Int. J. Electrochem. Sci., 11 **(2016)** 8109 – 8122, doi: 10.20964/2016.10.07

International Journal of ELECTROCHEMICAL SCIENCE
www.electrochemsci.org

Simultaneous Determination of Cd(II) and Pb(II) Based on Bismuth Film/Carboxylic Acid Functionalized Multi-Walled Carbon Nanotubes-β-cyclodextrin-Nafion Nanocomposite Modified Electrode

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Received: 29 June 2016 / *Accepted:* 2 August 2016 / *Published:* 6 September 2016

A bismuth film/carboxylic acid functionalized multi-walled carbon nanotubes-β-cyclodextrin-Nafion nanocomposite modified glassy carbon electrode (Bi/CMWCNTs-β-CD-Nafion/GCE) was fabricated and characterized for the sensitive detection of cadmium and lead using square wave anodic stripping voltammetry (SWASV). Cyclic voltammetry (CV), SWASV and chronoamperometry were utilized to study the electrochemical behavior of cadmium and lead detection. The electrode surface morphology has been characterized by scanning electron microscopy. Compared with β-CD and CMWCNTs, the enhanced stripping peak currents for both Cd(II) and Pb(II) were observed on Bi/CMWCNTs-β-CD-Nafion/GCE. Due to the synergistic effect, the resulting surface provided a favorable surface morphology for improving the efficiency of electrodeposition and accelerating electron transfer rate for the determination of trace amounts of heavy metal ions (HMs). The experimental results show that the CMWCNTs-β-CD-Nafion nanocomposite modified electrode can act as a kind of practical sensor for the simultaneous determination of Pb(II) and Cd(II) by SWASV. The optimized linear working range (S/N = 3) were 1 to 100μg/L for Cd(II) and Pb(II), and the limits of detection were 0.21μg/L for Pb(II) and 0.13μg/L for Cd(II), respectively. Moreover, the sensor was further used for the trace HMs detection in soil samples with satisfactory results.

Keywords: Multi-walled carbon nanotubes, β-cyclodextrin, Nafion, Cd(II) and Pb(II), Soil

1. INTRODUCTION

Cd(II) and Pb(II) are widely known to pose toxic effects on living organisms due to persistent toxicity and pose a substantial threat to human health, , which are mainly come from industrial emission and continuously exist in the soil [1,2]. HMs in soil can be transferred to humans through the food chain and can accumulate in human bodies. Therefore, trace levels of Cd(II) and Pb(II) in soil are of widespread concern, and the ability to detect these ions is important[3-6]. Some spectroscopic-based methods such as inductively coupled plasma mass spectrometry (ICP-MS) [9,10], atomic absorption spectroscopy (AAS) [7] and inductively coupled plasma atomic emission spectroscopy (ICP-AES) [8] are used for HMs detection. Reliable results with high sensitivities can be obtained using these spectroscopic methods. However, these methods have some shortcomings, including high operating costs, complex operation and poor suitability for on-site detection [11,12]. In order to meet the on-site detection of HMs, the detection methods which at low cost and easy to operate are urgent need. Compared with traditional spectroscopic methods, the electrochemical method of stripping voltammetry has the advantages of low cost, high sensitivity and fast response times; stripping voltammetry can also be implemented for in situ detection [11-13]. The modified materials for the electrode modification play an important role in the detection sensitivity, which determine the deposition efficiency of HMs on the electrode surface [14].

In recent years, the bismuth film electrode (BiFE) has become the most popular working electrode for anodic stripping voltammetry (ASV) [15-18] because of its low toxicity, simple fabrication and its ability to form alloys with many HMs [19-22].In addition, many efforts were made to design and prepare chemically modified electrodes (CMEs) for the determination of HMs [].

Multi-walled carbon nanotubes (MWCNT) are widely used for electrode modification due to their large specific surface area, unique electrical conductivity and highly efficient catalysts towards certain target analytes [33]. But the multi walled carbon nanotubes are not easy to disperse in the common solvents.β-cyclodextrin (β-CD), a macrocyclic oligosaccharide, has been employed as a modifier and dispersing reagents in voltammetry analysis of different analytes [34-36]. The combination of β-CD and MWCNTs as nanocomposites can be used for the modification of electrodes to quantify and study many analytes due to the interaction effects of both materials [37]. Nafion has the ability to preconcentrate HMs which is widely used for the electrode modification combining with mercury and bismuth film, due to its higher anti-interference ability and good mechanical stability on the surface of electrode [38,40]. The presence of Nafion might improve the deposition of heavy mental ions on the composite membrane [41]. However, as we know, very few reports on CMWCNTs-β-CD-Nafion/GCE could be found in electrochemical detecting Cd(II) and Pb(II).

In this study, we report the first example of the fabrication of a sensitive electrochemical sensor based on a CMWCNTs-β-CD-Nafion nanocomposite modified GCE , which was further explored to detect Cd(II) and Pb(II). Here, the use of CMWCNTs is helpful to get a good dispersion in the β-CD, due to their hydrophilic carboxyl groups. It was found that, CMWCNTs-β-CD-Nafion/GCE displayed stronger peak currents for both Cd(II) and Pb(II) compared with β-CD-Nafion modified GCE (β-CD-Nafion/GCE) and CMWCNTs-Nafion modified GCE (CMWCNTs-Nafion/GCE), and the CMWCNTs-β-CD-Nafion/GCE exhibited excellent electric conductivity as well as good anti-interference ability, which opens up a new route for the simultaneous detection of trace Cd(II) and Pb(II). Finally, the practicality and feasibility of sensor was verified by the real soil samples analysis.

2. EXPERIMENTAL

2.1. Reagents and instruments

CMWCNT (< 8 nm diameter, 10-30 μm length and > 95 wt% purity) were obtained from Shenzhen Nanotech Port Co., Ltd. (Shenzhen, China). β-cyclodextrin and Nafion were purchased from Aldrich (Sigma-Aldrich, USA). NA was then diluted to 1 wt% with pure ethanol. Stock solution of Bi(III), Cd(II) and Pb(II) (1000 mg/L) were purchased from the National Standard Reference Materials Centre of China and diluted as required. Acetate buffer solution (0.1 M) served as the supporting electrolyte for the detection of Cd(II) and Pb(II). All other chemicals were of analytical grade and used without further purification. Millipore-Q (18.2 MΩ) water was used for all experiments.

Scanning electron microscopy (SEM) was performed on a JEOL JSM-6701F (Japan) field-emission scanning electron microscope. SWASV, EIS and CV measurements were performed using a CHI660D electrochemical workstation (Shanghai CH Instruments, China). A three-electrode system consisting of a modified glassy carbon working electrode (⌀ 3 mm), an Ag/AgCl reference electrode and Pt wire counter electrode was used. All electrochemical measurements were conducted in a 25 mL cell. The test solutions were stirred using a magnetic stirrer during the deposition steps.

2.2. Preparation of GR-β-CD-Nafion/GCE

The surface of GCE was polished by 0.05 μm alumina powder and rinsed with 1:1 HNO_3, absolute ethanol and water. 32 milligram of β-cyclodextrin was added into 4 mL of a dimethylformamide (DMF) solution (2 wt%) with sonication until theβ-cyclodextrin was homogeneously dispersed. The dispersion of the CMWCNT was prepared by adding 1 mg of CMWCNT into 4 mL of above suspension to produce a 0.25 mg/mL black suspension with the aid of ultrasonic agitation for 3 h. Then, 450 μL 1 wt% Nafion was mixed to form a CMWCNT-β-CD-Nafion composite solution. Next, 5 μL of a CMWCNT-β-CD-Nafion suspension was cast onto the GCE surface and then solidified by irradiating with an infrared lamp for 10 min to obtain CMWCNT-β-CD-Nafion/GCE. For comparison, other electrodes were also prepared with the same procedures described above.

2.3. Electrochemical detection of Cd(II) and Pb(II)

The SWASV determination of Pb(II) and Cd(II) on Bi/CMWCNTs-β-CD-Nafion/GCE was achieved in 0.1 M acetate buffer solutions containing 600 μg/L Bi(III). A deposition potential of -1.2 V (vs. Ag/AgCl) and a deposition time of 140 s were applied to the working electrode under stirring conditions. After a 10 s equilibration period, the SWASV potential was scanned from -1.2 V to 0.2 V, and the solution was not stirred in these two steps. The pulse amplitude, step amplitude and frequency were 25 mV, 5 mV and 25 Hz, respectively. Before the next detection, the modified electrode was activated for 140 s at 0.31 V in a pH 5.5 acetate buffer to remove the residual metals and bismuth film on the surface of the GCE. The main fabrication and detection processes of the electrochemical sensor are shown in Fig. 1B.

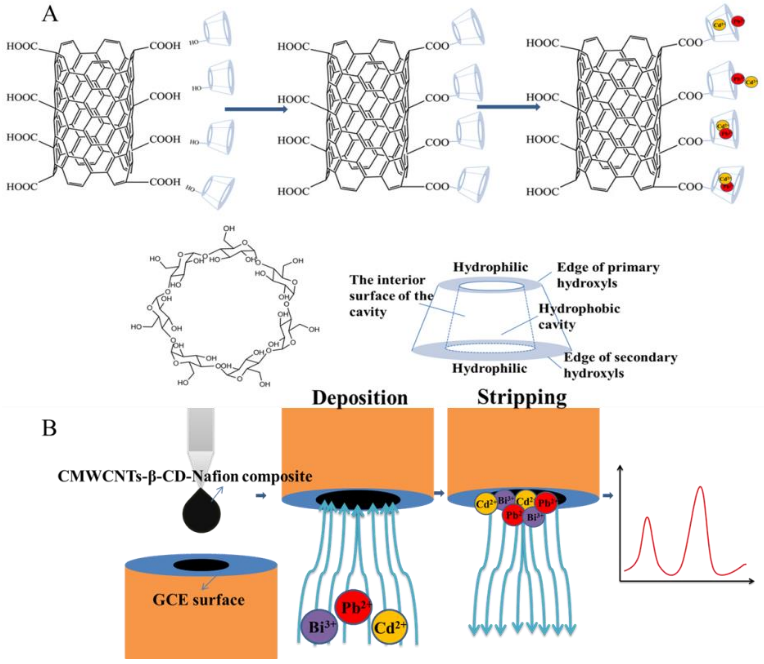

Figure 1. (A) Schematic of the synthesis procedure of CMWCNTs-β-CD-Nafion composite and the interaction between CMWCNTs-β-CD-Nafion composite and the heavy metal ions. (B) Schematic of main detection steps of Cd (II) and Pb (II) by means of SWASV method.

3. RESULT AND DISCUSSION

3.1. Basic characteristics of the modified electrodes

The morphologies of prepared electrodes were illustrated by SEM., The morphologies of CMWCNTs/GCE and CMWCNTs-β-CD-Nafion/GCE characterized by SEM was shown in Fig. 2. A crumpled structure composed of carbon nanotubes could be observed on the CMWCNTs/GCE, as shown in Fig. 2A. We could find that CMWCNTs-β-CD-Nafion composites more uniform dispersed than CMWCNTs, as shown in Fig. 2B. The uniform and crumpled coverage structure of CMWCNTs-β-CD-Nafion composite film indicated that high surface area of the electrode and active sites could be obtained among the carbon nanotubes, β-CD and Nafion components.

β-CD are common members of cyclodextrins with a hydrophilic exterior and a hydrophobic inner cavity, which can form stable host-guest inclusion complexes by selectively binding many kinds of inorganic, biological and organic molecules into their cavities attributed to their unique structure [42, 43]. β-CD can interact with CMWCNTs through covalent bond, van der Waals forces and hydrogen-bonding interaction between the adjacent β-CD molecules as the principal driving forces []. Additionally, β-CD, as excellent water-soluble and environmentally friendly supramolecules, have been used widely as dispersing reagents for nanomaterials such as carbon nanotubes[]. Therefore, the stability of CMWCNTs-β-CD-Nafion composites modified GCE was better than CMWCNTs modified GCE, moreover, CMWCNTs-β-CD-Nafion composite film further increased the physical adsorption amount of electroactive species on the electrode. The synthesis procedure of CMWCNTs-β-CD-Nafion composite and the interaction between CMWCNTs-β-CD-Nafion composite and the heavy metal ions were shown in Fig. 1A.

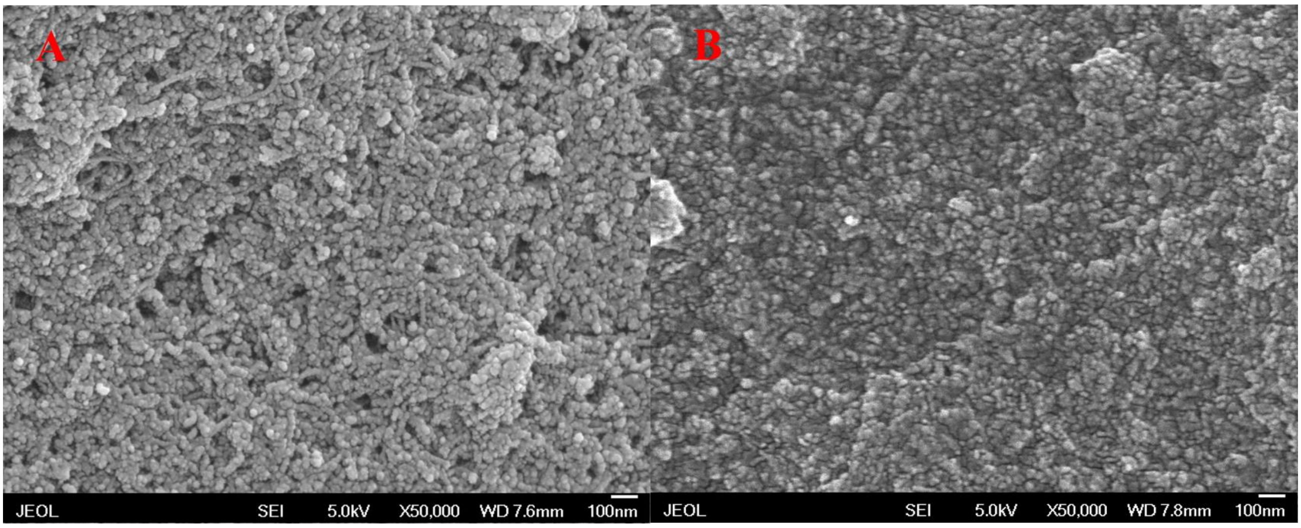

Figure 2. SEM images of surface morphologies of (A) CMWCNTs/GCE and (B) CMWCNTs-β-CD-Nafion/GCE.

The electrochemical properties of the modified electrodes were studied by CV using $[Fe(CN)6]^{3-/4-}$ as a redox probe.. Fig. 3 compares the CV responses of GCE, CMWCNTs-Nafion/GCE, β-CD-Nafion/GCE and MWCNTs-β-CD-Nafion/GCE in 5.0 mM $K_3[Fe(CN)_6]$ solution, respectively. Curve a showed a CV of the bare GCE in $K_3[Fe(CN)_6]$ and KCl mixture solution and a pair of well-defined redox peaks was observed, which was due to the reversible one-electron redox behavior of ferricyanide. As shown in curve b, after the modification of β-CD-Nafion composites on the GCE, the CV of β-CD-Nafion/GCE exhibited a pair of significantly decreased redox peaks, which indicated that the β-CD-Nafion composites acted as a block layer which made the interfacial charge transfer difficult. In contrast, an obvious increase in Stripping voltammetric response currents can be found at CMWCNTs-Nafion/GCE (curve c), which demonstrated that CMWCNTs-Nafion composites could improve the electron transfer rate on the surface of electrode due to the outstanding electric conductivity of CMWCNTs. However, when the GCE was modified with CMWCNTs-β-CD-Nafion composites, the redox peak currents (curve d) slightly decreased compare to the CMWCNTs-Nafion/GCE. This phenomenon may be due to the presence of β-CD which attenuating the electron transfer between soluble redox couple.

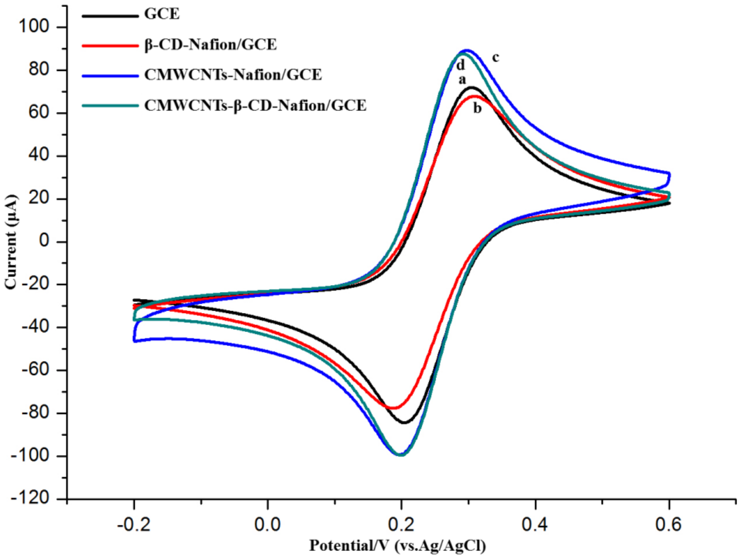

Figure 3. Cyclic voltammograms for 5 mM $K_3[Fe(CN)_6]$ in 0.1 M KCl, (a) GCE, (b) β-CD-Nafion/GCE, (c) CMWCNTs-Nafion/GCE and (d) CMWCNTs-β-CD-Nafion/GCE. Scan rate: 50 mV/s.

3.2. Optimization of experimental conditions

To improve the sensitivity for the SWASV detection of target HMs with the Bi/OMC-MW/CPE, we optimized the different SWASV parameters, including the deposition potential, pH value of the supporting electrolyte, concentrations of Bi(III) and the deposition time.

The effect of the pH in the range 3.5-6 on the stripping peak currents of target HMs was studied, as shown in Fig.4A. The maximum peak current appeared at pH 5.5, so the following experiments were conducted at pH 5.5. Fig. 4B demonstrates the effect of the Bi(III) concentration on the peak currents of target HMs. The peak currents increased with an increasing Bi(III) concentration from 100 to 600 μg/L and then decreased when the Bi(III) concentration exceeded 600 μg/L. Consequently, we chose 600 μg/L as the optimal Bi(III) concentration. The effect of the deposition potential on the peak currents of target HMs over a potential range of -0.8 to -1.6 V after accumulation 140 s was investigated, as shown in Fig. 4C. The highest peak currents were obtained at -1.2 V for target HMs. For further measurements, a value of -1.2 V was chosen as the accumulation potential. Fig. 4D shows the influence of the deposition time, which ranged from 30 to 450 s, on the sensitivity of the peak current of target HMs. The peak currents of target HMs at the MWCNT-EBP-NA/GCE increased with increasing deposition time. As deposition times longer than 140 s, the peak currents began to level off. Taking into account both the sensitivity and the efficiency, we used a deposition period of 140 s in subsequent experiments.

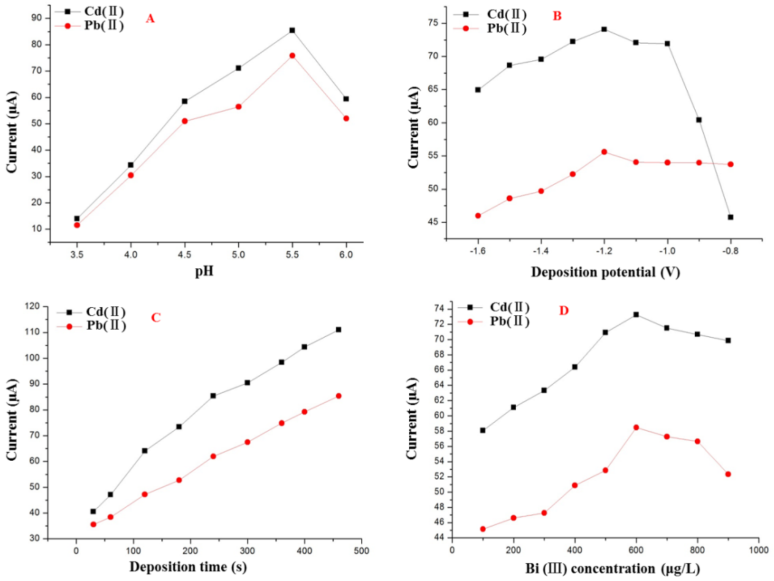

Figure 4. Effects of (A) pH value, (B) deposition potential, (C) deposition time, (D) Bi(III) concentration on the stripping peak currents of 50μg/L Cd(II) and Pb(II).

The stripping voltammograms were recorded in 0.1 mol/L pH 5.5 buffer solutions of PBS (Na_2HPO_4-NaH_2PO_4), disodium hydrogen phosphate-citric acid and NaAc-HAc to investigate the influence of supporting electrolytes with the CMWCNTs-β-CD-Nafion/GCE. Fig. 5 shows the current responses toward Cd (II) and Pb (II) in the three different buffer solutions. The best response for both studies was obtained with NaAc-HAc electrolyte solution at slightly acid pH values. Thus, NaAc-HAc buffer solution was chosen as the appropriate electrolyte because of its enhanced response to Cd (II), Pb (II) and Bi(III).

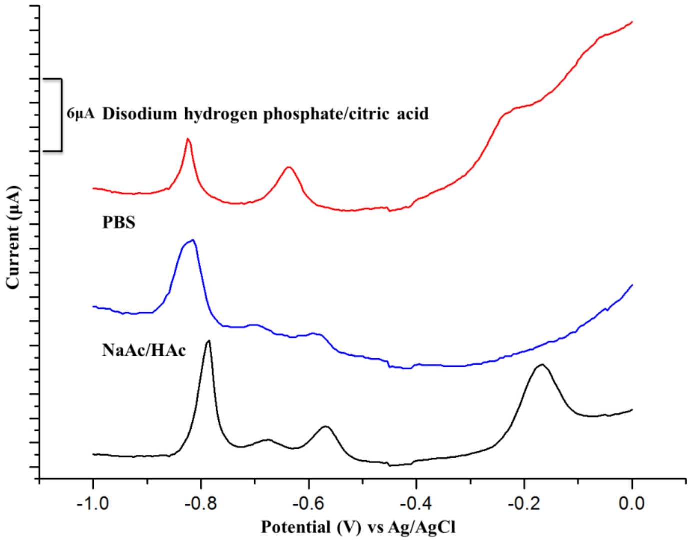

Figure 5. Influence of electrolytes on the stripping peak currents: 0.1 mol/L NaAc-HAc, PBS (Na_2HPO_4-NaH_2PO_4) and disodium hydrogen phosphate-citric acid buffer solution containing 40μg/L of Pb(II) and Cd(II) on CMWCNTs-β-CD-Nafion/GCE by in situ depositing bismuth film (600μg/L).

3.3. Stripping response of Cd(II) and Pb(II) at the CMWCNTs-β-CD-Nafion/GCE

3.3.1 Performance comparison of different coated metals modified electrodes

The comparison of CMWCNTs-β-CD-Nafion, Bi/CMWCNTs-β-CD-Nafion and Sn/CMWCNTs-β-CD-Nafion nanocomposite modified glassy carbon electrodes were investigated in 600µg/L of Sn(II) and Bi(III) solution, respectively, which both containing 50µg/L Cd(II) and Pb(II), as shown in Fig. 6. The CMWCNTs-β-CD-Nafion/GCE (curve a) shows stripping responses of the both of the target metals and the oxidation peak potentials of Cd(II) and Pb(II) were -0.8 V and -0.55 V, respectively. The Bi/CMWCNTs-β-CD-Nafion/GCE (curve c) had the excellent peak current to the both of the target metals, compared with CMWCNTs-β-CD-Nafion/GCE and Bi/CMWCNTs-β-CD-Nafion/GCE. The stripping response of Cd(II) on the Sn/CMWCNTs-β-CD-Nafion/GCE was the same with the stripping response of Cd(II) CMWCNTs-β-CD-Nafion/GCE, however, the stripping response of Pb(II) on the Sn/CMWCNTs-β-CD-Nafion/GCE was poor. Sn could form binary or multicomponent alloys with Cd and Pb, which was similar with bismuth [50]. These results can be explained as the following two reasons: on the one hand, compared with Pb, Cd was more likely to form alloy with Sn, which blocking the reduction of the Pb(II) onto the surface of the electrode at the accumulation step. On the other hand, this phenomenon may be because of the formation of multicomponent alloys, which affecting the normal stripping of Pb at stripping step.

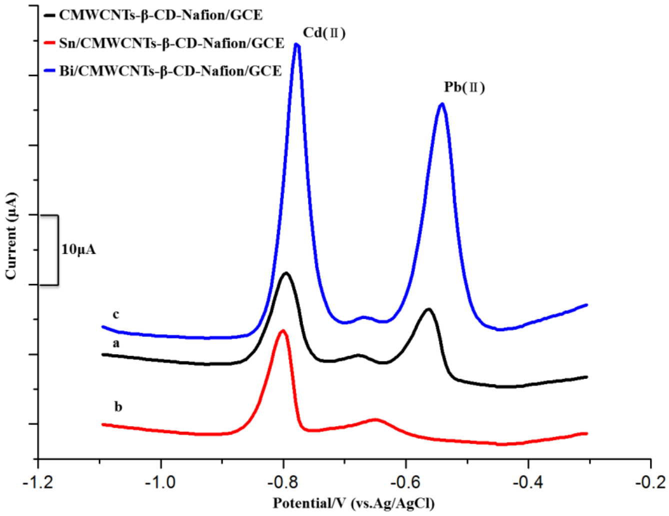

Figure 6. Square wave anodic stripping voltammograms of 50µg/L Cd(II) and Pb(II) in 0.1 M acetate buffer solution (pH 5.5) on the (a) CMWCNTs-β-CD-Nafion/GCE, (b) Sn/CMWCNTs-β-CD-Nafion/GCE and (c) Bi/CMWCNTs-β-CD-Nafion/GCE; Deposition time: 140 s. Deposition potential: -1.2 V. Concentration of Bi(III): 600 µg/L.

3.3.2. Electrochemical characterization of different modified electrodes

The stripping response performance of Bi/GCE, Bi/β-CD-Nafion/GCE, Bi/CMWCNTs-Nafion/GCE and Bi/CMWCNTs-β-CD-Nafion/GCE was initially investigated by SWASV, as shown in Fig. 7. The stripping voltammogram recorded at Bi/CMWCNTs-β-CD-Nafion/GCE (curve c) exhibited an enhanced, undistorted and well-defined Stripping voltammetric signal for both of the target HMs with peak potentials at -0.8 and -0.55V for Cd(II) and Pb(II), respectively. In contrast to the superior electroanalytical performance of Bi/CMWCNTs-β-CD-Nafion/GCE, Bi/GCE (curve a) and Bi/CMWCNTs-Nafion/GCE (curve b) yielded lower peak currents for both of the HMs. The highly electrochemical response of Bi/CMWCNTs-β-CD-Nafion/GCE could be due to the following facts: (1) the CMWCNTs-β-CD-Nafion provided a large specific surface area to increase the deposition amount of target HMs; (2) CMWCNTs could accelerate the electron transfer rate on the surface of electrode, and further amplify the Stripping voltammetric signal due to their outstanding electric conductivity; (3) The structural property of β-CD makes it readily undergo host–guest interaction with target HMs, due to their hydrophobic centers and hydrophilic outer tails [].(4) Nafion has the ability to improve the preconcentrating efficiency of heavy metal ions, and can prevent the interference molecules from approaching the electrode surface, moreover, Nafion can also improve the mechanical strength of the electrode surface modification layer [].All of these would improve the stripping voltammetric responses of HMs on the surface of Bi/CMWCNTs-β-CD-Nafion/GCE.

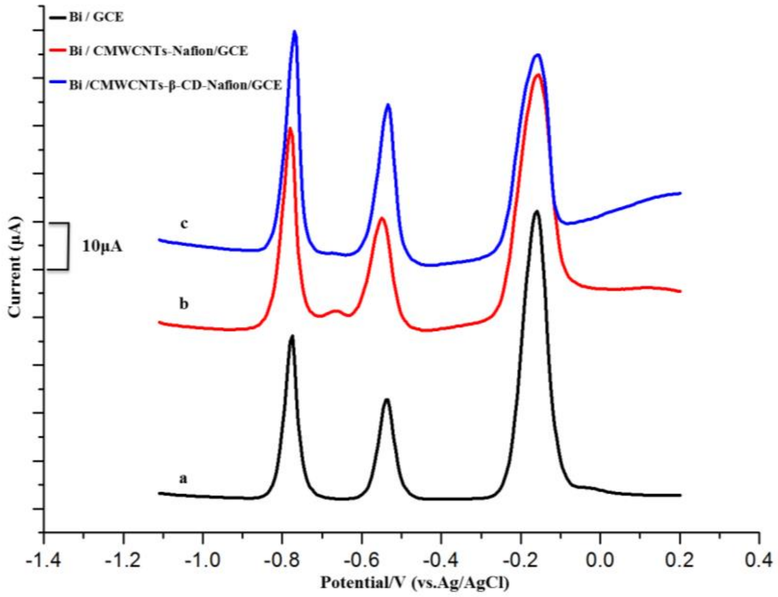

Figure 7. Square wave anodic stripping voltammograms of 50µg/L Cd(II) and Pb(II) in 0.1 M acetate buffer solution (pH 5.5) on the (a) Bi/GCE, (b) Bi/CMWCNTs-Nafion/GCE and (c) Bi/CMWSNTs-β-CD-Nafion/GCE. Deposition time: 140 s. Deposition potential: -1.2 V. Concentration of Bi(III): 600 µg/L.

The performance of residual metals and bismuth film removed from the electrode surface during electrode cleaning process directly affected the reusability of the electrode. Chronoamperometry was used as an electrode cleaning method to remove the residual metal film with a 120 s cleaning step at 0.31 V under stirring condition, as shown in Fig. 8. As you can see from Fig. 8A, after three times cleaning, the bare electrode still had a certain response current, which indicating that the metal film had not been completely removed. Until the fourth cleaning of the electrode, the response current was close to 0. As shown in Fig. 8B, in the first cleaning of Bi/CMWSNTs-β-CD-Nafion/GCE, the response current dropped sharply and was close to 0 (curve e and f), which revealing that the Bi/CMWSNTs-β-CD-Nafion/GCE had excellent performance of removing residual metal film, compared with the bare GCE. The excellent performance of removing residual metal film from the electrode surface would improve the reusability of the sensor.

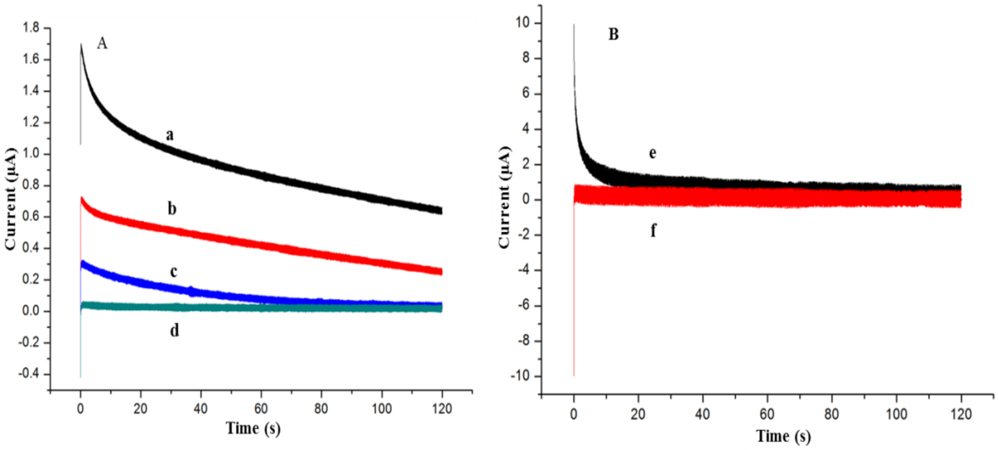

Figure 8. The current-time curves of electrodes cleaning. (A) Cleaning times of Bi/GCE, a-d: 1-4. (B) Cleaning times of Bi/CMWCNTs-β-CD-Nafion/GCE, e-f: 1-2.

Furthermore, in order to evaluate the reproducibility of the proposed Bi/MWCNT-EBP-NA/GCE, **six modified electrodes was used to** test the **reproducibility** via 10 repetitive measurements of 50 μg/L Pb(II) and Cd(II) in 0.1 M acetate buffer solution (pH 5.5)**. The relative standard deviation (RSD) was 3.8% for Cd(II) and 3.0% for Pb(II), respectively, which suggested acceptable reproducibility. The Bi/CMWSNTs-β-CD-Nafion composites modified electrode can be used for the simultaneous detection of trace target HMs in practical application at a low cost due to the good reusability and reproducibility.**

3.4. Analytical performance for simultaneous detection of Cd(II) and Pb(II)

Under the optimized conditions, the developed electrode was applied to the simultaneous determination of Cd(II) and Pb(II) by SWASV. A series of peak currents for different concentrations of Cd(II) and Pb(II) are illustrated in Fig. 9A. The stripping responses showed a good linear relationship with the concentrations of target HMs in the range 1.0-50 μg/L, as shown in the insets of Fig. 9B and Fig. 9C, respectively. The calibration curves and correlation coefficients were $y = 0.6622x + 41.9660$ (x: μg/L, y: μA, 1 to 100 μg/L, r = 0.991) for Cd(II) and $y = 0.3345x + 39.7616$ (x: μg/L, y: μA, 1 to 100 μg/L, r = 0.997) for Pb(II). The detection limits (S/N = 3) could be calculated as 0.13 μg/L for Cd(II) and 0.21 μg/L for Pb(II), respectively. Of course, lower detection limits can be obtained by extending the deposition time. A comparison between previous works and this work is shown in Table 1. It can be found from the Table 1 that the analytical performance of the

Bi/CMWSNTs-β-CD-Nafion/GCE is comparable and even better to the previous reports, which offering a wider range, lower detection limit and relatively less deposition time.

Table 1. Comparison of different electrodes for determination of Pb(II) and Cd(II).

Electrodes	Method	Deposition time(s)	Linear range(μg/L)		Detection limit(μgL/)		Reference
			Pb(II)	Cd(II)	Pb(II)	Cd(II)	
Bi/GCE	SWASV	250	5-150	5-150	1.9	3.2	[34]
Bi/GCE	SWASV	300	0-100	0-100	0.41	0.49	[35]
CB-15-crown-5/GEC	DPASV	300	10.9-186.5	15.7-191.1	3.3	4.7	[36]
BiOCl/MWCNT/GCE	SWASV	120	5-50	5-50	0.57	1.2	[37]
L-cys/GR-CS/GCE	DPASV	120	1.04-62.1	0.56-67.2	0.12	0.45	[38]
MWCNT/poly(PCV)/GCE	DPASV	420	1.0–200.0	1.0-300.0	0.4	0.2	[39]
Bi/poly(p-ABSA)/GCE	DPASV	240	1.0-130	1.0-110.0	0.8	0.63	[40]
Bi/CPE	SWASV	300	10-100	10-100	0.9	1.2	[41]
Bi-xerogel/Nafion/GCE	SWASV	240	1.04-20.72	0.56-11.24	1.3	0.37	[42]
Bi/CNT/SPE	SWASV	180	2-100	2-100	0.2	0.8	[43]
Bi/CMWSNTs-β-CD-Nafion/GCE	SWASV	140	1-100	1-100	0.13	0.21	This work

NMC: nitrogen doped microporous carbon, CB-15-crown-5: 4-carbox-ybenzo-15-crown-5, BioCl: bismuth-oxychloride, MWCNT: multi-walled carbon nanotube, L-cys: L-cysteine, GR: graphene, poly(PCV): poly(pyrocatecholviolet)

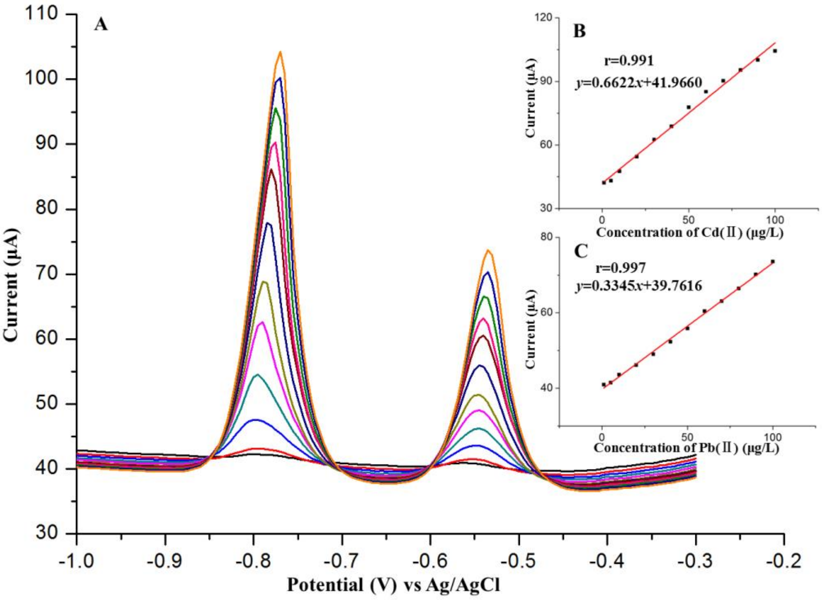

Figure 9. (A) Square wave anodic stripping voltammograms for different concentration of Cd(II) and Pb(II). From bottom to top, the concentrations are 1, 5, 10, 20, 30, 40, 50, 60, 70, 80, 90, and 100μg/L, respectively. (B) Calibration curve of Cd(II). (C) Calibration curve of Pb(II).

3.5. Interference study

The influence of various possible interference ions, such as Cu^{2+}, Na^{+}, As^{3+}, Cr^{2+}, K^{+}, Ca^{2+} and Zn^{2+}, on the SWASV detection of Cd(II) and Pb(II) was examined at an interference-ion-to-target-HM concentration ratio of 5:1 under the optimized conditions. At higher concentrations of interference ions, no significant changes were observed in the stripping peak currents of either HMs (changes in peak currents < 10%), except in the presence of Cu^{2+}, which negatively affected the stripping peak currents. In this study, Cu^{2+} was the most pronounced interference ion. The stripping peak currents of Cd(II) and Pb(II) increased by approximately 27.3% and 19.6%, respectively, in the presence of Cu^{2+}. This suppression effect was likely due to the formation of intermetallic compounds as well as competition toward active sites on the electrode surface. Nevertheless, the Cu^{2+} interference could be reduced by the addition of 0.1 mM ferrocyanide to the sample extract solutions, in which an insoluble and stable copper-ferrocyanide complex was formed with the help of a ligand [44].

3.6. Application to real sample analysis

To evaluate the applicability of the presented modified electrodes, the Bi/CMWSNTs-β-CD-Nafion/GCE was applied to the concrete analysis of Cd(II) and Pb(II) in real soil samples. The experiments were performed by the standard addition method. To reduce the interference of Cu^{2+} and to conduct an accurate quantitative determination of Cd(II) and Pb(II), we treated the soil samples by adding 0.1 mM ferrocyanide ions before the determination of Cd(II) and Pb(II). The HMs contents were calculated; the results are summarized in Table 2. The recovery test demonstrated the feasibility of using the developed Bi/CMWSNTs-β-CD-Nafion/GCE for the detection of target HMs in real soil samples. The average recoveries of Cd(II) and Pb(II) were 96.28% and 96.64%, respectively. Precision and recovery tests indicated that the proposed Bi/CMWSNTs-β-CD-Nafion/GCE could be applied to the analysis of trace heavy metals in real samples.

Table 2. Results for the simultaneous detection of Cd(II) and Pb(II) in several soil sample extracts.

Sample no.	Added (μg/L)		Found (μg/L)[a]		RSD (%)		Recovery (%)	
	Cd(II)	Pb(II)	Cd(II)	Pb(II)	Cd(II)	Pb(II)	Cd(II)	Pb(II)
1	-		1.79	4.39	3.3	4.1	-	-
	4		5.68	8.17	2.7	2.2	97.25	94.5
	8		9.43	12.16	1.6	3.6	95.5	97.13
2	-		3.59	6.51	1.8	4.2	-	-
	5		8.21	11.28	2.2	1.9	92.4	95.4
	10		13.18	16.32	1.4	1.3	95.9	98.1
3	-		2.37	2.08	3.1	3.7	-	-
	10		12.18	11.68	2.7	2.7	98.1	96
	15		17.15	16.89	1.5	3.3	98.53	98.73

[a] SWASV measurements were repeated five times (n=5)

4. CONCLUSION

In this study, a Bi/CMWSNTs-β-CD-Nafion composites modified GCE has been developed and further investigated for simultaneously detection of trace Cd(II) and Pb(II) by SWASV. Basic characteristics of the CMWCNTs-β-CD-Nafion/GCE were investigated by SEM and CV. Optimization of key measurement parameters (pH value, supporting electrolyte, concentration of Bi(III), deposition potential and deposition time) and practical application of the CMWCNTs-β-CD-Nafion/GC were investigated in detail. Due to unique properties and synergistic effects of CMWCNTs, β-CD, Nafion and bismuth film, the developed electrode exhibited some advantages over traditional GCE, such as large surface area, good sensitivity and stability, reusability and electronic conductivity. The proposed modified electrode was further applied to detect trace Cd(II) and Pb(II) in soil samples with satisfactory recovery results, which holds great promise for its wide applications in food safety and environmental pollution monitoring.

ACKNOWLEDGEMENTS
This work was supported by the National High Technology Research and Development Program of China (no.2013AA102302), Research Fund for the Doctoral Program of Higher Education of China (no.20120008110033), the Fundamental Research Funds for the Central Universities (no.2016 XD001) and the Shandong Provincial Natural Science Foundation of China (no.ZR2015CM016).

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