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Frontiers in Voltammetry

Edited by Shashanka Rajendrachari,
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and Shamanth Vasanth

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Meet the editors

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Contents

Preface

Frontiers in Voltammetry focuses principally on the different applications of various modern voltammetric techniques. The five chapters are all written in simple easy-to-understand language.

Chapter 1 mainly discusses the successful use of electrochemical impedance spectroscopy (EIS) to determine the molecular weight of compounds. The authors discuss the advantages of this technique over such conventional ones as Ostwald and Walker's method. Generally, the measurement of the vapor pressure of pure solvents in solutions is difficult and lengthy in Ostwald and Walker's method, while EIS is a simple, robust, accurate and non-destructive method of determining the molecular weight of polymers and proteins soluble in protic solvents.

Chapter 2 reports the use of carbon dot and chitosan nanocomposite-based sensors to detect copper ions using EIS. Prepared carbon dots and the modified glassy carbon electrode are characterized by transmission electron microscope, scanning electron microscope (SEM), Fourier-transform infrared spectroscopy (FTIR), X-Ray diffraction, and UV-visible spectroscopy. From their discussion of the stability, selectivity, specificity, sensitivity, dynamic range, and detection limits, the authors conclude that fabricated electrodes are economic, simple, and highly sensitive, and give better current response during copper ion detection.

Chapter 3 considers how the many applications of electrochemical sensors could enhance the sensitivity, selectivity, robustness, accuracy, and anti-fouling properties of the electrodes in various fields including healthcare, biomedical, pharmaceuticals, and agriculture. These types of electrochemical sensors are much sought after to meet global demand in various sectors [1–11]. Nanomaterials are a popular choice as a modifier of electrode sensors because of their possible immobilization of molecules, catalysis in electrosynthesis, facilitation of electron transfer between electrodes and biomolecules, and labeling of biomolecules.

Chapter 4, written by the editors, discusses the use of various electrochemical sensors to detect toxic heavy metals like arsenic, cadmium, and lead heavy metals which can cause malfunction of the gastrointestinal, nervous, kidney, and immune systems, birth defects, skin lesions, and cancer. The main source of heavy metal pollution is geological activities or agricultural and industrial wastes (**Figure 1**) [12, 13]. Cyclic voltammetry has proved to be one of the most popular methods of detecting various heavy metals using different modified carbon paste electrodes, carbon screen-printed electrodes, and glassy carbon electrodes. The authors also discuss the advantages of cyclic voltammetry over other non voltammetric methods for detecting heavy metals.

The final chapter discusses the importance of developing toxic organic and inorganic sensors for use in a wide variety of fields, including food sensors, drug and pharmaceutical sensors, biosensors, agricultural residue sensors, energy sensors, and forensic and environmental sensors, to avoid environmental health risks. The authors explain that electroanalytical techniques are better than spectrometric or chromatographic techniques in sensing applications. Among the electroanalytical techniques described are linear

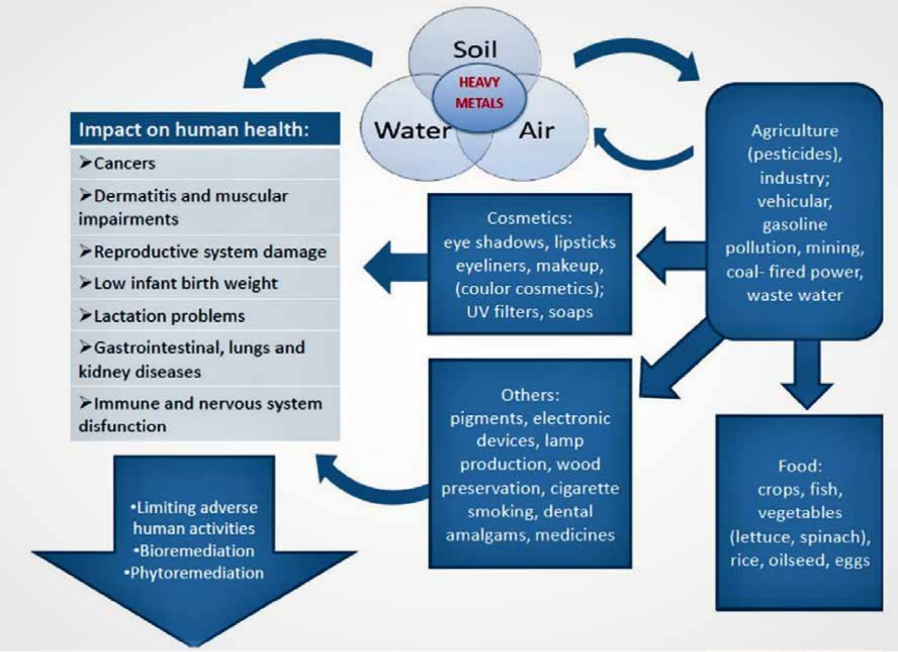

Figure 1.
Pictorial representation of heavy metal, their effect on human health, and their mechanism [12].

sweep voltammetry (LSV), cyclic voltammetry (CV), pulse voltammetry (PV), stripping voltammetry (SV), and chronoamperometry.

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Section 1

Applications of Electrochemical Impedance Spectroscopy (EIS) in Various Fields

Chapter 1

A New Method for Determination of Molecular Weight of Compounds Soluble in Protic Solvents by Electrochemical Impedance Spectroscopy

Subramaniam Rameshkumar, Panjaiyan Karthikeyan,
Iman Danaee and Manogaran Obulichetty

Abstract

This chapter deals with a new method for determining the molecular weight of chemical substances soluble in protic solvents. One of the well-known methods for the determination of molecular weight of a substance, based on one of the colligative properties, is Ostwald and Walker's method, which depends on relative lowering of vapor pressure of solvent. In this paper we proposed a new method for determining the molecular mass of the substances that are soluble in protic solvents such as water, methanol and ethanol employing electrochemical impedance spectroscopy (EIS) technique and Raoult's law. The moisture and vapor pressure dependent proton conductivity of some organic compounds and metal-organic frame works (MOFs) can be utilized to find the molecular mass of solutes soluble in protic solvents. This property is considered as key for determination of molecular weight of chemical substances using EIS and is simpler than Ostwald and Walker's method. This method is a non-destructive and also useful to determine the molecular weight of polymers and proteins soluble in protic solvents.

Keywords: impedance, molecular weight, vapor pressure, Raoult's law

1. Introduction

Electrochemical impedance spectroscopy (EIS) finds a special place among the various electrochemical techniques. It is a powerful tool for analyzing the interfaces formed in the heterogeneous systems. EIS supplies a large amount of informations, though it may not provide all the answers. EIS uses tools developed in electrical engineering and describes the behavior of the systems under study in terms of an equivalent circuit consisting of the circuit elements resistors, capacitors, Warburg impedance etc. The mathematical foundations of EIS were dealt by Heariside [1], through which it is possible to solve the integrodifferential equations appearing in the solutions of electrical circuits by converting them into a system of algebraic equations. The main advantage of EIS is the fact that it is based on the linear time invariant (LTI) theory and validity of the data may be verified using Kramers-Kronig integral transforms. Nernst was the first person who described the chemical applications of impedance spectroscopy through his work [2], followed by many others including those applications to the distribution of relaxation time constants by Cole and Cole [3] and Davidson and Cole [4]. The impedance of mass transfer was explained by Warburg using so called Warburg impedance, which extended EIS to apply for redox reactions [5]. With further development in the understanding of EIS, the structure of double layer in the absence and presence of adsorbed species was studied initially at dropping mercury electrode and then at solid electrodes using AC bridge. The analysis of electrochemical reactions using the electro analog circuit was introduced by Dolin and Ershler [6] and Randles [7, 8], where the age of electrical analog began [9] and continues up till now. The fundamental aspects of EIS give the idea to validate the data and to model the processes limited by diffusion, electrode kinetics and adsorption on different types of electrode geometries. The availability of modern instrumentation to obtain impedance data as well as computer programs to interpret the results have made this technique popular. Now a days, EIS finds applications in corrosion, biosensors, battery development, fuel cell development, drug cell membrane interaction [10], paint characterization, sensor development, polymers etc.

The development of organic proton conducting materials to substitute the per fluorinated polymers such as nafion is an important area of research in the field of fuel cell technologies [11–15]. Recent research in this field emerged some coordination polymers and metal-organic frame works (MOFs) for their proton transport capabilities, though the literature on these materials in other domains such as magnetism, catalysis, inclusion phenomenon and in supramolecular chemistry are quite extensive [16–23]. Under high humidity conditions or with water channels, MOFs show high degree of proton conductivities, comparable to nafion [24–28]. The proton conducting ability of these materials primarily depend on the existence of charge carrying molecular or ionic species such as H_3O^+, OH^-, or NH_4^+ Lewis acidic moieties. These molecular or ionic species with the complex network of hydrogen bonds or their arrangements with the water molecules play a vital role for proton conductivity. These characteristics are considered to be the important structural requirements of the proton conducting polymers and MOFs [29–33]. With the above-mentioned features, several new MOFs that exhibit Nafion-like proton conducting characters, under humidified and ambient temperature conditions have been reported [34]. The proton conducting ability of these materials was evaluated using EIS [34–36] which depends on humidity levels of the surroundings.

In this chapter, through an innovative approach we would like to propose a new method for the determination of molecular weight of compounds which are soluble in water and other protic solvents, using proton conducting ability of organic compounds or MOFs by EIS technique.

2. Electrochemical impedance spectroscopy—a tool to evaluate the proton conductivity of solid materials theory and discussion

Now a days proton conducting solid state electrolytes gained a considerable attention owing to their application in fuel cells1, electrochromic devices [37], humidity sensors [38] and gas separators [39]. Nafion, a perfluorinated polymer with sulphonic acid is used as solid-state proton conductor under hydrated conditions [40]. This polymer has many disadvantages, under high temperature (>80°C) the water clusters are lost in the pores of Nafion. At low humidity levels water clusters in the Nafion pores are low. Both factors reduce the conductivity of Nafion [40]. In addition to these drawbacks, high cost, high fuel cross over, non eco-friendly synthesis and variation of conductivity with degree of sulphonation limit its applications. These limitations made the researchers to look for alternate solid state proton conducting materials. Many coordination compounds and MOFs having proton conducting ability were not explored for their proton conductivities. Recent reports on proton conducting nature of MOFs promise their enhanced proton conductivity at high temperature and low fuel cross over.

It was reported that the organic compounds with heteroatoms incorporated within the pores of MOFs as guests with controlled loading. The amphoteric heterocyclic moiety has shown electrolytic conductance through proton. This system has shown an improved proton conductance even at higher temperatures and precisely the theoretical open circuit potential of hydrogen-oxygen fuel cell. Only few compounds have been studied for their proton conductivities. Their proton conducting properties can further be extended to calculate the molecular weight of solutes dissolved in the protic solvents and the vapor pressure of the protic solvents at any temperature knowing the normal boiling point. Conversely, this property can also be used for the calculation of molar enthalpy of vaporization of protic solvents. These applications have not been verified for these compounds. This method could be an alternate for Ostwald and Walker Method for determining molecular weight of substances and a useful technique for knowing the molecular weight of polymers soluble and an unknown substance in protic solvent. The proposed method is based on EIS technique.

EIS is a routine method for characterization of various electrical properties of different types of materials and the interfaces formed by the materials with electronically conducting materials. EIS is a simple non-destroying technique, where a system study is perturbed by an AC sinusoidal voltage of small amplitude at different applied frequencies and the resulting current varying with the applied frequency is used to extract the required kinetic informations.

2.1 Fundamentals of electrochemical impedance spectroscopy

The resistance of a system under study comes from the hindrance offered for the flow of electrical current through its circuit elements. The resistance, R, of the material is defined by Ohm's law, in terms of voltage, E and current I ratio:

$$R = \frac{E}{I} \tag{1}$$

Similar to resistance, the term impedance measures the ability of a material to resist the flow of charges in definite direction. However, impedance differs from resistance in two main aspects. First, it is associated with alternating current (AC); second, it is usually mentioned at a particular frequency.

Measurement of impedance is done by applying a sinusoidally varying an AC potential to the system under study and measuring the current through the system.

The response to the applied sinusoidally varying potential at a frequency is a sinusoidally varying current at the same frequency with shift in phase. The ratio of applied sinusoidally varying potential to the resulting sinusoidally varying current at the same frequency is called impedance, using which the information on conductivity of the system can be obtained.

The input or excitation signal, i.e. sinusoidally varying potential at a frequency can be expressed as a function of time as follows:

$$E(t) = E_0 \sin(\omega t) \tag{2}$$

Where,

$E(t)$ refers to the potential at time t, E_0 is the amplitude of the applied AC potential and ω is the angular frequency given by the expression $\omega = 2\pi f$ (f = applied frequency in Hz)

In a linear system the excitation of voltage at a frequency 'ω' provides a current 'I' at the same frequency. This generated current is different in amplitude and phase from voltage as given below:

$$I(t) = I_0 \sin(\omega t + \varphi) \tag{3}$$

In a non-linear system I-V relation gives a distorted response which is not purely sinusoidal, but it is still periodic [41].

An analogous expression to Ohm's law allows us to calculate the impedance of the system as:

$$Z = \frac{E(t)}{I(t)} = \frac{E_0 \sin(\omega t)}{I_0 \sin(\omega t + \varphi)} = Z_0 \frac{\sin(\omega t)}{\sin(\omega t + \varphi)} \tag{4}$$

The impedance is therefore expressed in terms of a magnitude, Z_0, and a phase shift (φ). Using Euler's relationship, the impedance is then represented as a complex number

$$Z = \frac{E(t)}{I(t)} = \frac{E_0 \sin(\omega t)}{I_0 \sin(\omega t + \varphi)} = Z_0(\cos\varphi + j\sin\varphi) \tag{5}$$

Accordingly, the impedance is a vector quantity since it has a magnitude, Z_0, and direction given by phase shift, φ.

When we apply the above concepts to a pure resistor, for which the phase angle (φ) is zero,

$$E(t) = E_0 \sin(\omega t) \tag{6}$$

$$I(t) = I_0 \sin(\omega t) \tag{7}$$

$$R = \frac{E(t)}{I(t)} = \frac{E_0 \sin(\omega t)}{I_0 \sin(\omega t)} = \frac{E_0}{I_0} \tag{8}$$

When the concept is applied for a capacitor, where, $\varphi = \frac{\pi}{2}$

Charge in the capacitor,

$$q = CE \tag{9}$$

Current,

$$I = \frac{\mathrm{d}q}{\mathrm{d}t} = C = \frac{\mathrm{d}E}{\mathrm{d}t} \tag{10}$$

$$I = CE_0\omega\cos(\omega t) \tag{11}$$

$$I = \frac{E_0}{X_\mathrm{C}}\sin\left(\omega t + \frac{\pi}{2}\right) \tag{12}$$

Where X_C is capacitive reactance, i.e. the resistance offered by a pure capacitor for the alternate current flows across it. Its value depends on frequency of AC excitation voltage and is given as:

$$X_\mathrm{C} = \frac{1}{\omega C} \tag{13}$$

Where, 'C' is capacitance of the pure capacitor (in F).

Since the current leads the voltage by a phase angle of $\frac{\pi}{2}$, the capacitive reactance is taken along the ordinate (Y-axis) and is given as imaginary component.

$$\text{i.e.} \ -iX_\mathrm{C} = \frac{-i}{\omega C} = \frac{E(t)}{I(t)} \tag{14}$$

Where, $i = \sqrt{-1}$, an imaginary number.

When a capacitor and a resistor are in series connection, the excitation voltage is given as,

$$E = E_\mathrm{R} + E_\mathrm{C} \tag{15}$$

$$E = IR - iX_\mathrm{C}I \tag{16}$$

$$\frac{E}{I} = R - iX_\mathrm{c} \tag{17}$$

Since the value of X_C depends on frequency, the total resistance in this series depends on the frequency of excitation voltage and is called impedance (Z).

$$Z = R - iX_\mathrm{C} \tag{18}$$

In general, the impedance can be represented as,

$$Z(\omega) = Z_\mathrm{Re} - iZ_\mathrm{Im} \tag{19}$$

Where, Z_Re = real part of impedance,

Z_Im = imaginary part of impedance.

The magnitude of impedance is given as,

$$|Z| = \sqrt{(Z_\mathrm{Re})^2 + (Z_\mathrm{Im})^2} \tag{20}$$

$$|Z| = \sqrt{R^2 + \frac{1}{\omega^2C^2}} \tag{21}$$

The phase angle φ is given as,

$$\varphi = \tan^{-1}(Z_{\mathrm{Im}}/Z_{\mathrm{Re}}) \tag{22}$$

$$\varphi = \tan^{-1}(X_C/R) \tag{23}$$

$$\varphi = \tan^{-1}(1/\omega CR) \tag{24}$$

It is well known that impedance is a specific form of the transfer function of the system [41]. If $\bar{I}(s)$ and $\bar{E}(s)$ are the Laplace transforms of the sinusoidal current and voltage respectively, the transfer function [41] is given as,

$$\mathrm{TF}(s) \cong \frac{E(s)}{\bar{I}(s)} \simeq \frac{E_0}{I_0}\left(\cos\varphi + \frac{s}{\omega}\sin\varphi\right) \tag{25}$$

Were, s is the Laplace complex variable or frequency,

$$s = i\omega \tag{26}$$

Now solutions to the Eq. (26) are confined to the frequency domain.

$$Z \cong \mathrm{TF}(i\omega) = \frac{E_0}{I_0}(\cos\varphi + i\sin\varphi) \tag{27}$$

2.2 Variation of frequency

When we consider a homogeneous system, it is represented by a conductance (G) or resistor (R) in parallel connection with a capacitor (C) as shown in **Figure 1**.

The corresponding Nyquist and Bode (phase and impedance) plots for the above equivalent circuit are presented in the **Figures 2** and **3** respectively.

By rule the net impedance of this homogeneous system, from the above equivalent circuit, is given as,

$$\frac{1}{Z} = \frac{1}{R} - \frac{1}{iX_C} \tag{28}$$

$$\frac{1}{Z} = \frac{1}{R} + \frac{\mathrm{i}}{X_C} \tag{29}$$

$$\frac{1}{Z} = G + i\omega C \tag{30}$$

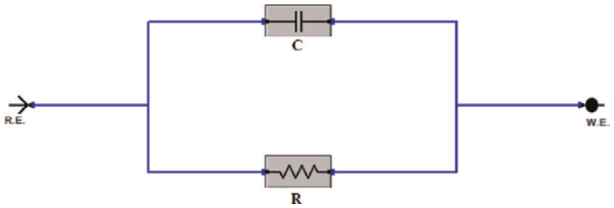

Figure 1.
An equivalent circuit for a homogeneous system.

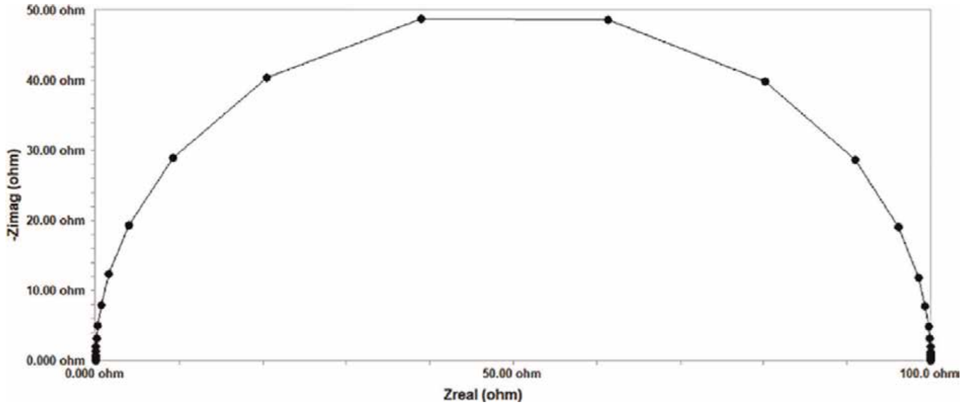

Figure 2.
Nyquist plot for the equivalent circuit proposed for homogeneous system (arbitrarily assumed value for R *is 100 Ω and* C *is* 5×10^{-6} *F).*

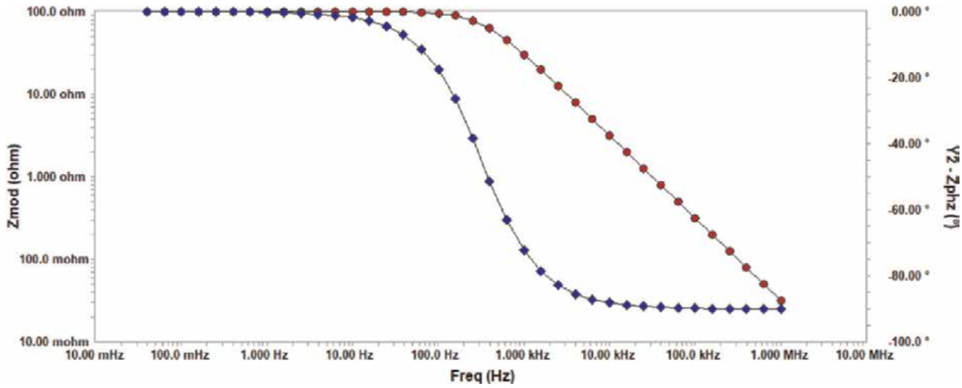

Figure 3.
Bode impedance and phase angle plots for the equivalent circuit proposed for homogeneous system (arbitrarily assumed value for R *is 100 Ω and* C *is* $5 \times 10-^{6}$ *F).*

$$Z = \frac{1}{G + i\omega C} \tag{31}$$

Conductance (G) and capacitance (C) of the homogeneous material describe its ability to conduct and store electric charge respectively. If the homogeneous material is considered as a slab of cross-sectional area 'A' and thickness 'l', these properties are given by the following expressions,

$$G = \sigma \frac{A}{l} \tag{32}$$

$$C = \varepsilon \frac{A}{l} \tag{33}$$

Where σ and ε are conductivity and permittivity of the homogeneous system respectively.

From Eqs. (27) and (31),

$$\frac{1}{G + i\omega C} = \frac{E_0}{I_0}(\cos\varphi + i\sin\varphi) \tag{34}$$

$$\frac{1}{G + i\omega C} = |Z|(\cos\varphi + i\sin\varphi) \tag{35}$$

$$G + i\omega C = \frac{1}{|Z|}(\cos\varphi - i\sin\varphi) \tag{36}$$

Therefore,

$$G = \frac{1}{|Z|}\cos\varphi \tag{37}$$

$$C = -\frac{1}{|Z|\omega}\ \sin\varphi \tag{38}$$

Using the above equations, we can measure the thickness of the homogeneous material.

Inspection of the above equation reveals that the impedance of the homogeneous material is dispersed with frequency and the dispersion is more pronounced for the frequencies greater than G/C,

$$\omega = \frac{G}{C} \tag{39}$$

Giving the condition at which, the impedance measurement provides the most accurate estimates of both properties. This characteristic frequency of the homogeneous system is called 'natural frequency' of the system.

A heterogeneous system can be considered to consist of a number of different materials or slabs sandwiched together. The total impedance of such a system is given as,

$$Z_{\mathrm{N}}(\omega) = \sum_{n=1}^{N} \frac{1}{\mathrm{G}_n + i\omega C_{\mathrm{n}}} \tag{40}$$

Each slab in the heterogeneous system has its own natural frequency defined by the expression $\omega = \frac{G}{C}$. If the magnitudes of impedance of corresponding N slabs are sufficiently different, then these slabs can be easily identified within the combined dispersions immediately.

For example, using the last expression, the total impedance of a heterogeneous system consisting of two different materials or slabs (P and M), the impedance dispersion can be written as,

$$Z_{\mathrm{N}}(\omega) = \frac{1}{G_{\mathrm{P}} + \mathrm{i}\omega C_{\mathrm{P}}} + \frac{1}{G_{\mathrm{M}} + i\omega C_{\mathrm{M}}} \tag{41}$$

Dispersion of conductance (G) and capacitance (C) with frequency are obtained by simplifying this equation as,

$$G = \frac{G_{\mathrm{M}}G_{\mathrm{P}}(G_{\mathrm{M}} + G_{\mathrm{P}}) + \omega^2\left(C_{\mathrm{M}}^2 G_{\mathrm{P}} + C_{\mathrm{P}}^2 G_{\mathrm{M}}\right)}{(G_{\mathrm{P}} + C_{\mathrm{M}})^2 + \omega^2(C_{\mathrm{P}} + C_{\mathrm{M}})^2} \tag{42}$$

$$C = \frac{C_{\mathrm{M}}G_{\mathrm{P}}^2 + C_{\mathrm{P}}G_{\mathrm{M}}^2 + (\omega^2 C_{\mathrm{M}}C_{\mathrm{P}})(C_{\mathrm{P}} + C_{\mathrm{M}})}{(G_{\mathrm{P}} + C_{\mathrm{M}})^2 + \omega^2(C_{\mathrm{P}} + C_{\mathrm{M}})^2} \tag{43}$$

The solid-state proton conducting electrolytes can be synthesized by simple solution crystallization method. The Nyquist plots recorded will not be straight forward to give the electrical properties of solid-state proton conductors. Equivalent circuits are used to derive the electrical properties of solid-state electrolytes. The equivalent circuit that fits well with the Nyquist plots will also provide the nature of arrangement of different dielectric slabs inside the soild-state protonic conductor. The mechanism for proton conduction could be derived from the temperature studies.

3. Determination of molecular mass using the electrochemical impedance spectra of solid-state proton conductors

Vapor pressure is a characteristic property of a substance in the condensed phase at constant temperature. It is the pressure exerted by the vapor molecules of a substance on the surface of the condensed phase of the same substance, when the vapor molecules are in equilibrium with its condensed phase at constant temperature. The vapor pressure of a liquid at constant temperature is constant and increases with temperature. At one temperature the vapor pressure of the liquid becomes equal to atmospheric pressure at which the liquid boils and temperature is called boiling point of the liquid. At the same temperature the vapor pressure of a liquid decreases when a non-volatile solute is dissolved in it which is called lowering of vapor pressure of the solvent. The proton conducting ability of coordination polymers and MOFs depends on the humidity levels or water vapor level in an environment. Greater the humidity level greater will be the proton conductivity. The proton conductivity of a coordination polymer or MOF is measured from the charge transfer resistance (R_{ct}) value obtained from EIS [34–36]. The charge transfer resistance measured using EIS is inversely proportional to proton conducting of the CPs or MOFs, which in turn directly proportional to humidity level or moisture level in the atmosphere.

Therefore, the charge transfer resistance (R_{ct}) of CPs or MOFs in the presence of known volume of pure water or protic solvents, measured in a closed container,

$$R_{\mathrm{ct}} \,\alpha\, \frac{1}{P^0} \tag{44}$$

Where P^0 is vapor pressure of pure protic solvent.

The charge transfer resistance measured after dissolving a known weight of solute in the same volume of water or protic solvents in the closed container at same temperature,

$$R'_{\mathrm{ct}} \,\alpha\, \frac{1}{P} \tag{45}$$

Where P is vapor pressure of solvent in solution
From Raoult's law

$$P = P^0 X_1 \tag{46}$$

or

$$X_1 = \frac{P}{P^0} \tag{47}$$

Where X_1 is mole fraction of protic solvent.
Therefore

$$X_1 = \frac{R_{ct}}{R'_{ct}} \tag{48}$$

$$\frac{n_1}{n_1 + n_2} = \frac{R_{ct}}{R'_{ct}} \tag{49}$$

Where $n_1$and n_2 are number of moles of solvent and solute respectively.

$$M_2 = \frac{W_2 M_1 R_{ct}}{W_1 \left(R'_{ct} - R_{ct}\right)} \tag{50}$$

Using Eq. (50) the molecular weight of the solute can be calculated.

This method is also applicable for determining molecular weight of the substances which are insoluble in water but soluble in methanol or ethanol, since some CPs or MOFs showing reversible proton conductivity in CH_3CH_2OH are also reported [35, 36].

4. Conclusion

The measurement of vapor pressure of solvents in pure form and in solutions is a tedious one in Ostwald and Walker's method of determining molecular mass from relative lowering of vapor pressure, the proposed method is easy with simple experimental setup and can be used to determine the molecular weight of substances and polymers soluble in protic solvents.

Abbreviations

EIS	electrochemical impedance spectroscopy
MOF	metal organic framework
R	resistance
C	capacitance
E	voltage
I	current

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Chapter 2

Development of An Impedimetric Nanoplatform for Cu(II) Detection Based on Carbon Dots and Chitosan Nanocomposite

Mosaab Echabaane and Chérif Dridi

Abstract

In this chapter, an impedemitric sensor based on carbon dots (CDs) and chitosan (CS) nanocomposite for Cu (II) detection has been studied. The synthesized carbon dots were characterized by TEM, FTIR, XRD, UV-visible, and PL. The obtained carbon dot/chitosan/GCE structure was characterized by scanning electron microscopy (SEM) and electrochemical impedance spectroscopy (EIS). The behavior, interface processes of GCE/electrolyte, and sensor properties of the studied structures were investigated. In particular, the performance of the proposed impedimetric sensor to Cu ions, such as sensitivity, dynamic range, detection limit, and selectivity, was studied. Subsequently, the proposed sensor was applied for the determination of copper ions in real water samples.

Keywords: carbon dots, chitosan, nanocomposite, copper(II), Impedimetric sensors, introduction

1. Introduction

Essential transition metals such as copper, zinc, iron, and manganese play vital roles in several biological processes [1]. One of the essential transition metal ions, copper is the most abundant metal ion in the human body. It contributes to blood formation, connective tissue development, transcriptional events, and the functioning of several enzymes [2, 3]. However, exposure to an excess level of copper ion can cause gastrointestinal disturbance, neurodegenerative diseases, and liver and kidney damage [4]. The maximum content of Cu^{2+} ions in drinking water is limited to 30 nM by the World Health Organization (WHO) [5].

Hence, it is very important to develop a simple, fast, economically advantageous, selective, and sensitive analytical technique for the determination of copper in aquatic environments to avoid side effects. Notably, numerous techniques have been used to determine the copper ion, including atomic absorption spectroscopy, chromatography spectrofluorimetry, and spectrophotometry [6–9]. These techniques can provide good accuracy and sensitivity, but they have various disadvantages, such as expensive equipment, time-consuming operation, and an inability to do onsite analysis. Thus, their use is restricted. Therefore, to circumvent these limitations, electrochemical sensors have attracted great attention for detecting trace levels of copper ions due to their inherent advantages, such as simple operation, low-cost, rapidity, excellent sensitivity, and selectivity [10]. Notably, the presence of numerous advanced electrode modified nanomaterials improved sensing performance significantly [11–15]. Amongst such nanomaterials, nanocomposites have been employed in electrochemical sensors for environmental analysis [16–21]. Nowadays, analytical measurements are altered by nanocomposites of various sizes, shapes, and compositions. Chitosan as well as carbonaceous nanoparticles have an interest in the construction of electrochemical sensors [22–28]. Chitosan exhibits interesting properties due to its nontoxicity, film-forming ability, high permeability, adsorption ability, and biocompatibility. It has been extensively used as a good biomaterial in designing sensors [29, 30]. As compared to other carbonaceous nanoparticles, carbon dots have considerable importance because of their simple synthetic routes, high surface area, high biocompatibility, and high conductivity [31, 32]. The aim of this chapter is to develop an impedimetric sensor for copper ion detection based on carbon dots and chitosan nanocomposite. The synthesized carbon dots were characterized by transmission electron microscope (TEM), X-ray diffraction (XRD), FTIR spectroscopy, UV–Vis absorption, and photoluminescence spectroscopy. The morphological and electrochemical properties of carbon dot/chitosan/GCE structure were investigated by scanning electronic microscopy (SEM) and electrochemical impedance spectroscopy (EIS). The weather sensors' performance was discussed. The proposed sensor can be used to determine copper ions in real water samples.

2. Experimental details

2.1 Reagents

Copper sulfate ($CuSO_4$, ≥ 99.9%), mercury nitrate monohydrate ($Hg(NO_3)_2.{\cdot}H_2O$, ≥ 99.9%), cadmium nitrate tetrahydrate ($Cd(NO_3)_2,{\cdot}4H_2O$, ≥ 99%), lead nitrate ($Pb(NO_3)_2$, ≥ 99%), nickel nitrate hexahydrate ($Ni(NO_3)_2{\cdot}6H_2O$, ≥ 98.5%), zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$, ≥ 98%), sodium chloride (NaCl, ≥ 99%), calcium chloride ($CaCl_2$, ≥ 96%), potassium chloride (KCl, ≥ 99%), glucose (≥ 99.5%), sulfuric acid (H_2SO_4, ≥ 99.9%), Deionized (DI) water, sodium hydroxide (NaOH, ≥ 97%), ammonium acetate (CH_3COONH_4, ≥ 98%), and chitosan (CS, ≥ 85%). All chemicals used in this work were purchased from of Sigma- Aldrich.

2.2 Instrumentations

For further investigation of the synthesized carbon dots (CDs), an X-ray diffractometer (Bruker AXS D8 Advance), Fourier Transform Infrared Spectroscopy (FTIR) (Perkin Elmer, Spectrum Two), UV–vis spectrophotometry (Specord 210 Plus), and a spectrophotometer (Perkin Elmer) were employed.

Scanning Electron Microscopy (SEM) (Jeol JSM-5400 emission) was used to characterize the CS-CDs film.

The electrochemical impedance measurements were carried out using an impedance analyzer (EC-LAB BIOLOGIC) with a sinusoidal excitation signal amplitude of 10 mV and a 0.01 Hz-100 kHz frequency range. The polarization potential used for

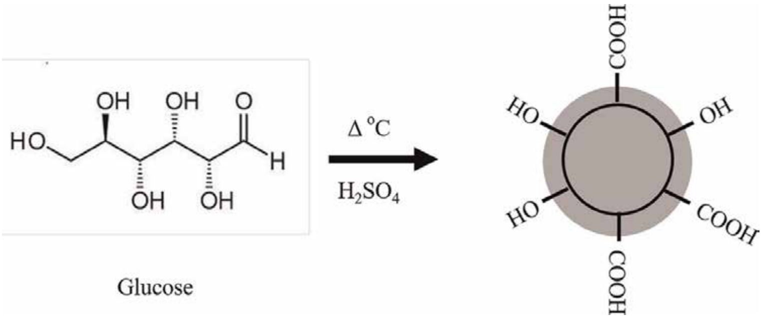


Figure 1.
Schematic representation of CDs formation from glucose.

these measurements was optimized at −600 mv. An aqueous ammonium acetate (solution of 0.1 M, with pH = 7, was used as an electrolyte in the electrochemical cell formed by three electrodes: a working electrode (GCE), a platinum counter electrode, and an Ag/AgCl electrode (SCE).

2.3 Synthesis of CDs

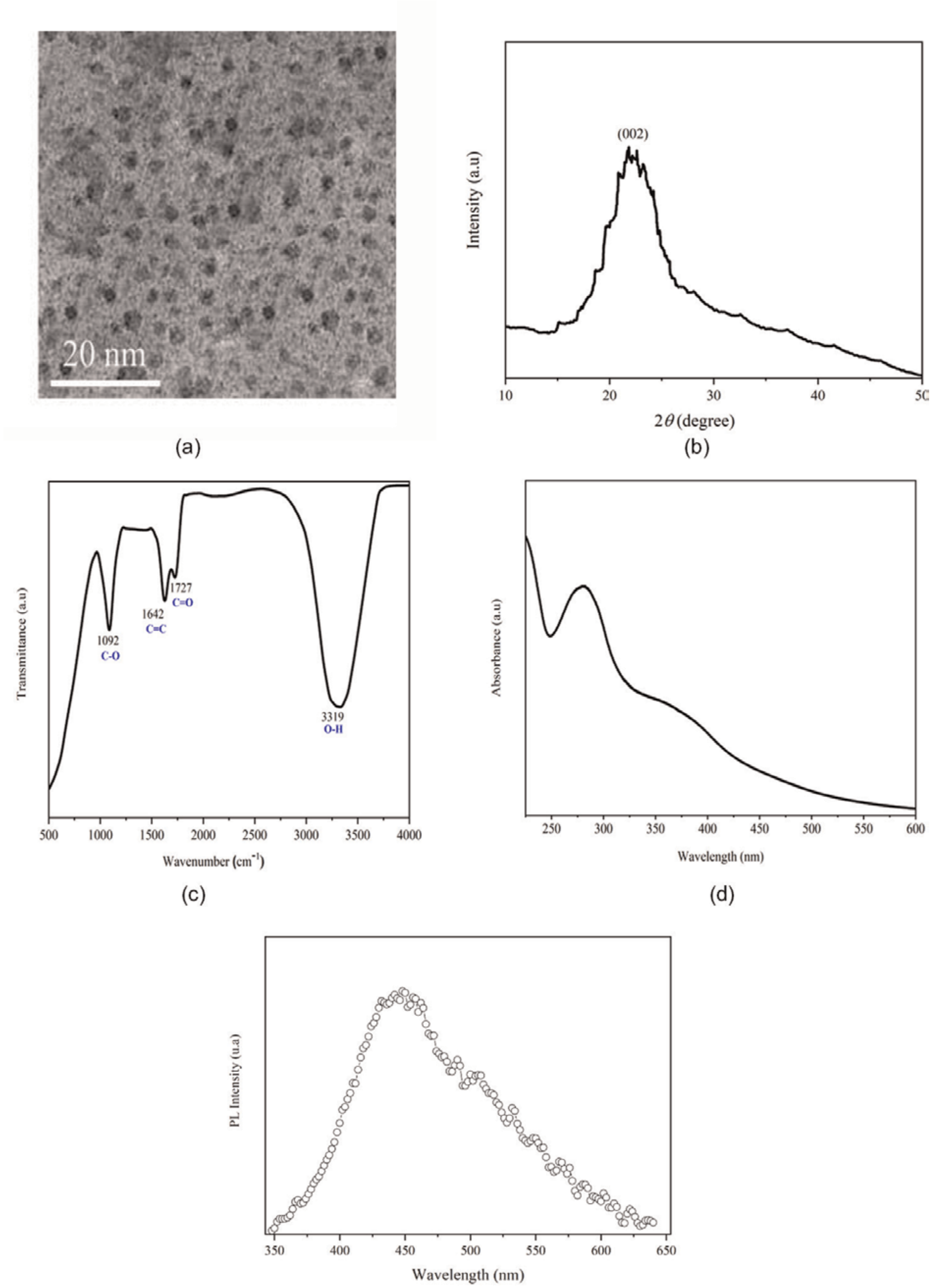
Glucose (3 g) and H_2SO_4 (1 ml) were dissolved in DI water (10 ml). Then, the mixed solution was heated for 30 min at a temperature of 100°C (**Figure 1**). The solution changed from colorless to yellow-brownish, signaling the formation of CDs. Then, this latter was neutralized using NaOH. In order to remove impurities, the prepared solution was centrifuged (14,000 rpm), filtered, and dried for 6 hours at a temperature of 80°C [33].

2.4 Preparation of modified glassy carbon electrode (GCE)

The surface of the GCE electrode was polished with 0.05 μm and 0.3 μm alumina powder. Then, the electrode was washed successively with distilled water, ethanol, and distilled water in an ultrasonic bath, and dried at room temperature. For the preparation of the CDs-CS nanocomposite solution: 0.5 mL of 1.0% CS solution was added to 1.5 mL of CDs solution by ultrasonication. Then, 2 μL of nanocomposite was dropped onto the surface of GCE and dried in the oven at 60°C for 30 min.

3. Characterization of CDs and CS-CDs/GCE

The TEM image of the synthesized CDs is shown in **Figure 2(a)**. It is noticed that the CDs are spherical in shape and their mean size is approximately 3.2 nm. The X-ray diffraction pattern of CDs is shown in **Figure 2(b)**. It exhibited a broad peak at $2\theta = 22.35^{\circ}$, corresponding to the (002) hkl plane of the graphitic structure (JCPDS card no. 26–1076). The FTIR transmittance spectrum of the CDs is presented in **Figure 2(c)**. The peaks at 3319 cm^{-1}, 1727 cm^{-1}, 1642 cm^{-1}, and 1092 cm^{-1} were assigned to O-H, C = O, C = C, and C-O. These indicate that carboxyl and hydroxyl groups may be found on the surface of CDs. The UV–Vis absorption spectrum of CDs exhibited two absorption bands located at 280 nm and 375 nm (**Figure 2(d)**), which are ascribed to



(a) (b)

(c) (d)

(e)

Figure 2.
Characterization of CDs: (a) TEM images, (b) XRD pattern, (c) FTIR spectra, (d) UV–visible spectra, (e) PL spectra.

π-π* and n-π* respectively. **Figure 2(e)** presents the PL spectra of the CDs. The fluorescence emission peak of CDs located at 470 nm is a blue light luminescent spectral region.

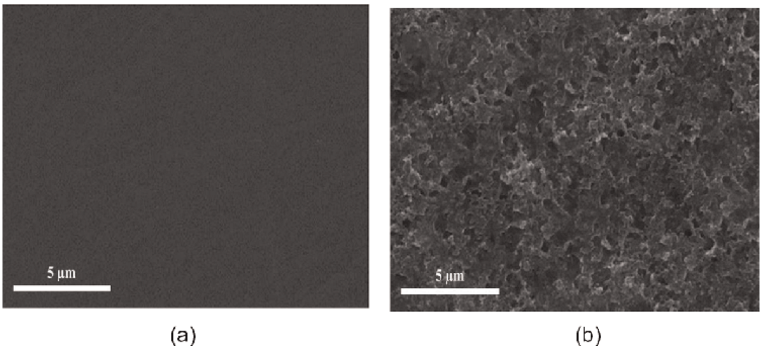


Figure 3.
Images SEM of (a) bare GCE electrode, (b) CS-CDs nanocomposite/GCE electrode.

SEM images of the bare GCE and the CS-CDs/GCE film are shown in **Figure 3**. It exhibits that the bare GCE electrode has a flat and smooth surface (**Figure 3(a)**), whereas the surface of the CS-CDs nanocomposite is rough with a few apparent pores (**Figure 3(b)**). This result shows that the CS-CDs film was deposited on the GCE surface.

4. EIS characterization of the CS-CDs/GCE electrode

Electrochemical impedance spectroscopy is a sensitive tool for investigating the characteristics of the electrode-solution interface. The Nyquist diagrams of the bare GCE electrodes and functionalized CS-CDs film are shown in **Figure 4**. The Nyquist of CS-CDs/GCE electrodes is higher than that of bare CGE electrodes. This is due to the immobilization of the film. Besides, **Figure 4** shows that the Nyquist plot of the CS-CDs/GCE structure is a single semicircle with a large diameter. This might be explained by the fact that it is an overlapping of two semicircles.

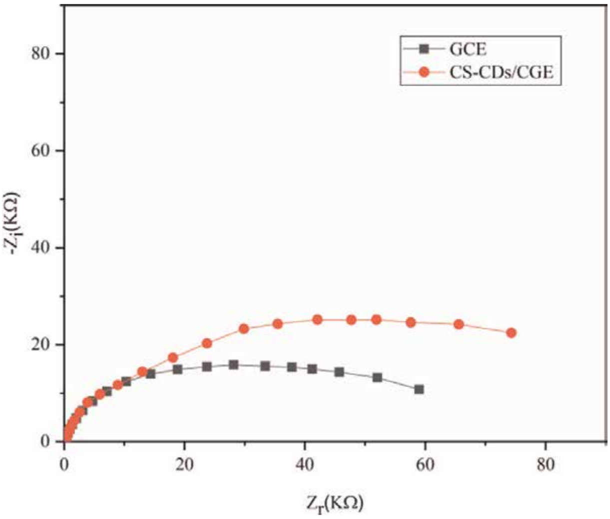


Figure 4.
Impedance spectra of bare GCE, and CS-CDs/GCE structures.

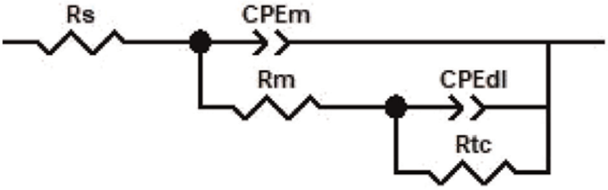


Figure 5.
Equivalent circuit used to fit the impedance spectra.

The EIS spectrum of the CS-CDs/GCE electrode was simulated with the equivalent electrical circuit presented in **Figure 5**. This circuit is an association of three components.

This circuit is an association of three components.

- The first one, in the low-frequency range, is used to represent the GCE/electrolyte interface, including in a parallel combination the constant phase element CPE_{dl} that substitutes the electrical double layer capacitance (C_{dl}) with the charge transfer resistance R_{ct}.

- The second component at higher frequencies is attributed to the film/electrolyte interface formed by a parallel combination of the resistance R_m and the capacitance CPE_m. Where R_m refers to the resistance of the film and CPE_m donates the constant phase element capacitance, is assigned to the electric capacitor consisting of the metal and the electrolyte, with the film as the dielectric.

- The last component is the series resistance of the electrolyte solution.

The two constant phase elements (CPE) are non-ideal capacitances and can be expressed by (Eq. (1)):

$$Z_{CPE} = {}^{1}\!/_{Q(j\omega)^{n}} \qquad (1)$$

where Q is a constant, j is the imaginary number, ω is the angular frequency, and $0 < n < 1$. CPE becomes more capacitive, when the value n tends to be 1.

Finally, the experimental EIS measurements were fitted using the ZView software. The different fits were made with a total error value of $\chi 2 \approx 10^{-4}$.

5. Impedance characterization for the detection of Cu ion

The electrochemical impedance response of copper at the CS-CDs/GCE is characterized using EIS. The Nyquist spectra of the CS-CDs film obtained after the addition of different concentrations of copper ions is shown in **Figure 6**.

It is noted that the Nyquist plot of the CS-CDs film clearly decreases as a function of Cu^{2+} concentration from 10^{-9} M to 10^{-5} M. The response of the CS-CDs modified electrode to copper ions is due to a complexation process. This is induced by coordination between the donor groups of nanocomposites and the copper ions. In fact, the

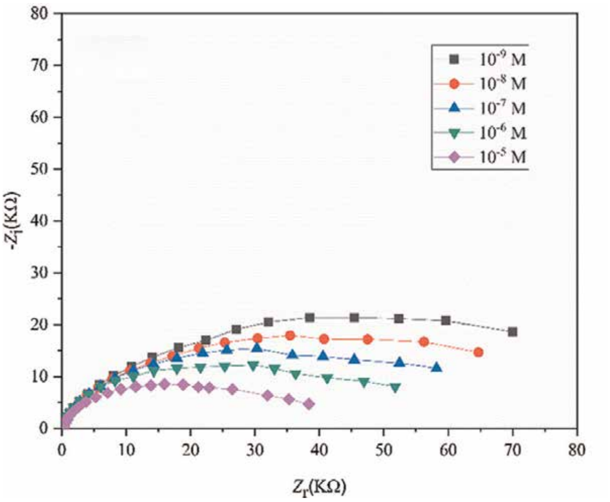


Figure 6.
Impedance spectra for different copper concentrations of CS-CDs/GCE.

$[Cu^{2+}]$ (M)	R_s (kΩ)	CPE_m (μF)	n_1	R_m (kΩ)	CPE_{dl} (μF)	n_2	R_{ct} (kΩ)	χ2 (10^{-4})
10^{-9}	0.11	1.70	0.90	17.40	9.20	0.59	67.24	2.7
10^{-8}	0.10	1.73	0.89	16.24	10.01	0.60	56.56	6.8
10^{-7}	0.11	1.60	0.88	15.01	9.22	0.60	45.05	7.3
10^{-6}	0.12	1.56	0.90	13.40	9.52	0.61	36.16	2.1
10^{-5}	0.13	1.66	0.88	12.50	10.10	0.62	27.72	4.2

Table 1.
Fitting parameters of CS-CDs/GCE versus copper concentrations.

interaction of the copper ions (Lewis acid, acceptor electrons) with the amide and hydroxyl groups of CS (Lewis base, donor electrons) is possible by the acid–base reaction. Furthermore, the negatively charged carboxyl and hydroxyl groups existing on the surface of CDs enable interactions with the positively charged copper ions. Thus, the interaction mechanism is evolved by an electrostatic interaction that occurs between the copper ions and the nanocomposite film.

Table 1 summarizes the circuit parameters of the CS-CDs film as determined by the fit to the previous equivalent circuit.

6. Physical meaning of parameters obtained from the Nyquist plots

Figure 7 shows the plot of the film resistance versus $p[Cu^{2+}]$. The value of film resistance (R_m) decreases when increasing the concentration of copper. This is may be explained by the increase in the ionic conductivity of the CS-CDs film.

Figure 8 represents the variation of the charge transfer resistance (R_{ct}) parameters upon the addition of Cu^{2+}. It was observed that R_{ct} decreased with increasing Cu^{2+} concentration. This can be due to improvement in the charge transfer at the GCE/CS-CDs electrode electrolyte interface.

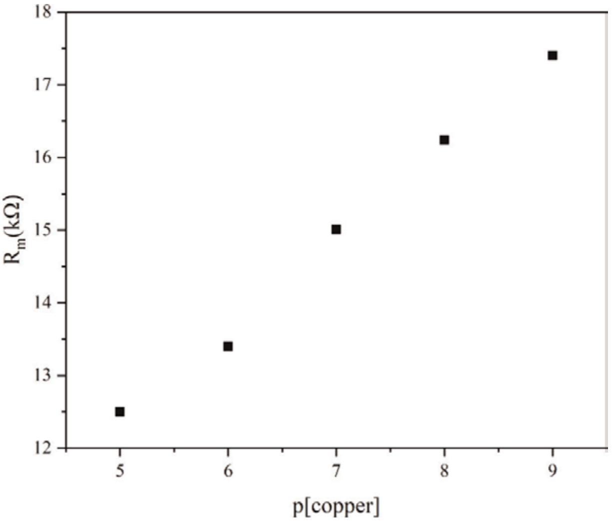


Figure 7.
Variation of the R_m of CS-CDs/GCE.

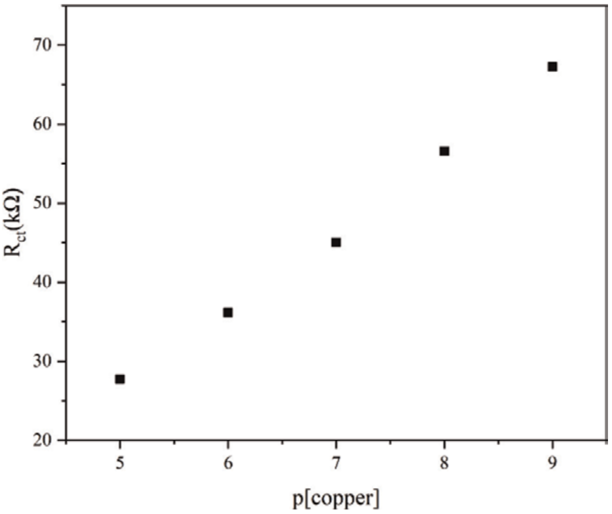


Figure 8.
Variation of the R_{ct} of CS-CDs/GCE.

Electrode/p [Cu^{2+}]	**R_m (KΩ)**	**R_{ct} (KΩ)**
CS-CDs/GCE	1.3	9.9

Table 2.
R_m and R_{ct} slope values of CS-CDs/GCE.

Table 2 presents the R_m and R_{ct} slope values. It is noted that the R_{ct} slope value is higher than the R_m slope value. This can indicate that the recognition process was at the electrolyte/GCE interface. Therefore, the R_{ct} is provided as the primary factor determining the sensors' response.

7. Analytical performance of impedimetric sensors

Figure 9 shows the variation of -log(R_{tc}/R_{tc0}) as a function of copper concentration, where R_{tc0} is the charge transfer resistance value without copper ions in the solution. Here, a linear behavior with a large detection range between 10^{-9} and 10^{-5} M was observed. The equation of linear regression is -log (R_{tc}/R_{tc0}) = 0.1 × log [copper] + 0.9, where the slope is 0.1 of the sensor sensitivity. The detection limit of our copper sensor was ≈ 5×10^{-10} M, according to the formula LOD = (3 × standard deviation)/slope.

8. Specificity

The specificity of the GCE/CS-CDs sensor has been studied towards some interfering cations: Hg^{2+}, Cd^{2+}, Pb^{2+}, Ni^{2+}, Zn^{2+}, Na^{+}, Ca^{+}, and K^{+}. **Figure 10** shows the relative signal change $\left(\left[\frac{R_{tc-R_{tc0}}}{R_{tc0}}\right]\right)$ as a function of the interfering cations. The results noted that GCE/CS-CDs displayed good selectivity for Cu^{2+} in the presence of other ions.

9. Determination of copper ion in water samples

To evaluate the practical feasibility of the GCE/CS-CDs sensor, it is applied for the detection of copper in water samples (tap water). 1 mL of sample solution (tap water) is added to 1 mL of electrolyte (acetate ammonium at pH 7). The impaled copper amounts are of 10^{-6} M and 10^{-8} M. The recovery percentage is calculated as $\frac{Found\ (M)}{Added\ (M)} \times 100$. It can be seen in **Table 3** that the recoveries are less than 5%. Therefore, the proposed GCE/CS-CDs impedimetric sensor is efficient for the detection of Cu^{2+} ions in real water samples.

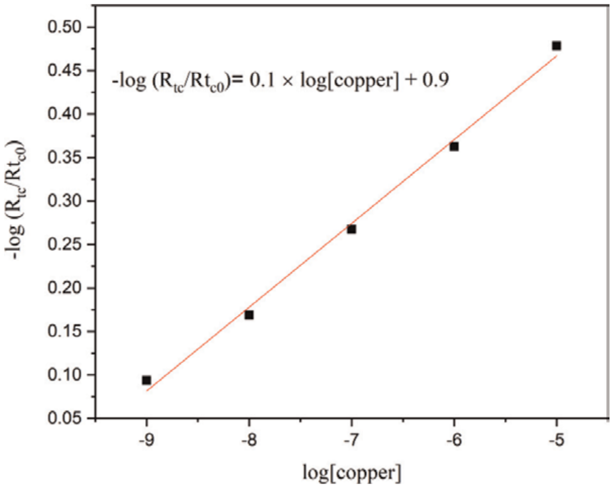


Figure 9.
Calibration curve of -log (R_{tc}/R_{tco}) versus log ([copper]).

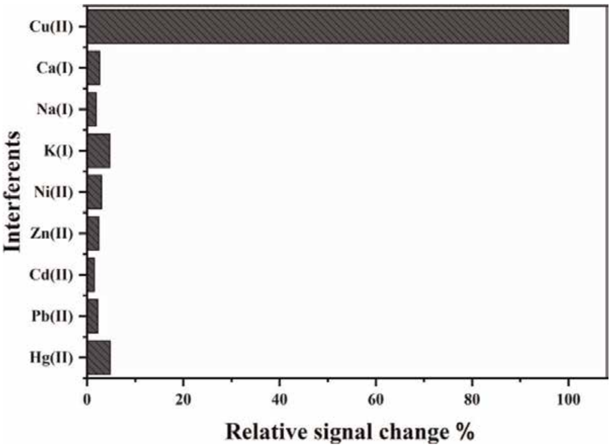


Figure 10.
Influence of interferences (10^{-4} M) on the response copper (10^{-6} M).

Sample	Added (M)	Found (M)	Recovery (%)	RSD (%)
Tap water	10^{-8}	9.70×10^{-9}	97.0	4.12
	10^{-6}	1.02×10^{-6}	102. 0	1.47

Table 3.
Determination of copper ion in tap water samples (n = 3).

10. Conclusion

In this chapter, we fabricate a highly sensitive, selective, impedimetric sensor for the determination of copper-based on carbon dots/chitosan nanocomposite modified glassy carbon electrode. A simple, fast, low-cost method to prepare carbon dots using glucose by heating has been demonstrated. The electrochemical performance of the copper sensor was examined by electrochemical impedance spectroscopy. Based on the excellent properties of CS-CDs/GCE, the impedimetric sensors had high sensitivity, a low limit of detection, and good selectivity. The newly developed impedimetric sensor for the determination of copper ions was applied in water for real samples with satisfactory results. Thus, this indicates that these sensors offer promising potential for water monitoring.

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Section 2

Nanoparticle Enhanced Voltammetric Applications

Chapter 3

An Overview of the Synergy of Electrochemistry and Nanotechnology for Advancements in Sensing Applications

Rajni Bais

Abstract

Electrochemical sensors have been widely employed in diverse domains of electrochemical analysis, biosensing, drug administration, healthcare, agriculture, and so on because of their special potential features that are closely related to their high selectivity, sensitivity and cycling stability. Various electrochemical techniques employed to transduct biological or chemical signal to electrical signal are voltammetry, conductometry, potentiometry and amperometry. Due to the high demand of global market and human interest in having a device to check the concentration of species in different samples that is simple and fast, researchers have been engaged in a fierce competition to design and build new sensors and biosensors in recent years. The performance of the sensors can be considerably improved by modifying the electrode surfaces using diverse nanomaterials. Further, electrochemical biosensors are promising diagnostic tools that can find biomarkers in bodily fluids including sweat, urine, blood or excrement. Nanoparticles have found propitious role in biosensors, because they aid in functions like immobilisation of molecules, catalysis in electrosynthesis, facilitation of electron transfer between electrodes and biomolecules and labelling of biomolecules. The advance in the research amalgamating electrochemistry and nanotechnology for electro (bio) sensing applications is the beginning of a promising future for mankind and global market.

Keywords: nanomaterials/ nanoparticles (NPs), electrochemical, sensor, biosensor

1. Introduction

The information carried by an electrochemical redox reaction (the reaction between electrode and analyte) is converted into an applicable quantitative or qualitative signal by electrochemical sensors. The sensors can generate electronic outputs in the form of digital signals that can be analysed further [1]. Depending on the mechanism involved in recognition, the sensors can be chemical or biological (biosensor). Electrochemistry is found to play a crucial role in medical technology, forensics, food, environmental sciences, defence settings, agriculture, among others [2, 3].

Electrochemical sensors and detectors are very appealing for applications, viz. on-site monitoring of environmental contaminants, addressing varied environmental needs, health monitoring, testing of adulterants in food samples, forensic drug analysis, and many more. Many of the specifications for on-site environmental scanning are met by sensing devices. They are intrinsically sensitive and selective to electroactive species and are fast, reliable, portable, compact and economical [4]. A transducer and a chemical recognition system are the two primary components of an electrochemical sensor, and collectively these two components constitute a sensing electrode. Other electrodes may also be used in electrical measurements like reference and counter electrodes (CEs) [5]. In electrochemical sensors, a potential difference is applied in between working and counter electrodes, and on the basis of redox reactions caused by the analyte at the electrode's interface, the resulting current response is measured. Voltammetry, conductometry, potentiometry, or amperometry can be used to study the transduction of biological or chemical signal to electrical signal. Since their invention, the electrochemical sensors are being studied extensively for their applications in efficient biosensors, immunosensors, special electrode design automated systems, and microelectrodes, etc. [6]. With the recent advancements in the designing and synthesis of nanomaterials along with the evaluation of intrinsic properties of nanoparticles (NPs) based on carbon [7] and many other types of base materials, the engine of nano-electrochemistry has begun to gain speed in the field of electrosensing.

2. Electrochemical signal transduction techniques

A transduction process involves efficient capture of biological or chemical recognition signals and their conversion into electrical, gravimetric, optical, electrochemical or acoustic signals. There are four main types of electrochemical signal transduction techniques that can be used in analysis, depending on the reaction under investigation:

i. Voltammetry

ii. Potentiometry

iii. Amperometry

iv. Conductometry

Each of these techniques is described in the following section in brief.

2.1 Voltammetry

Voltammetry is an electroanalytical method that obtains information about an analyte by modifying a potential and then measuring the resultant current. Here, the potential sweep is applied between working electrode (WE) and counter electrode (CE) with respect to reference electrode (RE), and the current so produced is measured as an analytical signal. Because the potential can be varied in many ways, many forms of voltammetry are available, such as direct current (DC) polarography, differential pulse polarography (DPP), differential staircase voltammetry, cyclic voltammetry, linear sweep voltammetry, normal pulse, and reverse pulse voltammetry [8–10]. Cyclic voltammetry is one of the most widely used electroanalytical methods.

2.2 Potentiometry

In potentiometry, the analytical signal is the open-circuit voltage between working electrode and reference electrode. Depending on the concentration of the analyte, this signal can increase or decrease [11]. Here, Nernst equation governs the relationship between concentration and potential. Useful information about ion activity in redox reaction is provided by potentiometry [12]. Ion-selective electrodes (ISEs) are often employed to achieve low detection limits for potentiometric sensors. Also the potentiometric sensors are ideal for measuring low concentrations of analyte in small sample volumes, because they do not chemically influence the sample [13].

2.3 Amperometry

It is similar to voltammetry with the difference that here a constant or stepped potential is employed to measure the current as electric signal, whereas in voltammetry, controlled variation of voltage is done to measure current. In fact, some scientists classify voltammetry as a type of amperometry only, because both these techniques employ measurement of current upon variation of potential. Here, a continuous measurement of current is done, and this current is produced by oxidation or reduction of an analyte in a biochemical reaction [9, 14]. Here, the peak value of the measured current (over a linear range of potential) is a direct indication of the bulk concentration of the electroactive species [15, 16]. Glucose biosensor is one of the most widely employed amperometric sensors. It is often claimed by many scientific practitioners that amperometric sensors are superior to potentiometric sensors when it comes to sensitivity [17].

2.4 Conductometry

Conductometry sensors are used to measure concentrations of electrolyte in aqueous solutions. The recorded electrical resistance of the solution is used to calculate the molar concentration of an identified electrolyte that causes solution conductivity [18]. Conductivity can be measured directly with a conductivity metre or indirectly with conductometric titration. Electrolyte conductometric analysis has long been used. Conductometric methods were used to analyse mineral waters and salt solutions by Henry Cavendish and Andreas Baumgartner [19].

3. Types of sensors

Sensors can be classified into two broad categories depending on their application or mode of transduction, as follows:

3.1 Types of sensors on the basis of application

i. **Chemical Sensors:** A chemical sensor converts an analyte's physical and/or chemical properties into a measurable signal [20]. The intensity of the measurable signal is normally proportional to concentration of the analyte [21]. The chemical sensors can further be classified as follows:

a. **pH Sensors:** These sensors are sensitive to even minute changes in pH of a solution and are used to measure acidity and alkalinity in aqueous and other solutions. When used properly, these devices can guarantee the safety and quality of a product as well as the processes that take place in a wastewater treatment or different manufacturing units in industries [22].

b. **Gas Sensors:** These sensors are employed to detect the type and amount or concentration of a gas in a specific environment. Any change in the composition of gas can be linked with electric signals through these sensors [23].

c. **Alcohol Sensors:** Technically known as a MQ3 sensor, an alcohol sensor is a non-contact breath sensor that is mostly used to detect ethanol in the air. When a drunk person breathes near an alcohol sensor, the sensor detects the ethanol in his breath and provides an output based on the concentration of alcohol [24].

d. **Ion-selective Sensors:** Ion-selective electrodes are a type of potentiometric devices. Many electrode systems exhibit a Nernstian relationship between the activity of a redox species in solution and measured electrode potential. The affinity of surface of the membrane for a typical redox species as well as minimum ion conductivity over the membrane are important requirements for the advancement of ion-selective electrodes [25].

e. **Humidity Sensors:** A humidity sensor is a device that detects, measures, and reports the relative humidity (RH) of air or the amount of water vapour present in a gas mixture (air) or pure gas. Humidity sensing is associated with the adsorption and desorption of water. Industrial and agricultural products are both monitored by humidity sensors. Incubators, sterilisers, and pharmaceutical processing plants all use humidity sensors [26].

ii. **Biosensors:** Biosensor is a powerful, efficient, and innovative analytical device that incorporates a biological sensing element and has a wide range of applications, like, environmental monitoring, diagnosis, biomedicine, food safety and processing, drug discovery, defence, and security [27–29]. In a biosensor, an electron exchange takes place in between layer of bioreceptor and an electrode, and this exchange of electrons (because of reduction or oxidation of the analyte) can be transduced into a readable signal [30].

3.2 Types of sensors on the basis of mode of transduction

i. **Amperometric Sensors:** The working of amperometric sensor is based on measuring current generated because of an electrochemical reaction at the electrode surface when a constant working potential is applied with respect to the reference electrode [31]. The amperometric set-up may consist of either two-electrode (WE and RE) or three-electrode (WE, RE, and CE) assembly.

ii. **Potentiometric Sensors:** These sensors are used to measure difference in potential applied between two electrodes when there is no current flowing between them. This measured potential is then used to detect or quantify the analyte of interest in the solution. In a general potentiometric sensor, the signal obeys Nernst Eq. [32].

iii. **Optical Sensors:** These are light-based sensors, which work on the principle of studying the change in wavelength of a particular light when the photosensitive analyte in the medium interacts with the recognition element [33]. Position-sensitive diode, phototransistor, photoresistor, photodiode, and diode array are some commonly used light sensors [34].

iv. **Piezoelectric Sensors:** In these sensors, environmental or mechanical energy changes are converted into electric signals or vice versa. The environmental or mechanical energy changes may include alteration in strain, vibration, pressure, force, etc. [35]. Piezoelectric sensors can be of two types, i.e. passive or active.

v. **Thermal or Calorimetric Sensors:** In these sensors, the concentration of analyte is correlated to amount of heat produced during a molecular recognition reaction. The working principle of calorimetric sensors is to detect the presence or measure the concentration of an analyte by studying the changes in enthalpy produced as a result of any physisorption process or chemical reaction in the medium under observation [36]. Calorimetric sensors are also known as chemoresistors, and the two types of chemoresistors are low-temperature chemoresistors and high-temperature chemoresistors.

4. Types of nanoparticles used in electrosensing

A nanoparticle has diameter approximately one lakh times smaller than that of a human hair strand. Nanomaterials, like in many other technological or scientific segments, have demonstrated their applicability and worthiness for electrochemical/biosensing applications. The astute use of such nanomaterials has resulted in clearly improved performance, with enhanced specificity, sensitivity, and extremely lowered limits of detection. Further, the high specific surface area of all nano-objects allows for the immobilisation of an increased number of bioreceptor units (in biosensors) [37]. The direct functionalisation of nanomaterials (during their synthesis) or coating of nanomaterials with specific functional polymers results in nanomaterials equipped with desired functions without altering their specific properties [38]. The commonly used nanoparticles in electrosensing applications are of following types:

i. **Gold nanoparticles (AuNPs)**

ii. **Quantum dots (QDs)**

iii. **Magnetic nanoparticles (MNPs)**

iv. **Carbon nanotubes (CNTs)**

A brief description of these nanoparticles is given as follows.

4.1 Gold nanoparticles

a. *Properties:* The characteristics of AuNPs, such as their optical and electronic properties, their biocompatibility, and their comparatively simple production and modification, make them of high priority and utility among the class of noble metal nanoparticles [38, 39]. The electrons of AuNPs when irradiated with light of a specific wavelength oscillate in the conduction band (resonant surface plasmons), and this optical behaviour of AuNPs makes them of immense applicability in the field of optical sensing. The use of surface plasmons resonance (SPR) transduction for sensing applications of gold nanoparticles is based on studying the changes in environment of gold films with reference to dielectric constant of propagating surface plasmons. Here, variation in intensity, angle or phase of the reflected light is used to monitor the analyte [40]. Phyto-AuNPs that are phytosynthesised with the aid of green chemistry approach are catalytically and biologically active, biocompatible, and stable. But despite their potent applications, these have not been explored sufficiently [41].

b. *Recent Research Trends:* Owing to the aforementioned properties, the use of AuNPs for the development of novel sensing techniques holds significant promises when it comes to research related to: drug determination [42–44]; anticancer and other biomedical applications [45, 46]; immuno-PCR (Polymerase Chain Reaction) assay and ELISA (Enzyme-Linked Immunosorbent Assay) [47, 48], and so on.

4.2 Quantum dots

a. *Properties:* QDs are nanoscale crystals created by scientists which are capable of electron transport. These semiconducting QDs show the property of emitting a variety of colours when UV light strikes them. These semiconductor nanoparticles have found varied applications in fluorescent biological labels, electrochemical sensing, solar cells and composites. The optical properties of a particle can be altered by controlling their size, and so, these particles can also be tuned or regulated in a way that they can absorb or emit light (colours) of specific wavelength [49]. Further, the shape (hollow/ solid), composition and structure are other crucial parameters of QDs that can affect their various properties. Another important application of QDs is as single-electron transistors. But studies have shown that these semiconductor nanoparticles may exert harmful effects on living systems in some cases [50].

b. *Recent Research Trends:* When carbon QDs are doped with heteroatoms [51], such as nitrogen [52], both sulphur and nitrogen [53], zinc [54], lanthanum [55] and $CuInS_2$ [56], then their optical/photoluminescent properties are found to improve prominently for sensing applications.

4.3 Magnetic nanoparticles

a. *Properties:* MNPs can be assimilated into transducer materials or scattered in the sample prior to being attracted to the active recognition surface of the sensor by an external magnetic field [57]. Because of the reduced number of magnetic domains in nanosized MNPs, these exhibit magnetic behaviours different than the bulk material, resulting in superparamagnetic behaviour. This means that in a very short time, magnetisation can rapidly and randomly flip directions, and when an external magnetic field is absent, the magnetisation denotes to be average zero. This is a temperature-dependent phenomenon which disappears when the magnetic moments are aligned by the application of an external magnetic field [58]. MNPs offer a highly sensitive technique of transduction in biosensors, optical sensors and electrochemical sensors [57, 58].

b. *Recent Research Trends:* In the recent times, the utility of MNPs has increased multifold. Some advanced sensing applications of MNPs are as follows: diagnosis of anticancer drug 6-mercaptopurine using cerium-based MNP as a fast-response and efficient fluorescence quenching sensor [59], Ihlamur leaves [60] and saffron flowers [61]-based biosynthesis of magnetic nanoparticles for antibacterial applications, use of silver MNPs to enhance the surface plasmon resonance signal for determination of leukocyte cell-derived chemotaxin-2 which is an important biomarker for the diagnosis of liver fibrosis [62], green synthesis of Fe_3O_4 nanoflakes and its utility as an electrocatalyst for the voltammetric determination of ascorbic acid [63], diversified biomedical applications of multifunctional MNPs [64], and many more.

4.4 Carbon nanotubes

a. *Properties:* Owing to the distinctive electronic properties (high conductivity and large surface-to-volume ratios) of CNTs, in recent years these have been widely investigated for their utility as electrosensing devices. Non-functionalised CNTs are not very selective for many chemicals, but functionalisation with different chemical moieties can be done to surpass this drawback. For their electrosensing applications, the CNTs can be functionalised with specific metals or functional groups [65]. The adsorption and binding of specific molecules on the surface of carbon nanotubes result in change in potential– current curves, and this forms the working principle of these devices [66]. The properties of CNTs as sensors are mainly dependent on their shape. The diameter of CNTs is of one to several nanometres, and their length may be of several microns. Well-ordered hexagonal carbon cycles or graphite rolls constitute their surface [67]. One to multilayered tubulenes (with closed or open terminations) may be formed, depending on the conditions of synthesis of these nanotubes.

b. *Recent Research Trends:* The characteristic properties of CNTs allow nanotechnology to provide promising platforms for sensing applications. Some of the emerging researches done in this field are as follows: designing of terahertz metasurface-based single-walled CNT [68], synthesis of sensing piezoresistive materials with carbon nanotubes [69], diagnosis of pancreatic and liver cancer employing CNTs [70], etc.

5. Role or functions of nanoparticles in (bio) sensing techniques

The various roles of NPs in (bio) sensing techniques are as follows.

i. **Immobilisation of molecules:** Chemical functional groups or biomolecules (antibody, DNA, enzymes, and cells) that are immobilised on transducer surface during the construction of a (bio) sensor decide for its stability, sensitivity, selectivity and reproducibility [71]. Hence, a number of methods are employed for immobilisation of desired (bio) molecules onto solid support materials. Some of these methods are adsorption, covalent bonding, entrapment, copolymerisation or crosslinking and encapsulation [72].

ii. **Catalysis in electrosynthesis/electrochemical reactions:** The use of solid nanoparticles as heterogeneous catalysts during electrosynthesis reactions has increased in recent times. Under green chemistry conditions, nanocatalysts can be employed efficiently to promote electrochemical reactions [73]. The incorporation of catalytic nanoparticles into electrochemical (bio) sensors can reduce overpotentials in many analytically crucial electrochemical reactions. Also the reversibility of some otherwise irreversible redox reactions (at traditional unmodified electrodes) can be enabled by nanocatalysts [74]. Production of hydrogen through splitting of water by renewable electricity [75], reduction of carbon dioxide into hydrocarbon products [73] and conversion of biomass products to high-value chemicals [73] are some of the commercially or energetically important electrochemical reactions that use nanocatalysts. Nanoparticles of metals like platinum, gold, silver, palladium, copper, nickel and iridium and also some oxide NPs have been used as catalysts in electrochemical reactions [74].

iii. **Enhancement of electron transfer between electrode surfaces and proteins:**

iv. The conductivity properties of metallic nanoparticles make them suitable for facilitating electron transfer between electrodes and active centres of proteins/enzymes, thereby ascertaining their role as ‘electrical wires’ or ‘mediators’ [74].

v. **Labelling of biomolecules:** The use of NPs for labelling biomolecules aids in retaining their interaction with cellular/molecular counterparts and also in maintaining their bioactivity. Stripping voltammetric technique is commonly used to measure the trace amounts of dissolved nanoparticle labels (usually semiconductor or metal NPs), which in turn is an indication of the concentration of biomolecule under investigation [74]. The NP labels can be introduced either actively (targeted) or passively (non-targeted) into cells under investigation [76]. The incorporation of nanoparticles in cells as labels allows enhanced visualisation of these cells in vivo using a variety of molecular imaging modalities, such as optical imaging, radionuclide imaging (positron emission tomography or PET), magnetic resonance imaging (MRI) and single-photon emission computed tomography (SPECT)) [77, 78].

vi. **Acting as reactant:** In some cases, significant difference is observed in chemical properties of bulk material and nanoparticles made from it because of high surface-to-volume ratio in case of NPs. This enhanced surface energy of NPs provides them amplified chemical activity. As a result, the nanoparticles have found significant applications in novel electrochemical analysis systems as special reactants [74]. For example, the high reactivity of manganese oxide

NPs (react directly with H_2O_2) in comparison with bulk MnO_2 (catalyses decomposition of H_2O_2) has made these NPs an important component of some electrochemical systems [79].

6. Recent advances in nanotechnology-based biosensors

Recently, techniques that are sensitive, selective, and cost-effective are being developed for detecting diseases and underlying medical issues. In this context, biosensors as nano-electroanalytical tools have taken the centre stage. Progress in the health sector enabled by nanotechnology has facilitated in the management of a number of diseases at an early stage [80]. When studying the electrosensing applications of NPs, transfer of electrons between substrate and active site of enzyme (biocatalyst) forms the basis for the functioning of enzymatic biosensors, and this transfer in turn is transduced to produce an electroanalytical signal [81]. Carbon nanostructures, nanotubes, nanorods, ceramic or polymeric matrices, derivatives of graphene, and other functionalised nanoparticles are some of the materials that have been explored and investigated widely by researchers for their electrosensing/ biosensing properties and applications [82–84]. The following recent researches further ascertain the efficiency and remarkable role of NPs in biosensors:

a. Shen et al. [85] showed that the DNA nanostructures can be used in a variety of biomedical applications such as biosensors and cancer therapy as these can interact with small biomolecules and cancer cells due to their specific engineering, unparalleled programmability, and innate biocompatibility and can also serve as nanocarriers for various therapeutic agents.

b. Outstanding physicochemical properties of nanoscaled polyaniline have captured the interest of scientists in the field of medical, as reported by Kazemi et al. [86]. These nanocomposites have shown the ability to immobilise enzymes, nucleic acids and antigen-antibodies on their surface and thus act as bioreceptors or biocatalysts.

c. A polydimethylsiloxane-based nanostructured immunosensor for the investigation of cortisol in human sweat was fabricated by Liu et al. [87].

d. The electrocatalytic and electrochemical features of nickel-cobalt nanoparticles (chemically reduced on functionalised multi-walled carbon nanotubes) were investigated voltametrically against glucose oxidation by Arikan et al. [88].

e. Polyaniline was sequentially electropolymerised on the surface of the functionalised gold electrode followed by electrodeposition of gold nanoparticles to design a nano-biosensor for rapid and ultrasensitive detection of insulin antibodies against diabetes antigens by Farrokhnia at al [89].

f. Electrochemical immunosensing properties of zirconium oxide nanoflowers integrated with quantum dots were investigated by Gupta et al. [90].

g. Recently Farzin et al. [91] have reviewed the biosensing applications of nanoparticles for early and accurate diagnosis of lentivirus HIV that leads to AIDS.

7. Conclusion

An extra advantage of the extensive use of nanoparticles in electrosensing techniques can be owed to their exceptional attributes, like remarkable selectivity and sensitivity, high surface energy, capability to show morphological as well as functional diversity, portability, cost-effectiveness, ease-of-construction and easy-to-operate. Thus, the merger of electrochemistry and nanotechnology has attributed to a wide range of electro (bio) sensing applications for the detection and quantification of chemical as well as biological target molecules. The role of electrode materials in high-performance electrosensing platforms is crucial and evident. Furthermore, when the simple electrode materials are functionalised with nanostructured and/or nanoengineered materials, significant improvement and enhancement in their conductivity, catalytic activity, biocompatibility, amplification of biorecognition events, acceleration of transduction signal, selectivity, specificity and sensitivity has been observed. Almost every passing day, some new innovation is reported in the field of nano-electrosensing, viz. incorporation of CNTs with metallic NPs aids in the development of highly improved nanocomposites for biosensing applications [86], a dramatic enhancement is observed in the electrical conductivity of rGO (reduced graphene oxide) by incorporation of AgNPs [92], nanowires have an exceptional potential as electrosensing probes because of their high surface-to-volume ratios, reproducibility and extraordinary optical, electrical, and magnetic properties [93], and successful designing of dye-sensitised solar cells based on green zinc oxide nanoparticles [94]. The field of nano-electrochemistry seems to expand its horizon continuously, and despite a significant amount of research done in this field, it just seems to be a new start.

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Section 3

Cyclic Voltammetric Applications with Recent Advancements

Chapter 4

A Review on Cyclic Voltammetric Investigation of Toxic Heavy Metals

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Rayappa Shrinivas Mahale, Shamanth Vasanth
and Sharath Peramenahalli Chikkegouda

Abstract

Heavy metals are one of the toxic pollutants threatening the human kind by causing various health issues. The detection of such polutants are of important environmental concern and we need a real-time monitoring equipment. Many researchers have established a number of approaches for the detection of these heavy metals so far. But, the development of one time use sensors for the quick, and real time detection of toxic heavy metals is in great demand. The electrochemical methods like cyclic voltammetry, is proved to be one of the best and popular methods, and are preferred over other electrochemical methods because of its high sensitivity, selectivity, anti-fouling, quick and accurate detection. In the present book chapter, we will discuss the various modifiers used to detect the arsenic, cadmium, and lead heavy metals using cyclic voltammetry.

Keywords: heavy metals, electrochemical sensors, cyclic voltammetry, electrodes, toxic pollutants

1. Introduction

Heavy metals occur either naturally by geological activities, or by agricultural and industrial wastes. Any elements exhibiting relatively high molecular weight and more than 5 g/cm^3 density are considered as heavy metals [1]. They are generally non-biodegradable and toxic in nature due to their ability to transform from one oxidation state to another easily. The heavy metals can cause bioaccumulation because of absorption of them by plants and animals living in that contamination areas [2] and causes various health effects like malfunction of gastrointestinal, nervous system, kidney and immune system, followed by birth defects, skin lesions, and cancer [3]. **Figure 1** depicts the different organs of humans affected by the consumption of various heavy metals.

The agricultural and industrial wastes like pesticides, fungicides, refineries, fertilizers, mining, smoking, nuclear fission plants, chemical industry, paint, electroplating, welding, automobiles, batteries, are the major sources of heavy metal ions [5]. Currently, there are more than 50 heavy metals are known and some of them are metalloids, actinides, transition elements and lanthanides [6]. The elements like lead, mercury, arsenic and cadmium are considered as very toxic and their consumption

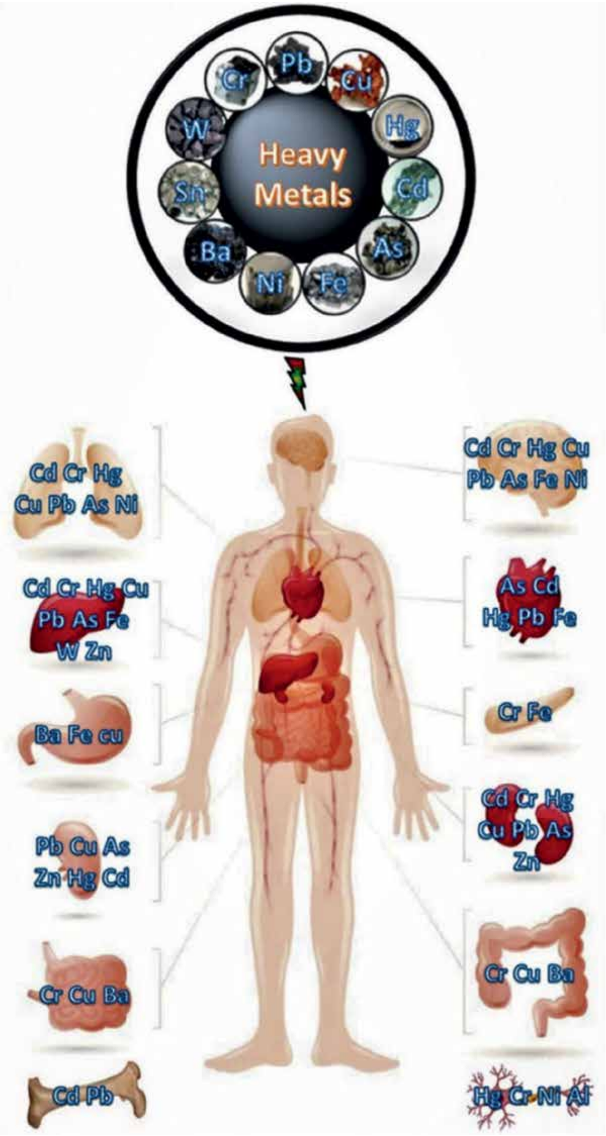

Figure 1.
Various heavy metals affecting the different organs of human [4].

in small amount can cause serious health issues. But, some of the heavy metals are human friendly and their consumption in trace amount can maintain good health. Therefore, regular determination of the heavy metals is advisable in the contamination areas. **Figure 2** depicts the possible ways of heavy metal exposure, their impact on human health and their mechanism.

Many researchers used cold vapor atomic fluorescence, atomic absorption, and emission spectroscopies and inductively coupled plasma techniques [8] to detect heavy metals. But these methods are time consuming, chances of contamination, requires huge manpower and area. Therefore, we need some standard analytical methods to detect the presence of heavy metal ions in foods, plants, animals, water, and soils. Electrochemical methods like cyclic voltammetry [9–16], stripping voltammetry,

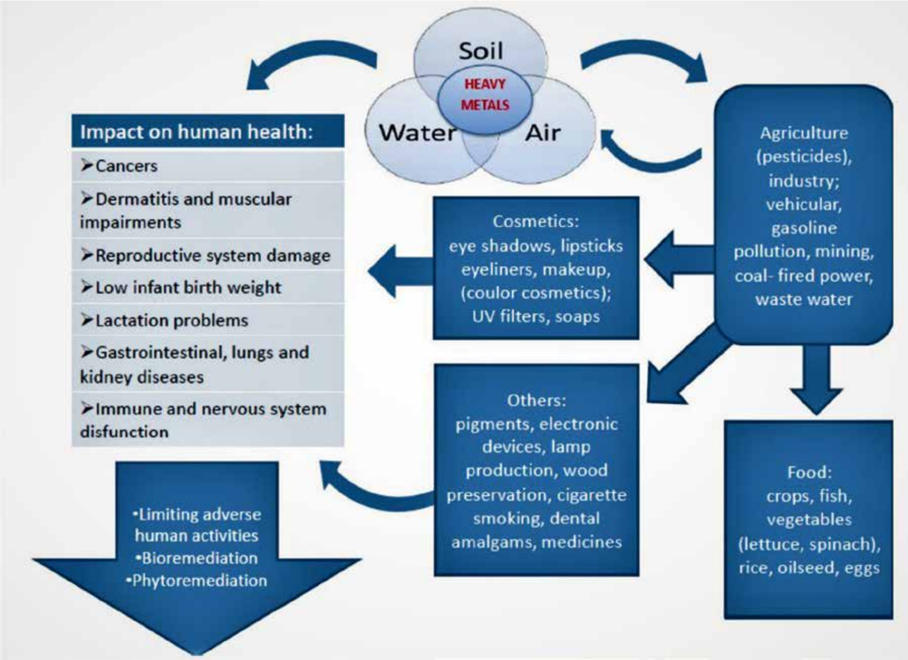

Figure 2.
The possible ways of heavy metal exposure, their impact on human health and their mechanism [7].

differential pulse voltammetry, and polarography are so far best and popular choice to determine the various heavy metals in the environment. These methods are cheap, highly accurate, quick, robust in nature. Among them, cyclic voltammetry is proved to be one of the better and highly advantageous electrochemical methods used to detect organic, inorganic, organometallic, and biological heavy metal ions. High sensitivity, fast response, live monitoring data acquisition, wide detection limit, and possibility of simultaneous detection of multi elements by surface functionalization has made it one of the popular choices among the environmentalists used to detect the heavy metals [6, 17–21]. The present book chapter focus on the recent developments, current challenges, and prospects for future research in cyclic voltammetric determination of lead, arsenic, and cadmium in the environment. We hope that this book chapter will be useful for all the environmental researchers working on heavy metals.

2. Electrochemical determination of Lead (Pb) using cyclic voltammetry

Lead is a bluish-gray metal generally found in the earth crust. Lead is very poisonous metal directly affect the human nervous system and causes severe headaches, and memory loss [22]. Lead is very dangerous woman especially during the pregnancy, when a pregnant woman consumes lead, then it reaches the fetus and causes premature childbirth, abnormal growth, and low weight of the fetus. Lead also affect the brain developments in children and causes the abnormalities [23]. Therefore, people working in lead contamination zone must regularly check the amount of lead in their body.

Mei et al. have reported the use of TC4 arene-modified screen-printed carbon electrode (SPCE) to detect lead ions in river water using cyclic voltammetry [22].

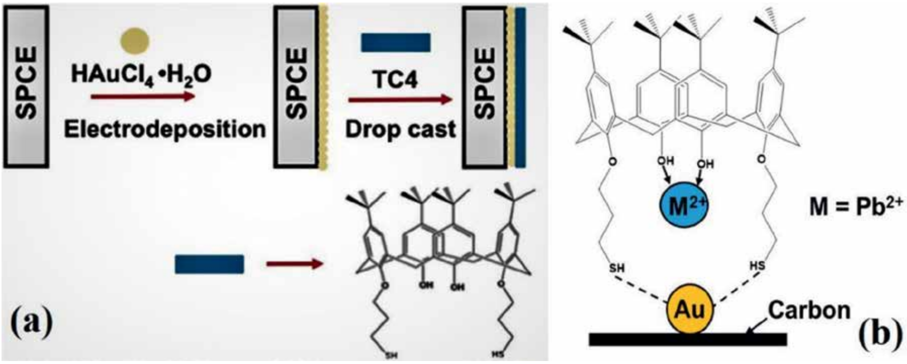

Figure 3.
(a) The schematic representation of electrode preparation to determine Pb2+, and (b) binding of electrode with Pb^{2+} *[22].*

Figure 3 demonstrates the schematic representation of electrode preparation to determine Pb^{2+}. They reported the 0.7982×10^{-2} ppm detection limit for Pb^{2+} followed by the excellent reproducibility and stability. **Figure 4** depicts the current response of the sensor detecting Pb^{2+} ions at different pH levels.

Riyanto has determined lead ions by cyclic voltammetry method using platinum wire as a working electrode in wastewater [24]. Authors reported that, they successfully detected the lead from wastewater with correlation of determination ($R^2 = 0.999$), LOD of 0.9029 mg/L, limit of quantification (LOQ) of 3.0098 mg/L and recovery of 100.67% respectively. They found that, the electro-oxidation of lead on Pt wire electrode occurs in a reversible system and reported that the analytical parameter from cathodic peak is better compared to anodic peak for analyzing of Pb using CV method. They claimed that, the fabricated electrode is simple, economic and showed an excellent selectivity, accuracy, sensitivity, reproducibility [24].

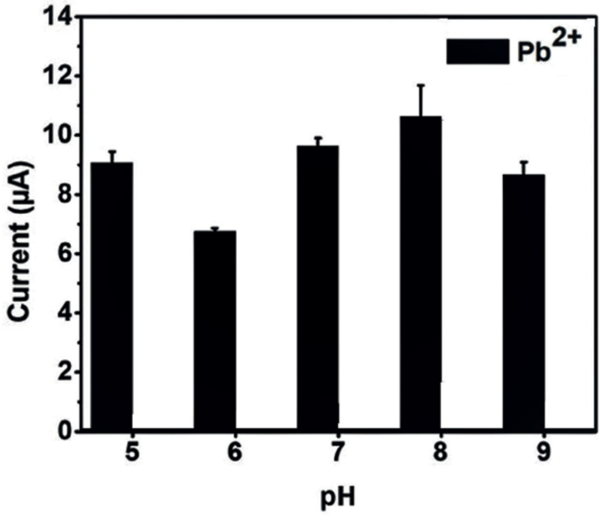

Figure 4.
Current response of electrode during electrochemical determination of lead ions in a KCl supporting electrolyte at different pH [22].

Khodari et al. İnvestigated the cyclic voltammetric behavior of lead ions well water samples using glassy carbon electrode [25]. Cyclic voltammogram showed an anodic peak at −520 mV for lead ions. Authors reported that, the glassy carbon electrode showcased an excellent linear response to a good linear response to Pb^{2+} in the concentration range from 8×10^{-6} M to 1×10^{-4} M with a detection limits of 2×10^{-7} M. They also studied the effect of scan rate, deposition time, deposition potential, and the pH of the supporting electrolyte on lead ions. They claimed that, the fabricated electrode is accurate, precise, highly selective in determining the lead ions in well water.

Honeychurch used carbon rod electrode extracted from zinc-carbon batteries to determine the traces of lead ions present in tap water sample using cyclic voltammetry [26]. Author studied the electrochemical behavior of Pb at different supporting electrolytes like ortho-phosphoric acid, HNO_3, HCl, CH_3COOH, KCl and malonic acid. They found the optimum electrochemical condition of a supporting electrolyte

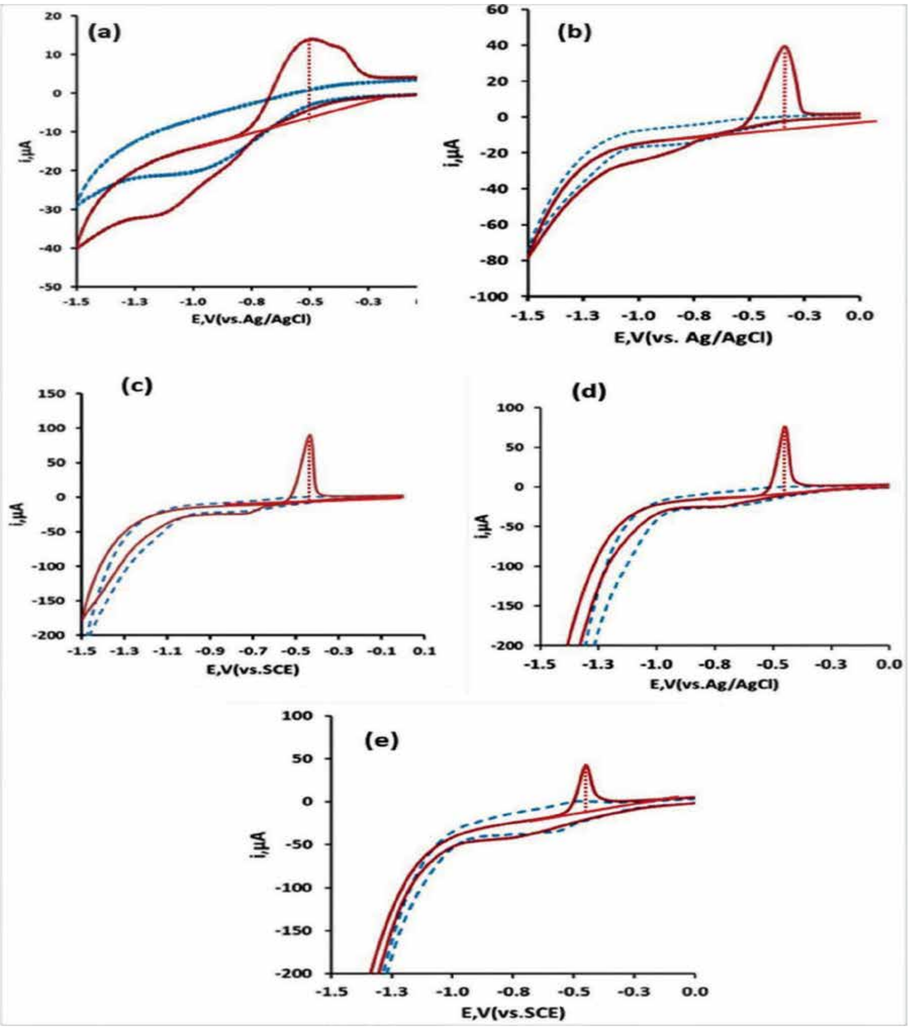

Figure 5.
Effect of acetic acid supporting electrolyte concentration on the cyclic voltammetric behavior of 116 µM Pb: (a) 0.0 M, (b) 0.03 M, (c) 0.1 M, (d): 0.66 M, and (e) 3.0 M [26].

of 4% v/v acetic acid, with a deposition potential and time of −1.5 V (vs. SCE) and 1100 seconds as per the **Figure 5**. They reported the linear range of 2.8 μg/L to 110 μg/L and a detection limit of 2.8 μg/L with 95.6% mean recovery.

3. Electrochemical determination of arsenic (As) using cyclic voltammetry

Arsenic is the 20th most abundant and high mobile element found in earth crust and exists as dust in air and dissolves in rain water and other water sources easily. The World health organization standard for As concentration must be 10 μg/L, but some parts of the World it exceeds the standard concentration. The excessive intake

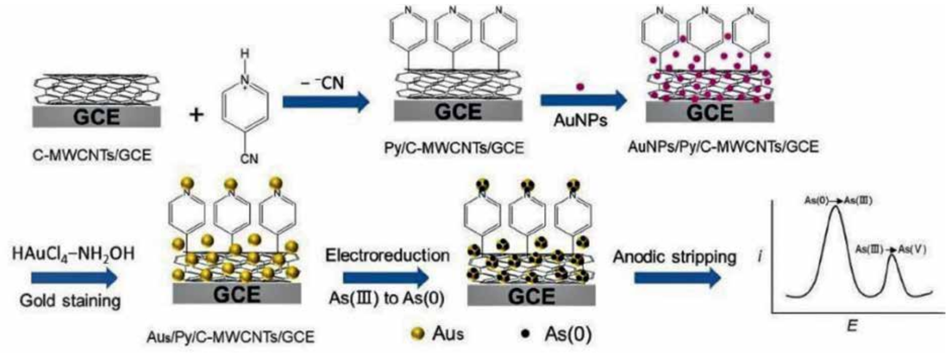

Figure 6.
Preparation of the electrode [28].

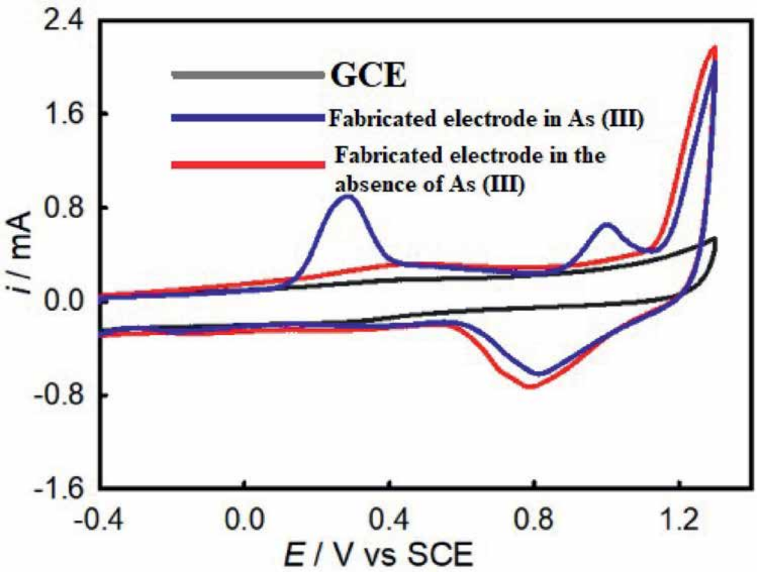

Figure 7.
Cyclic voltammogramms GCE and the fabricated Aus/Py/C-MWCNTs/GCE electrode in 0.1 M aqueous H_2SO_4 with 1 μM As(III) and without As (III) [28].

of As causes lung and skin cancer along with negative impacts on cognitive development and increased deaths [27]. Therefore, detection of arsenic in the environment is important for maintaining public health.

Du et al. fabricated a novel Au-stained Au nanoparticles/pyridine/carboxylated multiwalled carbon nanotubes/glassy carbon electrode for the detection of Arsenic (III) traces in real water samples using cyclic voltammetry [28]. The fabrication of the electrode is schematically represnted in **Figure 6**.

Authors observed the peak currents for oxidation of As (0) to As (III) are linear with a concentration of As (III) from 0.01 to 8 μM with a sensitivity of 0.741 mA μM^{-1} and an LOD of 3.3 nM respectively. Similarly, for the peak currents fort he oxidation of As (III) to As (V) are found to be linear from 0.01 to 8.0 μM with a sensitivity of 0.175 mA μM^{-1} and an LOD of 16.7 nM respectively. **Figure 7** depicts the cyclic voltammogramms of prepared and gassy carbon electrode (GCE) during the electrochemical behavior of As (III).

Ismail et al. fabricated low cost silica nanoparticles modified SPCE for the detection of As (III) using cyclic voltammetry as shown in the **Figure 8** [29]. They performed optimzation of the experimental conditions and reported that, the anodic peak current exhibited a linear range of 5 to 30 μg/L to the As(III) concentration, with a LOD of 6.2 μg/L. Authors claimed that, the fabricated electrode is very economic with high accuracy, high selectivity, sensitivity, stability with good reproducebility.

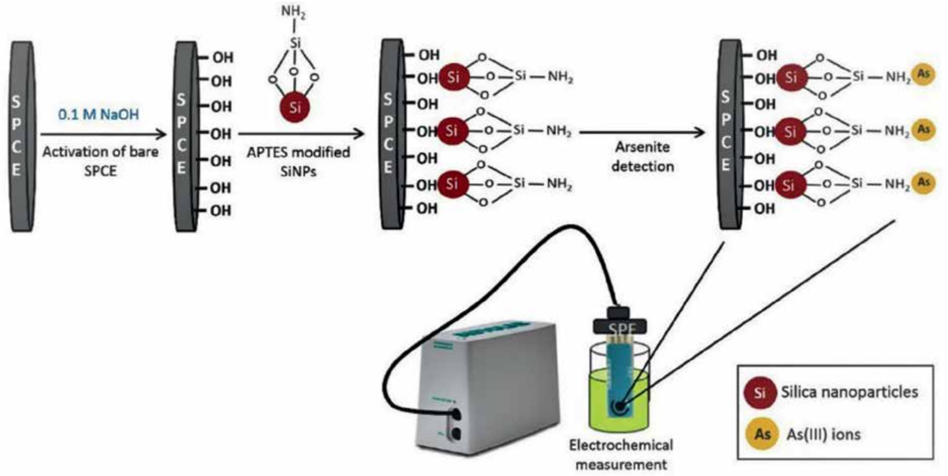

Figure 8.
Fabrication of silica nanoparticles modified SPCE [29].

Modified electrode	Linear range (μg/L)/ppb	LOD (μg/L)/ppb	Reference
Au/SPE	0.5–12	0.22	[30]
Au-Cu/GCE	30–130	5.64	[31]
Si/SPCE	5–30	6.2	[29]
Au/GCE	0.01–8	0.0033	[28]
Au/GCE	0.01–8	0.0167	[28]

Table 1.
Different electrodes used to detect arsenic by cyclic voltammetric method.

Trachioti et al. fabricated a sparked gold nanoparticles from eutectic Au/Si alloy for the determination of arsenic in drinking water using cyclic voltammetry [30]. They reported that the anodic peak current was proportional to the arsenic concentration over a linear range of 0.5 to 12 5 ppb, with a LOD of 6.2 ppb. The fabricated electrode exhibited excellent detection capability, high selectivity and reproducibility. Authors claimed that, the fabrication method of electrode is extremely simple and economic with wide scope of applicability. **Table 1** depicts the various electrodes used to detect arsenic by cyclic voltammetric method.

4. Electrochemical determination of cadmium (Cd2+) using cyclic voltammetry

Cadmium ion (Cd^{2+}) are one of most toxic heavy metals that contaminates water and causes deadliest diseases like cancer, kidney dysfunction, cardiovascular disease, bone degeneration, lung, and liver damage to humans [32]. Cadmium ions are considered to have a greater solubility in water than any other heavy metals and offering a great threat to the biosystem. The standard level of Cd^{2+} in drinking water is 0.003 mg/L as per the World Health Organization (WHO). Therefore, the detection of Cd^{2+} in drinking water samples is of utmost important.

Attaallah and Amine reported the use of enzymic membrane as a electrode without any pre-treatment to detect cadmium ions in drinking water using cyclic voltammetric method [32]. **Figure 9** depicts the fabrication of enzymic membrane electrode to detect cadmium ions. They also modified the fabricated electrode with screen printed electrodes to further increase the selectivity, sensitivity, reproducibility. They modified electrode has showed the linear calibration range between 0.02–100 ppb (R^2 = 0.990) and a detection limit of 50 ppt respectively. **Figure 10a** depicts the cyclic voltammogram of TMB/H_2O_2, HRP/TMB/H_2O_2, and HRP/Cd^{2+}/TMB/ H_2O_2. [TMB = 3,3′,5,5′-Tetramethylbenzidine, HRP = horseradish peroxidase] and **Figure 10b** represents the cyclic voltammograms of variation in the cadmium ions from 0.02 to 100 ppb, in 0.1 M acetate buffer.

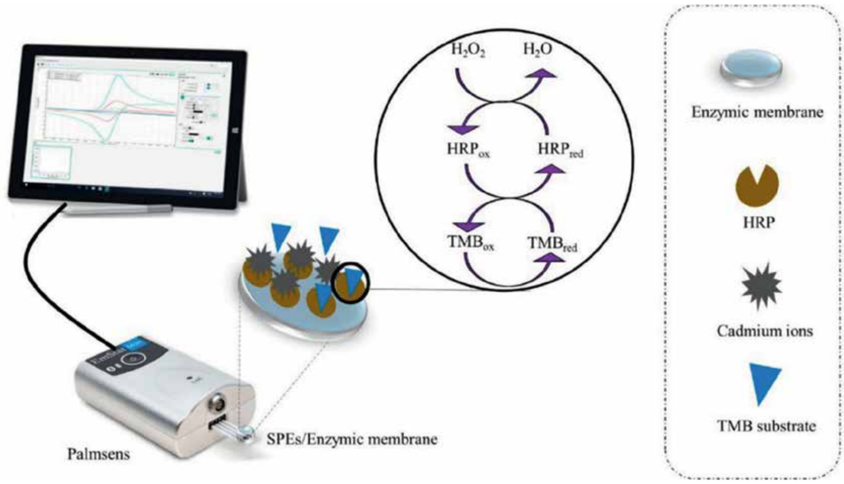

Figure 9.
Schematic representation of preparing enzymic membrane electrode to detect cadmium ions [32].

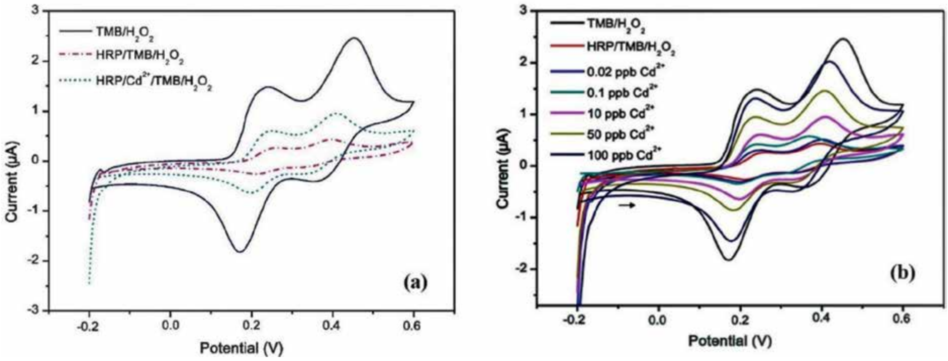

Figure 10.
(a) Cyclic voltammogram of TMB/H_2O_2, HRP/TMB/H_2O_2, and HRP/Cd^{2+}/TMB/ H_2O_2, and (b) cyclic voltammograms of variation in the cadmium ions from 0.02 to 100 ppb, in 0.1 M acetate buffer [32].

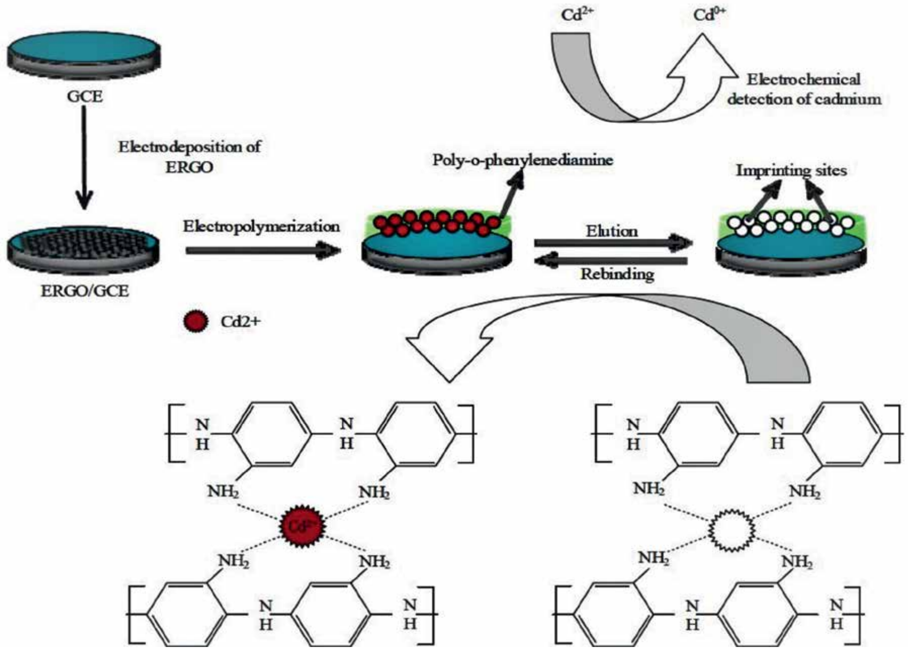

Figure 11.
The procedure diagrams for fabrication of the electrode [33].

Wang et al. electropolymerized ion imprinted poly (o-phenylenediamine) PoPD/ electrochemical reduced graphene (ERGO) composite on glass carbon electrode (GCE) to detect Cd^{2+} in water using cyclic voltammetry [33]. **Figure 11** depicts the procedure diagrams for fabrication of the electrode.

The prepared electrode exhibited a excellent selectivity toward the target Cd(II) ions in the presence multi heavy metal ions. Under optimized conditions, the electrochemical sensor showed a good linear relationship between Cd (II) concentration in the range of 1 to 50 ng/mL, with the limit of detection of 0.13 ng/mL respectively. **Figure 12** depicts the cyclic voltammetric curves of bare GCE, ERGO/GCE, Cd(II)-IIP/ERGO/GCE and IIP/ERGO/GCE.

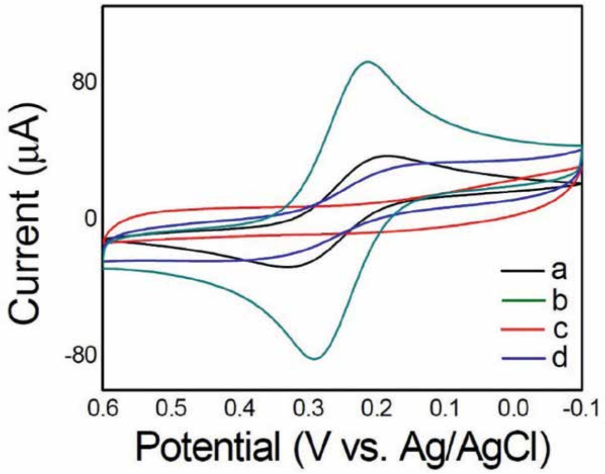

Figure 12.
CV curves on bare GCE (curve a), ERGO/GCE (curve b), Cd(II)-IIP/ERGO/GCE (curve c), and IIP/ERGO/GCE (curve d) between −0.2 V and 0.6 V at a scan rate of 50 mV/s [33].

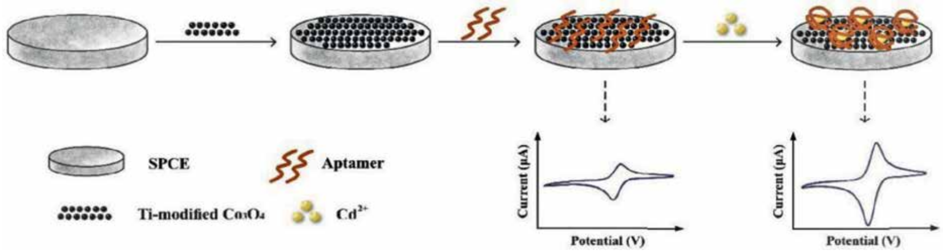

Figure 13.
Schematic representation of fabricting the electrochemical aptasensor used to determine Cd^{2+} [34].

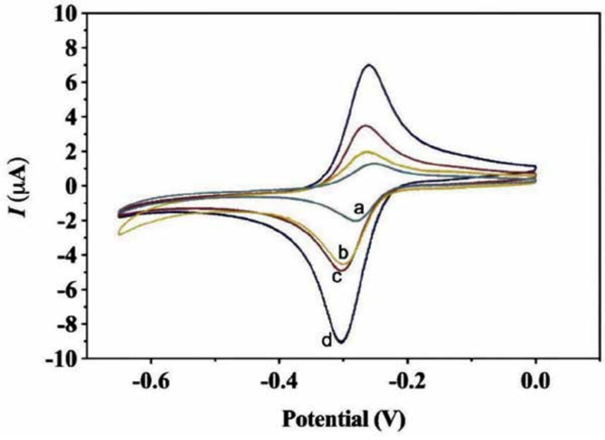

Figure 14.
The CV of (a) bare electrode, (b) Co_2Ti_1 modified electrode, (c) Co_2Ti_1/aptamer modified electrode, and (d) Co_2Ti_1/aptamer/Cd^{2+} modified electrode respectively at 100 mV/s scan rate [34].

Liu et al. prepared Ti-modified Co_3O_4-based electrochemical aptasensor to detect Cd (II) as shown in **Figure 13** [34]. Authors studied the effect of aptamer concentration, incubation time and pH of the solution to optimize the experimental condition to get good results. Under these conditions, peak current was proportional to the Cd (II) concentration over a wide linear range of 0.20 to 15 ng/mL, with a detection limit of 0.49 ng/mL respectively. Authors reported that, they have used cyclic voltammetry method not only to characterize each preparation and optimization step, but also to profile the bindings of aptamer to Cd^{2+}. **Figure 14** depicts the CV of bare electrode, Co_2Ti_1 modified electrode, Co_2Ti_1/aptamer modified electrode, and Co_2Ti_1/aptamer/Cd^{2+} modified electrode respectively.

5. Conclusion

The heavy metals like cadmium, arsenic and lead results in the bioaccumulation and causes adverse effect on gastrointestinal, nervous system, kidney and immune system, and also causes cancer. The detection of heavy metals and their ions is of utmost important in this world. As we discussed, cyclic voltammetry is one of the potential electrochemical method used to detect the heavy metals and their ions easily and quickly. The discussed method is one of the better method and exhibit excellent sensitivity, selectivity, good current response, and possible detection of multi heavy metals simultaneously compared to other electrochemical methods. The recent developments, challenges and future prospectus of the electrochemical detection of heavy metals by cyclic voltammetry is successfully discussed in this chapter. The electrochemical methods are more accurate, simple, robust methods compared to other traditional methods.

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Chapter 5

Recent Advances in Voltammetric Sensing

Harsha Devnani and Chetna Sharma

Abstract

The practical day to day life is largely affected by the products that we use, the air that we breathe, the soil that is used to grow crops, the water we drink and use for various household chores or industrial purposes. The purity analysis of these products or estimation of useful inorganic and organic analytes is of utmost importance for avoiding health and environment risk. Everyone wants to be aware that what they are eating or applying on their skin is safe for them. A diabetic patient needs to monitor their blood sugar levels constantly. The air, water and soil quality needs constant monitoring to avoid health hazards. Not just this, chemical analysis is crucial as a crime investigation technique to identify suspects. Fuel quality and storage needs to be tested for eliminating unwanted losses. The electrochemical techniques are inherently fast, selective and sensitive and some systems are portable as well which is a boon for on-site monitoring. Voltammetric techniques like cyclic voltammetry, stripping voltammetry, impedance spectroscopy, amperometry and other techniques provide specific information of the analytes to be tested. This chapter will highlight the voltammetric techniques used for different types of analyte sensing and the advances that have taken place recently related to voltammetric sensing.

Keywords: voltammetry, sensing, electrochemistry, cyclic voltammetry, stripping voltammetry

1. Introduction

The electrochemical sensor is a broad integrated area encompassing physical aspects, analytical science, material science, electronic fabrication, biochemistry along with statistical analysis. This chapter restricts to the electroanalytical methods involving analytical science and electrochemistry which lay the foundation for voltammetric sensing. Electroanalytical measurements are based on the measurement of potential (potentiometry), current (voltammetry) and the amount of electricity consumed or the matter transformed during electrolysis (coulometry). These techniques are inherently fast, sensitive, selective and offer low detection and quantification limits [1]. In contrast to other analytical techniques like chromatography, ICP-OES, MS and others, electrochemical analysis does not require heavy instrumentation and tedious sample preparation. In fact, miniaturized sensors are portable and are thus handy for on-site monitoring wherever required.

Each of the above mentioned electroanalytical measurement methods involve a specifically designed electrochemical cell. Although potentiometric sensors are more lucrative for on-site operations, voltammetric sensors are more sensitive and fast. Recently, there has been a surge in researching new underlying principles for electrochemical sensing. As a result, sensors are now being developed taking advantage of changes in ionic conductivity, resistivity and impedance [2]. An altogether new concept based on imaging of local electrochemical current utilizing the optical signal from the electrode surface (surface plasmon resonance) has been reported by Shan et al. in 2012 [3]. This derives foundation from the fact that the current density can be determined from the local surface plasmon resonance signal.

Electroanalytical techniques like linear sweep voltammetry (LSV), cyclic voltammetry (CV), pulse voltammetry (PV), stripping voltammetry (SV), chronoamperometry provide an in-depth qualitative and quantitative information for an electro-active species deeming them to be a potential alternative to more commonly used spectrometric or chromatographic techniques. The understanding of an electrode process helps to explore mechanisms for in vivo studies, which is beneficial in analyzing how a drug works when administered to a human body. It is being utilized to speciate and determine ultra trace analytes in complex clinical and industrial samples. Sensor development is a thrust area in the field of chemistry, biology and environmental sciences [4]. A chemical sensor is defined as, "a small device that as the result of a chemical interaction or process between the analyte and the sensor device, transforms chemical or biochemical information of a quantitative or qualitative type into an analytically useful signal" [5]. Chemical sensors find wide applications in industry, critical care, quality control, process controls, pollutant monitoring, safety alarms, clinical diagnostics, food adulteration testing, in agriculture and forensics.

With the advent of electrochemistry, initially the voltammetric methods posed a lot of difficulties as a result of which they could not be much benefited from at the time. Gradually, with significant advancements over a period of time, voltammetric sensing soon became popular as an attractive analytical method. All the voltammetric techniques fundamentally involve the application of an electrode potential (E) and measuring the corresponding current (i) in the respective electrochemical cell. In most voltammetric techniques, the applied potential (E) is varied and the resulting current (i) is measured over a period of time (t). The applied potential relates to the change in electroactive species which can undergo a redox reaction and thus there is change in its concentration, which can be related to the corresponding current of the cell [6].

The voltammetric sensors have lured the researchers as they offer high sensitivity for inorganic as well as organic species along with a wide linearity range using a variety of electrolytes over a wide range of temperatures. Moreover, it has a fast response time and offers simultaneous determination of analytes at times. Voltammetric studies extend a deep insight into the kinetics and mechanism of the electrochemical process under study, making them attractive for sensing applications. Stripping analysis by far is the most sensitive voltammetric technique which boasts the advantages that it does not require derivatization and is also less sensitive to matrix changes in comparison to other analytical techniques [7, 8]. It is being widely used for analysis of heavy metals present in trace amounts in environmental samples. Cathodic stripping voltammetry (CSV) and anodic stripping voltammetry (ASV) have also been used for achieving sensitive determination of various analytes like nucleotides, nucleosides and nucleobases [9].

2. Voltammetric sensors

The voltammetric sensors initially were developed from mercury, carbon materials and inert metals as working electrodes. The use of mercury has long been forbidden due to its toxic nature and the noble metals demand high cost. The mercury electrode is almost out of the picture due to its difficult handling and limited anodic potential range. The carbon electrodes are still in use in a number of forms viz. glassy carbon, diamond, fullerene, graphite, nanotubes, graphene and graphene oxide [2]. In the past few years, carbon paste electrodes have gained momentum as working electrodes as they can be screen printed for production at mass scale. Another set of electrodes is the screen printed electrodes which are used as a robust miniaturized version and are viable for commercial technology. Most of the electrochemical sensors in the market, like the glucose sensor, employ screen printed electrodes as the working electrode [10, 11]. There is immense potential for electrochemical sensors to be established in markets other than that of glucose. The recent COVID-19 pandemic has demanded an urgent need for fast diagnostic processes which can help prevent spread of infectious diseases and provide timely diagnosis of neurodegenerative disease which is a crucial factor [12–14]. The voltammetric sensors hold promise for such diagnostic methods as they are fast, simple in operation, offer real time analysis and can be mass-produced for portable use as they can be miniaturized compared to other existing diagnostic methods [15–17].

The research is now targeted in the direction of new electrode materials which could offer comparable sensitivity and cost economical. Carbon and gold based electrodes are more popular owing to their biocompatibility, stability and good electron transfer kinetics. The bare electrodes often lack sensitivity and selectivity needed for the analysis due to poor charge transfer at the electrode surface. This requires modification of electrode surfaces to enhance charge transfer kinetics and avoid interferences [18, 19]. In this light, the nanomaterials are paving the way for smart electrochemical sensors as they provide enhanced electrochemical surface area with large surface area to volume ratio allowing improved interfacial kinetics exhibiting electrocatalytic activity for sensitive and selective determination of analytes [18–20]. The synergistic effect of nanomaterials is also being actively pursued by combining two or more nanomaterials to form a composite which would derive advantages from all individual components based on the sensing need [7, 8, 21–24]. Although nanomaterials have proved to be beneficial, there are certain challenges yet to overcome like handling sophisticated instruments and the stability of nanoparticles utilizing stabilizers or capping agents in certain cases to avoid agglomeration which will disrupt electrode-electrolyte interfacial kinetics [25, 26].

There are mainly three major hurdles encountered in the development of electrochemical sensors: the attainment of a low limit of detection (LOD); limiting the interaction of unwanted interfering species; maintaining sensor stability and achieving reproducibility in complex real matrices [27]. The LOD indicates the lowest concentration/quantity that could be detected for an analyte and is a major criterion for a sensor performance as many times we are dealing with analytes that are present at trace levels in real samples. With the advancement of nanomaterial modified surfaces, picomolar level of detection has been achieved [28–30]. These modified surfaces still pose the challenge of stability and reproducibility. Moreover, the sensor needs to be validated for real samples otherwise it does not hold importance in the market. The test of an electrochemical sensor as a diagnostic tool is only validated if it is stable and functional in a real matrix [31–33]. Real matrices involve interferences that hinder electrode performance. In the area of medical applications, this is being dealt with by exploring advanced materials to improve electrode surfaces. While the passive methods involve the use of polymers to create a hydrophilic and non-charged layer to limit protein absorption, active methods aim to develop stronger shear forces than the adhesion forces of the bound interferents on the surface [34, 35]. Recently, the use of sol–gel materials along with ceramics and nanomaterials for electrode surfaces have proven to enhance the stability of the sensor [36, 37]. The research has progressed over the years to overcome these challenges and establish effective diagnostic tools in the market for various applications. This chapter highlights the advancement that has taken place in recent years in the development of voltammetric sensors for a variety of applications.

2.1 Voltammetric food sensors

Food is prone to contamination of heavy metals, pesticides and adulterants. Metals come from a variety of natural and anthropogenic sources. However, man-made activities such as urbanization and agriculture can increase their levels, pollute water and soil, and damage the environment. Moreover, pesticides and food additives when added beyond their permissible limits are making way through the food chain, affecting human health invariably [38]. Ingestion of dangerous metal-rich vegetables, crustaceans and other foods can damage stable cells, alter metabolism, lead to carcinogenic mutations and toxicological effects on human organs [39]. The consequences of these elements on human health have inspired extensive analysis of major contaminants in food samples. The well-established spectrometric techniques viz. atomic emission or absorption spectroscopy [40], mass spectroscopy (MS) and inductively coupled plasma-MS (ICP-MS) have been widely used for this analysis in the past decade. Locatelli and Melucci (2013) detected levels of copper, mercury, lead, zinc and cadmium in several vegetables using a rectangular ASV approach and a standard addition method. The study was performed using two electrodes, gold electrode for detection of mercury and the other made of mercury to determine lead, copper, zinc and cadmium. For these studies, lettuce, spinach, and tomatoes were differentiated as washed and unwashed categories. The two groups were mineralized after treatment with an acid mixture in different amounts [41, 42]. The investigation showed that the values for lead and cadmium exceed the regulatory limits of the European Council. **Table 1** lists the range of voltammetric techniques used recently to sense a variety of heavy metals with nanomolar detection limits being achieved at robust electrode systems.

Zabihpour et al. (2020) have reported a robust vanillin (flavoring agent) electrochemical sensor derived from carbon paste electrode (CPE) substrate enriched with $NiFe_2O_4$ nanoparticles and 1-hexyl-3-methylimidazolium chloride (1H3MCl). $NiFe_2O_4$ nanoparticles were formed using a co-precipitation approach and the characterization findings pointed to a spherical $NiFe_2O_4$ nanoparticle with a diameter of 22 nm [52]. The CV technique was used to measure the vanillin oxidation peaks at potentials of +690 and + 650 mV on the surface of CPE and $NiFe_2O_4$/1H3MCl/CPE. The DPV analysis at $NiFe_2O_4$/1H3MCl/CPE showed a strong electrocatalytic capacity towards the electrooxidation of vanillin and revealed two distinct oxidation signals at potentials of 640 and 1050 mV. $NiFe_2O_4$/1H3MCl/CPE was thus successfully used as an analytical sensor to determine vanillin and tryptophan levels in coffee, milk, chocolate and cookie samples [52, 53].

It is also required to estimate nutraceuticals or phytopotentials of certain plants for therapeutic purposes. Voltammetry provides a gateway to such analysis with high sensitivity and selectivity. Zheng et al. (2022) have reviewed the evaluation of

Sample	Target	Technique	Electrode	LOD	Reference
Tomato, potato, and mango	Cu, Cd, and Pb	CV and DPSV	PGE modified with MWCNTs	1.03 μg l^{-1} for Cd, 2.12 μg l^{-1} for Cu, and 1.62 μg l^{-1} for Pb	[43]
Fish liver	Cu	SWV	Hanging mercury drop electrode	0.6 nmol l^{-1} and 0.9 nmol l^{-1}	[44]
Fish	Zn, Cd, Cu, Pb, and Hg	Zn, Cd, Cu, Pb, and Hg	Hanging mercury drop electrode	1–10 ng l^{-1},	[45]
Rice	Cd	DPASV	Au nanoparticle modified CPE	1.94 nmol l^{-1}	[46]
Chicken, duck, and turkey	Roxarsone (ROX)	DPV	SPCE modified with lanthanum molybdates	12.4 nmol l^{-1}	[47]
Apple, potato and lemon	Cd	SWV	PGE/bimetal oxide nanoparticles/graphene oxide	1.85 ng l^{-1}	[48]
Beans and corns	Pb, Cd, and Cu	LSASV	GCE	0.1 mol l^{-1}	[49]
Mushroom	Zn, Cu	DPASV	Amalgam electrode	10.3 mg kg^{-1}; 72.9 mg kg^{-1}	[50]
Canned tuna fish	Hg	DPV	GCE/Cu-MOF nanocubes	0.0633 nmol l^{-1}	[51]

LSASV: Linear Sweep Anodic Stripping Voltammetry, DPV: Differential Pulse Voltammetry, SWV: Square Wave Voltammetry, DPASV: Differential Pulse Anodic Stripping Voltammetry, GCE: Glassy Carbon Electrode, SPCE: Screen Printed Carbon Electrode, PGE: Pencil Graphite Electrode, MWCNT: Multiwalled Carbon Nanotubes, MOF: Metal Organic Framework.

Table 1.
Literature survey of metal analysis in food samples.

antioxidant activity using electrochemical sensors. The development of research in this area has been outlined with its initial stages in 1999, thereafter gaining momentum in 2010 and has remained so ever since. A total of 758 articles were published during this period. Electrochemical methods were used for the first time mainly for quantitative analysis, as well as other analytical approaches. Subsequently, CV was used to directly measure the electrochemical properties of various antioxidants and evaluate their antioxidant capacity. There were several advantages in this scenario when compared to the conventional DPPH assay [54]. The most direct application scenario for the evaluation of antioxidant capacity is in the food industry as it can have a direct impact on their price and nutritional value. One of the most widespread and produced antioxidants present commonly in food is vitamin C, which is electrochemically active and thus can be detected by electrochemical sensors. The development of an electrochemical sensor for Vitamin C brought a major breakthrough in the field of analytical chemistry [55]. Bounegru and Apetrei (2020) reported a nanomaterial based voltammetric sensor for the qualitative and quantitative determination of caffeic acid using CV (**Figure 1**). Carbon nanofibre (CNF) and MWCNT modified carbon based SPEs (C-SPE) were utilized to study the electrochemical behavior of caffeic acid in aqueous solution (pH 3.6). The LOD and LOQ values were seen to be in the range of 10^{-7} – 10^{-9} M (**Figure 1**) which indicates good sensitivity and in fact the

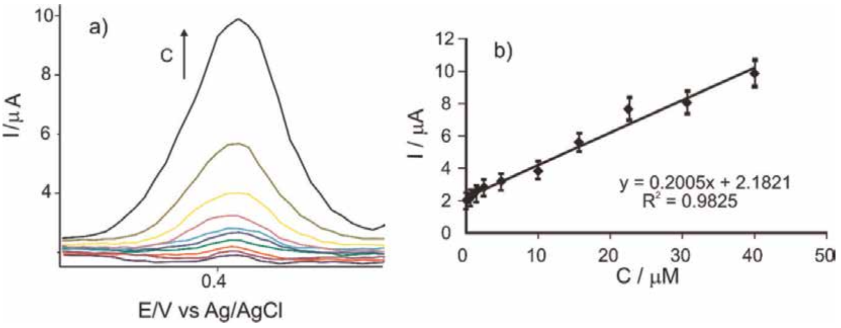


Figure 1.
(a) Zoomed-in view of the anodic peak zone of the CV registered with CNF/C-SPE immersed in caffeic acid solutions with the concentrations in the 0.1–40 μM range. (b) Linear dependence between the anodic peak current and the concentration of the caffeic acid solution [56].

electrochemical results were also compared to the spectrophotometric data. Also, among the two naomaterials used CNF based sensor proved to be better in terms of sensitivity and performance. The optimized sensor (CNF/C-SPE) was also tested for real samples (Active Detox (Herbagetica), DVR-Stem Glycemo (DVR Pharm) and green tea (Alevia) as depicted in **Figure 2** yielding satisfactory results [56].

Qin et al. (2020) reported a TiO_2/electro reduced graphene oxide (TiO_2/ErGO) nanoparticles based electrochemical sensor for the simultaneous analysis of ponceau 4R and tartrazine. The nanocomposite was prepared by ultrasonically dispersing TiO_2 nanoparticles in the grapheme oxide solution followed by an electro-reduction step. The TEM analysis (**Figure 3**) indicated the uniform distribution of the TiO_2 nanoparticles in ErGO nanoflakes confirming the nanocomposite formation which resulted in enhanced adsorptive stripping DPV current response as is expected because of the synergistic effect of the nanomaterials. The two colorants could be detected in a nanomolar range using the respective sensor with selectivity, sensitivity and stability. The sensor was also applied for real sample which was orange juice in this case [57].

2.2 Voltammetric sensing of drug & pharmaceuticals

As pharmaceutical firms evolve to keep pace with expanding population of humans globally, the global pharmaceutical industry reached $1.25 trillion in 2019 and is expected to reach $1.5 trillion by 2023. The implications of this data suggest that the pharmaceutical sales grew by 207.9 percent between 2005 and 2019. As a result, two main problems emerged: many drugs are misused/abused thus pressing the need for researching economical, portable, and effective sensors for monitoring drug overdose or biomedical monitoring; and secondly, tracking or monitoring of pharmaceutical or other contaminants in water sources to maintain human and ecological health is also necessity of today's world [58]. Based on the unique electrochemical interfaces between the nanomaterials and the analyte at hand, there are several approaches that may be more suitable for the detection of pharmaceuticals [59]. Voltammetry, potentiometry, amperometry, and electrochemical impedance spectroscopy (EIS) are examples of common electrochemical methods. Due to their higher sensitivity than CV, pulse methods such as normal pulse voltammetry (NPV), DPV and SWV are more commonly utilized for electrochemical detection. These pulse approaches

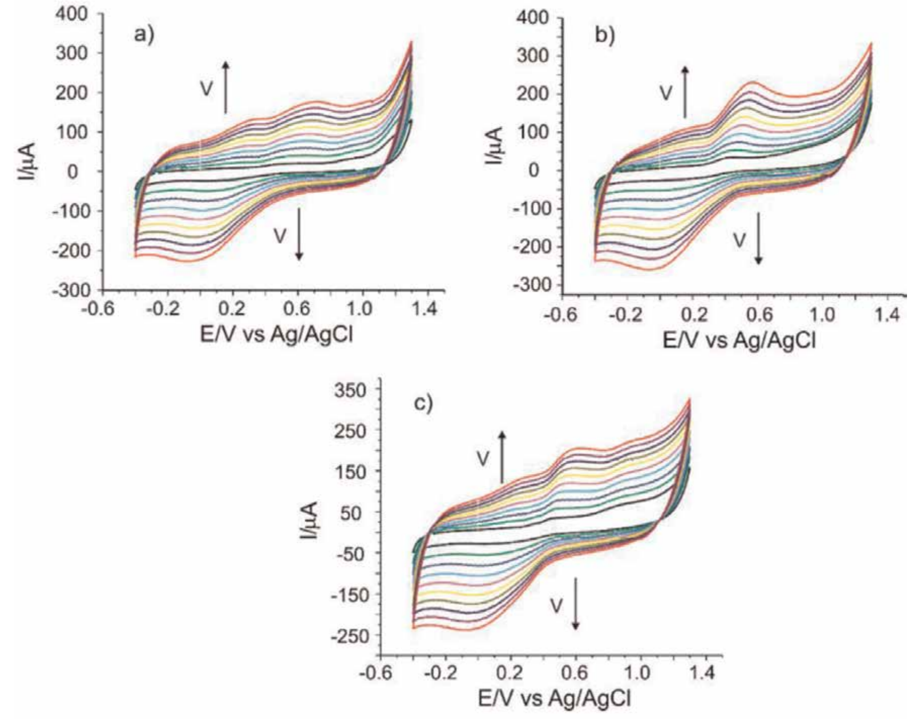


Figure 2.
CVs of CNF/C-SPE immersed in solutions of (a) active detox, (b) DVR-stem Glycemo and (c) green tea, recorded at scan rates between 0.1 and 1.0 V·s^{-1} [56].

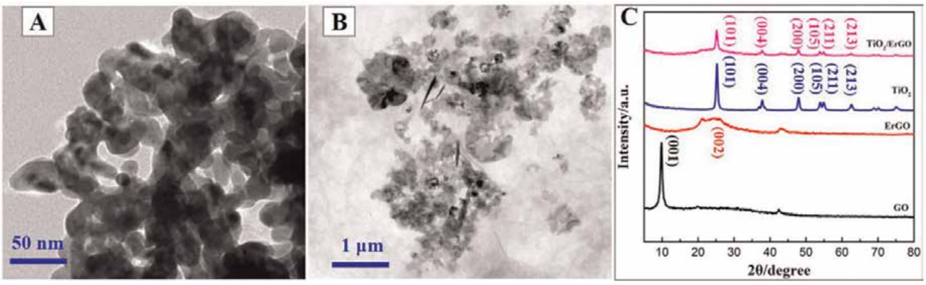


Figure 3.
TEM images of TiO$_2$ nanoparticles (A) and TiO$_2$/GO nanocomposites (B); XRD patterns of nanomaterials (C) [57].

significantly increase the signal of interest corresponding to the analytes compared to the capacitive current response [60].

Voltammetry and polarography are the most commonly used electroanalytical methods in pharmaceutical and biological analysis. In the 1930s and 1940s, the first examples of pharmaceutical analysis using polarographic techniques were documented. Most pharmaceutically active chemicals have been found to be electrochemically active [61]. Electrochemistry is a well-established and rapidly growing field with numerous potential applications in the pharmaceutical industry as is evident from **Table 2** [56]. The use of solid electrodes in the voltammetric determination

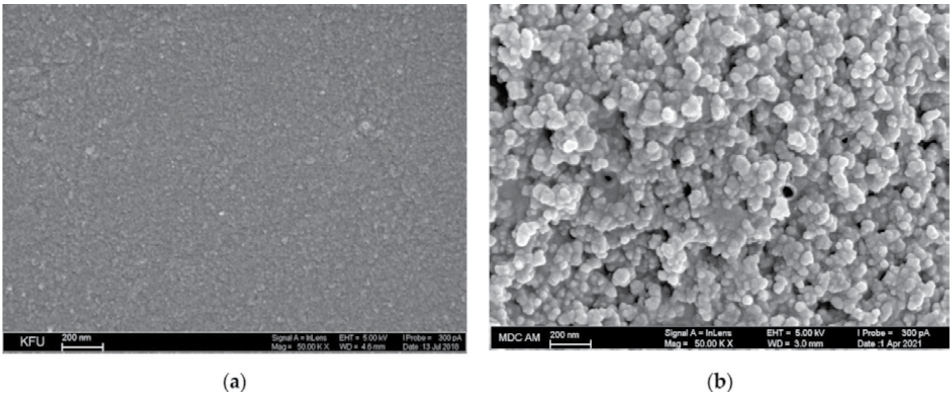
Sample	Target	Technique	Electrode	Drug	Linear Range	LOD	Reference
Non toxic Material	HCl	DPV	CPE	Dexamethosone	0.5–1 μg l^{-1}	4,10 μg l^{-1}	[62]
Non toxic Material	HCl	DPV	CPE	Prednisolone	0.5–1 μg l^{-1}	4,10 μg l^{-1}	[63]
Non toxic Material	HCl	DPV	CPE	Hydrocortisone	0.5–1 μg l^{-1}	4,10 μg l^{-1}	[64]
MWCNT	HCl	CV	CPE	Tinadozol	4.9 μg l^{-1}	8.3 μg l^{-1}	[65]
River Water	Buffer	CV	SPE	Ibufuran	1.6 μg l^{-1}	4.7 μg l^{-1}	[66]
River Water	Buffer	DPV	SPE	Flunitrazepam	2 μg l^{-1}	1 μg l^{-1}	[67]
Coca cola	Buffer	DPV	SPE	esomeprazole	3.5 μg l^{-1}	10 μg l^{-1}	[68]
Alco-pop	Buffer	DPV	SPE	gemifloxin	0.4 μg l^{-1}	2 μg l^{-1}	[69]

Table 2.
Literature survey of electrochemical analysis in drug & pharmaceuticals.

of drugs is gaining popularity due to its simple modification providing a large electrochemical active surface area for fast charge transfer kinetics.

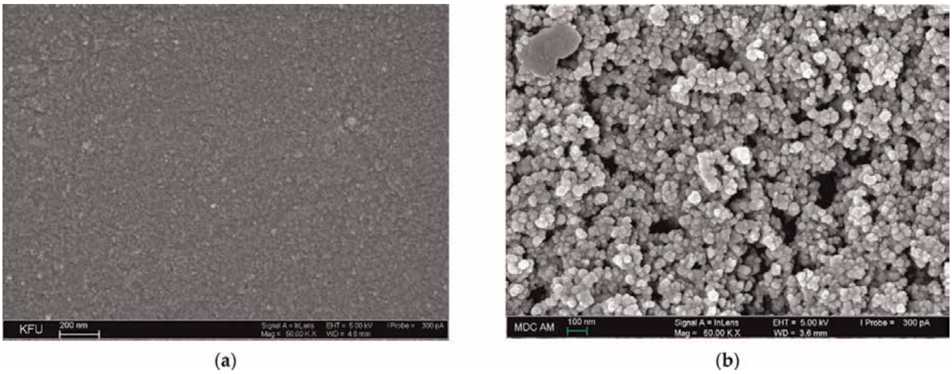
Various modifiers were used to improve the recorded current intensity and the sensitivity of the electrode for the detection of pharmaceutical traces. Additionally, since the solid electrode is non-toxic, it can be used with minimal safety precautions. The phrase disposable electrode makes electrochemical drug determination easier than it was in the 1940s. This word is associated with solid electrodes, the most common home-made conventional solid electrodes, including carbon paste electrodes, screen-printed electrodes, boron-doped diamond electrodes, and pencil graphite electrodes. Both screen-printed and pencil graphite electrodes are single-use electrodes [70].

Mehmandoust et al. (2021) reported gold/silver core–shell nanoparticles (Au@Ag CSNPs) with conducting polymer poly(3,4-ethylenedioxythiophene) polystyrene-sulfonate (PEDOT: PSS) and functionalized multi-carbon nanotubes (F-MWCNTs) on glassy carbon electrodes to create a novel and sensitive voltammetric nanosensor for the first time to monitor trace levels of favipiravir [70]. Under optimized conditions and at a typical working potential of + 1.23 V (vs. Ag/AgCl), Au@Ag CSNPs/ PEDOT: PSS/F-MWCNT/GCE revealed linear quantitative ranges from 0.005 to 0.009 and 0.009 to 1.95 μM with a detection limit of 0.046 nM (S/N = 3) with acceptable relative standard deviations (1.1–4.9 percent) for pharmaceuticals, urine samples, and human plasma without any sample pretreatment (1.12–4.93 percent) [71]. Amino acids, biologics, and antiviral drugs had little or no effect, and the sensing system exhibited exceptional reproducibility, repeatability, stability, and reusability. The results showed that this approach has potential applications in the diagnosis of FAV in clinical samples. The increased surface area and the synergistic interaction between the bimetallic core-shell nanoparticles and the entrapped carbon structures by the conducting polymer resulted in high sensing properties [72]. Ziyatdinova and Gimadutdinova (2021) developed a $CeO_2.Fe_2O_3$ nanoparticles based sensor for the estimation of lipoic acid which is extensively used in medicine as drug therapy. The SEM analysis (**Figure 4**) indicated the uniform distribution of nanoparticles on the electrode surface resulting in enhanced catalytic oxidation currents, reduced overpotential and improved electron transfer kinetics. The designed optimized sensor



(a) (b)

Figure 4.
Surface morphology of bare GCE (a) and $CeO_2.Fe_2O_3$ *nanoparticles modified GCE [73].*



(a) (b)

Figure 5.
SEM images of bare GCE (a) and SeO_2*-CPB/GCE (b) [74].*

was also successfully tested in pharmaceutical dosages for the lipoid acid [73]. Kavieva and Ziyatdinova (2022) subsequently reported a sensor based on SeO_2nanopartciles and surfactant (cetylpyridinium bromide; CPB) for the determination of indigo carmine which is a widely used colorant in pharmaceutical industry. The immobilization of SeO_2 nanoparticles on the electrode surface was confirmed with SEM analysis presented in **Figure 5**. The sensor was characterized using CV (**Figure 6**), chronoamperometry and electrochemical impedance spectroscopy (EIS) dictating reduction in charge transfer resistance at the fabricated sensor accompanied with roughly 4 times higher electroactive surface area [74].

2.3 Voltammetric biosensors

Since the first documented glucose biosensor more than half a century ago, biosensors have developed at an exponential rate. The use of biosensors in many fields such as diagnostics, environment, healthcare, and pharmaceuticals has resulted in the biosensor business growing into a multi-million dollar market that is expected to thrive in the coming years. In this massive biosensor sector, new advances in biosensors in terms of nanobiosensors should expand the range of such technologies in the market.

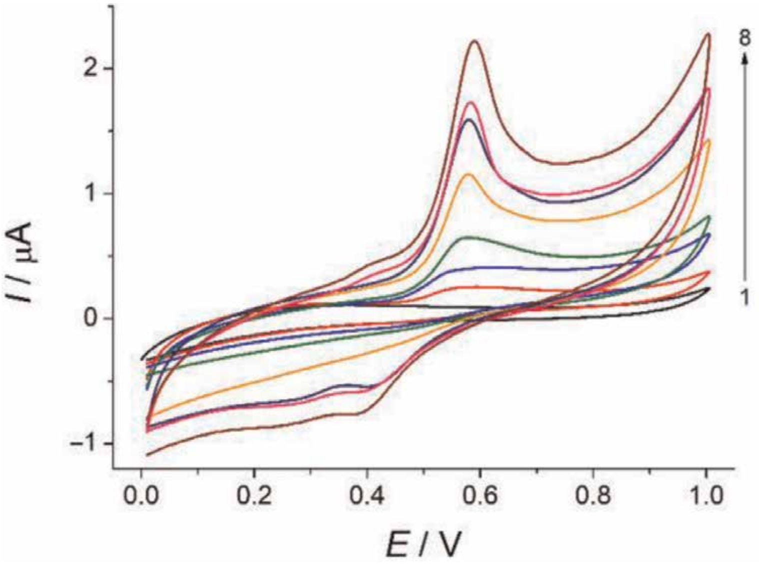


Figure 6.
CVs of 50 μM indigo carmine at SeO_2-CPB/GCE at various scan rates in pH 5 phosphate buffer [74].

Biosensors are generally based on the interaction of target species with the surface of a biomolecular receptor coupled to a transducer to generate a signal. A biosensor system can therefore be categorized based on how the detection was performed, such as electrochemical, mass, or optical. The method of detection can also be used to describe a nanobiosensor; however, the transducer used in such circumstances is usually from the field of nanotechnology, i.e. the use of nanoparticle or nanostructured interfaces. Optical nanoprobes detect various analytes using highly active metal nanoparticles such as gold or silver [75]. Although biosensors include well-established bioanalytical techniques, nanobiosensors have seen significant improvements in their sensitivity, resulting in a significant shift in the research trend from biosensors to the development of nanobiosensors. **Table 3** lists the range of electrochemical biosensors reported for analytes of importance in various sectors with their respective detection limit.

Kusior (2022) has reported a very interesting study for the determination of glucose without an enzyme receptor at copper oxide nanomaterial modified electrode wherein the facet exposition of Cu_2O nanoparticles has been linked to the current-potential profiles. The nanoparticles were synthesized using a wet chemical approach and different facets were exposed to current analysis for glucose determination (**Figures** 7 and **8**). It is claimed that the electrochemical sensing or biosensing of Cu_2O nanoparticles depended on {100} and {111} facets, with former possessing more neutral states and the latter positive state. The study was performed by synthesizing particles in different sizes by addition of surfactants and the electrochemical performance was tested by CV and amperometry [76].

2.4 Voltammetric sensors for agriculture purposes

Contamination of pesticides and herbicides in soil, groundwater, rivers, lakes, storm water and air is a major problem. Pesticides are widely used in agriculture around the world and are a key tool for controlling weeds, insects and infections. They were defined as chemicals or mixtures designed to resist, eliminate, prevent or limit

Electrode	Modifier	Electrochemical Method	Analytes	Linear Range	Detection Limit	References
CPE	1,4-BBFT/IL	SWV	Isoproterenol	6.0×10^{-8}–7.0×10^{-4} M	12.0 nM	[77]
LIG	Salmonella typhimurium	SWV	Aptamer	10 CFU/mL	67–6.7×10^{5} CFU/mL	[78]
CPE	FC/CNT	DPV	N-acetylcysteine	1.0–400.0 μM	0.6 μM	[79]
SPE	S. pullorum & S. gallinarum	CV	Antibody	1.61×10^{1} CFU/mL	10^{1}–10^{9} CFU/mL	[78]
		DPV		3 CFU/mL	10–10^{7} CFU/mL	[80]
CPE	FC/MWCNT	DPV	Cysteamine	0.7–200 μM	0.3 μM	[81]
			folic acid	5.0–700 μM	2.0 μM	[82]
GME	S. typhimurium	CV	Au	2.4×10^{2} to 2.4×10^{7}	2.4×10^{2} cfu/mL	[83]
		DPV		3.1×10^{-5}–3.3×10^{-3} M	9.0×10^{-6} M	[84]
CPE	FC/CNT	DPV	Norepinephrine	0.47–500.0 μM	0.21 μM	[85]
CPE	2CBF/GO	SWV	Hydrochlorothiazide	5.0×10^{-8}–2.0×10^{-4} M	20.0 nM	[86]
CPE	FM/TiO_2 nanoparticle	DPV	Methyldopa	2.0×10^{-7}–1.0×10^{-4} M	8.0×10^{-8} M	[87]
CPE	FCD/CNT	DPV	Norepinephrine	0.03–500.0 μM	22.0 nM	[88]
CPE	2CBF/CNT	SWV	N-acetylcysteine	5.0×10^{-8}–4.0×10^{-4} M	2.6×10^{-8} M	[88]

Table 3.
Electrochemical biosensor developed for the detection of some analytes.

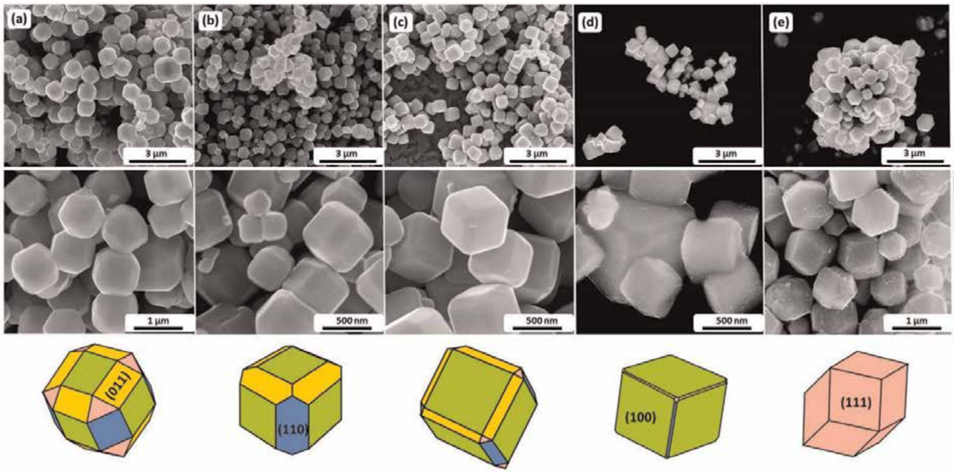


Figure 7.
SEM images of obtained polyhedral Cu_2O particles depending on surfactant used [76].

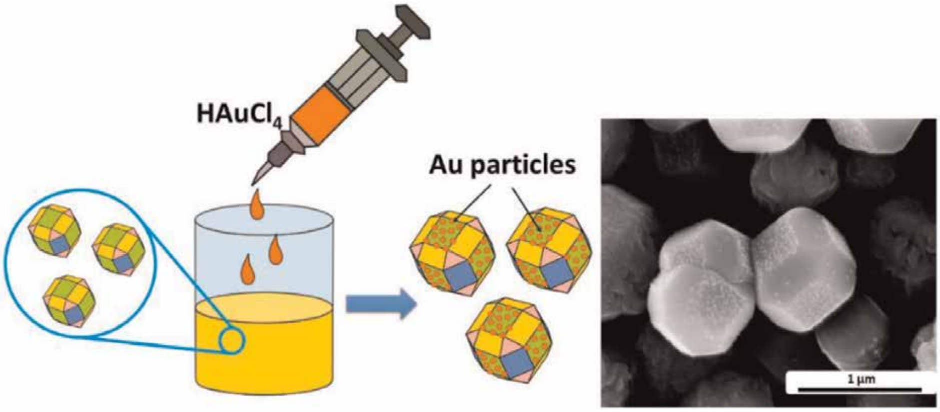


Figure 8.
Schematic representation of Au particle adsorption at the polyhedral surface with SEM image of modified Cu_2O grains [76].

the presence or effect of biological organisms capable of causing crop damage [89]. Since 1960, the increased use of pesticides has allowed farmers to significantly increase productivity while avoiding crop losses caused by pests [90]. Herbicides are pesticides that are used to kill or slow the growth of weeds. They were categorized based on their activity (contact or systemic), use (soil, pre-emergent or post-emergent) and mode of action on plant biochemical mechanisms [91, 92]. In addition, their target is classified as non-selective (kills all surrounding plants) or selective (attacks only weeds and leaves the crop alone) [93]. Glyphosate (N-(phosphonomethyl)glycine) was the most commonly used herbicide, followed by atrazine (2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine) and 2,4D-dichlorophenoxyacetic acid) [94]. Priscila discussed the detection of herbicides (1990–2018) to obtain certain qualities and increase the detection limit, the matrix can be changed using metals, metal oxides, polymers, clay materials or micro or nanoparticles.

Sample	Transducers	Analyte	Biosensing Elements	Reference
Soil	Amperometric	2,4-D	Acetyl-Cholinesterase	[95]
Soil	Bioluminescense	Diuron, paraquat	Cyanobacterial	[96]
Soil	Potentiometric	Simazine	Peroxidase(Biocatalytic)	[97]
Soil	Impedance	2,4-D	Antibody	[99]
Soil	Potentiometric	Hydrazide	Acetyl-Cholinesterase	[101]
Drinking Water	Potentiometric	Isoproturon	Antibody	[100]
Waste Water	Potentiometric	Simazine	Peroxidase(Biocatalytic)	[102]
Orange Juice	Amperometric	Atrazine	Antibody	[98]

Table 4.
Sensors developed for the detection of some herbicides.

Electrochemical sensors are good candidates for environmental monitoring and have been successfully fabricated using various types of electrode materials. The applicability and advantages of voltammetric techniques over traditional methods have been well established. Surface modification of the electrode improves its properties, allowing small amounts of a specific analyte to be detected or quantified; for metals or metal oxide electrodes are now able to detect non-electroactive herbicides. Nanostructures have also been shown to have several advantages and are a promising field of study. There are a significant number of biosensor papers that provide exciting new potential to increase their performance for herbicide detection (**Table 4**). Most of the work presented used real samples such as tap and lake water, poisoned soil and food hazardous substances (fruits and vegetables), but there is still a need to incorporate these new devices into commercial analysis or industries.

2.5 Electrochemical energy sensors

Fuels are an essential part of today's civilization with significant economic and ecological importance. The current search for new sustainable alternative fuels to fossil fuels was based on minimizing the emission of pollutants into the atmosphere such as CO_2. Biofuels, as they were widely known, were commonly produced from vegetable oils and their composition can vary depending on their origin, resource types and their matrices. Metals and toxins in fuels, regardless of their origin, such as fossil or alternative, remain a problem that needs to be solved. A large number of metals can be used as catalysts in the oxidation processes of fuels when combined with gasoline, either by contamination or adulteration, and the results can damage automotive engine components [100]. Among many types of current fuels, it is customary to examine and assess the metal contamination in their composition, which exceeds the limitations of regulatory authorities to avoid economic and environmental losses associated with the concentration of specific metals in fuel matrices. There are several variables that affect the maximum amount of metal allowed in gasoline. It was determined by the regulatory body, the type of fuel and even the metal involved. Lead was not permitted in gasoline in Europe and manganese is limited to 2 mg/l [88]; however no metals are permitted in gasoline in the United States [101]. There was extensive literature on the evaluation of metals in fuels using a variety of approaches, most of which have a high material and resource analysis. Due to its mobility, high sensitivity and low cost compared to other approaches, electrochemical techniques offer a promising alternative route for these kinds of studies.

Dos Santos and Ferreira discussed in a 2020 publication the analysis of Pb^{2+} and Cu^{2+} in microemulsified biodiesel using a boron-doped diamond electrode [90]. This process has been used to produce biodiesel from corn oil, according to the researchers [102]. In comparison to other traditional detection methods, the results obtained were good. The analysis was performed despite the fact that these metals are not controlled in biodiesel. Ferreira and co-workers in 2021 used B-doped diamond electrodes in ethanol solution with ASV to measure Fe^{3+}, Cu^{2+}, Zn^{2+}, Pb^{2+} and Cd^{2+}. Combining interactions and interferences between species, was investigated [103]. A sample of fuel ethanol was tested in a hydroethanolic environment using this approach after the experimental parameters were tuned, with concentrations of investigated ions below the detection limits for the proposed method (**Table 5**).

2.6 Voltammetric environmental sensors

Some benefits are likely to emerge in the existing water monitoring environment when the mode of analysis moves based on sampling techniques to exclusively Conductivity-Temperature-Depth (CTD) probes have been used underwater since the 1980s, there has been a clear shift towards decentralized techniques approaches in a portfolio of known analytical techniques show clear promise for use in An evaluation of submersible devices in terms of their analytical properties, autonomy, miniaturization, and portability [111]. Plant modified carbon paste electrodes have been reported in literature recently for the estimation of heavy metals. One study was done in 2016 wherein bagasse (waste from sugarcane) was used as a biomaterial in a sensor to detect the hazardous metals Pb and Cd. An electrochemical approach was used to investigate the performance of the bagasse-based carbon paste sensor [112]. SEM, FTIR, CV and BET analysis were used to characterize the modifier's surface which indicated mesoporous pore distribution of bagasse and the specific surface area was calculated to be 89.3 m^2/g [100]. The accumulation was carried out in pH 6 acetate buffer and stripping analysis was done in HCl at a scan rate of 50 mV/s. The linearity was observed for lead and cadmium in the concentration ranges of 100–600 gL^{-1} and 500–1200 gL^{-1} with detection limits of 10.1 and 170.64 gL^{-1}, respectively for 10 mins of accumulated time.

Sample	Target	Technique	Electrode type	LOD	Reference
Biodiesel	Cu	DPASV	Hg film electrode	4.69 nmol-^{1}	[104]
Biodiesel	Pb	DPASV	Hg film electrode	2.91 nmol-^{1}	[105]
Bio-Ethanol fuel	Fe	LSSV	Nafion	2.4 μmol-^{1}	[106]
Bio-Ethanol fuel	Cu	DPSV	CNT	170 nmol l-^{1}	[107]
Biodiesel	Ca	SWV	GCE	1.6 nmol l^{-1}	[108]
Biodiesel	Tin	SWASV	Bi Film electrode	0.14 μmol l^{-1}	[109]
Bio-Ethanol fuel	Zn	SWASV	GDE	5 μg l^{-1}	[110]
Biofuel	Cu	SWASV	Vulcan functionalized	1.2 nmol l^{-1}	[111]

Table 5.
Electrochemical energy sensors for metal analysis.

Electrochemical sensors have proven ideal for this function, particularly in ion detection. Maria Cuartero reported (2021) an investigation of electrochemical sensors that showed promise for measuring ions in seawater such trace elements, nutrition, and carbon species The preceding five years were chosen as the major era for investigation, but older contributions to the area or goods introduced are included when important technical advancements are highlighted. There was a distinct absence of electrochemical sensors used in in-situ applications, which exacerbated when saltwater was considered: only a few examples have been demonstrated under such difficult conditions.

A glassy carbon electrode (GCE) modified by simultaneous electropolymerization of L-lysine (L-lys) and -cyclodextrin (-CD) film (P-CD-L-lys/GCE) was described as a novel electrochemical platform for the detection of pymetrozine. Using CV in 0.1 M H_2SO_4, the electrochemical activity of P-CD-L-lys/GCE towards pymetrozine was investigated [113]. The sensor's potential value was shown using LSV to estimate pymetrozine concentration analytically. The linear range is 4.0108 mol/L to 1.0106 mol/L. Pymetrozine's detection limit was determined to be 1.3108 mol/L (S/N = 3). We were able to acquire satisfactory pymetrozine results in real sample analysis using this approach. The usage of amino acid materials and cyclodextrin in environmental analysis was supported in this study. Chaiyo et al. (2020) reported a simple, low-cost, and highly sensitive voltammetric sensor based on a Nafion, ionic liquid, and graphene composite, modifying a screen-printed carbon electrode for the simultaneous determination of Zn^{2+}, Cd^{2+}, and Pb^{2+} in drinking water at the nanomolar level [114]. Del Valle and co-workers reported the immobilization of 4-carboxybenzyl-18-crown-6 and 4-carboxybenzo-15-crown-5 on monolayers of aryldiazonium salts anchored on the surface of graphite-epoxy composite electrodes for the simultaneous determination of Cd^{2+}, Pb^{2+} and Cu^{2+} in synthetic water samples at to the ppb level (ca. nanomolar) using differential pulse anodic stripping voltammetry (DPASV) [115]. Then, using a comparable electrode modification, Perez-Rafols et al. developed an electronic tongue for the detection of Cd^{2+}, Pb^{2+}, Tl^{+} and Bi^{3+} in synthetic water samples [101]. For the detection of trace metals, molecularly imprinted polymers [102–104] and metal-shaped nanoparticles [116, 117] have also been proposed. Voltammetric analysis of Pb^{2+} in enriched water has been reported using MoS_2/rGO flower composite with ultrathin nanosheets [118], Ni/NiO/MoO_3/chitosan 3D foam at the p-n junction interfacial barrier for micromolar level Cu^{2+} detection [119] and Mn-mediated MoS_2nanosheets have been reported recently as a new approach to Pb^{2+} sensing [120]. A VIP (Voltammetric In-Situ Profiler) for the detection of Cu^{2+}, Pb^{2+}, Cd^{2+} and Zn^{2+} using a Hg-based electrode [121] and a kayak equipped with Zn^{2+}voltammetric sensors based on liquid crystal polymer bismuth film [122] are the only two cases reported in the literature that demonstrated in-situ operation in seawater. Single and multiple analyte detection methods have been investigated in the last five years. Maria's (2021) report includes a number of electrochemical techniques for the detection of trace metals, although demonstrated applications in unspiked saline samples are quite limited (**Table 6**). For nitrogenous nutrients, two in-situ solutions were effectively used to produce NO_3 and NO_2 profiles in saltwater.

After seawater treatment, potentiometric detection of NO_3 and NO_2 at relatively low doses is possible utilizing multiple electrodes combined in a flow cell. Amperometric NO_x and NO_2 biosensing is possible using various bacterial chambers in an electrode configuration that can be deployed in any water system using an analyzer or submerged device allowing direct contact of the sensors with the water column at

Sensor	Analyte	Electrode	LOD	Reference
SWSV	Trace Metals Cu^{2+}	Hg	10^{-11} M	[123]
SWSV	Trace metal Pb^{2+}	Hg	10^{-11} M	[124]
SWSV	Trace metal Cd^{2+}	Hg	10^{-11} M	[125]
SWSV	Trace metal Zn^{2+}	Hg	10^{-11} M	[126]
SWSV	Trace metal Zn^{2+}	Bi	1 nM	[127]
ISE	Nutrients NO^{3-}	Iniline acid	1 μM	[128]
ISM	Nutrients NO^{2-}	Disalination	1 μM	[129]
ISM	TAN	GC/POT with nonactine	1 μM	[130]
SWV	Phosphate	Au,Mo-P	1 μM	[131]
ISM	Carbon species	GC/CNT/ISM with ionophores	μM, pH = 9	[132]
Acid base titration	Alkanility	Solid electrode	pH < 4	[133]
Amphoteric biosensor	NO_x^-	Bacteria chamber	1 μM	[134]

Table 6.
Electrochemical environmental sensors for metal analysis.

micromolar concentration with separate electrodes. There are no demonstrated in-situ uses of electrochemical devices for in-situ detection of ions in saltwater, according to studies. At the laboratory scale, new advancements are ongoing, with in-situ installation compatibility promised but rarely fulfilled. The few sensors that have been integrated in submersibles appear to be in the early stages of commercialization. As a result, meaningful data is only gathered through the inventors' measurements [135]. Electrochemical sensors have the potential to transform seawater analysis programs, but bringing this vision to fruition would need well-planned phases and targeted research.

2.7 Electrochemical sensing in forensics

Homicide cases usually involve weapons that release many compounds when fired. These compounds are identified in gunshot residue that may be found at a crime scene, on a suspects' clothing or other items, which then become useful in the investigation of a crime by providing evidence. This gunshot residue (GSR) consists of both inorganic and organic parts that need analysis for a successful investigation. In addition, elements such as antimony, lead, bismuth and copper present in GSR are hazardous to human health and the environment and therefore their determination is necessary [136]. Increasing security needs necessitate the deployment of field-deployable detectors capable of detecting GSR and nitro-aromatic explosive compounds in real time.

Erden et al. (2011) presented the measurement of antimony and lead in gunshot residues using differential pulsed cathodic adsorptive stripping (DPCAS) and square-wave cathodic adsorption stripping voltammetry (SWCASV) [137]. A hanging drop of mercury was used as a working electrode for GSR samples obtained during test firings at the Police Criminal Laboratory from the shooters' hands. The results demonstrated that both the DPCAdSV and SWCAdSV approaches could be used to successfully determine metals in GSR, both qualitatively and quantitatively. Vuki et al. (2012) then reported the simultaneous detection of Pb and Sb. along with other organic components of GSR at propellant on a glassy carbon electrode using CV and cyclic-SWV [138]. The thin film Hg GCE was used for Ba analysis because it requires detection of the presence of mercury [139].

Ceto et al. (2012) reported Zn, Pb, Cu, and nickel amalgams on bare and modified SPE by SWV in samples obtained straight from shooters at a nearby shooting range. The fascinating element is that they were able to validate several handling situations including secondary contact with the GSR, loading the handgun, and finally discharging. The subject that fired the firearm was identified other than the ability to distinguish the time of contact with the GSR with respect to different subjects. The use of microelectrodes for lead analysis in GSR was demonstrated by Salles et al. (2012) using the SWV technique [140]. Microelectrodes have substantial benefits for analysis, such as the capacity to deal with small-volume samples, downsizing of equipment, and the removal of mixing in the pre-concentration process. Their study suggested the possibility of linking lead originating from the GSR to discrimination between different types of weapons and ammunition. Wearable, completely stiff finger sensors for quick on-site voltammetric assessment of GSR and explosive surface residues were described by Bandodkar et al. (2013). To build new forensic fingers, they screen-printed the three-electrode arrangement onto a nitrile finger pad and overlay another finger pad with an ionogel electrolyte layer [141]. The novel integrated sampling/detection system uses “microparticle voltammetry” (VMP) to transmit minute quantities of surface-confined analytes directly onto a fingertip-based electrode array. Voltammetric measurements of sample residues are performed by bringing the working electrode into direct contact with a second finger bed coated in ionogel electrolyte (worn on the thumb), therefore completing the solid-state electrochemical cell [142]. The sampling and screening process took less than four minutes and results in GSR and explosives having distinct voltammetric signatures. The use of a solid, flexible ionogel electrolyte eliminates any liquid handling, reducing leakage, portability, and contamination concerns. The fingertip detection gadget demonstrated great specificity for detecting GSR and nitroaromatic chemical residues. It can tolerate constant mechanical stress without losing its attractiveness, a low-cost way for conducting on-site crime scene investigations in a range of forensic settings [143]. Hashim et al. 2016 reported gold modified screen printed electrode for Cu (II) analysis in GSR using CV (**Figure 9**). It was also compared with ICP-OES analysis with 94% accuracy [144].

The research area was long forgotten, but is now re-emerging as a result of the sensitivity and adaptability that this approach provides. Ott et al. published a paper in 2020 on the analysis of Pb, Sb, and Cu by SWASV employing bare SPE. Two samples were taken in this investigation, one from the hands of volunteers with no direct touch and the other from the hands of those who had recently discharged a weapon. They examined data from 395 genuine shooter samples and 350 background samples, making it the biggest GSR research yet done [145]. Using a simple, quick, and sensitive voltammetric assay, they were able to identify all metals as well as organic bullet residues at the same time. It was detailed how to make a biochar-modified carbon paste electrode. Oliveira et al. used DPAdSV in 2021 to assess lead ions in gunshot residue and hair coloring samples. GSR samples were acquired using an IMBEL 9 mm pistol and 100% cotton fabric, with no hair color specified. To eliminate interference from other metals contained in gunpowder components such as Sb (III), Cu (II), Cr (III), and Fe (II), this work employed the conventional addition technique to measure lead in the acquired samples [146].

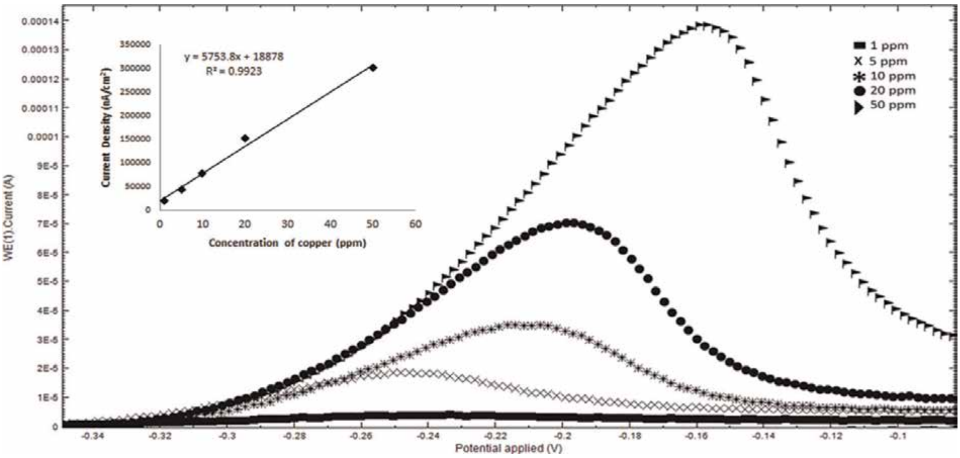


Figure 9.
CV at gold modified SPE for various Cu(II) concentration with inset showing calibration plot [144].

Bessa et al. (2021) presented a different approach to lead detection in *Lucilia cuprina*, a necrophagous insect that functioned as a GSR biomarker due to GSR consumption, As a result, an intriguing lead in forensic investigations is provided. Their survival rates were investigated, as well as the influence of lead on their embryonic growth [147]. As a working electrode, a bismuth film was deposited in an SPCE using the SAWASV process. The results showed that lead could be detected on larval samples even in the presence of interference such as Cu, Ba, and Cd. The effect of lead on mortality and larval development time was also successfully investigated [148, 149]. The revival of this area has opened up a whole new avenue for research leading to breakthrough in criminal investigations.

3. Conclusion

Voltammetry holds the key to future diagnostic tools for fast, real-time and sensitive analysis. It has found use in almost every spectrum of environment, medical care, agriculture, forensic, investigation, food and cosmetic industries for a range of analytes to be determined selectively or simultaneously depending on the requirement. The resurgence of the interest in electrochemical methods for the lucrative metal analysis required for various applications is derived from the advantages it caters to, like sensitivity and versatile application. Nanomaterials and polymers are the advanced materials being explored for their synergistic effect to modify electrode surfaces to overcome the challenges that stand in the way. The research is targeted to develop fast, stable, reproducible, miniaturized real-time sensors for use in various fields.

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Conflict of interest

The authors declare no conflict of interest.

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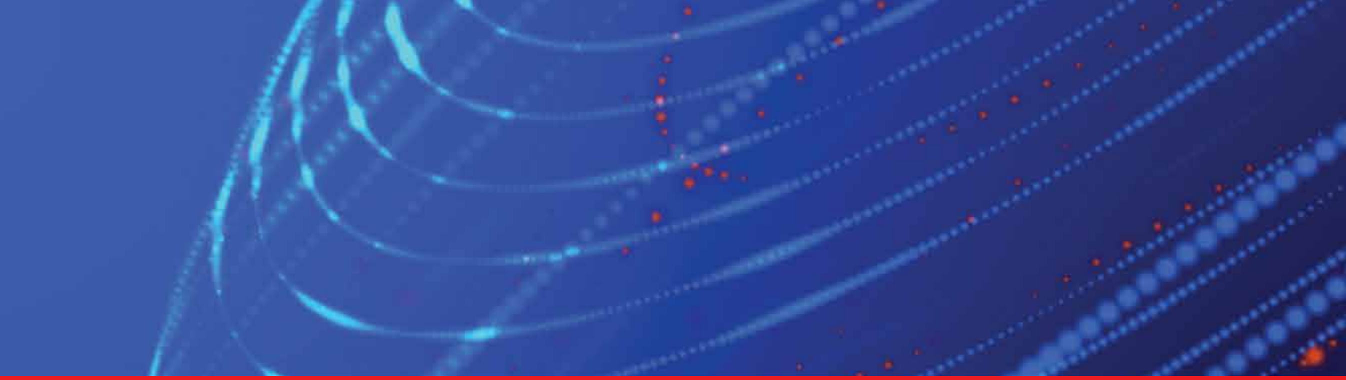

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This book provides a detailed analysis of recent advances in the various voltammetric techniques used to determine different analytes. It describes the basic concepts of voltammetry and its applications in a simple, easy-to-understand way. The book will suit anyone who wants to learn more about electrochemical sensors, different voltammetric methods, and their advanced applications, including undergraduate, postgraduate and research students.

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