ and the smallest by the modification with n-MgO and n-ZnO.

4.3. The effect of temperature at heating and modification by SiO_2 nanoparticles on the radiation stability of TiO_2 powders

A comparison of the ρ_{λ} spectra of heated TiO₂ powders shows (**Figure 7**) that with an increase in the heating temperature from 150 to 400°C, the reflection coefficient varies in different regions of the spectrum according to various regularities [26]. In the region from the absorption edge up to 600 nm, it increases so that an absorption band with a maximum at 400–405 nm is formed in the difference spectrum determined by the relation:

$$\Delta \boldsymbol{\rho}_{\lambda} = \boldsymbol{\rho}_{\lambda 150} - \boldsymbol{\rho}_{\lambda 400} \tag{9}$$

where $\rho_{\lambda 150}$ and $\rho_{\lambda 400}$ are the reflection coefficients of the powder heated at a temperature of 150 and 400°C, respectively.

In the 600–900 nm region, the reflection coefficient slightly decreases with a minimum value of 1.7% at 700 nm. In the longer wavelength region, it increases in accordance with power law of the wavelength [30, 31].

An increase in the heating temperature up to 800°C leads to the appearance of an absorption band at 380–390 nm in the difference spectrum ($\Delta \rho_{\lambda} = \rho_{\lambda 150} - \rho_{\lambda 800}$). At 450–680 nm, the changes are close to zero, and in the region of 680–2100 nm, a power function of the wavelength with a maximum value $\Delta \rho = 8.7\%$ is recorded.

Modification of the TiO₂ powder with SiO₂ nanoparticles and heating at 400°C, both lead to a decrease in the reflection coefficient over the entire spectrum (**Figure 8**). At the same time, an absorption band is recorded in the region from the absorption edge up to 600 nm with a maximum at 500 nm, and in the longer wavelength region, the reflection coefficient changes without certain regularities, the $\Delta \rho$ values are 2–3%.

An increase in the heating temperature up to 800° C at modifying TiO₂ powder leads to a decrease in the reflection coefficient in the region from the absorption edge up to 600 nm and



Figure 7. The diffuse reflection spectra of unmodified titanium dioxide powders heated at various temperatures.



Figure 8. Diffuse reflection spectra of TiO_2 powders heated at different temperatures and modified with SiO_2 nanopowders.

its increase in the longer wavelength region. The $\Delta \rho$ values are no more than 1% except for two regions: the bands with a maximum at 400–405 nm and the "tail" of absorption in the range of 900–2100 nm reaching 3.5% and 3.7%, respectively.

Analysis of the ρ_{λ} spectra of heated and modified by nanoparticles at different temperatures of titanium dioxide powders shows that the change in the reflection coefficient in the entire spectral region is determined by several processes, which lead to the appearance of qualitatively different dependences. A band with a maximum at 400–500 nm caused by defects of cationic sublattice (interstitial ions or absorption vacancies) is on the first region in the range from the absorption edge to 600 nm of TiO₂. The range from 680 or 900 nm to 2100 nm is the second region and can be described by a power-law dependence of the absorption coefficient from the wavelength because of electron transitions between levels in the conduction band of TiO₂. In the interval between these two regions, the difference values of the reflection coefficient change insignificantly or form an absorption band with a maximum at 700 nm.

Therefore, heating the TiO₂ powder at 400 and 800°C without nanoparticles and in mixtures with SiO₂ nanoparticles leads to a change in the concentration of native point defects and free electrons on the surface. Such changes are determined by the desorption of physically and chemically sorbed gases, the release of bonds, their filling with other molecules and atoms, i.e., redistribution of defects and electronic state on the surface.

Exposure with electrons leads to a decrease in the reflection coefficient over the entire spectrum as a result of the formation of radiation defects and the appearance of the absorption bands induced by them. With an increase in the heating temperature from 150 to 400°C, very slight changes in the absorption coefficient occur (**Figure 9**).

Since the heating at 150°C does not give noticeable changes in the absorption coefficient a_{sr} then the Δa_s values of the heated powder at 150°C are taken as the values of the initial (unheated) powder, and the efficiency of the TiO₂ micropowder modification by the SiO₂ nanopowder in an amount of 7 mass% at a temperature of 400 or 800° C was computed as follows: Investigation of Optical Properties and Radiation Stability of TiO₂ Powders before and after... 497 http://dx.doi.org/10.5772/intechopen.74073

$$\eta = \Delta a_s^{150} / \Delta a_s^T \tag{10}$$

where Δa_s values after irradiation with 0.5, 1, and 2 × 10¹⁶ cm⁻² electron fluence: Δa_s^{150} – TiO₂ powders heated at 150°C, Δa_s^{T} are the Δa_s values of TiO₂ powder modified with 7 mass% of SiO₂ nanoparticles at a temperature of 400 or 800°C.

With an increase in the electron fluence from $F = 1 \times 10^{16} \text{ cm}^{-2}$ to $F = 2 \times 10^{16} \text{ cm}^{-2}$, the coefficient η varies insignificantly for all values of the heating and modifying temperature (**Figure 10**) in comparison to its changes in the range of $F = (0.5-1) \times 10^{16} \text{ cm}^{-2}$. This allows us to assume that the values obtained at $F = 2 \times 10^{16} \text{ cm}^{-2}$ are close to the steady-state values.

The decrease in the efficiency of silica nanopowder modification with increasing exposure time or electron fluence is, probably, determined by the contribution of the surface preradiation defects in the total concentration of radiation defects formed by irradiation both in the TiO_2 micropowder and in SiO_2 nanoparticles.

When the electron fluence is less than 0.5×10^{16} cm⁻², the main contribution to the change in the diffuse reflection spectra and the integral absorption coefficient is made by preradiation defects on the grain surface of the crystal lattice of the TiO₂ powder.

Upon irradiation by accelerated electrons with prethreshold energies (e*), the processes of formation and separation of charge carriers in titanium dioxide proceed according to the scheme:

a. Hole-electron formation

$$\operatorname{TiO}_2 + e^* \to e^- + p^+ \tag{11}$$

b. Hole drift toward negatively charged surface, then an interaction with sorbed radicals and their oxidation

$$p^+ + R \to \mathrm{RO}^- \tag{12}$$

c. Neutralization of surface oxygen by holes

$$p^+ + O_s(O_l) \to O \tag{13}$$

d. Oxygen formation and its escape in vacuum

$$O + O \rightarrow O_2 \uparrow$$
 (14)

Holes move to the surface, where they first interact with surface oxygen, then with the oxygen of the lattice that leads to its radiolysis. If there are defects on the surface, then holes relax on these defects and SiO_2 nanoparticles do not play a special role in increasing the radiation stability. And only at an optimal value of the nanoparticle concentration which is sufficient to create the necessary number of relaxation centers along with the available native surface defects – native relaxation centers, the modification becomes effective.

Based on the results of studies of the temperature effect on optical properties (**Figures 9** and **10**) at the TiO_2 powders heating and their modification by SiO_2 nanoparticles, the following can be concluded:

- 1. Heating at 400°C does not give a noticeable increase in optical properties stability during electron exposure in comparison with the heating at 150°C. The increase is significant for modified powders, and the coefficient η is 2.38, 1.8, and 1.73 for electron fluence (0.5, 1, and 2) × 10¹⁶ cm⁻², respectively.
- 2. Heating at 800°C leads to an increase in the radiation stability of both types of powders. In this case, the coefficient η is 1.82, 1.48, and 1.43 for unmodified and 2.65, 2.31, and 2.26 for modified powders for electron fluence (0.5, 1, and 2) × 10¹⁶ cm⁻², respectively.
- 3. A comparison of these values shows that, with respect to the coefficient η and its dependence on the electron fluence, the modification at a temperature of 400°C leads to approximately the same effect (η = 2.38, 1.8 and 1.73) as the heating at 800°C (η = 1.82, 1.48, and 1.43). The effectiveness of such a method of processing powders is manifested: modification at a reduced temperature gives the same effect as heating at a higher temperature.
- **4.** The lack of improvement in radiation stability from heating at 400°C can be a consequence of the fact that at such a temperature, the surface of titanium dioxide particles is released only from physically bounded water on the surface and OH⁻ groups. Surface bonds are not released, and there is no chemisorption of oxygen, which does not give noticeable changes in the concentration of anionic sublattice defects.
- 5. A noticeable improvement in the radiation stability of the powder modified at 400°C testifies to the effect of SiO₂ nanoparticles, which are on the surface of grains and granules of titanium dioxide, as centers of relaxation of electronic excitations arise upon irradiation. This effect is more pronounced at low electron fluences ($\eta = 2.38$ at $F = 0.5 \times 10^{16} \text{ cm}^{-2}$), i.e., when the surface preradiation defects in titanium dioxide determine a degradation. At such a temperature and electron fluence of 0.5×10^{16} and 1×10^{16} , these defects, basically, transform to color centers. This is evidenced by the almost complete equality of the absorption coefficient at an increase in the heating temperature from 400–800°C: $\Delta a_s = 0.029$ for T = 400°C and $\Delta a_s = 0.026$ for T = 800°C. From this point, the following can be concluded that in the case of small values of the electron fluence (or absorbed dose), a rather low heating temperature (400°C) is sufficient at modification with nanoparticles.
- 6. If the electron fluence increases to $(1-2) \times 10^{16}$ cm⁻², then the change in Δa_s values of specimens heated at 400 and 800°C increases from 0.03 up to 0.1 and 0.13, respectively. This means that for large values of fluence, the SiO₂ nanoparticles on the surface of TiO₂ grains and granules are not sufficient to perform the function of relaxation centers of electronic excitations. Therefore, in order to clean the surface from chemosorbed gases, the appropriate conditions, such as heating at 800°C, should be provided.

The fact that the radiation stability at the same heating temperature is higher in mixtures of $TiO_2 + SiO_2$ powders than TiO_2 powders may indicate about a change in the catalytic activity, specific surface area, and concentration of chemisorbed gases upon the addition of SiO_2 nanoparticles. The reduction in the catalytic activity which depends on the anionic vacancy concentration and excess titanium on the surface [32] will occur at heating in an atmosphere with a large oxygen concentration. Such a heating, in turn, will lead to an increase in radiation stability.

Investigation of Optical Properties and Radiation Stability of TiO₂ Powders before and after... 499 http://dx.doi.org/10.5772/intechopen.74073



Figure 9. Dependence of Δa_s values on the electron fluence with 30 keV energy of TiO₂ powder heated at the temperature of 150, 400, and 800°C and modified with SiO₂ nanoparticles in an amount of 7 mass% by heating at the same temperature values.



Figure 10. Effectiveness of the heating and TiO₂ powder modification (η) with SiO₂ nanoparticles.



Figure 11. X-ray diffraction patterns of TiO₂ powders modified with SiO₂ nanoparticles at a variety of heating temperatures.

The heating of TiO₂ powder mixtures with SiO₂ nanoparticles at a temperature of 150, 400, and 800°C cannot lead to the formation of new phases, because even at a higher heating temperature (900, 1000, and 1200°C) of TiO₂ + SiO₂ powder mixtures, the Ti_(1-x)Si_xO₂ solid solution is not formed [33].

A certain contribution to the increase in radiation stability at the highest heating temperature in the present studies, equaled to 800° C, can be made by changing the phase state of TO₂ powder—the conversion of anatase to rutile, which is carried out at a temperature of 450–900°C. The transition temperature is determined by the degree of crystallinity of the compound (films, polycrystals, and single crystals), the concentration of defects, and other factors [34, 35].

When SiO₂ particles are added to the TiO₂ powder, the phase transition is facilitated: transition temperature reduces and the relative rutile concentration increases [33]. Therefore, the TiO₂ powder mixtures with SiO₂ nanoparticles heated at 800°C can give an increase in the relative rutile concentration, a change in the particle size and specific surface area, the concentration of absorbed gases, and stability to an impact of electron exposure. A confirmation of the increase in rutile concentration with increasing temperature is the results of X-ray phase analysis (**Figure 11**), which show that an increase in the heating temperature from 150–400°C does not change the phase ratio, and further increase to 800°C leads to the formation of rutile in an amount 10 mass%.

5. Conclusions

In this chapter, the optical properties and radiation stability of titanium dioxide powders before and after modification by nanopowders of various oxide compounds (Al₂O₃, ZrO₂, SiO₂, TiO₂, ZnO, and MgO) are considered.

The reflectivity of modified powders can both increase, in comparison to the initial powders, and decrease. The reflection coefficient is determined by the grain sizes and, with their decrease, it increases, which occurs when nanopowders are added. The decrease in the reflection coefficient may be due to a large absorption by native point defects in the UV and visible ranges and by chemisorbed gases in the near-IR range of the spectrum, determined by the larger specific surface area of nanopowders.

Modification with nanopowders leads to an increase in the radiation stability of reflective powders, which is determined by the relaxation of electronic excitations on the surface of nanoparticles and by a smaller concentration of absorption centers formed upon irradiation. The maximum effect of increasing radiation stability is achieved by modification by nanopowders with a larger specific surface area and a smaller particle size. An additional factor affecting the increase in radiation stability is the heating during the modification, and the largest effect was obtained at $T = 800^{\circ}C$.

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References

- Ma Y, Wang X, Jia Y, Chen X, Han H, Li C. Titanium dioxide-based Nanomaterials for Photocatalytic fuel generations. Chemical Reviews. 2014;114(19):9987-10043. DOI: 10.10 21/cr500008u
- [2] Akpan UG, Hameed BH. Parameters affecting the photocatalytic degradation of dyes using TiO2-based photocatalysts: A review. Journal of Hazardous Materials. 2009;170(2–3): 520-529. DOI: 10.1016/j.jhazmat.2009.05.039

- [3] Chihiro I, Iwahashi K, Kan'no K. Photogeneration of charge carriers in titanium oxides. Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms. 2002;191(1–4):271-274. DOI: 10.1016/S0168-583X(02)00574-8
- [4] Zhang L. Chen Rong-min. TiO2-Siloxane thermal control coatings for protection of spacecraft polymers. Chinese Journal of Aeronautics. 2004;17(1):53-59. DOI: 10.1016/S1000-9361(11)60203-3
- [5] Dobrzański LA, Szindler M. Sol gel TiO2 antireflection coatings for silicon solar cells. Journal of Achievements in Materials and Manufacturing Engineering. 2012:**52**(1):7-14
- [6] Baraton M-I. Nano-TiO2 for solar cells and Photocatalytic water splitting: Scientific and technological challenges for commercialization. The Open Nanoscience Journal. 2011;5: 64-77. DOI: 10.2174/1874140101105010064
- [7] Khan MA, Khan SMM, Mohammed MA, Sultana S, Islam JMM, Uddin J. Sensitization of Nanocrystalline titanium dioxide solar cells using natural dyes: Influence of acids medium on coating formulation. American Academic & Scholarly Research Journal. 2012;4(5)
- [8] Chen X, Mao SS. Titanium dioxide nanomaterials: Synthesis, properties, modifications and applications. Chemical Reviews. 2007;**107**(7):2891-2959. DOI: 10.1021/cr0500535
- [9] Mikhailov MM, Utebekov TA, Neshchimenko VV. Radiation stability of powders in mixtures with Al2O3 nanoparticles. Radiation Effects and Defects in Solids. 2013;168(2): 106-114. DOI: 10.1080/10420150.2012.693084
- [10] Mikhailov MM, Verevkin AS. Optical properties and radiation stability of thermal control coatings based on doped zirconium dioxide powders. Journal of Materials Research. 2004;19(2):535-541. DOI: 10.1557/jmr.2004.19.2.535
- [11] Li XW, Song RG, Jiang Y, Wang C, Jiang D. Surface modification of TiO₂ nanoparticles and its effect on the properties of fluoropolymer/TiO₂ nanocomposite coatings. Applied Surface Science. 2013;276:761-768. DOI: 10.1016/j.apsusc.2013.03.167
- [12] Mikhailov MM, Lapin AN. Influence of the temperature of aluminum oxide micropowder modification with Al2O3 nanopowders on the optical properties and radiation resistance of coatings manufactured on their basis. Russian Physics Journal. 2011;53(11):1131-1139. DOI: 10.1007/s11182-011-9541-3
- [13] Mikhailov MM, Neshchimenko VV, Li C. The degradation kinetics of the optical properties under proton irradiation for ZnO pigments modified by Al2O3 and Al2O3 CeO2 nanopowders. Radiation Effects and Defects in Solids. 2012;167(1):26-36. DOI: 10.1080/ 10420150.2011.588231
- [14] Mikhailov MM, Neshchimenko VV, Li C. Radiation stability of zinc oxide pigment modified by zirconium oxide and Aluminum oxide Nanopowders. AIP Conf. Proc. 2009:680-690. DOI: 10.1063/1.3076886

- [15] Kositsyn LG, Mikhailov MM, Kuznetsov NY, Dvoretskii MI. Apparatus for study of diffuse – Reflection and luminescence spectra of solids in vacuum. Instruments and Experimental Techniques. 1985;28:929-932
- [16] Johnson FS. The solar constant. Journal of Meteorology. 1954;11(6):431-439. DOI: 10.1175/ 1520-0469(1954)011<0431:TSC>2.0.CO;2
- [17] Mikhailov MM, Neshchimenko VV, Yuryev SA. Optical properties and radiation stability of submicro- and nanopowders titanium dioxide measured in situ. Radiation Physics and Chemistry. 2016;121:10-15. DOI: 10.1016/j.radphyschem.2015.12.006
- [18] Pidgeon CR. In: Balkanski M, eds. Handbook on Semiconductors. North Holland: Amsterdam. 1980
- [19] He J, Behera RK, Finnis MW, Li X, Dickey EC, Phillpot SR, Sinnott SB. Prediction of hightemperature point defect formation in TiO2 from combined ab initio and thermodynamic calculations. ActaMater. 2007;55:4325-4337. DOI: 10.1016/j.actamat.2007.04.005
- [20] Chen J, Lin L-B, Jing F-Q. Theoretical study of F-type color center in rutile TiO2. Journal of Physics and Chemistry of Solids. 2001;62:1257-1262. DOI: 10.1016/S0022-3697(01)00018-X
- [21] Seebauer Edmund G, Kratzer MC. Charged point defects in semiconductors. Materials Science and Engineering R. 2006;55:57-149. DOI: 10.1016/j.mser.2006.01.002
- [22] Nakamura I, Negishi N, Kutsuna S, Ihara T, Sugihara S, Takeuchi K. Role of oxygen vacancy in the plasma-treated TiO2 photocatalyst with visible light activity for NO removal. Journal of Molecular Catalysis A: Chemical. 2000;161:205-212. DOI: 10.1016/ S1381-1169(00)00362-9
- [23] Kuznetsov VN, Serpone N. On the origin of the spectral bands in the visible absorption spectra of visible-light-active TiO2 specimens. Analysis and assignments. Journal of Physical Chemistry C. 2009;113:15110-15123. DOI: 10.1021/jp901034t
- [24] Mikhailov MM, Chundong L, Neshchimenko VV. Optical property degradation of titanium dioxide micro- and nanopowders under irradiation. Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms. 2014;333:52-57. DOI: 10.1016/j.nimb.2014.04.014
- [25] Mikhailov MM, Vlasov VA, Yuryev SA, Neshchimenko VV, Shcherbina VV. Optical properties and radiation stability of TiO2 powders modified by Al2O3, ZrO2, SiO2, TiO2, ZnO, and MgO nanoparticles. Dyes and Pigments. 2015;123:72-77. DOI: 10.1016/j. dyepig.2015.07.024
- [26] Mikhailov MM, Yuryev SA, Remnev GE, Sazonov RV, Kholodnaya GE, Ponomarev DV. Effect of temperature on radiation resistance of TiO₂ powders during heating and modification by SiO₂ nanoparticles. Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms. 2014;336:96-101. DOI: 10.1016/j. nimb.2014.07.002

- [27] Blanco M, Coello J, Ityrriaga H, Maspoch S. Near-infrared spectroscopy in the pharmaceutical industry. The Analyst. 1998;123:135-150. DOI: 10.1039/A802531B
- [28] Blanco M, Vilarroya I. NIR spectroscopy: A rapid-response analytical tool. Trac trends in Analytical Chemistry. 2002;21:240-250. DOI: 10.1016/S0165-9936(02)00404-1
- [29] Mikhailov MM, Neshchimenko VV, Li C. Effect of the heat treatment on reflective Spectrum of the zinc oxide powders. Journal of Materials Research. 2009;24(1):19-23. DOI: 10.1557/JMR.2009.0033
- [30] Hunsperger RG. Integrated Optics: Theory and Technology. Springer; 2009. 513 p. DOI: 10.1007/b98730
- [31] Peter YU, Cardona M. Fundamentals of Semiconductors: Physics and Materials Properties. Springer; 2010. 778 p. DOI: 10.1007/978-3-642-00710-1
- [32] Mitsuhara K, Matsuda T, Okumura H, Visikovskiy A, Kido Y. Oxygen deficiency and excess of rutile titania (1 1 0) surfaces analyzed by ion scattering coupled with elastic recoil detection. Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms. 2011;269(16):1859-1864. DOI: 10.1016/j.nimb.2011.05.007
- [33] Tobaldi DM, Tucci A, Škapin AS, Esposito L. Effects of SiO₂ addition on TiO₂ crystal structure and photocatalytic activity. Journal of the European Ceramic Society. 2010; 30(12):2481-2490. DOI: 10.1016/j.jeurceramsoc.2010.05.014
- [34] Nowotny J. Titanium dioxide-based semiconductors for solar-driven environmentally friendly applications: Impact of point defects on performance. Energy & Environmental Science. 2008;1:565-572. DOI: 10.1039/B809111K
- [35] Lu Z, Jiang X, Zhou B, Wu X, Lu L. Study of effect annealing temperature on the structure, morphology and photocatalytic activity of Si doped TiO₂ thin films deposited by electron beam evaporation. Applied Surface Science. 2011;257(24):10715-10720. DOI: 10.1016/j.apsusc.2011.07.085



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Titanium dioxide is currently being used in many industrial products. It provides unique photocatalytic properties for water splitting and purification, bacterial inactivation, and organics degradation. It has also been widely used as the photoanode for dye-sensitized solar cells and coatings for self-cleaning surfaces, biomedical implants, and nanomedicine. This book covers various aspects of titanium dioxide nanomaterials including their unique one-dimensional, two-dimensional, mesoporous, and hierarchical nanostructures and their synthetic methods such as sol-gel, hydrothermal, anodic oxidation, and electrophoretic deposition, as well as its key applications in environmental and energy sectors. Through these 24 chapters written by experts from the international scientific community, readers will have access to a comprehensive overview of the recent research and development findings on the titanium dioxide nanomaterials.

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