Research Article

Preparation of Electrode Material Based to Bismuth Oxide-Attached Multiwalled Carbon Nanotubes for Lead (II) Ion Determination

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Bi2O3 was proven an attractive compound for electrode modification in heavy metal electrochemical analysis. A novel method for synthesizing Bi2O3-attached multiwalled carbon nanotubes (Bi2O3@CNTs) in solution is successfully developed in this study. Characteristics of the obtained Bi2O3@CNTs were proven by modern techniques such as X-ray diffraction, Raman spectroscopy, scanning electronic microscopy, transmission electron microscopy, cyclic voltammetry, electrochemical impedance spectroscopy, and anodic stripping voltammetry. Microscopy images and spectra results reveal that Bi2O3 particles are mainly attached at defect points on multiwalled carbon nanotubes (MWCNTs) walls. Paste electrodes based on the MWCNTs and synthesized Bi2O3@CNTs were applied for electrochemical measurements. The redox mechanism of Bi2O3 on the electrode surface was also made clear by the cyclic voltammetric tests. The recorded cyclic voltammograms and electrochemical impedance spectroscopy demonstrate that the Bi2O3@CNTs electrode was in lower charge transfer resistance than the CNTs one and in the controlled diffusion region. Investigation on the electrochemical behavior of Pb2+ at the Bi2O3@CNTs electrodes found a significant improvement of analytical response, resulting in 3.44 μg/L of the detection limit and 2.842 μA/(μg/L) of the sensitivity with linear sweep anodic stripping voltammetry technique at optimized conditions.

1. Introduction

Currently, researchers are focusing on controlling the level of heavy metals in waterways through developing novel sensors for detecting heavy metals such as lead. As low concentrations of lead (II) can cause severe ecological damage and harm human health (such as anemia, weakness, and kidney and brain damage) [1], developing a fast and highly efficient method for accurately detecting lead in wastewater is extremely necessary. Anodic stripping voltammetry (ASV) is a powerful, sensitive and selective electrochemical technique for determining heavy metal ions such as Pb [1]. These ionic species are first deposited on the working electrode (WE) in the accumulation step under a reduction potential. Followed by a potential scan, the analyte is stripped back into the solution in the stripping step, resulting in a current response proportional to its concentration [2, 3]. These redox processes occur on the WE surface, where mass and electrons are transported, and these processes depend significantly on the properties of the electrode material.

Existing literature provides an overview of several suitable electrochemical materials for WE construction [4]. Although the traditional mercury electrode has advantages, replacing it with other suitable materials is necessary owing to its toxicity to humans and the environment [5, 6]. Advanced carbon forms have been considered promising electrode replacements as they are ecofriendly and exhibit excellent electrical conductivity, chemical stability, structural versatility, and broad potential windows [3]; moreover, they require simple modifications for their application as electrodes. Carbon nanotubes (CNTs) [7], graphene [8], graphene oxide [9], and carbon nanofibers [10] are extremely useful as carbon paste electrodes to trace heavy metals from different sources. The sensing applications of MWCNTs are
Bi2O3@CNTs were prepared using ultrasonication to enhance the performance of the WE surface is formed owing to the reduction of Bi3+ in a weakly acidic electrolyte, the Bi3+ was dispersed and oxidized for 2h at room temperature. The solid material was then collected by centrifugal separation. The obtained sediment was dispersed in water and transferred into a vacuum filtration system for filtration and washing until a neutral solution was obtained. These oxidized CNTs were dried overnight at 110°C and used for Bi2O3 attachment.

Next, 3 g of the oxidized CNTs was mixed with 50 mL of Bi(NO3)3 solution (20, 50, and 70 mmol/L), which was acidified using 5 mL of HNO3 solution (0.1 M). Interactions between CNTs and Bi3+ occurred for 30 min under stirring. Next, NaOH solution (0.1 M) was slowly dropped into the mixture (at intervals of ~10 s) until the pH reached 6.5. Subsequently, the mixture was sonicated for 10 min. The solid was then filtered and washed several times. The obtained materials were heated to 270°C and held for 2 h. The final products were labelled as Bi2O3@CNTs-20, Bi2O3@CNTs-50, and Bi2O3@CNTs-70, corresponding to concentrations of 20, 50, and 70 mmol/L of the used Bi(NO3)3 solution.

2.2. Preparation of the Bi2O3@CNTs. Approximately 20 g CNTs was added to 1500 mL of HNO3 (68%) in a flask, which was placed in an ultrasonic tank. The CNTs were dispersed and oxidized for 2h at room temperature. The solid material was then collected by centrifugal separation. The obtained sediment was dispersed in water and transferred into a vacuum filtration system for filtration and washing until a neutral solution was obtained. These oxidized CNTs were dried overnight at 110°C and used for Bi2O3 attachment.

2.3. Electrode Fabrication. Mixtures of CNTs (or Bi2O3@CNTs) and paraffin oil (80:20 wt.%, respectively) were dispersed in n-hexane under ultrasonication until pastes were formed. The obtained fresh pastes were packed and pressed into the end of the cavity with a 3 mm inner diameter in the polytetrafluoroethylene (PTFE) electrode body. A copper wire was used to conduct electrical signals. The electrode surface was polished on a weigh paper before each electrochemical measurement.

2.4. Electrochemical Measurements. A solution mixture of 0.1 M KCl and 0.1 M acetate buffer (pH 4.0) was used as the electrolytic support for all electrochemical tests. The cyclic voltammetry (CV) measurements with the potential ranging from -0.2 V to 1.0 V at different scan rates (10, 20, 30, 40, 50, 70, 100, 150, and 200 mV/s) and electrochemical impedance spectroscopy (EIS) with a 5 mV amplitude over a frequency range of 1-105 Hz were conducted on the electrodes in the electrolyte containing 50 mM K3Fe(CN)6.

The Pb2+ concentrations in the electrolyte were quantified using linear sweep anodic stripping voltammetry (LSASV). WE was first subjected to an accumulation potential (Eacc) for an accumulation time (tacc) while the solution was stirred. Following the accumulation step, stirring was stopped to reach an equilibrium period of 10 s, and stripping voltammograms were recorded by sweeping the potential from Eacc to -0.2 V at a rate of 50 mV/s. The Eacc, tacc, and pH of the electrolyte were optimized.
3. Results and Discussion

3.1. Characterization of Electrode Materials. Figure 1(a) presents the XRD patterns of the CNTs and Bi$_2$O$_3$@CNTs. The characteristic diffraction peaks of CNTs at 2θ = 26.4° and 43.2° were assigned to the C(100) and C(002) planes [21]. These two peaks indicate the existence of amorphous phases in the CNTs owing to their low intensity and large width [22]. The diffraction peaks for α-Bi$_2$O$_3$ are observed at 2θ = 28.0° (021), 32.3° (220), 46.3° (222), and 54.7° (023) in the XRD patterns of the Bi$_2$O$_3$@CNTs, corresponding to the JCPDS file no. 76-1730. These results indicate that the synthesized Bi$_2$O$_3$ exhibits monoclinic symmetry, as observed in an earlier study [23, 24]. The XRD patterns of Bi$_2$O$_3$@CNTs-20, Bi$_2$O$_3$@CNTs-50, and Bi$_2$O$_3$@CNTs-70 show increased peak intensities at 2θ = 28.0°, resulting from the increased Bi$_2$O$_3$ loading [25]. Average crystallite size of Bi$_2$O$_3$ particles was found to be 15.8, 16.8, and 14.9 nm for Bi$_2$O$_3$@CNTs-20, Bi$_2$O$_3$@CNTs-50, and Bi$_2$O$_3$@CNTs-70, respectively, by applying the Debey-Scherer equation: 

$$D = \frac{0.99 \lambda}{B \cos \theta}$$

where $\lambda$ is wavelength, $B$ is full width at half maximum, and $\theta$ is Bragg’s angle [26].
Differences in the microstructures and photon and electron quantum confinements of the electrode materials could be identified from their Raman spectra, as shown in Figure 1(b). Three prominent Raman bands of the CNTs appear at 1325 cm\(^{-1}\) (D-band), 1582 cm\(^{-1}\) (G-band), and 2656 cm\(^{-1}\) (G'-band). The D-band confirms the presence of amorphous carbon owing to structural defects, with strong dispersion leading to double resonance peaks [27, 28]. The G- and G'-bands indicate graphitic rings with sp\(^2\) hybridized C=C bonds [27, 29]. Increased intensity ratios of the D- and G-bands (\(I_D/I_G\)) [27] indicate increased microstructural disorder, which is higher for the Bi\(_2\)O\(_3\)@CNTs than the CNTs. The intensity ratios, \(I_G'/I_G\), of the CNTs, Bi\(_2\)O\(_3\)@CNTs-20, Bi\(_2\)O\(_3\)@CNTs-50, and Bi\(_2\)O\(_3\)@CNTs-70 (0.75, 0.70, 0.66, and 0.40, respectively) decreased, demonstrating the increased formation of Bi\(_2\)O\(_3\) according to the used Bi\(^{3+}\) concentrations [27]. The above results could probably be attributed to the attachment of the Bi\(_2\)O\(_3\) particles to the CNTs sidewall defects. Finally, the minor D'-band at 1614 cm\(^{-1}\) corresponds to the defective graphite structure in the CNTs, typically amorphous hydrogenated carbon (\(\alpha\):C-H) [30]. For Bi\(_2\)O\(_3\)@CNTs, the dominant vibration band emerged at a low frequency (181 cm\(^{-1}\)), ascribed to the displacements of the O atoms in Bi\(_2\)O\(_3\) and the overtone vibrations of Bi [31]. This would have probably originated from CNTs. Furthermore, we could not confirm the origin of the relatively weak band at 277 cm\(^{-1}\); however, it is close to the band at 288 cm\(^{-1}\) corresponding to multiple regions in the Brillouin zone with a number of photon branches [31].

The SEM micrographs of the electrode materials are shown in Figure 2. Figure 2(a) clearly shows that the individual CNTs exist as tubular fibers with diameters less than 50 nm and are randomly twisted together, generating a three-dimensional network. The presence of Bi\(_2\)O\(_3\) particles in the Bi\(_2\)O\(_3\)@CNTs is obvious owing to the increased utilization of Bi\(^{3+}\) in the solutions, as observed in Figures 2(b)–2(d). The Bi\(_2\)O\(_3\)@CNTs-20 sample presents a sparse distribution of Bi\(_2\)O\(_3\) particles (Figure 2(b)). In contrast, Bi\(_2\)O\(_3\)@CNTs-50 and Bi\(_2\)O\(_3\)@CNTs-70 indicate widespread, discrete, and relatively homogeneous distributions of Bi\(_2\)O\(_3\).
particles attached to the CNTs sidewalls. When the used Bi^{3+} quantity exceeds the necessary amount, Bi$_2$O$_3$ clusters are formed, as shown in Figure 2(d). This may be disadvantageous to the sensitivity of the Bi$_2$O$_3$@CNTs-70 electrode owing to the low electrical conductivity of Bi$_2$O$_3$ (~1 S/cm) [32] compared to that of the bulk CNTs (~100 S/cm) [33]. The CNTs serve as skeletons for attaching Bi$_2$O$_3$ particles. TEM analyses of the CNTs and Bi$_2$O$_3$@CNTs samples were performed in order to characterize the particle size distribution, and the results are shown in Figure 3. Most of

![Cyclic voltammograms](image)

**Figure 4:** Cyclic voltammograms of (a) CNTs and Bi$_2$O$_3$@CNTs-50 electrodes in electrolyte without K$_3$Fe(CN)$_6$ and (b) electrode in electrolyte containing 50 mM K$_3$Fe(CN)$_6$. Conditions: pH 4 and scan rate of 50 mV/s.

![Influence of scan rate](image)

**Figure 5:** Influence of scan rate on peak current determined from CV measurements. Conditions: 50 mM K$_3$Fe(CN)$_6$ in the electrolyte at pH 4.
the CNTs are tubular porous structures with nonsmoothed surfaces caused by the defective CNTs sidewalls. Impurities in CNTs did not present through the TEM images (Figure 3(a)) as well as XRD pattern for CNTs (Figure 1(a)). The morphology of Bi$_2$O$_3$@CNTs-50 (Figures 3(b) and 3(c)) shows that the Bi$_2$O$_3$ particles are discretely attached to the CNTs. The arrow in Figure 3(b) points to a smooth CNT with little or no Bi$_2$O$_3$ attached to it. Figure 3(c) shows that Bi$_2$O$_3$ nanoparticles are present on the outer walls of the CNTs at defect points but do not enter the hollow channels inside the CNTs, indicating excellent agreement with the Raman spectra analyses. A recent study by Dighole et al. [23] also proved the formation of Bi$_2$O$_3$-decorated multiwalled carbon nanotubes via TEM imaging. However, the TEM studies conducted by Dighole et al. did not show the presence of Bi$_2$O$_3$ on the outer walls of the CNTs.

3.2. Electrochemical Properties of the Electrodes. The electrochemical characteristics of the electrodes were investigated from CV and EIS measurements, as illustrated in Figures 4–6. The area of the CV curve (Figure 4(a)) of the CNTs electrode is 1.48-folds higher than that of the Bi$_2$O$_3$@CNTs-50 electrode, indicating the reduced specific capacitance of the CNTs with attached Bi$_2$O$_3$ [34]. This characteristic of the Bi$_2$O$_3$@CNTs-50 electrode is advantageous for distinguishing the Faradic current in the analytical signals [35]. The current curves in Figure 4(a) appear as a knob hill at +0.25 V. This may be attributed to the multistep redox reactions between the O atoms in the C–O or/and C=O bond(s) present in the CNTs, although the CNTs were treated at a high temperature [36]. In the CV curve of the Bi$_2$O$_3$@CNTs-50 electrode (Figure 4(a)), the small peak C1 at +0.15 V demonstrates the partial reduction of Bi$_2$O$_3$ into BiO$^{2-}$; peak C2 at −0.61 V corresponds to the successive reduction of BiO$^{2-}$ into BiO$_2$ and subsequently to Bi$^0$ [37]. The anodic potential scan results showed that the Bi$^0$ on the surface Bi$_2$O$_3$@CNTs-50 electrode was oxidized to BiO$^+$ through an active dissolution process [37, 38], resulting in the appearance of peak A1 (Figure 4(a)) at −0.44 V. Peak A2 (+0.48 V) corresponds to the oxidation of Bi$^0$ to

| Table 1: Fe$^{2+}$/Fe$^{3+}$ peak potentials and currents obtained from CV curves. |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| Electrodes      | CNTs            | Bi$_2$O$_3$@CNTs-20 | Bi$_2$O$_3$@CNTs-50 | Bi$_2$O$_3$@CNTs-70 |
| $i_{pa}$ (mA)   | 0.613           | 0.634           | 0.677           | 0.649           |
| $E_{pa}$ (V)    | 0.384           | 0.373           | 0.301           | 0.321           |
| $i_{pc}$ (mA)   | 0.736           | 0.672           | 0.658           | 0.675           |
| $E_{pc}$ (V)    | 0.067           | 0.143           | 0.148           | 0.132           |

Figure 6: (a) Nyquist and (b) Bode plots developed from EIS data of the electrodes. Conditions: 50 mM K$_3$Fe(CN)$_6$ in the electrolyte, pH 4.
The double layer, which is formed at the electrode surface, plays a crucial role in the electrochemical processes. The double layer capacitance, $C_{dl}$, is directly proportional to the surface area and inversely proportional to the thickness of the electrical double layer (EDL). The $C_{dl}$ values are calculated using the following equation:

$$C_{dl} = \frac{Q}{V}$$

where $Q$ is the charge and $V$ is the potential difference.

The electrochemical impedance spectroscopy (EIS) measurements provide valuable information about the electrode/electrolyte interface. The impedance spectrum is often represented in the form of a Nyquist plot, which shows the relationship between the real part of the impedance, $Z'$, and the imaginary part, $Z''$, as a function of frequency.

The Nyquist plot is composed of two regions: the high-frequency and low-frequency regions. The high-frequency region is associated with the Faradaic processes, while the low-frequency region is associated with the capacitive processes.

The equivalent circuit model used to interpret the EIS data is given by the following equation:

$$Z_{eq} = R_{ct} + \frac{1}{j\omega C_{dl}} + R_{f}$$

where $R_{ct}$ is the charge transfer resistance, $C_{dl}$ is the double layer capacitance, and $R_{f}$ is the resistance due to the electrolyte.

The $C_{dl}$ values are calculated using the following equation:

$$C_{dl} = \frac{Q}{V}$$

where $Q$ is the charge and $V$ is the potential difference.

The $R_{ct}$ values are calculated using the following equation:

$$R_{ct} = \frac{V}{I}$$

where $V$ is the potential difference and $I$ is the current.

The $R_{f}$ values are calculated using the following equation:

$$R_{f} = \frac{1}{\frac{1}{R_{ct}} + \frac{1}{R_{dl}}}$$

where $R_{ct}$ is the charge transfer resistance and $R_{dl}$ is the double layer resistance.

The EIS spectra of the electrodes in Figure 6(a) indicate that the interfacial process is a combination of controlled charge transfer (indicated by semicircles) and mass diffusion (indicated by arcs).

The “knee” in the EIS spectrum of the CNTs electrode (Figure 6(a)) shows the existence of a transition region between charge transfer and mass diffusion [48]. Moreover, the radius of the semicircle is large in the EIS spectrum of the CNTs electrode, indicating the dominance of charge transfer, thereby resulting in the nonlinear relationship between the peak current and the square root of the scan rate (Figure 5(a)). For the Bi$_2$O$_3$@CNTs electrodes, the contribution of the charge transfer decreased and that of mass diffusion increased. Steep arcs exceeding 45° at low frequencies indicate the pore narrowing phenomenon on the electrode surface with depth penetration [49]. For porous electrodes, the complex electron transfers occur through the electrolyte, EDL, electrode material itself, and diffusion of the electrolyte onto the electrode [50, 51], represented by the $R_{ct}$, $(C_{dl}/R_{ct})$, $(C_{dl}/R_{f})$, and $W_s$ elements in the equilibrium circuit shown in Figure 6(a).

Table 2 presents the parameters obtained from the EIS data fitting.

| Electrodes | CNTs | Bi$_2$O$_3$@CNTs-20 | Bi$_2$O$_3$@CNTs-50 | Bi$_2$O$_3$@CNTs-70 |
|------------|------|---------------------|---------------------|---------------------|
| $R_s$ (Ω)  | 4.3  | 14.0                | 19.3                | 24.4                |
| $C_{dl}$ (F) | $3.3 \times 10^{-4}$ | $3.1 \times 10^{-7}$ | $1.7 \times 10^{-7}$ | $1.5 \times 10^{-7}$ |
| $R_{ct}$ (Ω) | 6.6  | 211.2               | 171.7               | 156.6               |
| $C_s$ (F)  | $9.7 \times 10^{-7}$ | $10.2 \times 10^{-4}$ | $7.0 \times 10^{-4}$ | $9.2 \times 10^{-4}$ |
| $R_s$ (Ω)  | 281.7 | 81.4                | 58.5                | 45.4                |
| $W_s$ (Ω)  | 387.0 | 266.0               | 78.4                | 87.8                |

The anodic and cathodic peak currents of the Fe$_2$+/Fe$_3^+$ couple determined from the CV curves of the electrodes as a function of the scan rate (v) from 10 to 200 mV/s are shown in Figure 5. Good linear correlations between the peak currents and current are a function of the scan rate (v) from 10 to 200 mV/s are shown in Figure 5. Good linear correlations between the peak currents and square root of the scan rate (v$^{1/2}$) are observed for the Bi$_2$O$_3$@CNTs-50 and Bi$_2$O$_3$@CNTs-70 electrodes (Figure 5(a)), indicating that the redox process involves controlled diffusion [43]. However, this behavior is not observed for the CNTs and Bi$_2$O$_3$@CNTs-20 electrodes; at low scan rates, the peak current increased with the increasing scan rate for these electrodes, the opposite of what occurred at high scan rates. This trend was also observed in an earlier study [44]. The porous electrode surface generates a complex and thick EDL [45], resulting in a heterogeneous electron transfer rate; therefore, the intensity of the peak current decreases at a high scan rate [46]. However, understanding of this influence is limited in the literature. Consequently, Bi$_2$O$_3$ enhanced the electrochemical performance of the electrode, thus proving its potential for analytical applications. Moreover, the poor linear correlations between the peak responses and scan rates are evident in Figure 5(b), verifying that the adsorptive resistance can be neglected [47].

The EIS spectra of the electrodes in Figure 6(a) indicate that the interfacial process is a combination of controlled charge transfer (indicated by semicircles) and mass diffusion (indicated by arcs).

The “knee” in the EIS spectrum of the CNTs electrode (Figure 6(a)) shows the existence of a transition region between charge transfer and mass diffusion [48]. Moreover, the radius of the semicircle is large in the EIS spectrum of the CNTs electrode, indicating the dominance of charge transfer, thereby resulting in the nonlinear relationship between the peak current and the square root of the scan rate (Figure 5(a)). For the Bi$_2$O$_3$@CNTs electrodes, the contribution of the charge transfer decreased and that of mass diffusion increased. Steep arcs exceeding 45° at low frequencies indicate the pore narrowing phenomenon on the electrode surface with depth penetration [49]. For porous electrodes, the complex electron transfers occur through the electrolyte, EDL, electrode material itself, and diffusion of the electrolyte onto the electrode [50, 51], represented by the $R_{ct}$, $(C_{dl}/R_{ct})$, $(C_{dl}/R_{f})$, and $W_s$ elements in the equilibrium circuit shown in Figure 6(a).

Table 2 presents the parameters obtained from fitting the EIS data to this circuit. The EDL capacitance ($C_{dl}$) of the Bi$_2$O$_3$@CNTs electrode is significantly lower than that of the CNTs one, indicating the planar surface of the Bi$_2$O$_3$@CNTs electrode owing to the attachment of Bi$_2$O$_3$ particles on the CNTs sidewalls at the defect points. Moreover, the Warburg element ($W_s$) of the electrode decreased in the presence of Bi$_2$O$_3$, proving that Bi$_2$O$_3$ contributed toward decreasing the porosity of CNTs, thereby limiting the diffusion of the electrolyte onto the electrode [52]. The enhanced charge transfer in Bi$_2$O$_3$@CNTs electrodes is demonstrated by the lower electrical resistance ($R_s$) when compared to that of the CNTs because of the hybridization reactions between the Bi-6p$^3$
and CNT-π^2 orbitals, leading to reduced bandgaps in Bi_2O_3 and CNTs [53]. A similar trend was also observed earlier [44]. However, the capacitance (C_e) of Bi_2O_3@CNTs is higher than that of the CNTs owing to the high permittivity of Bi_2O_3 [54]. The multistep mechanism of the electrochemical process on the electrode surface in the presence of Bi [40] affects the charge transfer resistance (R_cl) of the EDL [55] that may have led to a higher R_cl of the Bi_2O_3@CNTs electrode than that observed for the CNTs electrode. However, the values of (R_cl + R_e) for the Bi_2O_3@CNTs electrodes are generally lower than that for the CNTs electrode, indicating the positive effect of Bi_2O_3 on electrical signal conductivity. These results agree with the CV measurements shown in Figure 4(b).
3.3. ASV Studies. The electrochemical responses of the different electrodes to Pb\(^{2+}\) (Figure 7(a)) were examined via ASV measurements in 0.1 M acetate buffer solution containing 30 \(\mu\)g/L of Pb\(^{2+}\). At an \(E_{\text{acc}}\) of \(-0.1\) V, Bi\(_2\)O\(_3\) was reduced to Bi\(^0\) (indicated in Figure 4(a)), which further enriched Pb by forming Bi-Pb alloys [15]. Consequently, the Bi\(_2\)O\(_3@CNTs\) electrodes exhibited enhanced Pb\(^{2+}\) sensing properties compared to those of the CNTs electrode, as indicated by their improved anodic peak currents. The peak potential was approximately \(-0.40\) V for the CNTs electrode, whereas it was approximately \(-3.83\) V for the Bi\(_2\)O\(_3@CNTs\) electrodes. This positive shift reveals a more complex reduction of Pb\(^0\) because of Bi-Pb alloy formation [15] on the Bi\(_2\)O\(_3@CNTs\) electrodes than on the CNTs electrode, indicating differences in the interaction mechanism between Pb\(^{2+}\) and the CNTs and between Pb\(^{2+}\) and Bi\(_2\)O\(_3@CNTs\) electrode surfaces [58]. The sensitivity for Pb\(^{2+}\) detection increases in the following order: CNTs, Bi\(_2\)O\(_3@CNTs\)-20, Bi\(_2\)O\(_3@CNTs\)-70, and Bi\(_2\)O\(_3@CNTs\)-50 electrodes. Therefore, the Bi\(_2\)O\(_3@CNTs\)-50 electrode is a favorable candidate for Pb\(^{2+}\) detection applications.

Important parameters of the LSASV technique (\(E_{\text{acc}}, t_{\text{acc}}, \) and pH) were considered to optimize Pb\(^{2+}\) detection using the Bi\(_2\)O\(_3@CNTs\)-50 electrode. Figures 7(b)–7(d) show the peak currents obtained from the ASV measurements under different conditions.

The CV measurements presented in Figure 4(a) indicate that Bi\(^{3+}\) in Bi\(_2\)O\(_3\) is reduced to Bi\(^0\) at \(-0.61\) V, revealing the upper \(E_{\text{acc}}\) limit for electrochemical analyses involving Pb\(^{2+}\). Figure 7(b) shows that the stripping response of Pb\(^{2+}\) depends on the accumulation potential in the interval from \(-1.4\) V to \(-0.6\) V. The Pb oxidative peak signal increases with a negative shift of the \(E_{\text{acc}}\) from \(-0.6\) V to \(-1.0\) V resulting from the enhanced microstructural parameters of the deposited Bi\(^0\) particles such as their size and distribution [59], thus improving the Pb-Bi alloy formation [60]. However, the hydrogen evolution reaction on the electrode surface begins to occur at \(-1.2\) V in an acidic electrolyte [16], which could have prevented Pb\(^{2+}\) deposition and damaged the Bi\(^0\) film. This led to a substantial decrease in the stripping response at a high negative \(E_{\text{acc}}\). Consequently, \(E_{\text{acc}} = -1.0\) V was considered the optimum accumulation potential and applied in the accumulation time (\(t_{\text{acc}}\)) studies. Figure 7(c) presents the effects of different \(t_{\text{acc}}\) values, namely, 30, 60, 90, 120, and 150 s, on the stripping signals. With a prolonged \(t_{\text{acc}}\) the amount of Pb deposited on the electrode surface increased until saturation, resulting in a rapidly increasing peak current with \(t_{\text{acc}}\) up to 120 s and then tending to remain constant at a longer \(t_{\text{acc}}\). Thus, \(t_{\text{acc}} = 120\) s was chosen as the suitable accumulation time for subsequent experiments. As depicted in Figure 7(d), the pH has a significant influence on the peak signal. At low pH, the stripping current decreases due to protonation of the CNTs structure with the increasing bandgap [61]. Moreover, the potential for hydrogen evolution shifts to more positive values at low pH; thus, the peak current is low at low pH. In contrast, at high pH, Pb\(^{2+}\) and intermediate forms of Bi could be converted to insoluble hydroxide complexes [62], leading to decreasing peak currents with increasing pH. Figure 7(d) shows that the optimum sensitivity of the electrodes for Pb\(^{2+}\) is at pH = 5.0.

To evaluate the applicability of the Bi\(_2\)O\(_3@CNTs\)-50 electrode for Pb\(^{2+}\) detection, the relationships of current responses with Pb\(^{2+}\) concentrations were determined from the electrochemical measurements using the LSASV technique using the following optimal parameters: \(E_{\text{acc}} = -1.0\) V, \(t_{\text{acc}} = 120\) s, and pH = 5.0. The obtained voltammograms are presented in Figure 8, along with the calibration plot of Pb\(^{2+}\) in the range of 2–40 \(\mu\)g/L (in the insert). The peak current is directly proportional to the Pb\(^{2+}\) concentration according to the following linear regression equation: \(i(\mu\text{A}) = 2.842 \times C_{\text{Pb}^{2+}}(\mu\text{g/L}) + 0.07\) (correlation coefficient \(R^2 = 0.9986\)). The limit of detection (LOD) was 3.44 \(\mu\)g/L according to the 3\(\sigma\) criteria (\(N = 6\)). Table 3 compares the obtained LOD and sensitivity with those in previous reports, proving the applicability of the fabricated Bi\(_2\)O\(_3@CNTs\) electrodes for Pb\(^{2+}\) detection.

3.4. Application to River Water Media. Water from the Saigon River was collected, filtered through a 0.45 \(\mu\)m membrane, and sonicated for ICP-MS and ASV measurements. Because the Pb\(^{2+}\) concentration in the sample was lower than the LOD of the ICP-MS method, this natural water was used as the medium for preparing the ASV analytical solution containing 5 \(\mu\)g/L Pb\(^{2+}\), 0.1 M KCl, and 0.1 M acetate buffer (pH 4.0). Under the optimal conditions, the
trode for Pb2+ determination at the trace level. These results prove the excellent applicability of the Bi2O3@CNTs electrodes for Pb2+ detection using the LSASV technique, namely, the detection limit was 3.4 μg/L, which is lower than that of the CNTs electrode. The optimal parameters for Pb2+ detection were determined: accumulation potential, accumulation time, and pH of the solution, were determined. The obtained detection limit and sensitivity from the Pb2+ calibration curve revealed the excellent applicability of the Bi2O3@CNTs electrodes for detecting heavy metal ions. In the future, the interaction mechanisms between Bi2O3 and CNTs and other applications of the Bi2O3@CNTs electrodes will be investigated.

### Data Availability

The experimental data used to support the findings of this study are included within the article.

### Conflicts of Interest

The authors declare that they have no conflicts of interest.

### References

1. A. L. Wani, A. Ara, and J. A. Usmani, “Lead toxicity: a review,” *Interdisciplinary Toxicology*, vol. 8, no. 2, pp. 55–64, 2015.
2. A. J. Borrell, N. E. Reily, and J. V. Macpherson, “Addressing the practicalities of anodic stripping voltammetry for heavy metal detection: a tutorial review,” *Analyst*, vol. 144, no. 23, pp. 6834–6849, 2019.
3. M. Oliveira Salles, A. P. Ruas de Souza, J. Naozuka, P. V. de Oliveira, and M. Bertotti, “Bismuth modified gold microelectrode for Pb(II) determination in wine using alkaline medium,” *Electroanalysis*, vol. 21, no. 12, pp. 1439–1442, 2009.
4. A. García-Miranda Ferrari, P. Carrington, S. J. Rowley-Neale, and C. E. Banks, “Recent advances in portable heavy metal electrochemical sensing platforms,” *Environmental Science: Water Research & Technology*, vol. 6, no. 10, pp. 2676–2690, 2020.
5. J. A. Barón-Jaimez, J. L. Marulanda-Arévalo, and J. J. Barba-Ortega, “Electrodes friendly with the environment for detect heavy metal,” *Dyna*, vol. 81, no. 187, pp. 122–128, 2014.
6. P. Zuman, “Role of mercury Electrodes in contemporary analytical chemistry,” *Electroanalysis: An International Journal Devoted to Fundamental and Practical Aspects of Electroanalysis*, vol. 12, no. 15, pp. 1187–1194, 2000.
7. A. Vimala and C. Vedhi, “Electrochemical sensors for heavy metals detection in *Gracilariia corticata* using multiwalled carbon nanotubes modified glassy carbon electrode,” *Journal of Analytical Chemistry*, vol. 74, no. 3, pp. 276–285, 2019.
8. M. Pumera, A. Ambrosi, A. Bonanni, E. L. Chng, and H. L. Poh, “Graphene for electrochemical sensing and biosensing,” *TrAC Trends in Analytical Chemistry*, vol. 29, no. 9, pp. 954–965, 2010.
9. X. Xuan, M. F. Hossain, and J. Y. Park, “A fully integrated and miniaturized heavy-metal-detection sensor based on micropatterned reduced graphene oxide,” *Scientific Reports*, vol. 6, no. 1, article 33125, 2016.
10. J. Wu, Z. Xu, X. Wang et al., “Cadmium-sensitive measurement using a nano-copper-enhanced carbon fiber electrode,” *Sensors*, vol. 19, no. 22, p. 4901, 2019.
11. J. Manjunatha, “A new electrochemical sensor based on modified carbon nanotube-graphite mixture paste electrode for voltammetric determination of resorcinol,” *Asian Journal of Pharmaceutical and Clinical Research*, vol. 10, no. 12, pp. 295–300, 2017.
12. G. E. Uwaya and O. E. Fayemi, “Electrochemical detection of choline at f-MWCNT/Fe3O4 nanocomposite modified glassy
carbon electrode,” *Materials Research Express*, vol. 8, no. 5, article 055403, 2021.

[13] C. Hu and S. Hu, “Carbon Nanotube-Based Electrochemical Sensors: Principles and Applications in Biomedical Systems,” *Nanomaterials for Chemical Sensing Technologies*, vol. 2009, article 187615, pp. 1–40, 2009.

[14] L. Pujol, D. Evrard, K. Groenen-Serrano, M. Freyssinier, A. Ruffien-Cizsak, and P. Gros, “Electrochemical sensors and devices for heavy metals assay in water: the French groups’ contribution,” *Frontiers in Chemistry*, vol. 2, 2014.

[15] J. Wang, “Stripping analysis at bismuth electrodes: a review,” *Electroanalysis*, vol. 17, no. 15–16, pp. 1341–1346, 2005.

[16] G. Hwang, W. Han, J. Park, and S. Kang, “Determination of trace metals by anodic stripping voltammetry using a bismuth-modified carbon nanotube electrode,” *Talanta*, vol. 76, no. 2, pp. 301–308, 2008.

[17] N. Serrano, A. Alberich, J. M. Díaz-Cruz, C. Ariño, and L. Pujol, D. Evrard, K. Groenen-Serrano, M. Freyssinier, M. Esteban, “Preparation and characterization of bismuth oxide nanoparticles-decorated carbon nanotubes: an Effective nanoelectrode for Enhanced electrocatalytic 4-nitrophenol reduction,” *Frontiers in Chemistry*, vol. 8, 2020.

[18] A. Economou, “Screen-printed electrodes modified with “green” metals for electrochemical stripping analysis of toxic Elements,” *Sensors*, vol. 18, no. 4, p. 1032, 2018.

[19] A. T. Kuhn and C. Y. Chan, “pH changes at near-electrode surfaces,” *Journal of Applied Electrochemistry*, vol. 13, no. 2, pp. 189–207, 1983.

[20] C. Dossi, D. Monticelli, A. Pozzi, and S. Recchia, “Exploiting chemistry to improve performance of screen-printed, bismuth film electrodes (SP-BiFE),” *Biosensors (Basel)*, vol. 6, no. 3, p. 38, 2016.

[21] R. Das, S. B. A. Hamid, M. E. Ali, S. Ramakrishna, and W. Yongzhi, “Carbon nanotubes characterization by X-ray powder diffraction – a review,” *Current Nanoscience*, vol. 11, no. 1, pp. 23–35, 2015.

[22] L. Xu, Y. Zhang, X. Zhang et al., “Designed synthesis of tunable amorphous carbon nanotubes (a-CNTs) by a novel route and their oxidation resistance properties,” *Bulletin of Materials Science*, vol. 37, no. 6, pp. 1397–1402, 2014.

[23] R. P. Dighole, A. V. Munde, B. B. Mulik, and B. R. Sathe, “Bi2O3 nanoparticles decorated carbon Nanotube: an Effective nanoelectrode for Enhanced electrocatalytic 4-nitrophenol reduction,” *Frontiers in Chemistry*, vol. 8, 2020.

[24] A. P. Periasamy, S. Yang, and S.-M. Chen, “Preparation and characterization of bismuth oxide nanoparticles-multiwalled carbon nanotube composite for the development of horseradish peroxidase based H2O2 biosensor,” *Talanta*, vol. 87, pp. 15–23, 2011.

[25] Z. Jian and W. Hejing, “The physical meanings of 5 basic parameters for an X-ray diffraction peak and their application,” *Chinese Journal of Geochemistry*, vol. 22, no. 1, pp. 38–44, 2003.

[26] R. I. Jibrael and M. K. A. Mohammed, “Production of graphene powder by electrochemical exfoliation of graphite electrodes immersed in aqueous solution,” *Optik*, vol. 127, no. 16, pp. 6384–6389, 2016.

[27] L. Bokobza, J. L. Bruneel, and M. Couzi, “Raman spectra of carbon-based materials (from graphite to carbon black) and of some silicone composites,” *Journal of Carbon Research*, vol. 1, no. 1, pp. 77–94, 2015.

[28] D. S. Ahmed, M. K. A. Mohammed, and M. R. Mohammad, “Sol–gel synthesis of Ag-doped titania-coated carbon nanotubes and study their biomedical applications,” *Chemical Papers*, vol. 74, no. 1, pp. 197–208, 2020.

[29] M. Zdrojek, W. Gebicki, C. Jastrzebski, T. Melin, and A. Huczko, “Studies of multiwall carbon nanotubes using Raman spectroscopy and atomic force microscopy,” *Solid State Phenomena*, vol. 99–100, pp. 265–268, 2004.

[30] F. K. Tung, M. Yoshimura, and K. Ueda, “Direct fabrication of carbon nanotubes STM tips by liquid catalyst-assisted microwave plasma-enhanced chemical vapor deposition,” *Journal of Nanomaterials*, vol. 2009, Article ID 612549, 5 pages, 2009.

[31] J. S. Lannin, J. M. Calleja, and M. Cardona, “Second-order Raman scattering in the group-V7, semimetals: Bi, Sb, and As,” *Physical Review B*, vol. 12, no. 2, pp. 585–593, 1975.

[32] R. Mandfield, “The electrical properties of bismuth oxide,” *Proceedings of the Physical Society. Section B*, vol. 62, no. 8, pp. 476–483, 1949.

[33] H. L. Zhang, J. F. Li, B. P. Zhang, K. F. Yao, W. S. Liu, and H. Wang, “Electrical and thermal properties of carbon nanotube bulk materials: experimental studies for the 328–958K temperature range,” *Physical Review B*, vol. 75, no. 20, article 205407, 2007.

[34] M. Nawwar, R. Poon, R. Chen, R. P. Sahu, I. K. Puri, and I. Zhitomirsky, “High areal capacitance of Fe3O4-decorated carbon nanotubes for supercapacitor electrodes,” *Carbon Energy*, vol. 1, no. 1, pp. 124–133, 2019.

[35] F. Scholz, “Voltammetric techniques of analysis: the essentials,” *ChemTexts*, vol. 1, no. 4, article 17, 2015.

[36] M. T. Caccamo, G. Mavilia, and S. Magazù, “Thermal investigations on carbon nanotubes by spectroscopic techniques,” *Applied Sciences*, vol. 10, no. 22, p. 8159, 2020.

[37] V. Vivier, A. Régis, G. Sagon, J. Y. Nedelec, L. T. Yu, and C. Cachet-Vivier, “Cyclic voltammetry study of bismuth oxide Bi2O3 powder by means of a cavity microelectrode coupled with Raman microspectrometry,” *Electrochimica Acta*, vol. 46, no. 6, pp. 907–914, 2001.

[38] W. S. Li, X. M. Long, J. H. Yan, J. M. Nan, H. Y. Chen, and Y. M. Wu, “Electrochemical behaviour of bismuth in sulfuric acid solution,” *Journal of Power Sources*, vol. 158, no. 2, pp. 1096–1101, 2006.

[39] C. Lee, S. Jeong, N. Myung, and K. Rajeshwar, “Preparation of Au-Bi2O3 Nanocomposite by anodic electrodeposition combined with galvanic replacement,” *Journal of The Electrochemical Society*, vol. 161, no. 10, pp. D499–D503, 2014.

[40] T. T. P. Nguyen, X. G. Trinh, and D. T. T. Uyen, “Using electrode made of carbon nanotubes and bismuth oxide for the determination of metal concentration by anodic stripping voltammetry,” *Journal of Chemistry*, vol. 2019, Article ID 6170967, 7 pages, 2019.

[41] T. Trunzer, T. Stummvoll, M. Berzensmeier, P. Fraga-García, and S. Berensmeier, “Using elec trode made of carbon nanotubes and bismuth oxide for the determination of metal concentration by anodic stripping voltammetry,” *Journal of Electroanalytical Chemistry*, vol. 797, no. 1, pp. 265–268, 2014.

[42] Y. Choudhary, L. Jothi, and G. Nageswaran, “Electrochemical characterization,” in *Spectroscopic Methods for Nanomaterials Characterization*, S. Thomas, R. Thomas, A. Zachariah, and R. Mishra, Eds., pp. 19–54, Elsevier Inc., U.S., 2017.

[43] J. E. B. Randles, “A cathode ray polarograph. Part II.—the current-voltage curves,” *Transactions of the Faraday Society*, vol. 44, pp. 327–338, 1948.
[44] Y. Suzuki, Y. Fukunaka, and T. Goto, “Interfacial phenomena associated with Li electrodeposition on liquid Ga substrates in propylene carbonate,” *Electrochemistry Communications*, vol. 100, pp. 20–25, 2019.

[45] H. Tao, C. Lian, and H. Liu, “Multiscale modeling of electrolytes in porous electrode: from equilibrium structure to non-equilibrium transport,” *Green Energy & Environment*, vol. 5, no. 3, pp. 303–321, 2020.

[46] S. Sarkar, P. Chaturvedi, L. Yan et al., “Synergistic effect of iron diselenide decorated multi-walled carbon nanotubes for enhanced heterogeneous electron transfer and electrochemical hydrogen evolution,” *Electrochimica Acta*, vol. 270, pp. 138–146, 2018.

[47] N. Elgrishi, K. J. Rountree, B. D. McCarthy, E. S. Rountree, W. Kwon, J. M. Kim, and S. W. Rhee, “A new equivalent circuit model for porous carbon electrodes in charge transfer reaction of iodide/triiodide redox couples,” *Electrochimica Acta*, vol. 65, no. 14, pp. E826–E831, 2018.

[48] S. J. Cooper, A. Bertei, D. P. Finegan, and N. P. Brandon, “Simulated impedance of diffusion in porous media,” *Electrochimica Acta*, vol. 251, pp. 681–689, 2017.

[49] W. Kwon, J. M. Kim, and S. W. Rhee, “A new equivalent circuit model for porous carbon electrodes in charge transfer reaction of iodide/triiodide redox couples,” *Electrochimica Acta*, vol. 68, pp. 110–113, 2012.

[50] N. F. Sylla, N. M. Ndiaye, B. D. Ngom et al., “Effect of porosity enhancing agents on the electrochemical performance of high-energy ultracapacitor electrodes derived from peanut shell waste,” *Scientific Reports*, vol. 9, no. 1, article 13673, 2019.

[51] R. Attias, B. Dlugatch, M. S. Chae, Y. Goffer, and D. Aurbach, “Changes in the interfacial charge-transfer resistance of Mg metal electrodes, measured by dynamic electrochemical impedance spectroscopy,” *Electrochemistry Communications*, vol. 124, article 106952, 2021.

[52] L. W. Tack, M. A. Azam, and R. N. A. R. Seman, “Structural and electronic properties of transition metal oxides attached to a single-walled CNT as a lithium-ion battery electrode: a first-principles study,” *Journal of Physical Chemistry A*, vol. 121, no. 13, pp. 2636–2642, 2017.

[53] S. Sharma, S. K. Mehta, A. O. Ibhadon, and S. K. Kansal, “Fabrication of novel carbon quantum dots modified bismuth oxide (α-Bi2O3/C-dots): material properties and catalytic applications,” *Journal of Colloid and Interface Science*, vol. 533, pp. 227–237, 2019.

[54] D. Qu, G. Wang, J. Kafle et al., “Electrochemical impedance and its applications in energy-storage systems,” *Small Methods*, vol. 2, no. 8, article 1700342, 2018.

[55] R. Manikandan, C. J. Raj, M. Rajesh, B. C. Kim, J. Y. Sim, and K. H. Yu, “Electrochemical behaviour of lithium, sodium and potassium ion electrolytes in a Na2O·33V2O5 Symmetric pseudocapacitor with high performance and high cyclic stability,” *ChemElectroChem*, vol. 5, no. 1, pp. 101–111, 2018.

[56] K. Koteshwara Reddy, M. Satyanarayana, K. Yugender Goud, K. Vengatajalabathy Gobi, and H. Kim, “Carbon nanotube ensemble hybrid nanocomposite electrode for direct electrochemical detection of epinephrine in pharmaceutical tablets and urine,” *Materials Science and Engineering C*, vol. 79, pp. 93–99, 2017.

[57] Y. Xie, T. Gan, D. Sun, and K. Wu, “Application of multi-walled carbon nanotubes/nafion composite film in electrochemical determination of Pb,” *Fullerenes, Nanotubes, and Carbon Nanostructures*, vol. 16, no. 2, pp. 103–113, 2008.

[58] A. Królacka and A. Bobrowski, “Bismuth film electrode for adsorptive stripping voltammetry - electrochemical and microscopic study,” *Electrochemistry Communications*, vol. 6, no. 2, pp. 99–104, 2004.

[59] L. T. Tufa, K. Siraj, and T. R. Soreta, “Electrochemical determination of lead using bismuth modified glassy carbon electrode,” *Russian Journal of Electrochemistry*, vol. 49, no. 1, pp. 59–66, 2013.

[60] M. S. Strano, C. B. Huffman, V. C. Moore et al., “Reversible, band-gap-selective protonation of single-walled carbon nanotubes in solution,” *Journal of Physical Chemistry B*, vol. 107, no. 29, pp. 6979–6985, 2003.

[61] S. Lee, J. Oh, D. Kim, and Y. Piao, “A sensitive electrochemical sensor using an iron oxide/graphene composite for the simultaneous detection of heavy metal ions,” *Talanta*, vol. 160, pp. 528–536, 2016.

[62] C. Hao, Y. Shen, J. Shen et al., “A glassy carbon electrode modified with bismuth oxide nanoparticles and chitosan as a sensor for Pb(II) and Cd(II),” *Microchimica Acta*, vol. 183, no. 6, pp. 1823–1830, 2016.

[63] J. C. Quintana, F. Arduini, A. Amine et al., “Part I: A comparative study of bismuth-modified screen-printed electrodes for lead detection,” *Analytica Chimica Acta*, vol. 707, no. 1–2, pp. 171–177, 2011.

[64] R. Pauliukaite, R. Metelka, I. Švancara et al., “Screen-printed carbon electrodes bulk-modified with Bi2O3 or Sb2O3 for trace determinations of some trace metals,” *Scientific Papers of the University of Pardubic*. Series A, vol. 10, pp. 47–58, 2005.

[65] R. O. Kadara and J. E. Tothill, “Development of disposable bulk-modified screen-printed electrode based on bismuth oxide for stripping chronopotentiometric analysis of lead (II) and cadmium (II) in soil and water samples,” *Analytica Chimica Acta*, vol. 623, no. 1, pp. 76–81, 2008.

[66] R. O. Kadara, N. Jenkinson, and C. E. Banks, “Disposable bismuth oxide screen printed electrodes for the high throughput screening of heavy metals,” *Electroanalysis*, vol. 21, no. 22, pp. 2410–2414, 2009.