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Electrochemical Determination of Trace Cadmium in Soil by a Bismuth Film/Graphene-β-cyclodextrin-Nafion Composite Modified Electrode

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In this study, a novel bismuth film/graphene-β-cyclodextrin-Nafion composite modified glassy carbon electrode (GR-β-CD-Nafion-GCE) was developed for trace cadmium detection using square wave anodic stripping voltammetry (SWASV). The morphologies and electrochemistry properties of the modified electrode were characterized by SWASV, chronoamperometry, cyclic voltammetry (CV)and scanning electron microscopy (SEM). It was found that the GR-β-CD-Nafion-GCE exhibited remarkable enhancement effects towards cadmium ions detection which remarkably facilitate the electron transport and enlarge the specific surface area of the electrode. With ideal circumstance, the anodic stripping currents displayed a good linear relationship to concentration in the ranges from 1 to 500μgL^{-1} and 800 to 2000μgL^{-1} with a detection limit of 0.3μg/L (S/N=3). The sensor was further applied to the detection of cadmium ions with satisfactory results in soil extracts and exhibited a good reusability and stability.

Keywords: Bismuth, Graphene, β-cyclodextrin, Nafion, Cadmium, Soil

1. INTRODUCTION

Cadmium is one of the most serious pollutants in soil, which can enter the body through the food chain and damage nervous system, immune system, reproductive system and digestive system [1]. With the industrial development, all kinds of wastes discharged from industrial production were discharged into the environment, which heavily polluted in our environment, especially the soil [2]. The soil was contaminated by toxic heavy metals and other pollutants. Foods intake is one of the main ways to enter the human body. [3]. That is to say, there are potential hazards to the plants and the meat of animals that have been contaminated by heavy metals in tainted agricultural land. [4]. Therefore, it is essential to control the heavy metals pollution in the soil, but to do so must be on the premise that the effective methods for heavy metals detection in soil have been spatially analyzed. [5–7].

Presently, various traditional analytical methods for the trace cadmium in soil samples have already been proposed, such as atomic absorption spectrometry (AAS), flame atomic emission spectroscopy, inductively coupled plasma atomic emission spectroscopy (ICP-MS) [8–15]. These methods have high sensitivity and excellent selectivity. However, there are also many drawbacks, such as the complex operation, ancillary equipment is expensive, high level of operator skills, expensive detection costs, not applicable for in situ detection. Anodic stripping voltammetry as a rapid and effective electrochemical method is widely used in the detection of heavy metals in soil samples [16-18]. Seeing that the working electrode plays a critical role in the stripping analyses of heavy metals, the toxicity and risks of hanging drop mercury electrode and mercury film electrode during disposal make the use of them were undesirable.

In recent years, carbon-based nanostructural materials, especially GR [19–22] have received increased interest to improve the heavy metals electrochemical detection performance of sensing electrodes, due to their environmental friendliness, efficient electron transfer capability, unique structural properties and physics and chemistry characteristics. However, due to the existence of strong π-π stacking and van der Waals interactions, the dispersibility of graphene is poor, which limits the application in electrode modification [23]. Thus, people spend a lot of efforts to functionalize graphene by noncovalent strategies or covalent [24, 25]. CDs have excellent physical and chemical properties, which has attracted a lot of researchers for its theoretical research and application research

β-CD are common members of CDs and with a toroidal shape which consisting of a hydrophilic exterior and a hydrophobic inner cavity. β-CD, as a novel material, has wide scope of applications, such as molecular recognition, increasing solubility, environmental protection and catalysis[26]. The interesting characteristics can enable them to form nanostructured supramolecular assemblies or stable host–guest inclusion complexes, in their hydrophobic cavity. Therefore, it can show enantioselectivity and high molecular selectivity [27–29] and improve the solubility and stability of functional materials, such as GR [30-32]. Among the different membranes applied to bismuth-film electrodes, Nafion is one of the most widely used materials [33–35]. GR-β-CD nanocomposite combined with Nafion might improve the absorption of cadmium ion on the film and enhance the stability of the film by forming a negatively perfluor sulfonated ion-exchange polymer [36].

It can be supposed that the multifunctional nanocomposite obtained from graphene, β-CD and Nafion has the advantages of GR, β-CD and Nafion, including the large surface area, efficient electron transfer capability, high selective recognition properties and enrichment capability properties [37–39]. However, to the best our knowledge, the electrochemical propertiesof GR-β-CD-Nafion composite modified bismuth film electrode has not been explored by now. On the basis of the above consideration and in combination with the characteristics of GR, β-CD and Nafion, in this paper, we synthesized GR-β-CD-Nafion composite modified bismuth film GCE by SWASV for electrochemical determination of trace cadmium in soil. The experimental results indicated that the developed electrode exhibited more excellent voltammetric response to cadmium ion than the classical GCE.

2. EXPERIMENTAL

2.1. Reagents and instruments

β-cyclodextrin and Nafion were obtained from Aldrich (Sigma-Aldrich, USA). Pure ethanol was used to dilute Nafion from 5 wt% to 1 wt%.

Graphite powder (spectrum pure, size <30 μm) and Stock solution of Cd(II) (1,000 mg L^{-1}) were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China)and national standard reference materials center of China respectively and stock solution was diluted as required. Acetate buffer solution (0.1 M) was served as the supporting electrolyte for the detection of cadmium ion. Millipore-Q (18.2 MΩ) water was used throughout.

SEM analysis was carried out on JSM-6701F field emission scanning electron microscope (FE-SEM) produced by JEOL Ltd. (Japan). CV of the ferricyanide system, chronoamperometry and electrochemical measurements were performed on a CHI660D electrochemical workstation (Shanghai CH Instruments, China). The Ag/AgCl (3 M KCl) electrode, platinum wire and modified glassy carbon working electrode (Φ=3 mm) were used as reference, counter and working electrode, respectively. All electrochemical measurements were carried out in a 25 mL cell

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

Prior to the modification, the GCE was polished by 0.05μm alumina powder and rinsed with 1:1 HNO_3, absolute ethanol and water, respectively. 32 mg β-cyclodextrin was added into 4 mL of dimethylformamide (DMF) solution (2 wt%) by sonicating until β-cyclodextrin disperse equably. Then 1 mg graphene was added to the above suspension to give a 0.25 mg mL^{-1} black suspension with the aid of ultrasonic agitation for 3h. Next, 450μL Nafion (1 wt%) was added to the mixture to form a homogeneous black dispersion through ultrasonication. The obtained highly dispersed black suspension would be named as GR-β-CD-Nafion. A 5μL of GR-β-CD-Nafion suspension was coated on the GCE surface and then solidified by irradiating with infrared lamp for 15 min to obtain GR-β-CD-Nafion /GCE.

2.3. Electrochemical measurement procedure

The determination of cadmium ion was carried out using SWASV, which was performed in 0.1 M acetate buffer solutions with 600μgL^{-1} Bi(III). In the deposition process, the working electrode is provided with -1.4 V for 140 s, under the stirring conditions. When the deposition process is over, there is an equilibration process in 10s. A potential scan range from -1.2 V to 0 V was used for SWASV detection. The potential step, square wave amplitude and frequency were 5 mV, 25 mV and 25 Hz, respectively. In order to remove the residual metal film, before the next electrochemical detection, clean step must be carried out at 0.3V for 30s under stirring condition. The main steps of Cd(II) detection was illustrated by Fig.1.

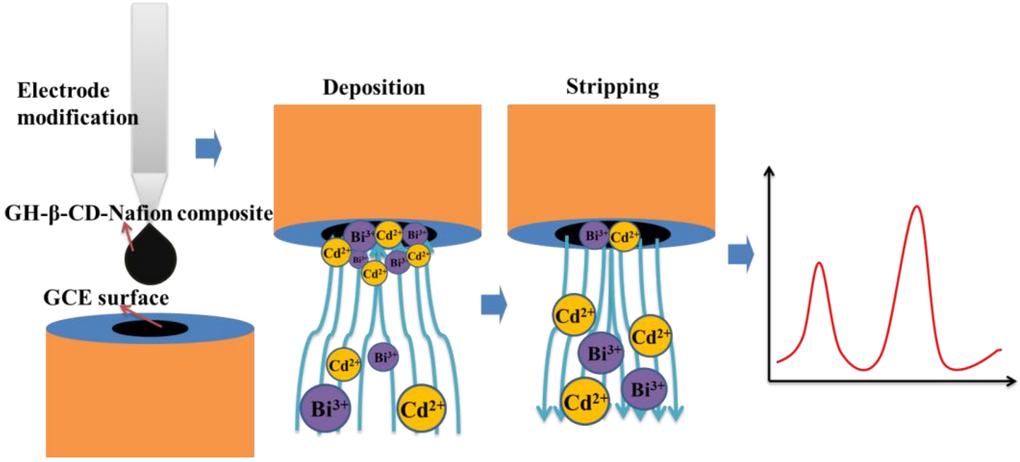

Figure 1. Schematic diagram of main measurement steps of Cd(II) by means of SWASV method.

3. RESULT AND DISCUSSION

3.1. Basic characteristics of the modified electrodes

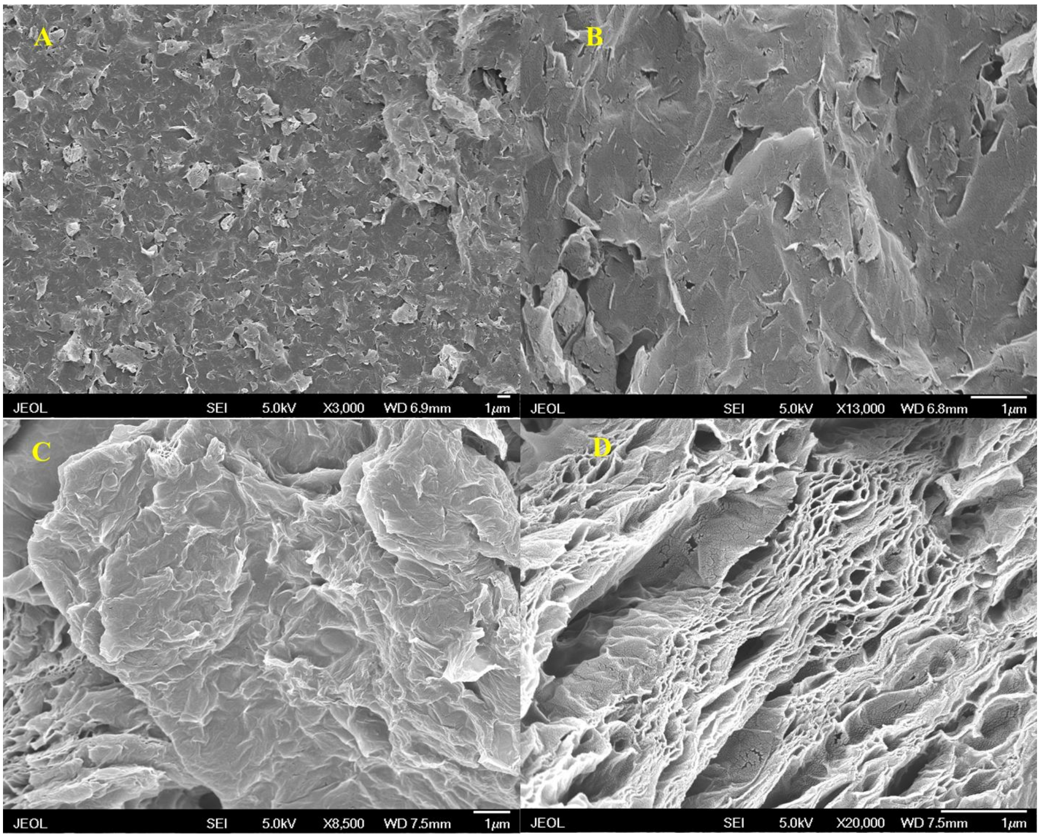

Figure 2. SEM images of surface morphologies of GR /GCE (A and B), GR-β-CD-Nafion/GCE (C and D).

SEM was used for the characterization of prepared electrodes morphological features. Graphene was first characterized with SEM. As shown in Fig. 2(A and B), a fractured and wrinkled paper-like structure could be observed on the GR/GCE, indicating the forming of GR nanosheets on the electrode surface. Fig. 2(C and D) shows the image of the wrinkled GR-β-CD-Nafion composite membrane on the electrode surface, which corrugated, scrolled and polylaminate. Moreover, the graphene had completely embedded into the composite structure composed by graphene, cyclodextrin and Nafion, the stability and compatibility of the film could be enhanced by this composite structure Characteristics of each modified electrode surface can be monitored by CV based on ferricyanide system which is convenient and valuable [32]. Cyclic voltammograms of different modified electrodes in 5.0 mM $K_3[Fe(CN)_6]$ solution were shown in Fig.3. On the bare GCE, a weak redox peaks was observed, indicating the sluggish electron transfer rate at the interface. After the bare GCE was modified by the GR-β-CD-Nafion composite film, an obvious increase of peak current could be observed compared to bare GCE electrode, which could owe to the high electrocatalytic activity and excellent ionic conductivity of GR. After GR-Nafion was coated on the GCE, an obvious reduced amperometric response was appeared. The obvious decreased peak current could be attributed to the poor dispersibility of graphene in solvents.

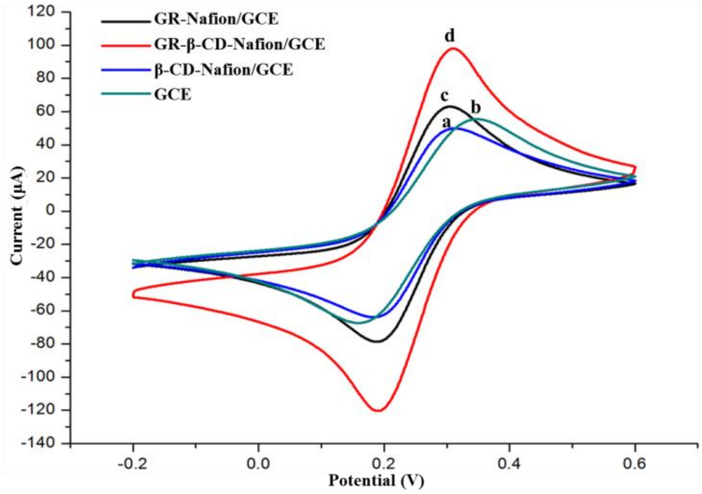

Figure 3. Cyclic voltammograms for 5 mM $K_3[Fe(CN)_6]$ in 0.1 M KCl, (a) β-CD-Nafion/GCE, (b) GCE, (c) GR-Nafion/GCE and (d) GR-β-CD-Nafion/GCE. Scan rate: 50 mV s^{-1}.

3.2. Optimization of experimental conditions

In order to get high detection performance of Cd(II), a solution containing 80μg L^{-1} of Cd(II) was used to optimize the various parameters of square wave anodic stripping voltammetry for Cd(II) detection. The effect of Bi(III) concentration on the stripping responses was demonstrated by Fig. 4A. As shown, In the range of 0 to 600μg L^{-1}, with the increase of the concentration of Bi(III), the stripping peak currents of the cadmium ions increased, too. When the Bi(III) concentration got 600μg L^{-1}, the current value reached the maximum. This phenomenon may be due to the high concentration Bi(III) so that the electrode surface formed a thick bismuth film, the thick bismuth film will affect the stripping of cadmium ion. Consequently, we chose 600μg L^{-1} Bi(III) concentration as the optimal coating concentration.

The SWASV responses to 80μg L^{-1} of Cd(II) on GR-β-CD-Nafion composite modified electrodes were studied in acetate buffer solution with different pH values. As shown in Fig. 4B, the best responses to Cd(II) was shown at pH 5.5. When pH valve is low, the H^+ will be reduced on the surface of working electrode to H_2, The hydrogen evolution reaction will hinder the deposition and stripping of the target cadmium ion on the electrode surface. When the solution with stronger alkaline, the hydrolysis reaction of heavy metals in the environment may affect the detection results which would influence dissolution response of cadmium ion. Finally, the follow-up experiments were carried out with the pH value of 5.5.The influence of deposition potential on the stripping voltammetry detection of cadmium ion was discussed, as shown in Fig. 4C. When the deposition potential was in the range of -0.8V to -1.4V, the peak current increased with the increased of the deposition potential, which may due to the further reduction of cadmium ions But when the deposition potential continued to increase on the basis of -1.4V, the peak current will gradually decreased, which may be due to the occurrence of hydrogen evolution reaction. Therefore, we chose -1.4V as the deposition potential of this methodThe metal accumulation time was investigated in the range of 30–480 s in a solution containing 80μg L^{-1} of Cd(II) and 600μg L^{-1} of Bi(III) in acetate buffer solution. From Fig. 4D, we could find that the peak current increased with the increased of deposition time. But when the deposition time was more than 140s, the peak current increased slightly with the increase of time. However, as deposition time longer than 140 s, the curve of peak currents versus time began to increase slightly, which may be due to the effective area of the electrode surface and the saturation effect of the Bi(III) film. In view of the simultaneous consideration of timeliness and sensitivity, 140 s was selected for deposition.

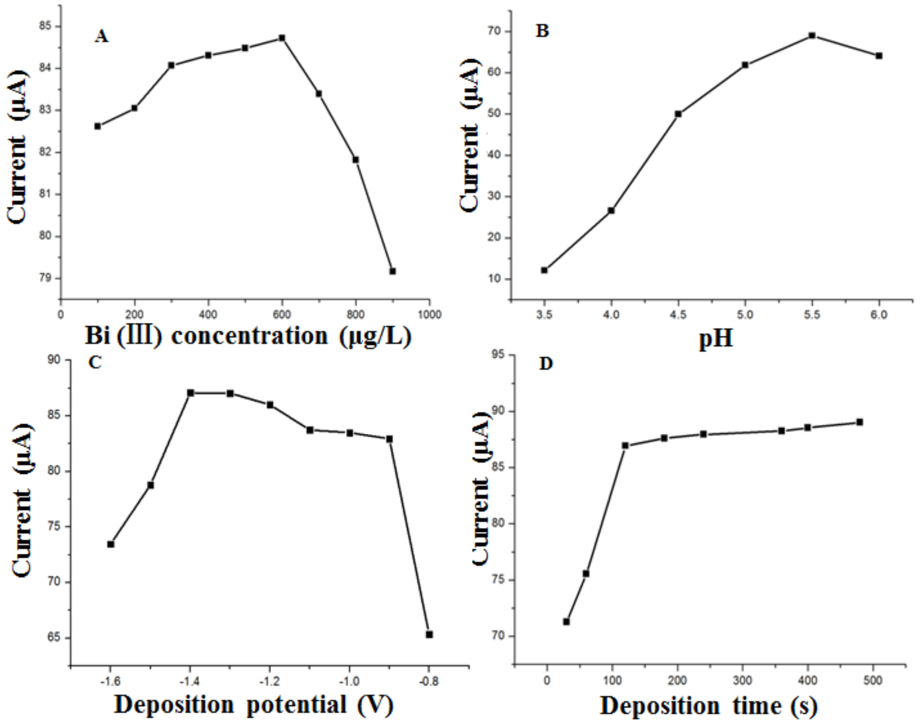

Figure 4. Effects of (A) Bi(III) concentration, (B) pH value, (C) deposition potential, (D) deposition time on the stripping peaks current of 80μg L^{-1} Cd(II).

3.3. Stripping behavior of cadmium at the modified electrode

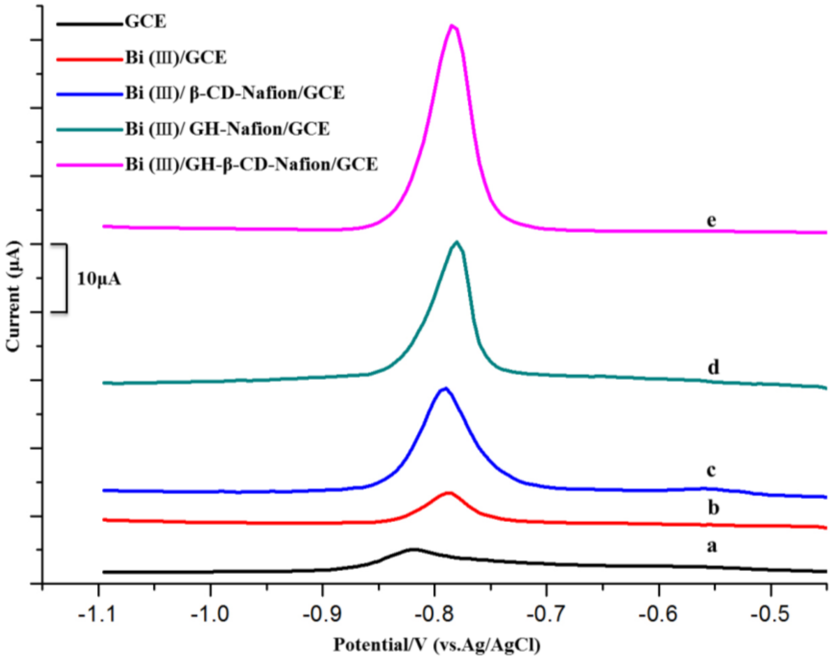

Figure 5. Square wave anodic stripping voltammograms of 50μgL^{-1}Cd(II) in 0.1 M acetate buffer solution (pH 5.5) on the (a) GCE, (b) Bi(III)/GCE, (c) Bi(III)/β-CD-Nafion/GCE (d) Bi(III)/GR-Nafion/GCE and (e) Bi(III)/GR-β-CD-Nafion/GCE. Deposition time: 140 s. Deposition potential: -1.4 V. Concentration of Bi(III): 600 μgL^{-1}.

Fig.5 compares the SWASV responses of 50μgL^{-1} Cd(II) on different working electrodes. The response of Cd(II) at the bare GCE was very poor with a small peak current (curve a). After adding 600 μgL^{-1} Bi(III), the peak current at the Bi(III)/GCE was remarkably enhanced (curve b). This phenomenon arises may be due to bismuth can form an “alloy” with the target heavy metal ions and make cadmium ion is easy to be reduced on the electrode surface. Moreover, Bi(III)/GR-β-CD-Nafion/GCE exhibited higher stripping responses toward Cd(II) detection than Bi(III)/GCE, which revealed that the effect of GR-β-CD-Nafion/GCE on the enhancement of SWASV responses was better than bare GCE. As shown in fig.5, two relatively weak stripping peaks were observed on Bi(III)/β-CD-Nafion/GCE (curve c) and Bi(III)/GR-Nafion/GCE (curve d). While at Bi(III)/GR-β-CD-Nafion/GCE, a higher sensitivity toward Cd(II) detection (curve e) was observed.

Such improvement could be attributed to two factors: one is that the combination of β-CD and GR, in which the β-CD can selectively hold the cadmium ion and the GR provides a large specific surface area to increase the deposition of cadmium ion. Meanwhile, good electrical conductivity of graphene can accelerate the transfer efficiency of the electron on the electrode surface and amplify the electrochemical signal. The other is that Nafion has the sulfonate groups which were negatively charged and, as a result, the polymeric membrane with cation exchange function can facilitate the non-faradaic electro-deposition of heavy metal ions [47].

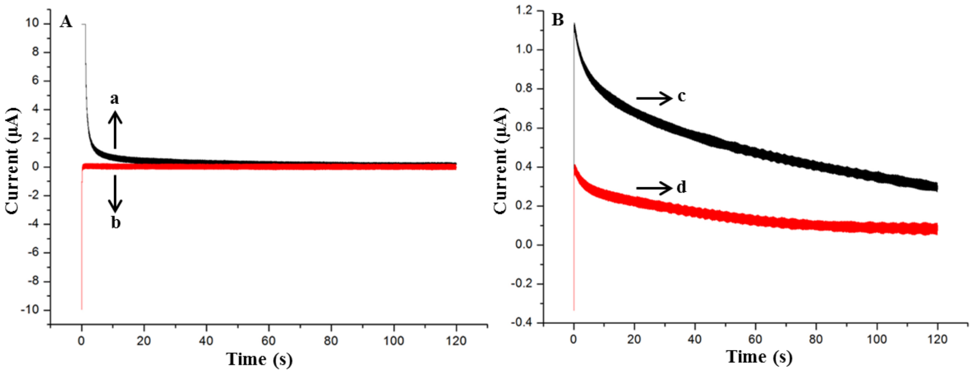

Figure 6. Chronoamperometry of electrode cleaning to remove the residual metal film. (A) Bi(III)/GR-β-CD-Nafion/GCE (a) the first cleaning (b) the second cleaning. (B) Bi(III)/GCE (c) the first cleaning (d) the second cleaning.

The cleaning performance directly affects the reusability of the electrode. Chronoamperometry was used to remove the residual metal film with a 30 s clean step at 0.3 V under stirring condition, as shown in Fig.6. As you can see from Fig.6A, the metal cations stripped rapidly on the GR-β-CD-Nafion/GCE surface at the potential of 0.3V. In the first cleaning process the stripping current rapidly decreased from 10μA and approached 0μA in about 2s (curve a) and the stripping current during the second cleaning process was almost remain in 0μA which revealing that the residual metal film has been cleaned almost completely. In contrast, after two cleaning, the bare electrode still had a certain residual metal film, as shown in Fig.6B (curve c and d) which revealing that the reusability of the bare electrode was not as good as the GR-β-CD-Nafion composite modified electrode. Furthermore, in order to evaluate the proposed electrochemical sensors' reproducibility, five modified electrodes were used to detect Cd(II) of 50μgL^{-1}repeatedly.The relative standard deviation (RSD) was 3.62%, which suggested that the accuracy and repeatability were acceptable.. The good reusability and reproducibility make the GR-β-CD-Nafion composite modified electrode be an ideal sensor suitable for the trace cadmium ion detection or analyzing in practical application at a low cost.

3.4. Analytical performance of Bi/GR-β-CD-Nafion/GCE

Cadmium detection was carried out used the developed electrode by SWASV in ideal circumstances. A series of stripping responses for different concentrations of Cd(II) were discussed in Fig.7A. The peak currents had a good linear relationship with the concentrations of Cd(II) in the range of 1 to 500μgL^{-1} and 800 to 2000μgL^{-1}, as shown in Fig.7B and Fig.7C. The calibration curves and correlation coefficients were $y = 0.1165x + 64.5604$ (x: μgL^{-1}, y: μA, 1 to 500 μgL^{-1}, r = 0.993) and $y = 0.0181x + 126.4133$ (x: μgL^{-1}, y: μA, 800 to 2000 μgL^{-1}, r = 0.991) for Cd(II). The detection limits and quantification limits was used to evaluate the detection performance of the proposed electrode. The limits of detection (LOD) and limits of quantification (LOQ) were calculated based on three times and ten times of standard deviation of the blank signals (S/N = 3 and S/N = 10) and the LOD and LOQ were 0.3 μgL^{-1}and 0.9 μgL^{-1}for Cd(II), respectively. Of course, an even lower LOD and LOQ could be obtained by extending the deposition time. A comparison between previous works and this work was shown in Table 1, which indicated that the GR-β-CD-Nafion/GCE offered a wider range, lower detection limit and better timesaving.

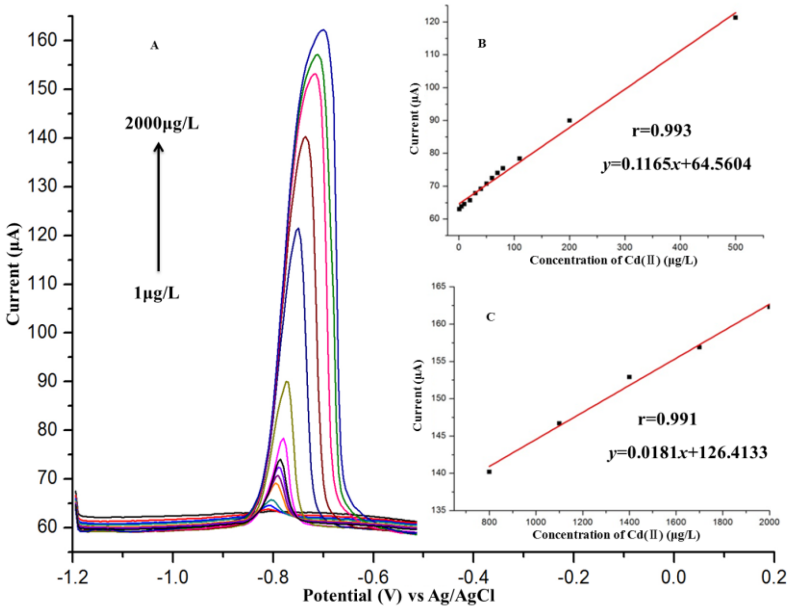

Figure 7. (A) SWASVs for different concentration of Cd(II). From bottom to top, the concentration are 1, 5, 10, 20, 40, 50, 60, 70, 110, 200, 500, 800, 1100, 1400,1700 and 2000μgL^{-1}, respectively. (B) The corresponding correlation plot with the range from 1 to 500μg/L. (C) The corresponding correlation plot with the range from 800 to 2000μg/L.

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

Electrodes	Method	Deposition time (s)	Linear range(ugL^{-1})	Detection limit(ugL^{-1})	Refenrence
Bi/GCE	SWASV	250	5-150	3.2	[42]
Nafion/Bi/NMC/GCE	SWASV	150	0.5 -10	1.5	[43]
Bi/GCE	SWASV	300	0-100	0.49	[44]
SnF/CPE	SWASV	150	2.0–90.0	1.13	[45]
BiOCl/MWCNT/GCE	SWASV	120	5-50	1.2	[46]
L-cys/GR–CS/GCE	DPASV	120	0.56–67.2	0.45	[47]
MWCNT/poly(PCV)/GCE	DPASV	420	1.0–300.0	0.2	[48]
Bi-D24C8/Nafion SPCE	SWASV	180	0.5-60	0.27	[49]
Bi/poly(p-ABSA)/GCE	DPASV	240	1.0–110.0	0.63	[50]
Bi/CPE	SWASV	300	10–100	1.2	[51]
Bi-xerogel/Nafion/GCE	SWASV	240	0.56–11.24	0.37	[52]
Sn/NaDBS/MWCNTs/GCE	DPASV	240	5-100	0.8	[53]
Bi/CNT/SPE	SWASV	180	2-100	0.8	[54]
Bi/GR-β-CD-Nafion/GCE	SWASV	140	1-500 and 800-2000	0.3	This work

NMC: nitrogen doped microporous carbon, BioCl: bismuth-oxychloride, MWCNT: multi-walled carbon nanotube, L-cys: L-cysteine, GR: graphene, poly (PCV): poly (pyrocatecholviolet), D24C8: dibenzo-24-crown-8, poly (p-ABSA): poly (p-aminobenzene sulfonic acid), NaDBS: sodium dodecyl benzene sulfonate, CNT: carbon nanotubes, GCE: glassy carbon electrode, CPE: carbon paste electrode, SPE: screen-printed electrode, SPCE: screen-printed carbon electrode.

3.5. Interference study

In an ideal situation, the anti-interference ability of the proposed electrode was evaluated by Cd(II) detection in the presence of some foreign ions. Mn^{2+}, Ba^{2+}, Ca^{2+}, Mg^{2+}, Al^{3+}, K^{+} , Cr^{3+}, Na^{+}, SO_4^{2-}, PO_4^{3-}, Cl^{-}, NH_4^{+}, NO_3^{-} were commonly found in soil environment, which were added into acetic acid buffer containing 50.0 μgL^{-1}Cd(II) and 600 μgL^{-1} Bi(III), in order to explore the interference of these ions on the electrode. The experimental results showed that the above ions had no significant effect on the stripping signal of cadmium ion. Such experimental results may be due to the molecular recognition ability and strong interaction of GR-β-CD-Nafion composite for Cd(II).In addition to the above ions, the experimental results showed that the Cu^{2+} had serious interference to the stripping signal of cadmium ions, which affected the detection results seriously. When 2-fold of Cu^{2+} was added, stripping signal of Cd(II) was decreased by about 29.6%. This inhibiting effect may be due to the competition of active sites on the surface between Cu^{2+} and Bi(III) competing. The intermetallic compound formed by the copper and cadmium would seriously affected the stripping signal of the cadmium ion on the electrode surface. But the interference of copper ions could be easily eliminated by adding ferrocyanides into the detection solution to produce an insoluble and stable copper-ferrocyanide complex [55].

3.6. Application to real sample analysis

In order to evaluate the practical application of the sensor, the GR-β-CD-Nafion/GCE was applied to the detection of Cd(II) in soil samples. Standard addition method was used to detect the Cd(II) in actual soil samples. The detection results were further verified by experiments with atomic absorption spectrometry and recovery ratio experiment. Table 2 showed that there were no significant differences between the two detection methods. It was proved that the described method was suitable for quantitative detection of cadmium ions in soil by samples detection and recovery tests with an average recovery of 96.80%.

Table 2. Recovery tests and the comparison of GR-β-CD-Nafion/GCE and AAS for the determination of Cd(II) in several soil sample extracts

Sample no.	Added (μgL^{-1})	Found by SWASV (μgL^{-1})	Found by AAS (μgL^{-1})	Recovery (%)
1	-	2.23±0.29	2.35±0.06	-
	4	6.18±0.11		95.75
	8	9.98±0.18		95.38
2	-	4.61±0.08	4.7±00.2	-
	5	9.64±0.10		98.80
	10	14.43±0.12		97.30
3	-	7.17±0.09	7.26±0.04	-
	10	16.76±0.17		95.00
	15	22.05±0.16		98.60

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

[b] Mean value ± standard deviation

4. CONCLUSION

In summary, environment friendly, low-price, and fully electrochemical synthesis methodology was used to prepare bismuth film/GR-β-CD-Nafion composite modified electrode for the sensitive determination of trace cadmium ions, which was further investigated by SEM, CV, Chronoamperometry and SWASV. Due to the combination of graphene, β-cyclodextrin and Nafion, their respective advantages are fully integrated in the new composite membrane which was modified on the electrode surface. Compared with the glassy carbon electrode, the modified electrode had a good performance for determination of Cd(II), for example, good stability, anti-interference ability, sensitivity, reusability and ion interaction. Several experimental parameters were optimized and the influence caused by different ions was investigated. The detection performance of the proposed electrode for cadmium was further verified by the detection of the actual soil samples, and the results were satisfactory. This work introduced a “green”, highly stable and sensitive cadmium ion sensor by using nanomaterials and “mercury-free” metal composite modification, which showed well detecting performance to cadmium recognition in soil.

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