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A Bismuth Modified Hybrid Binder Carbon Paste Electrode for Electrochemical Stripping Detection of Trace Heavy Metals in Soil

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A novel carbon paste electrode for simultaneous determination of lead and cadmium was fabricated by using the mixture of ionic liquid, 1-butyl-3-methylimidazolium hexafluorophosphate, and paraffin oil as binder. This electrode overcame the huge background current of the carbon paste electrode which completely used ionic liquid as binder, and presented a better signal-to-noise ratio and electrochemical activities compared with the traditional carbon paste electrode which employed the paraffin oil as binder. With the electrochemically deposited bismuth film, the developed electrode exhibited well-defined and separate stripping peaks for cadmium and lead. Several parameters, such as the most suitable paste composition, concentration of bismuth, deposition time, deposition potential and pH value were investigated in detail. Under the optimal conditions, the linear range for both metal ions was from 1 to 90 μgL^{-1}, and the detection limit was 0.12 μgL^{-1} for cadmium and 0.25 μgL^{-1} for lead, respectively. The electrode was further applied to determine lead and cadmium in soil extracts, and the obtained results were compared with the standard atomic absorption spectroscopy method.

Keywords: ionic liquid; carbon paste electrode; bismuth; soil; heavy metals

1. INTRODUCTION

Heavy metals are considered to be one of the main sources of pollution in the environment, since they have a significantly negative effect on ecological quality. The heavy metals in soil can be absorbed by the crops and entered the human bodies through food chain that caused immediately poisoning or long-term health problems to the organisms [1,2]. Therefore, the development of a sensitive and simple method for the rapid evaluation of heavy metals contamination in soil is highly desirable for agriculture and food safe applications.

Electrochemical stripping analysis (ESA) has been widely recognized as a powerful technique for simultaneous measurement of multiple trace metals in various samples. It possess some intrinsic advantageous features such as quick analysis speed, high precision and accuracy, relatively portable and inexpensive instrumentations, and thus can be used for "on-site" measurements for biomedical, environmental and industrial applications [3,4].

In the stripping analysis, the proper choice of the working electrode is crucial for the success of measurement. Traditionally, mercury-based electrodes such as hanging drop mercury electrodes (HDMEs) and mercury film electrodes (MFEs) are preferred for ESA due to their high reproducibility and sensitivity [5]. However, the health considerations and safety regulations severely restrict its application due to the toxicity of mercury. The bismuth electrode was introduced by Wang as an attractive alternative to common mercury electrodes [6]. Such electrodes display many excellent properties such as low toxicity, ability to form alloys with many metals, wide cathodic potential window as well as its insensitivity to dissolved oxygen, etc [7,8].To date, many bismuth electrodes have been reported for environmental, clinical and food analysis as "environmentally friendly" sensors to replace mercury-based electrodes[9-11].

Carbon paste electrode (CPE) is made from a mixture of carbon powder and a suitable binder. These electrodes are simple to make and offer easily renewable surface for electron exchange [12]. Bismuth film, metallic bismuth powder or bismuth precursors (Bi_2O_3) have been successfully employed to modify CPE for stripping analysis [13–15]. However, CPE also suffer several disadvantages such as low reproducibility and mechanical stability, compared with the bare solid electrodes [16,17]. Moreover, the use of nonconductive binders such as paraffin or silicone oils may weaken the electrochemical performance of the CPE [18].

Recently, room temperature ionic liquid (RTIL) has received much attention due its unique advantages such as good chemical and thermal stability, excellent ionic conductivity, non-volatility and wide electrochemical windows [19]. Preparation of carbon paste electrodes in which the non-conductive binder was replaced with IL has been reported in several studies for detection of myoglobin, nitrite, dopamine, ascorbic acid and metal ions, etc [20-23]. However, those IL-based paste electrodes are found to suffer from very large background current caused by capacitive charging. This high background charging current would obscure the analytical faradaic current of interest, especially at low analyte concentration. One approach to overcome this problem was as proposed by Maleki which used a solid IL (n-octylpyridinum hexafluoro-phosphate, OPFP) as binder [24]. After being heated to the melting point of the IL (65 °C), the electrodes provided very low background current and high electrochemical response. However, the heating process of the electrode preparation is very complex, and can not be applied to the other liquid IL. Another way to overcome the large capacitive currents was demonstrated by the use of linear sweep voltammetry at rotating disk IL-based paste electrode [25].Under hydrodynamic condition, the charging current was reduced by the enhanced mass transport, and the measurement sensitivity was improved. But this strategy to process electrode is far more intricate and time-consuming.

In this paper, we apply a simple way to prepare a high performance carbon paste electrode by using the mixture of liquid IL and paraffin oil as binder (rather than using IL as the sole binder), and expand the range of applications of IL in carbon paste electrode. We find that the electrode possesses very low charging current and favourable signal-to-background ratio under the presence of small amount of IL in conventional carbon pastes. After in situ deposition bismuth film, the electrode was successfully used to simultaneously determine Cd(II) and Pb(II) in soil samples by using square-wave anodic stripping voltammetry (SWASV). According to our knowledge, it was the first time to use this composite electrode to determine heavy metal ions in soil samples.

2. EXPERIMENTAL

2.1 Reagents

All chemicals were of analytical grade and used without any further purification. Ionic liquid 1-Butyl-3-methylimidazolium hexafluorophosphate ([BMIM]PF_6) was obtained from Shanghai Chengjie Co., Ltd. (Shanghai, China). Graphite power (spectrum grade, size<20μm) and paraffin oil were obtained from Sinopham Chemical Reagent Co., Ltd. (Shanghai, China). Stock solution of Bi(III), Cd(II) and Pb(II) (1000 mgL^{-1}) were obtained from national standard reference materials center of China and diluted as required. An acetate buffer solution (0.11 $molL^{-1}$, pH 4.5) was served as the supporting electrolyte. Millipore-Q (18.2 MΩ) water was used for all experiments.

2.2 Apparatus

Voltammetric measurements were carried out using a CHI660D electrochemical workstation (Chenhua Instrumental Corporation, Shanghai, China). Electrochemical impedance spectroscopy (EIS) was performed on a PARSTAT 2273 electrochemical workstation (AMETEK, USA).The electrochemical cell was assembled with a conventional three-electrode system: an Ag/AgCl (saturated KCl) reference electrode, a platinum wire counter electrode and the prepared carbon paste working electrodes. A PC controlled magnetic stirrer was used to stir the solution during the deposition and cleaning step. All electrochemical experiments were carried out at room temperature.

2.3 Soil sample preparation

Soil samples were collected form an agriculture department in china, which is near a chemical industrial area. The treatment of soil samples was performed according to the published literature [26,27]. In brief, soil sample was dried in an oven at 60°C for two hour. Then, the sample was grinded in a pestle and mortar, and further sieved by a 200 μm sieve. A portion (1 g) of soil sample was placed in an extraction tube with 40 mL of 0.11M acetic acid (pH 2.8) added and shaked for 16 h at room temperature. Then the mixture was centrifuged for phase separation, and the aqueous phase was filtered with a membrane (0.2 μm pore size). After these processes, the heavy metal ions of the water and acid soluble fraction in soil are extracted. Before the measurement, the pH of the extract solutions was adjusted to 4.5 by 0.11M NaOH solution.

2.4 Preparation of electrodes

The hybrid binder carbon paste electrode (HCPE) was prepared by hand-mixing 0.7 g graphite powder with 0.3 g an appropriate ratio of [BMIM]PF_6 and paraffin oil. Mixing proceeded for about 30 min to produce a homogeneous paste. Then a portion of the resulting paste was packed firmly into one end of a glass tube (inner diameter: 1.8 mm) and a bare copper wire was inserted through the opposite end to produce electrical contact. For comparison, an traditional carbon paste electrode (CPE) consisting of graphite powder and paraffin oil (70/30, w/w) and an ionic liquid binder carbon paste electrode (CILE) consisting of graphite powder and [BMIM]PF_6 (70/30, w/w) were prepared in a similar way. A new surface on these working electrodes was obtained by polishing the electrodes with weighing paper.

2.5 Measurement Procedures

The square wave anodic stripping voltammetry (SWASV) measurements were performed in 0.11 M acetate buffer solutions in the presence of 300 μgL^{-1} Bi(III) and appropriate target metals. The deposition potential of –1.2V was first applied to the working electrode for 120s under stirring conditions. Then the stirring was stopped, and after a 10s equilibration period, the SWASV potential scan was carried out from -1.2V to +0.3V (square wave amplitude, 25 mV; potential step, 5 mV; frequency, 25 Hz). Prior to the next measurement, a clean step at potential of +0.3V was applied for 30s. All experiments procedures were carried out in the presence of dissolved oxygen in the test solutions.

3. RESULT AND DISCUSSION

3.1 Optimized the composition of HCPE

In order to choose the most suitable composite for HCPE, electrodes of different mass ratio of graphite/[BMIM]PF_6/paraffin oil with 70:20:10, 70:15:15, 70:10:20 were prepared, respectively. All of prepared electrodes yielded a uniform surface and consistent composites which shows the good adherence of ionic liquid with graphite and paraffin oil. Figure 1 compared the cyclic voltammetric responses of the $[Fe(CN)_6]^{3-/4-}$ solution (Fig. 1A) and acetate buffer solution (Fig. 1B) at HCPE, CILE and CPE, respectively. It is clear that the CILE exhibited a very large background current as can be seen in Figure1 A(a) and B(a), which has been suggested by Li [28]. This phenomenon can be explained by the reactant was transferred to the internal of electrode across IL, and caused a very large electrochemical reaction areas that increased the double-layer capacitance [29]. The high charging current reduced the signal to background ratio and limited the monitoring of analytical faradaic current toward $[Fe(CN)_6]^{3-/4-}$. By gradually doping paraffin oil into the paste, the background current of electrodes was significantly reduced (Fig.1B a→d). The best well-defined redox peaks for $[Fe(CN)_6]^{3-/4-}$ and the smaller background current was observed at the graphite/[BMIM]PF_6/paraffin oil ratio was 70:10:20, with the peak-to-peak separation was 93 mV. On the contrary, a very weak redox peaks for $[Fe(CN)_6]^{3-/4-}$ were observed at CPE with the peak-to-peak separation was 205 mV (Fig. 1Ae), suggesting paraffin oil acted as the blocking material for the diffusion of $[Fe(CN)_6]^{3-/4-}$ toward the electrode surface. On the basis of this study, the HCPE prepared with a graphite/[BMIM]PF_6/paraffin oil mass ratio of 70:10:20 was selected for subsequent work.

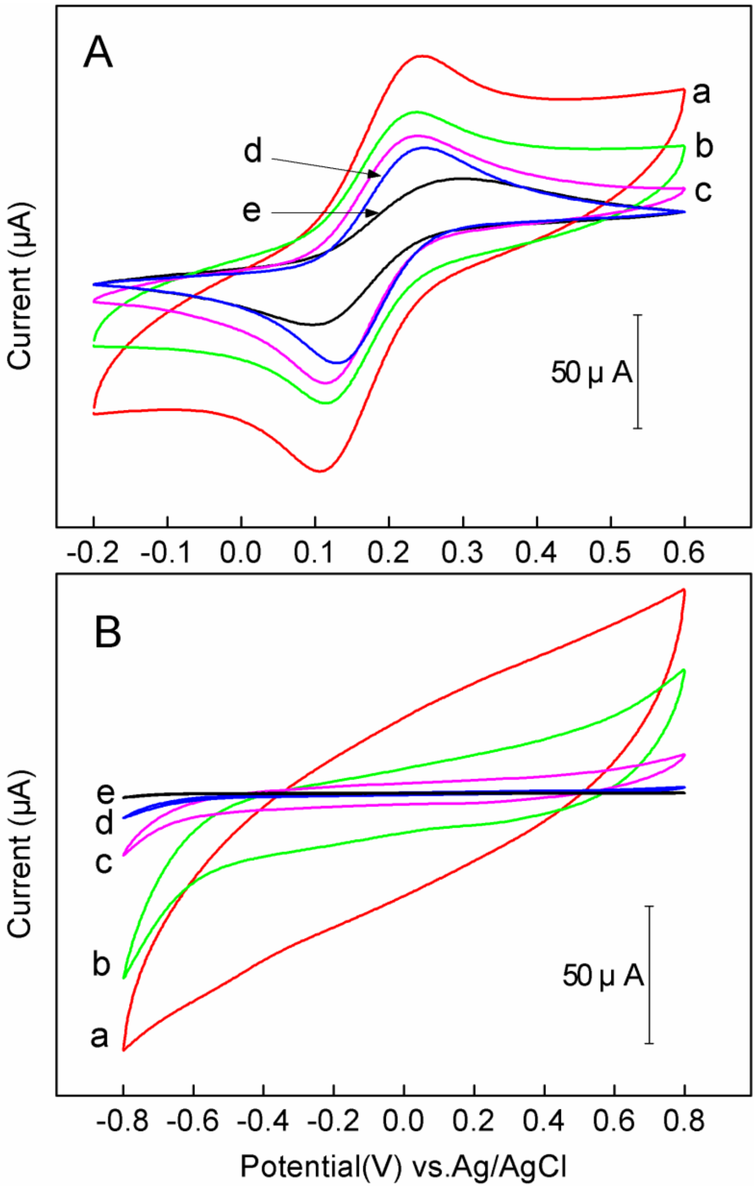

Figure 1. Cyclic voltammograms for (A) 10mM $[Fe(CN)_6]^{3-/4-}$ in 0.1 M KCl and (B) 0.11M acetate buffer solution using graphite powder/[BMIM]PF_6/paraffin oil composite with different mass ratios: (a)70:30:0(CILE), (b) 70:20:10, (c)70:15:15, (d)70:10:20 and (e) 70:0:30 (CPE). Scan rate: 100 mV/s.

3.2 Electrochemical impedance spectroscopy

The interfacial properties of prepared electrodes were explored by electrochemical impedance spectroscopy (EIS). Figure 2 showed the Nyquist plots of the fabricated CPE and HCPE in the solution of 10 mM $[Fe(CN)_6]^{3-/4-}$ in 0.1 M KCl, respectively. In measured plot, the semi-circle part at higher frequency range was related to the electron transfer limit process, while the straight line section at lower frequency range was related to the diffusion limit process. The diameter of the semi-circle in the Nyquist plots equals to the charge transfer resistance (R_{ct}), which represents the difficulty of electron transfer of the redox probe between the solution and the electrode surface. It was clear that the R_{ct} of the HCPE (about 600Ω) was much smaller than those of the CPE (about 12KΩ), indicating that the presence of the $[BMIM]PF_6$ in the carbon paste can obviously reduce the impedance and accelerate the electron transfer rate of the electroactive species.

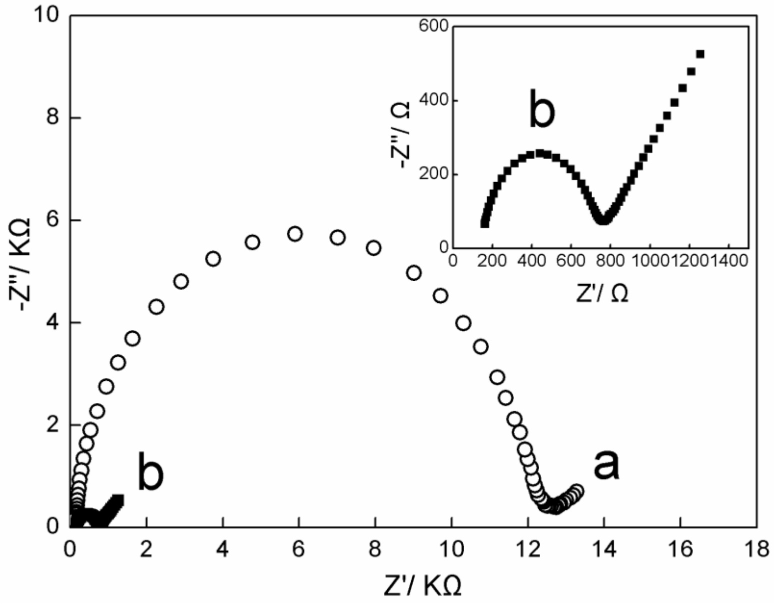

Figure 2. Electrochemical impedance spectroscopy for (a) CPE and (b) HCPE, in the presence of 10mM $[Fe(CN)_6]^{3-/4-}$ and 0.1M KCl solution. The applied perturbation amplitude was 10mV and the frequencies swept from 10^6 to 1Hz.

3.3 Stripping response of HCPE

Figure 3 showed the square wave anodic stripping voltammograms of 50 μgL^{-1} Pb(II) and Cd(II) at the bare HCPE, the bismuth film modified HCPE (BiF/HCPE), bismuth film modified CPE (BiF/CPE) and the bismuth film modified CILE (BiF/CILE) in acetate buffer solution. As can be seen, the response at the bare HCPE was very weak with two small peaks (Fig. 3b). After adding 300 μgL^{-1} Bi(III) into the deposition solution, the signal at the BiF/HCPE was remarkably enhanced and showed two sharp and separate stripping peaks toward Pb(II) and Cd(II) (Fig. 3c). The signal enhancement could be ascribed to the bismuth can form “fusible” alloys with target metal ions which facilitates the heavy metals to reduce more easily [30]. In comparison, the stripping response at the BiF/CPE (Fig.

3a) was lower than that of BiF/HCPE due to the poor conductivity of paraffin oil. Figure 3d showed the response of BiF/CILE under the same conditions. However, the voltammetric response of Pb(II) and Cd(II) was very weak and the signal accompanied with a great background noise. We deduced that the electrode prepared in this method showed a remarkably charging current that interfered with the analytical faraday current, and hence reduced the detection sensitivity toward Pb(II) and Cd(II). So in this experiment, completely using ionic liquid as binder to prepare the electrode is not recommended.

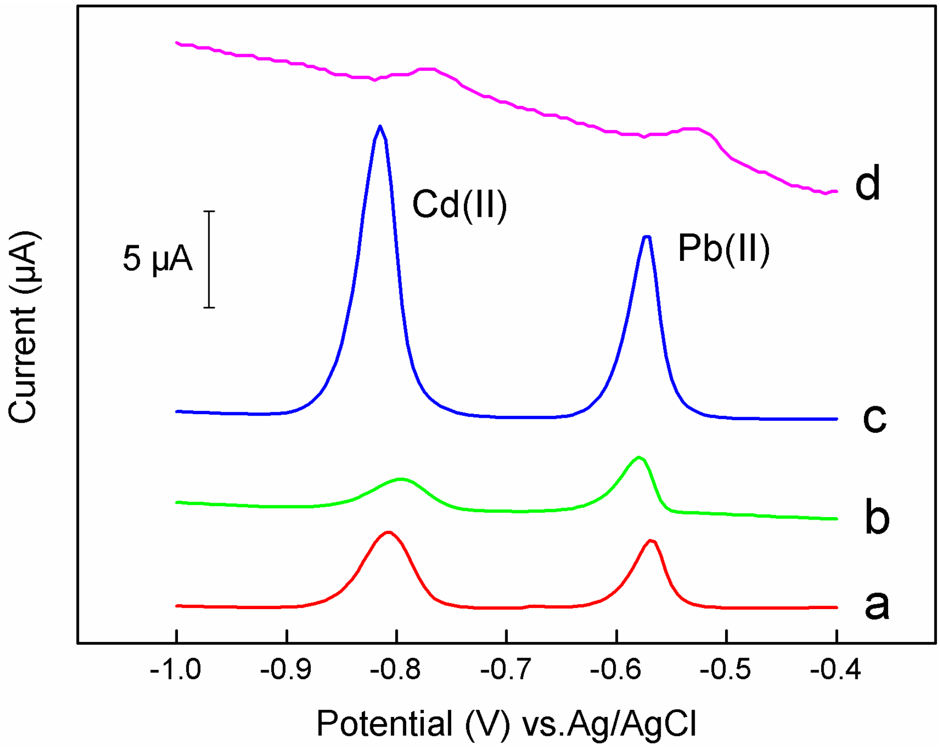

Figure 3. Square wave anodic stripping voltammograms of 50 μgL^{-1} Pb(II) and Cd(II) in 0.11 M acetate buffer solution (pH4.5) at the (a) BiF/CPE, (b) bare HCPE, (c) BiF/HCPE and (d) BiF/CILE. Deposition time: 120 s. Deposition potential: -1.2 V. Concentration of Bi(III): 300 μgL^{-1}.

3.4 Effect of experimental parameters

To optimize the performance of the BiF/HCPE for the determination of Pb(II) and Cd(II) in aqueous solution, the parameters influencing the response of the target metals ions including the concentration of Bi(III), pH of supporting electrolyte, deposition potential and deposition time were investigated.

3.4.1 Concentration of Bi(III)

The concentration of Bi(III) controlled the thickness of the bismuth film which had a profound effect on the electrochemical performance of modified electrode. Figure 4(a) showed the influence of

Bi(III) concentrations varied in the range of 0 to 600 μgL^{-1} on the stripping responses of 50 μgL^{-1} Cd(II) and Pb(II). As shown, the peak currents of both metals increased rapidly upon the raising of Bi(III) concentration from 0 to 300 μgL^{-1}. However, with subsequent additions of bismuth ions into the solution, the stripping signals were decreased gradually. This phenomenon could be explained by the formation of thick bismuth layer on the electrode surface which hampered the target metal ions diffusing out of the bismuth film during the stripping step [31]. Similar results for Hg electrodes were also reported [32]. Hence, a Bi(III) concentration of 300 μgL^{-1} was used for the subsequent measurements.

3.4.2 pH of supporting electrolyte

Figure 4(b) displayed the influence of pH of the acetate buffer solution on the stripping responses. As shown, the peak currents increased along with the increase of pH from 3.0 to 4.5. The reason of lower responses at a relative acid electrolyte was probably due to the excessive hydrogen evolution that could interfere with the deposition process [33]. On the other hand, when the pH of solution was higher than 4.5, a sharp decrease of striping signals for both metals was observed. This results might be attributed to the Bi(III) ions were very susceptible to hydrolysis in neutral and alkaline media according to the reaction[7]:

$$\mathrm{Bi^{3+} + 3H_2O \rightarrow Bi(OH)_3 + 3H^+}$$

Therefore, all further experiments were carried out at the acetate buffer with a pH value of 4.5.

3.4.3 Deposition potential

Figure 4(c) demonstrated the effect of deposition potential upon the stripping responses. When the deposition potentials shifted from −0.8V to −1.0V, the signals for both metal ions were increased remarkably. With the deposition potential shift toward more negative, the stripping signal for Cd(II) kept increasing and reached the maximum value at -1.2V, and then started to decrease. Whereas the signal for Pb(II) did not change obviously in the range of -1.0V to -1.4V, but appeared significant decline at -1.5V.The decrease of stripping signals at a more negative potentials was probably due to the hydrogen evolution was occurred at such potentials and the hydrogen bubbles might damage the bismuth film on the surface of electrodes. Consequently, -1.2V was used as optimal deposition potential to obtain the good sensitivity and better responses in the measurement.

3.4.4 Deposition time

Deposition time is another crucial parameter for stripping analysis that influences the sensitivity of the determination. As depicted in Figure 4(d), with the prolong of deposition time from 60 to 360 s, the stripping signals for Pb(II) and Cd(II) increased almost linearly with the deposition time. While, when the deposition time exceeded 360s, the curves of peak current versus time began to leave off, which due to the saturation effect of the bismuth film on the carbon paste surface [34]. On the basis of this study, a time of 120s was selected for deposition based on the compromise between sensitivity and length of analysis.

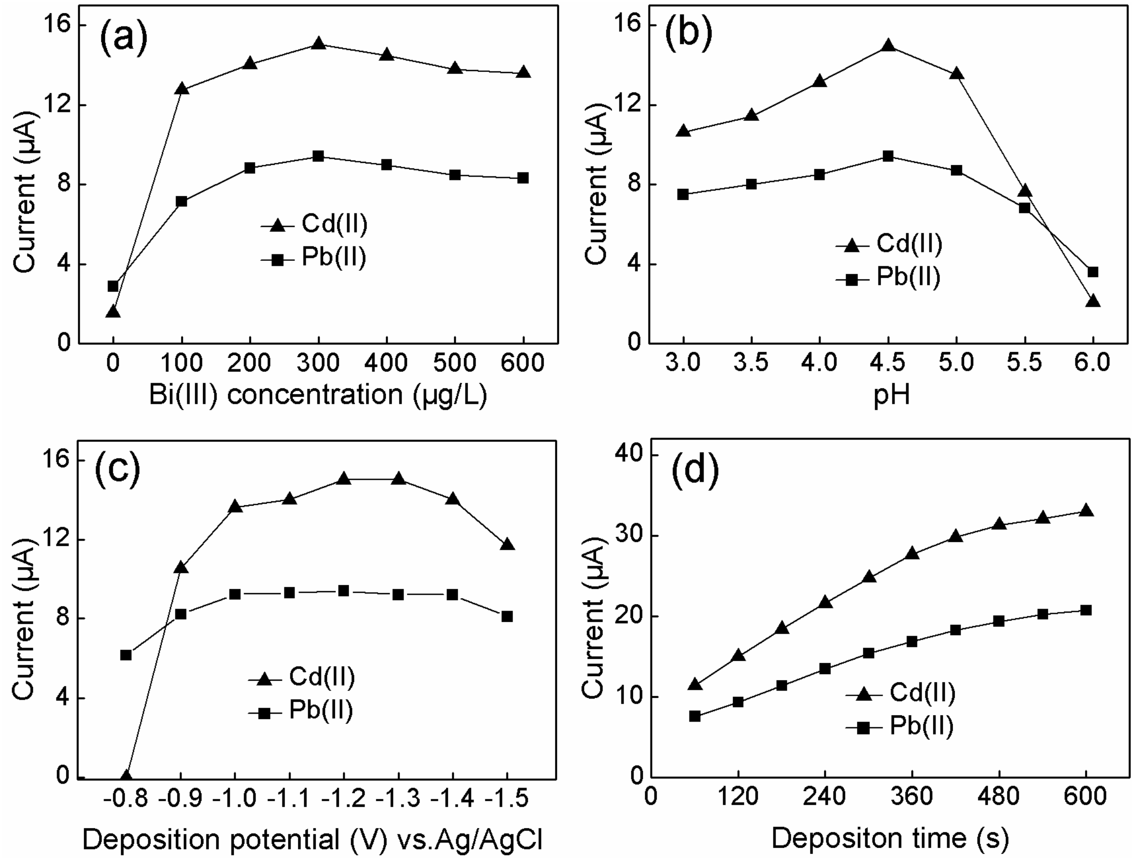

Figure 4. Effects of (a) Bi(III) concentration, (b) pH of supporting electrolyte, (c) deposition potential and (d) deposition time on the SWASV peak currents for 50μgL^{-1} Cd(II) and Pb(II) in 0.11molL^{-1} acetate buffer solution at the BiF/HCPE. Other conditions were as in Figure 3.

3.5 Analytical performance

Figure 5 illustrated a series of stripping voltammetric responses with simultaneously increasing the concentrations of Pb(II) and Cd(II). It can be seen that the peak currents have a good linear relationship with the concentration of Cd(II) and Pb(II) in the range from 1.0 to 90.0 μgL^{-1}, with the linear correlation coefficients of 0.9971 and 0.9963 for Cd(II) and Pb(II), respectively. Based on three times the standard deviation of the baseline (S/N = 3), the limits of detection were estimated to be 0.12 μgL^{-1} for Cd(II) and 0.25 μgL^{-1} for Pb(II) using 120 s deposition time. Lower detection limits for both metal ions can be expected by prolonging the deposition time. The reproducibility and stability of the developed electrode was evaluated using a buffer solution containing 20 μgL^{-1} each of Pb(II) and Cd(II). For a single electrode, the relative standard deviations (RSD) were 2.2 % for Pb(II) and 2.6 % for Cd(II) in five times repetitive measurements. The RSD of six different electrodes prepared by the same way were 3.6 % for Pb(II) and 4.5 % for Cd(II), respectively. The long-term stability of the same electrode was investigated for a period of three weeks, during which the electrode was used daily. The experimental results show that the currents response only deviates about 5.3%.

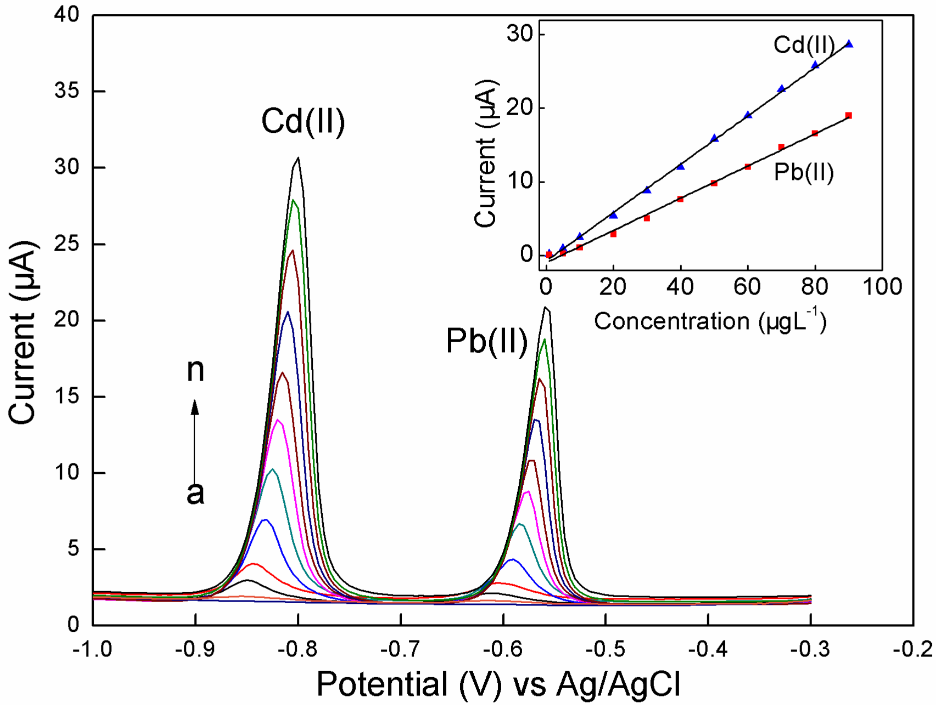

Figure 5. Voltammograms for additions of 0, 1, 5, 10, 20, 30, 40, 50, 60, 70, 80 and 90 μgL^{-1} Cd(II) and Pb(II) from a to n. Inset: the calibration curves of Cd (II) and Pb (II). Other conditions were as in Figure 3.

3.6 Interference study

It is reported that the surfaces of solid electrodes, such as glass carbon electrode and carbon paste electrode, are prone to being fouled by the surface active compounds and cause the decrease of response in the analysis of natural media [11, 35]. In this work, three types of surfactants, including cetyltrimethylammonium bromide (CTAB), Triton X-100 and sodium dodecyl sulfate (SDS), were added to investigate the possible effects on the measurements of Cd(II) and Pb(II) at the BiF/HCPE and BiF/CPE. The peak currents of target metal ions before (I_{pmax}) and after (I_p) adding surfactants were recorded. Table 1 summarized the data on the normalized current I_p/ I_{pmax} for the measurement of 50 μgL^{-1} Cd(II) and Pb(II). As shown, three types of surfactants cause different level of interference on stripping signals for target metals. However, compare with the BiF/CPE, the BiF/HCPE exhibited more tolerance to the presence of surfactants. This resistance to surfactants was attributed to the ionic liquid can form an ionic conductivity layer on the outside of carbon particles that prevent the transport of macromolecules to the electrode surface [36].

The interferences from other metal ions were also investigated. Under the ±5.0% tolerated ratios, it was found that 1000-fold K^+, Na^+, Ag^+ and Mg^{2+}; 500-fold Fe^{3+} and Al^{3+}; 200-fold Ca^{2+}; 20-fold Zn^{2+} and Cr^{3+} have no evident influences on the signal of 20 μgL^{-1} of Pb(II) and Cd(II). Hg^{2+} was found to increase the stripping signals of Pb(II) and Cd(II), which was due to that Hg^{2+} can form amalgam with Pb and Cd that cause Pb(II) and Cd(II) to be reduced more easily. In contrast, Cu^{2+} was found to have an obvious suppressing effect even in low mass ratio. This influence is related to the formation of inter-metallic compounds which the Pb(II) and Cd(II) were co-deposited with Cu^{2+} instead of Bi^{3+} [33]. The interference caused by Cu^{2+} could be released by the addition of ferricyanide as suggested by previously paper [37].

Table 1. Normalized current, I_p/ I_{pmax}, expressed as a percentage, for 50 μgL^{-1} Cd(II) and Pb(II) at 10 mgL^{-1} of surfactants for the BiF/HCPE and BiF/CPE.

Metal ion	Electrode	I_p/I_{pmax} (%)		
		CTAB	Triton X-100	SDS
Pb(II)	BiF/HCPE	62	68	88
	BiF/CPE	55	62	80
Cd(II)	BiF/HCPE	58	65	83
	BiF/CPE	51	56	74

3.7 Soil Sample Analysis

The feasibility of the BiF/HCPE for the determination of lead and cadmium in real samples was verified by the analysis of soil sample extracts. Concentrations of target metal ions were determined by standard addition method.

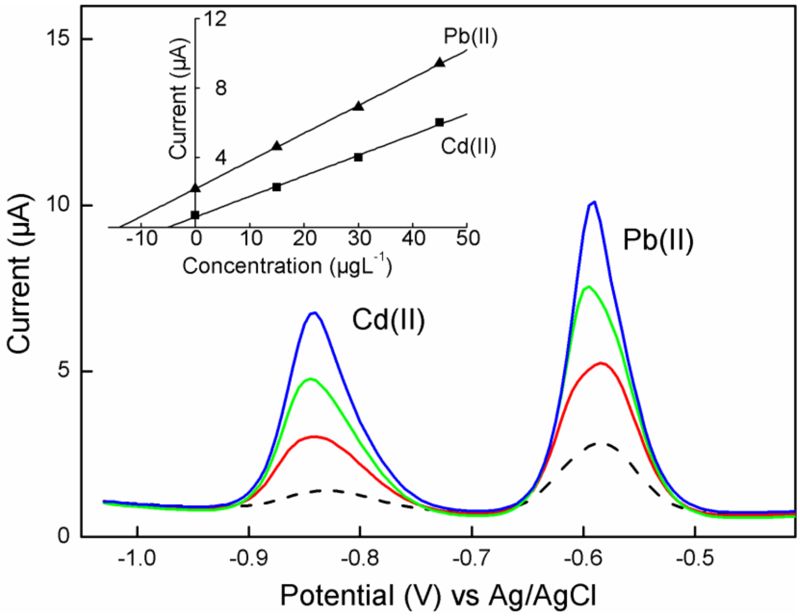

Figure 6. Voltammograms for the determination of Cd(II) and Pb(II) in a soil sample extracts (dashed line) together with three consecutive standard additions of 15.0 μgL^{-1} Cd(II) and Pb(II) (full lines). Inset: the corresponding standard addition plot. Other conditions are as in Figure 3.

Table 2. Recovery for the determination of Cd(II) and Pb(II) in soil sample extracts.

Metal ion	Added (μgL^{-1})	Found (μgL^{-1})[a]	RSD (%)	Recovery (%)
Cd(II)	-	4.72	1.9	-
	5.0	9.57	2.6	98.42
	10.0	15.29	3.7	103.86
	20.0	23.55	4.8	95.27
Pb(II)	-	13.65	2.2	-
	5.0	18.17	3.7	97.45
	10.0	22.89	4.2	96.78
	20.0	24.20	4.7	102.34

[a] Mean of five repetitive measurements

A typical analysis from these tests is shown in Figure 6, The SWASV responses of the prepared sample and three consecutive standard additions of 15 μgL^{-1} Cd(II) and Pb(II). As shown, the lead and cadmium content were clearly found in the sample by the presence of stripping peaks at potentials of approximately -0.58V and -0.84V in the voltammograms (dash line), which confirmed the suspicion of heavy metals pollution in this areas.The determined concentration of Cd(II) and Pb(II) was 4.72±0.05 μgL^{-1} and 13.65±0.13 μgL^{-1} (n=5), respectively. The obtained results were validated with the independent analysis of atomic absorption spectroscopy (AAS), with the values of 4.85±0.04 μgL^{-1} for Cd(II) and 13.37±0.09 μgL^{-1} (n=5) for Pb(II), respectively. The difference of the measured data of Cd(II) and Pb(II) concentrations obtained by the BiF/HCPE and AAS was less than 5%. To better validate the feasibility of the BiF/HCPE, further recovery tests were carried out. The results (summarized in table 2) showed that the stripping method using the BiF/HCPE produced satisfactory recovery results, with an average recovery of 99.18% for Cd(II) and 98.85% for Pb(II). All of these results demonstrate that the as-prepared electrode can be successfully applied to the determination of Cd(II) and Pb(II) in complex sample matrices even in the presence of dissolved organic material.

4. CONCLUSIONS

In this work, a novel carbon paste electrode based on the mixture of IL and paraffin oil as binder was fabricated for the determination of lead and cadmium. Comparing with completely using ionic liquid as binder, the hybrid binder decreases the background current and improves the signal-to-noise ratio of electrode. Combining the high conductivity and good antifouling capacity of ionic liquid and high sensitivity of the bismuth film, the developed electrode exhibited very good analytical performance. The detection limits for Cd(II) and Pb(II) were 0.12 μgL^{-1} and 0.25 μgL^{-1}, respectively. Several experimental parameters were optimized and the influence caused by surfactants and other metal ions were investigated. In addition, the electrode was applied to detect trace metal ions in soil samples with satisfactory results. This work proposed a low cost, high sensitive, reproducible and stable sensor, which holds great promise for its wide applications in trace metal ions monitoring for environmental and food analysis.

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