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Electrochemical Determination of Trace Pb (II) by The Modified Glassy Carbon Electrode Compositing Multi-Walled Carbon Nanotubes-Nafion-Bi Film

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Abstract

A modified glassy carbon electrode (GCE) compositing multi-walled carbon nanotubes (MWCNTs), Nafion and bismuth film was prepared and applied for the sensitive detection of trace Pb (II). MWCNTs were dispersed into ethanol by ultrasonication in the presence of Nafion and the nanotubes are coated onto the bare GCE. After that, an extra Nafion adhesion agent is added to the electrode. By the in situ plating, a bismuth film was fabricated on the MWCNTs-NA/GCE, making the desired electrode, MWCNTs-NA-Bi/GCE. The modified electrode was characterized by differential pulse anodic stripping voltammetry, scanning electron microscopy, and cyclic voltammetry. A deposition potential of –1.4 V (vs. Ag/AgCl) and a deposition time of 300 s were applied to the working electrode under stirred conditions after optimizing. Nanotubes and Nafion concentrations and pH were carefully optimized to determine trace lead ions by using the electrode as an electrochemical-sensing platform. Nafion effectively increased the stability and adhesivity of the composite film. The MWCNTs-NA-Bi film modified electrode can remarkably increase the anodic peak current of Pb^{2+}. The sensitivity of MWCNTs-NA-Bi/GCE is 4.35 times higher than that of the bare GCE with bismuth film. The prepared electrode showed excellent stability and reproducibility and can be applied for determination of Pb^{2+} contained wastewater.

Highlights

- A method of detection and determination of heavy metals from water is proposed
- Multi-walled carbon nanotubes with Nafion as the dispersant and the adhesion agent or protector are used for the determination
- Effects of several important experimental conditions are discussed
- The peak current increases linearly with the increase of Pb^{2+} concentrations

Keywords: Pb(II); Nafion; multi-walled carbon nanotube; bismuth film electrode; sensor

Introduction

Lead (Pb), a kind of undesirable heavy metal in groundwater, drinking water or oil, can be accumulated in the human body through the food chain to induce a severe threat to human health, even in trace quantity. Usually, Pb is in the form of lead ions (Pb^{2+}). Thus, detection and quantification of trace lead ions is crucial [1]. Many analytical methods have been developed for heavy metal detection such as inductively coupled plasma-mass spectrometry (ICP-MS) [2], inductively coupled plasma-atomic emission spectrometry (ICP-AES) [3], flame atomic absorption spectroscopy (AAS) [4] and electrochemical methods [5-7]. However, owing to the expensive and complex instrumentation requirements, spectrometric methods are unsuitable for in situ measurements. Instead, electrochemical methods have the superiority of high sensitivity, low cost and easy to be miniaturized, becoming a kind of promising technique. In the electrochemical methods, anodic stripping voltammetry (ASV) is a powerful electroanalytical technique for trace metal analysis [8, 9]. A three-electrode system is employed in the ASV method to perform a detection and a glassy carbon electrode (GCE) is usually selected for the working electrode (WE). GCE can be modified with different materials for specific recognition of metal ions. From 2000, in order to replace the toxic mercury electrodes, the bismuth film electrodes which are more environmentally friendly are proposed by J. Wang et al. [10, 11].

Bismuth-film GCE can be prepared by an in situ method, exhibiting high sensitivity associated with well-defined, undistorted and reproducible signals, and offering good stripping performance, because of its fusing alloy formation with specific metals. Such operation simplifies the experimental process and minimizes the influence of uncontrolled conditions, making the detection faster and more reliable [12-14]. The detection limit can go down to μg/L level, e.g. 5 μg/L for copper and around 4 and 2 μg/L for thallium and indium separately [15]. However, for trace metal detection, one of the challenges is to improve the selectivity using electrochemical techniques.

On the aspect of GCE, modifying different carbon based materials such as carbon nanotubes (CNTs) and graphene, can bring specific performance [16-21]. Graphene was used by Lee et al. to detect the heavy metal ions such as Zn^{2+}, Cd^{2+}, and Pb^{2+}. The GCE was modified through electrode position of exfoliated graphene oxide (GO) and in situ plating bismuth film. The detection limit was 0.11 μg/L for Pb^{2+} [22]. Hwang et al. have prepared four carbon based electrodes, i.e. CNTs, glassy carbon, activated carbon and graphite pastes. Compared to the other carbon materials, CNTs exhibited superior performance and showed higher electrochemically sensitivity with more active sites in the results of cyclic voltammetry. The limit of detection was 1.3 μg/L for lead [16]. CNTs have many unique properties such as strong electrical conductivity, high chemical stability, high specific surface areas, relatively high adsorptive ability, and good tensile properties, making it perform well in adsorbing heavy metals from contaminated water.

However, CNTs are insoluble in water. Nafion, as a solubilizing agent for CNTs, provides a useful avenue for preparing CNTs-modified electrodes [23-25]. The Nafion coating improved the mechanical stability of the bismuth film and its resistance to the interference of surfactants. The good dispersibility, large specific surface area, rich active sites, and strong adsorption property contributed to the enhanced stripping signals of heavy metal ions [26, 27]. When preparing nitrogen doped micro porous carbon electrode, Nafion and N, N-Dimethylformamide were used to be the dispersing solution and the synergistic effects of Nafion and bismuth-film contributed to the enhanced signals of the electrode. Nafion was added since perm selective Nafion membrane can be used as an antifouling coating to

decrease the interference of the surface-active compounds [28]. Yu et al. have synthesized a porous graphene based Nano composite by a chemical and thermal reduction of graphite oxide in the assistance of calcium lignosulfonate. Nafion was also used to modify the GCE. This sensor showed a wide detection range for Pb^{2+} (0.05–5.0 μM) with the limit of detection and limit of quantification 0.01 and 0.03 μM, exhibiting improved electrochemical performance [29]. A Bi/multi-walled carbon nanotube-emeraldine base polyaniline-Nafion composite modified GCE was used to determine the concentration of Cd(II) and Pb(II). This electrode can achieve a lower detection limit for Pb(II) of 0.08 μg/L [30]. In order to clarify the performance of Nafion, Wang et al. have compared four different electrodes, (a) Nafion film modified GCE; (b) multi-walled carbon nanotube-Nafion (MWCNT-NA) modified GCE; (c) Nafion-bismuth modified GCE; (d) MWCNT-NA-bismuth modified GCE. The experimental results show clearly that the last one is the best, giving a strong proof for the advantage of MWCNT-NA modified electrode [17]. In this work, the Nafion and MWCNTs are used for modifying the electrode and Nafion is added twice in the preparing process with different roles. The detection effects are improved and the electrode has good stability and reproducibility.

Experimental

Reagent

All the chemicals were analytical grade without further purification. Pure MWCNTs were obtained from Hengqiu Tech. Inc. (China). The standard solutions of Pb^{2+} and Bi^{3+} were bought from Aladdin (China). All the ion solutions with different concentrations were prepared by dilution of the standard solutions. Nafion (5wt.% solution in a mixture of water and alcohol) was also purchased from Aladdin (China) and different concentrations of dilute Nafion solution were prepared with absolute ethanol. A mixed acetic acid (HAc) and sodium acetate (NaAc) buffer solution (0.1 mol/L, pH=4.6) served as the supporting electrolyte. Phosphate buffer solution (PBS, pH=7) acted as dispersion liquid.

Apparatus

All the voltammetric measurement were performed in a three-electrode system using a CHI660E electrochemical workstation (Chenhua Instruments, Shanghai, China). A bare GCE (d=3 mm) or MWCNTs-NA-Bi modified GCE served as the working electrode. The Ag/AgCl (Saturated. KCl) acted as the reference electrode and platinum wire acted as counter electrode. The scanning electron microscopy (SEM) was performed with a FEI Nova Nano SEM 450 microscope (USA). All glassware was carefully cleaned by soaking in 0.1 mol/L HNO_3 over 48 h, followed by thoroughly rinsing with copious amounts of ultrapure water.

Preparation of MWCNTs-NA/GCE

Before preparing the composite modified electrode, the bare GCE was pretreated carefully with 1, 0.3, and 0.05 μm alumina slurry on a polishing cloth, rinsed thoroughly with HNO_3, and washed with pure ethanol and redistilled water to achieve a clean GCE. 1 mL 5wt. % Nafion solution and 4 mL 0.05 mol/L PBS were mixed to act as a dispersion. 10 mg of MWCNTs were dispersed in 5 mL of this dispersion, sonicating about 4h. Then a uniform dispersion of black MWCNTs and Nafion suspension with a MWCNT concentration of 2 g/L was obtained. The Nafion here is called a dispersant. The GCE was coated with 10 μL MWCNTs and Nafion suspension twice (once 5 μL) and solidified by irradiating for 5 minutes with an infrared lamp. This electrode is called MWCNTs/GCE hereafter. Note that Nafion dispersant is incorporated in MWCNTs/GCE.

Afterwards, 2 μL Nafion solution was pipetted onto the MWCNTs/GCE electrode surface and solidified by irradiating. Here, Nafion acted as adhesion agent or protector. Finally, a MWCNTs-NA/GCE electrode was

obtained. The electrode was cleaned at 0.3 V for 60 s under stirring using galvanostatic method after each determination.

Analytical procedures

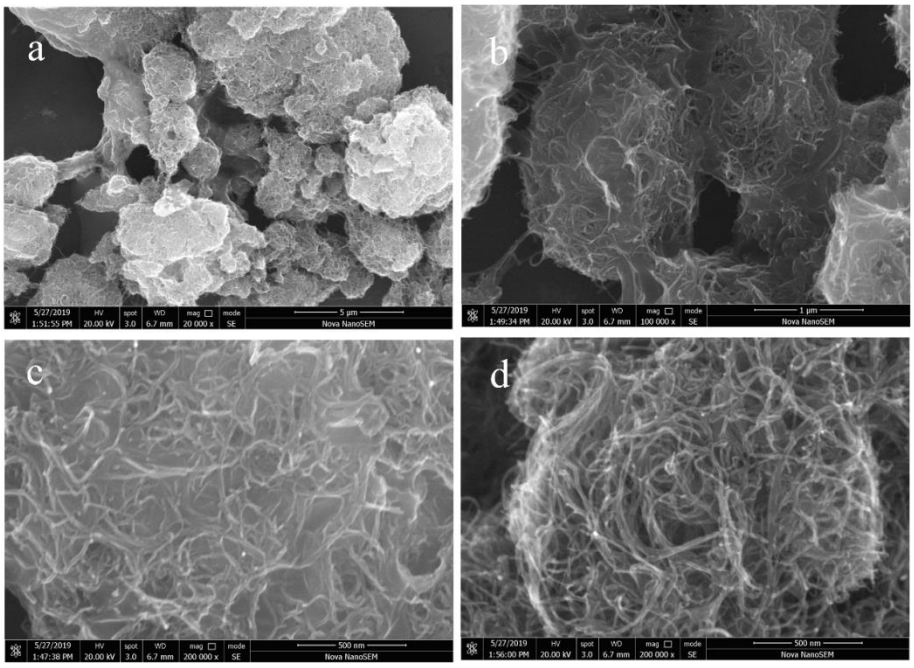
The differential pulse anodic stripping voltammetry (DPASV) determination of Pb^{2+} on MWCNTs-NA/GCE was achieved in 0.1 mol/L HAc–NaAc buffer solution containing different concentration Pb^{2+} and 400 μg/L Bi^{3+}. An in-situ method for bismuth plating was used. Under stirring condition, a fixed deposition potential was applied to the working electrode for a certain deposition time, depositing lead ions and bismuth film onto the composite electrode. After a 10 s equilibration period without stirring, the DPASV potential was scanned from –1.4 V to 0 V. The pulse amplitude, step amplitude and frequency were 25 mV, 5 mV and 25 Hz, respectively. After each determination, the modified electrode was cleaned at 0.3 V for 60 s to remove the residual metals and bismuth film on the surface under stirring.

Results and discussion

Characterization of the modified electrode

The SEM images of MWCNTs with Nafion as a dispersant and adhesion or protector are shown in (Figure 1 (a), (b) and (c)), with different magnifications of 20000,100000 and 200000. Each MWCNT holds a length of more than 1 μm. The average diameter of the carbon nanotube bundles reaches 13 nm. MWCNTs are dispersed well in Nafion. Nafion wraps around the hydrophobic MWCNT surface and effectively separate the MWCNTs by its hydrophobic and hydrophilic regions. But there are many envelopes on the surface of the electrode forming layered structures. Between the blocks, there are many pores.

Figure (1): SEM images of MWCNTs with Nafion composite film after (a, b, c) and before (d) adding Nafion as adhesion agent.

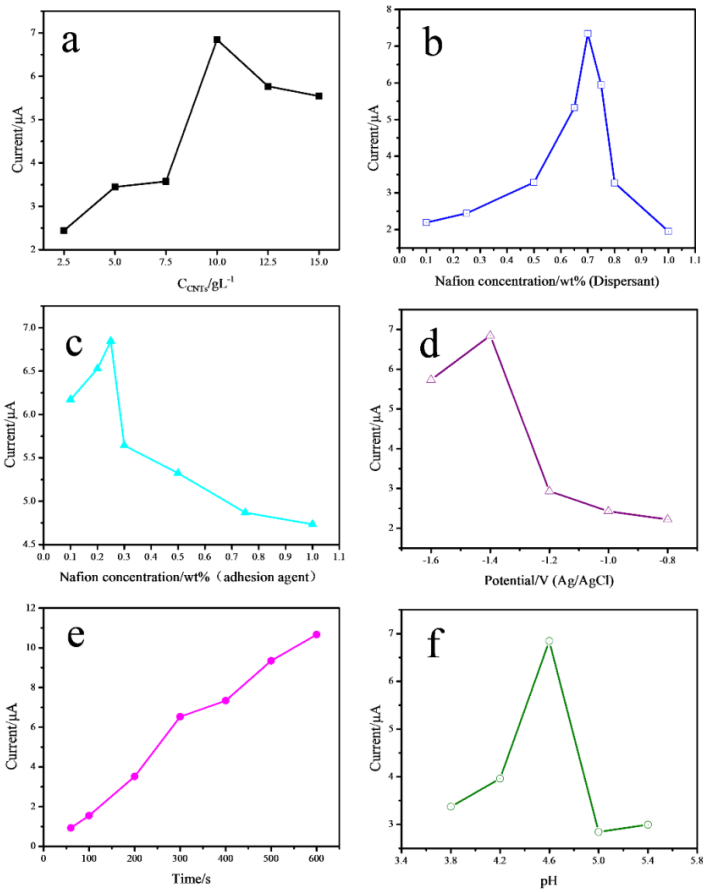


Nafion combines the MWCNTs uniformly and tightly together, not only increasing the specific surface area of the electrode when adsorbing heavy metals, but also fixing the well-defined three dimensional structures, making the composite material stronger and not easy to peel off. (Figure 1 (d)) with a magnification of 200000, is without the 2 µL Nafion binder, but only the 10 µL MWCNTs-NA suspension on the electrode. Compared to (Figure 1 (c)), the MWCNTs are clearer. There's an extra layer of Nafion membrane protecting the electrode in (Figure 1 (c)), which does not affect the MWCNT structures.

Selection of the experimental conditions

Several important experimental conditions are optimized in order to obtain the optimal voltammetric response for the DPASV determination of trace metal Pb^{2+}, including the concentration of MWCNTs, concentration of Nafion as a dispersing agent, concentration of Nafion as an adhesion agent, deposition potential, deposition time and pH. All the experiments were carried out in 0.1 mol/L HAc-NaAc buffer solution containing 60 µg/L Pb^{2+} and the results are displayed in (Figure 2).

Figure (2): The effects of several important experimental parameters on the stripping peak current for 60 µg/L Pb^{2+} solution on MWCNTs-NA-Bi/GCE including (a) MWCNTs concentration, (b) Nafion concentration as a dispersing agent, (c) Nafion concentration as a binder, (d) deposition potential, (e) deposition time and (f) pH.



The concentration of MWCNTs influences the thickness of the composite material on the electrode. Six different concentrations are considered and the effects on the stripping signal of Pb^{2+} are shown in (Figure 2 (a)). The peak current for Pb^{2+} increased with increasing MWCNTs concentration from 2.5 g/L to 10 g/L and decreased from 10 g/L to 15 g/L, suggesting that the best concentration is 10 g/L. A thick layer of carbon nanotubes may reduce the adsorption abilities for heavy metal ions. The effect of Nafion concentration on the Ip of Pb^{2+} was displayed in (Figure 2 (b) and (c)). For dispersing Nafion, concentration of 0.1% to 1% is considered. The Ip of Pb^{2+} increased with the Nafion concentration from 0.1% to 0.7% and decreased from 0.7% to 1%. With the concentration growing up, the dispersibility of MWCNTs becomes better and better. When the concentration goes larger, it will restrict the electron transmission from the electrode surface. Therefore, 0.7% Nafion solution is selected as the dispersing agent for carbon nanotubes. From (Figure 2 (c)), it could be clearly observed that the best concentration of Nafion adhesion agent is 0.25%. Over 0.25%, the stripping peak currents decline rapidly.

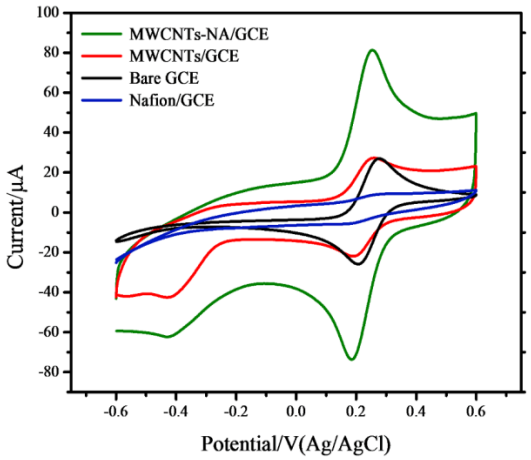
The deposition potential over the range from −1.6 V to −0.8 V was explored and the effects to the stripping responses of heavy metal ions are displayed in (Figure 2 (d)). It clearly showed an increasing trend with the increase of the deposition potential from −1.6 V to −1.4 V, suggesting that the deposition amount of Pb^{2+} increased with the increase of deposition potential. When the deposition potentials further increased to −0.8 V, the stripping peak currents were weakened. So −1.4 V was chosen as the optimal deposition potential for high sensitivity of detecting Pb^{2+}. The influence of the deposition time was investigated ranging from 60 s to 600 s. As shown in (Figure 2 (e)), the peak current increased accordingly when the deposition time increased, indicating that the longer deposition time would profit the deposition of more metal ions on the surface of MWCNT-NA/GCE. However, when the deposition time was longer than 300 s, the increasing trend become slower. This is because longer deposition time results in nearly saturation of the surface active sites of the modified materials on the electrode surface. Therefore, 300 s was chosen as the best deposition time.

The effect of pH on the stripping peak current was studied in 0.1 mol/L NaAc-HAc buffer solution with pH values ranging from 3.5 to 5.5. As displayed in (Figure 2 (f)), the maximum value of Ip appears at pH=4.6. The lower pH values resulted in the protonation of Nafion binding sites, reducing the absorption of Pb^{2+} on the surface of modified electrode while the higher pH values decreased Ip due to the possible formation of metal hydroxide complexes [31-32]. Therefore, pH=4.6 was chosen for the following analysis.

Electrochemical characterization

The $[Fe(CN)_6]^{3-/4-}$ redox couple was used as a probe by cyclic voltammograms (CV) to characterize the electrochemical properties of the electrode. The CV curves of four different electrodes are compared in (Figure 3). The CV recorded at bare GCE shows a low current and that at Nation modified GCE shows even lower current for the $[Fe(CN)_6]^{3-/4-}$ couple due to the electrostatic repulsion between the negatively charged $[Fe(CN)_6]^{3-}$ and SO_3 groups in the Nafion film [21]. Also the insulated Nafion can impede the current. When we dispersed MWCNTs in Nafion to obtain the MWCNTs/GCE, the electrochemical behavior was improved compared to both the bare and Nafion modified GCE. It is because the MWCNTs have good electron transfer capacity, providing the conduction pathway. In addition, the green line in Figure 3 shows the CV of MWCNTs-Nafion/GCE prepared by adding 2 μL Nafion as adhesion agent or protector on the MWCNTs/GCE, indicating a significantly increase of the redox peaks by nearly three times. Therefore, Nafion as an adhesion agent can effectively increase the conductivity of MWCNTs. The MWCNTs-Nafion modified electrode exhibited a higher electroactive area compared to the other three electrode.

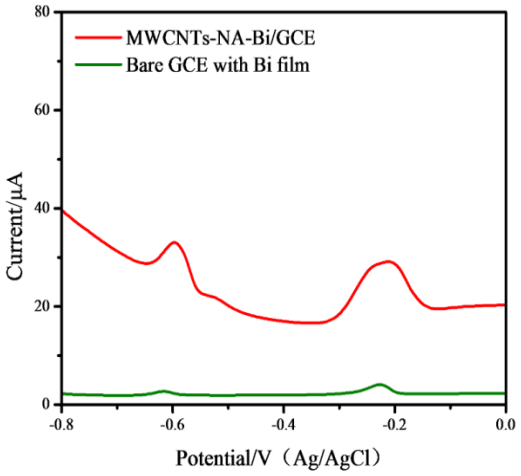
Figure (3): CV recorded at modified (a-green) MWCNTs-Nafion , (b-red) MWCNT, and (d-blue) Nafion, and unmodified (c-black) GCEs in 0.1 mol/L KCl solution containing 5 mmol/L $[Fe(CN)_6]^{3-/4-}$ at a scan rate of 50 m*V/s*.



Stripping behavior of Pb^{2+} on modified electrode

In order to probe the effect of MWCNTs-NA modified electrode on the electrochemical response of Pb^{2+} ions, the electrodes of bare GCE and MWCNTs-NA/GCE were prepared and used for the determination. After the Nafion binder was added to the electrode, bismuth was plated by an in situ method. The stripping current responses for 60 μg/L Pb^{2+} using DPASV for the bare GCE and MWCNTs-NA/GCE electrodes are compared in (Figure 4). HAc-NaAc buffer solution was chosen as the supporting electrolyte [27] and the concentration of Bi^{3+} is 400 μg/L [17, 22]. Two oxidation peaks at about −0.60 V and −0.20 V were clearly observed, which can be ascribed to the stripping process of reduced Pb^{2+} and Bi^{3+}. The stripping peak current (Ip) for Pb^{2+} at the Bi modified GCE was very low with Ip = 2.669 μA. In contrast, a prominent peak with a peak current value of 33.07 μA was observed in the MWCNTs-NA-Bi modified electrode. The composite electrode has good conductivity and the electron transfer is greatly enhanced. The sensitivity improvement is attributed to two reasons. The presence of the MWCNTs effectively improved the electron mobility on the electrode surface and possibly enhanced the uniform distribution of Pb^{2+} on the electrode surface. Meanwhile, Nafion imparts a higher anti-interference ability to surface active species and improves the mechanical stability of the modified layer on the electrode surface [33].

Figure (4): DPASV of 60 μg/L Pb^{2+} on bare GCE and MWCNTs-NA-Bi/GCE



Calibration curve of MWCNTs-NA-Bi/GCE

Under the optimized experimental conditions, the analytical performance of MWCNTs-NA-Bi/GCE for quantitative analysis of Pb^{2+} was evaluated by DPASV. The concentration of Pb^{2+} is from 10 μg/L to 350 μg/L, in 0.1 mol/L NaAc-HAc buffer containing 400 μg/L Bi^{3+} solutions. The stripping signals of DPASV response for different concentrations of Pb^{2+} are plotted in (Figure 5 (a)). The peak current increases linearly with the increase of Pb^{2+} concentration and the regression equation is Ip = 0.0965 C – 0.884 (Ip: μA, C: μg/L) (n=3) with a correlation coefficient of 0.9996. Based on a signal-to-noise ratio characteristic of 3 (S/N=3), the detection limit of Pb^{2+} was estimated to be 0.0928 μg/L.

The heavy metal ion detection performance of the proposed MWCNTs-NA-Bi/GCE composite sensor was compared with previously reported Bi-modified electrodes and the results were summarized in (Table 1). The results show that the current electrode has superior or comparable detection limits with respective to the other materials modified electrodes for the determination of

Pb^{2+}, exhibiting outstanding analytical performance of the composite of MWCNT and Nafion.

Figure (5): Relationships between stripping peak currents (Ip) and the concentrations (C) of Pb^{2+} (red dots, n=3) and the calibration curves for detection of Pb^{2+} (black line).

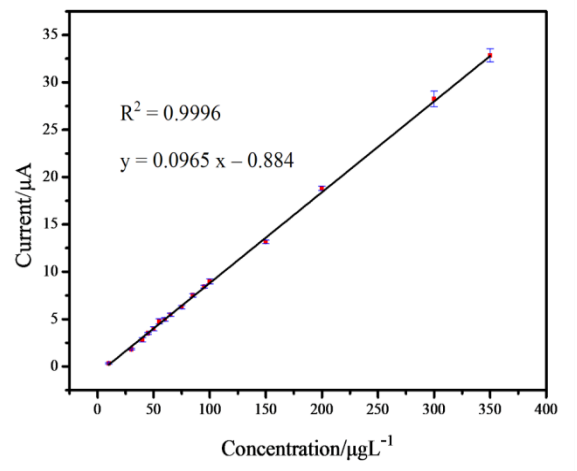


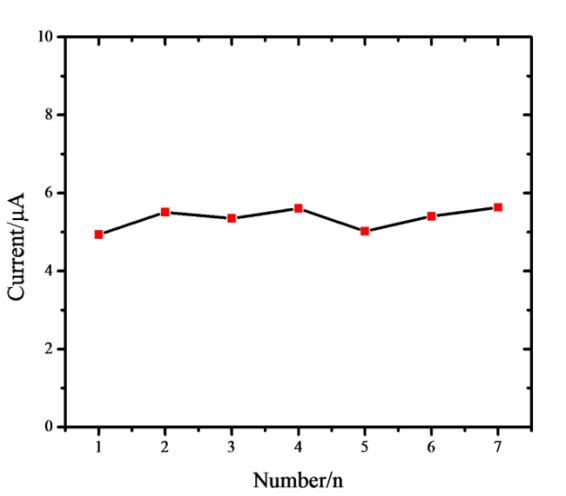
Table (1): Comparison of the analytical performance of the electrodes and electrochemical methods for the detection of Pb^{2+}.

Electrode	Measurement technique	Detection Range (μg/L)	Detection limit for Pb^{2+} (μg/L)	Refs
Bi/CNT/GCE	SWASV	20-100	1.3	[16]
Bi/CNT/SPE	SWASV	2-100	0.2	[31]
Bi/Graphene/MWCNT/GCE	DPASV	5-30	0.2	[19]
Bi/Nafion/Graphene/GCE	DPASV	0.5-50	0.02	[34]
Bi/EG/GCE	DPASV	1-100	0.11	[22]
Bi/MWCNT-EBP-NA/GCE	SWASV	1-50	0.08	[30]
MWCNTs-NA-Bi/GCE	DPASV	10-350	0.0928	This work

Stability and reproducibility of the modified electrode

In order to verify the stability of the modified electrode, repetitive measurements were carried out for the detection of 60 μg/L Pb^{2+}. After the first measurement, the electrode was reduced in a 0.1 mol/L NaAc-HAc buffer at a potential of 0.3 V for 60 s to remove the residual metals and bismuth film on the surface under stirring, then placed in a beaker for one hour before the next measurement. The DPASV responses in each experiment was obtained and are shown in (Figure 6). The relative standard detion (RSD) of seven measurements for Pb^{2+} at one single modified electrode was 4.75%. Therefore, the MWCNTs-NA-Bi/GCE composite electrode has excellent stability and repeatability.

Figure (6): The stripping peak currents of seven repetitive measurements of 60 μg/L Pb^{2+} on MWCNTs-NA-Bi/GCE.



Analysis of real samples

To evaluate its accuracy in practical applications, the fabricated electrode was employed to determine Pb^{2+} in real water samples that collected from Liaohe River. Liaohe River is the largest river in the south of northeast China and one of the seven major rivers in China. Two water samples were collected from the estuary and the middle of the river, separately. 2 mL sample solution

was diluted to 5 mL by adding 0.2 mL 1 mg/L Bi^{3+} solution and some 0.1 mol/L NaAc-HAc buffer (pH=4.6). Each sample were analyzed five times but the Pb^{2+} concentration is too low to detect. Different concentrations of Pb^{2+} were added to the river water and the found concentrations (the mean value ± standard detion) and the recoveries of the Pb^{2+} ions were summarized in (Table 2). Precision and recovery tests indicated that the proposed MWCNTs-NA-Bi/GCE could be applied to the analysis of trace heavy metals in real samples.

Table (2): Determination of trace Pb^{2+} in Liaohe River (n=5).

Added (μg/L)	Found (μg/L)		Recovery (%)	
	The estuary of the river [a]	The middle of the river [a]	The estuary of the river	The middle of the river
-	Not detectable	Not detectable	-	-
20	18.39±0.54	17.83 ± 0.33	91.95 %	89.13
30	32.98±0.84	33.55 ± 1.40	109.95 %	111.83
[a]Mean value ± standard detion.				

Conclusions

In this work, a MWCNTs-NA-Bi composite modified electrode was proposed with an improved process. Nafion dispersing agent played an important role in dispersing the MWCNTs. The protecting film of Nafion made the electrode more efficient and enhanced sensitivity to detect trace metal iron of Pb^{2+}. The CV curve showed that the modified MWCNTs-NA-Bi/GCE exhibited excellent electrochemical activity and accelerated charge transfer kinetics due to the presence of conductive MWCNTs. The environmentally friendly bismuth film has replaced mercury membranes and showed a better performance in recognizing Pb^{2+}. The DPASV method was used for determination and six important experimental conditions were optimized in order to obtain the optimal voltammetric responses. The sensor was successfully applied for determination of Pb^{2+} in concentrations ranging from 10 to 350 μg/L and exhibited good linear relationship between the striping current and the iron concentration. The detection limit of analyzation Pb^{2+} was 0.0928 μg/L. In addition, the MWCNTs-NA-Bi/GCE demonstrated excellent reproducibility and stability. Finally, a real water sample collected from Liaohe River is detected by the fabricated MWCNTs-NA electrode and the average RSD is 4.75 %. Therefore, the composite electrode we prepared will have a good application prospect in water detection.

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Conflict of interest

The authors declare that they have no conflict of interest.

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