We are IntechOpen, the world’s leading publisher of Open Access books
Built by scientists, for scientists

6,600 Open access books available
177,000 International authors and editors
195M Downloads

154 Countries delivered to
TOP 1% Our authors are among the most cited scientists
12.2% Contributors from top 500 universities

WEB OF SCIENCE™
Selection of our books indexed in the Book Citation Index in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com
Chapter

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 impedimetric 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$_3$)$_2$·H$_2$O, ≥99.9%), cadmium nitrate tetrahydrate (Cd(NO$_3$)$_2$·4H$_2$O, ≥99%), lead nitrate (Pb(NO$_3$)$_2$, ≥99%), nickel nitrate hexahydrate (Ni(NO$_3$)$_2$·6H$_2$O, ≥98.5%), zinc nitrate hexahydrate (Zn(NO$_3$)$_2$·6H$_2$O, ≥98%), sodium chloride (NaCl, ≥99%), calcium chloride (CaCl$_2$, ≥96%), potassium chloride (KCl, ≥99%), glucose (≥99.5%), sulfuric acid (H$_2$SO$_4$, ≥99.9%), Deionized (DI) water, sodium hydroxide (NaOH, ≥97%), ammonium acetate (CH$_3$COONH$_4$, ≥98%), and chitosan (CS, ≥85%). All chemicals used in this work were purchased from 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
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 $H_2SO_4 (1 \text{ ml})$ 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 $\mu$m and 0.3 $\mu$m 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 $\mu$L 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
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.
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 GCE 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 3.
Images SEM of (a) bare GCE electrode, (b) CS-CDs nanocomposite/GCE electrode.

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

\[
Z_{CPE} = \frac{1}{Qj\omega^n}
\]  

(1)

where Q is a constant, j is the imaginary number, \(\omega\) 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
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.

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

<table>
<thead>
<tr>
<th>[Cu^{2+}] (M)</th>
<th>$R_s$ (kΩ)</th>
<th>$\text{CPE}_{\text{m}}$ (μF)</th>
<th>n_1</th>
<th>$R_m$ (kΩ)</th>
<th>$\text{CPE}_{\text{dl}}$ (μF)</th>
<th>n_2</th>
<th>$R_{ct}$ (kΩ)</th>
<th>$\chi^2$ (10^{-4})</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^{-9}$</td>
<td>0.11</td>
<td>1.70</td>
<td>0.90</td>
<td>17.40</td>
<td>9.20</td>
<td>0.59</td>
<td>67.24</td>
<td>2.7</td>
</tr>
<tr>
<td>$10^{-8}$</td>
<td>0.10</td>
<td>1.73</td>
<td>0.89</td>
<td>16.24</td>
<td>10.01</td>
<td>0.60</td>
<td>56.56</td>
<td>6.8</td>
</tr>
<tr>
<td>$10^{-7}$</td>
<td>0.11</td>
<td>1.60</td>
<td>0.88</td>
<td>15.01</td>
<td>9.22</td>
<td>0.60</td>
<td>45.05</td>
<td>7.3</td>
</tr>
<tr>
<td>$10^{-6}$</td>
<td>0.12</td>
<td>1.56</td>
<td>0.90</td>
<td>13.40</td>
<td>9.52</td>
<td>0.61</td>
<td>36.16</td>
<td>2.1</td>
</tr>
<tr>
<td>$10^{-5}$</td>
<td>0.13</td>
<td>1.66</td>
<td>0.88</td>
<td>12.50</td>
<td>10.10</td>
<td>0.62</td>
<td>27.72</td>
<td>4.2</td>
</tr>
</tbody>
</table>

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.
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 $-\log \left( \frac{R_{tc}}{R_{tc0}} \right)$ 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 $-\log \left( \frac{R_{tc}}{R_{tc0}} \right) = 0.1 \times \log [\text{copper}] + 0.9$, where the slope is 0.1 of the sensor sensitivity. The detection limit of our copper sensor was $\approx 5 \times 10^{-10}$ M, according to the formula $\text{LOD} = \left( 3 \times \text{standard deviation} \right) / \text{slope}$. 

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 $\left( \frac{R_{tc}}{R_{tc0}} \right)$ 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 $\frac{\text{Found (M)}}{\text{Added (M)}} \times 100$. 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.
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.

**Table 3.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Added (M)</th>
<th>Found (M)</th>
<th>Recovery (%)</th>
<th>RSD (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tap water</td>
<td>$10^{-8}$</td>
<td>$9.70 \times 10^{-9}$</td>
<td>97.0</td>
<td>4.12</td>
</tr>
<tr>
<td></td>
<td>$10^{-6}$</td>
<td>$1.02 \times 10^{-6}$</td>
<td>102.0</td>
<td>1.47</td>
</tr>
</tbody>
</table>

**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.
Development of An Impedimetric Nanoplatform for Cu(II) Detection Based on Carbon Dots...
DOI: http://dx.doi.org/10.5772/intechopen.105924

Author details

Mosaab Echabaane* and Chérif Dridi
NANOMISENE Lab, LR16CRMN01, Centre for Research on Microelectronics and Nanotechnology CRMN of Technopark of Sousse, Sousse, Tunisia

*Address all correspondence to: mosaab.echabaane@gmail.com

IntechOpen

© 2022 The Author(s). Licensee IntechOpen. This chapter is distributed under the terms of the Creative Commons Attribution License (http://creativecommons.org/licenses/by/3.0), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.
References


[5] Wu T, Xu T, Ma Z. Sensitive electrochemical detection of copper ions based on the copper (II) ion assisted etching of Au@ Ag nanoparticles. Analyst. 2015;140:8041-8047. DOI: 10.1039/C5AN01888A


[24] Li Y, Li Y, Yang Y. A new amperometric H_{2}O_{2} biosensor based on nanocomposite films of


