

Carbon Paste Electrode Modified with Bismuth Oxychloride as a Sensor for the Determination of Pb²⁺ and Cd²⁺

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Received: 21 December 2018 / Accepted: 13 February 2019 / Published: 10 April 2019

Herein, porous BiOCl microspheres were successfully fabricated by using a hydrothermal method. The as-obtained porous BiOCl microspheres were used as a bulk modifier to decorate a carbon paste electrode (CPE) for the simultaneous determination of Cd²⁺ and Pb²⁺ by square-wave anodic stripping voltammetry (SWASV). The BiOCl-modified CPE showed better detection sensitivity for Pb²⁺ and Cd²⁺ ions than that of a bare CPE. Furthermore, the effect of the preparation conditions (hydrothermal temperature and time) of BiOCl, mass ratio of BiOCl in the carbon paste, pH of the electrolyte solution and preconcentration conditions (deposition potential and time) on the detection sensitivity of target ions was investigated. Under optimized conditions, stripping voltammetric measurements demonstrated that the modified electrode has a wide linear working range (from 10.0 to 400.0 µg L⁻¹ for Pb²⁺ and from 10.0 to 450.0 µg L⁻¹ for Cd²⁺), a favorable detection limit (0.42 µg L⁻¹ for Pb²⁺ and 0.76 µg L⁻¹ for Cd²⁺) and good reproducibility. The BiOCl-modified CPE is a very promising candidate for the user-friendly and convenient determination of heavy metal ions.

Keywords: bismuth oxychloride; carbon paste electrode (CPE); heavy metal ions; anodic stripping voltammetry

1. INTRODUCTION

Heavy metals are important environmental and biological contaminants due to their accumulation in food chains, highly toxic effects and nonbiodegradable characteristics. In recent years, the natural environmental pollution caused by heavy metals has attracted more attention because of industrial, agricultural and mining activities [1,2]. The detection and identification of toxic heavy metal ions in the environment is of great importance to prevent and treat heavy metal contamination. In recent decades, electrochemical stripping analysis has been recognized as one of the most desirable techniques for the determination of trace heavy metal ions owing to its low cost, high sensitivity, easy

operation and ability to analyze element speciation [3]. In electrochemical stripping analysis, the working electrode plays a key role in the electrochemical detection of trace heavy metal ions. Mercury electrodes have been widely accepted for the electrochemical stripping analysis of heavy metal ions. However, the toxicity of mercury hinders its application as an electrode material and impels us to develop a facile, low-cost and environmentally friendly electrode material [4,5]. Thus, bismuth-film electrodes (BFEs) have been considered as an alternative candidate for mercury film electrodes (MFEs) because they are environmentally friendly and have roughly comparable analytical properties to those of MFEs in voltammetric analysis [6–10].

In general, BFEs are prepared by plating a thin bismuth layer on a suitable substrate material, such as glassy carbon [11], carbon paste [12,13], carbon fibers [14], pencil lead [15,16], or gold and platinum wires [17,18]. Among these substrates, carbon paste is a convenient substrate material because it is inexpensive, is simple to make and activate, and offers an easily renewable electrode surface. The method of combining bismuth with a substrate plays a critical role in the stripping performance of the resulting BFEs. There are three methods for the modification of the substrate surface with deposited bismuth, as follows: (1) preplating or ex situ plating method: the bismuth film is electroplated onto the substrate surface before analysis [19]; (2) in situ plating method: the bismuth film is deposited on the substrate surface during analysis [20–22]; and (3) the modification of the electrode bulk with metallic bismuth powder or bismuth precursors (BiF , Bi_2O_3 and $(\text{BiO})_2\text{CO}_3$) [10,12,20,23–25]. The latter method is easy to prepare and simplifies the analysis procedure by generating a bismuth film in situ without adding Bi ions to the solution. However, to the best of our knowledge, the selection of bismuth precursors to promote the stripping performance of the resulting BFEs is still challenging.

In this work, we investigate the electrochemical detection of Pb^{2+} and Cd^{2+} ions in aqueous solution using a carbon paste electrode with BiOCl (bulk modifier) by the electrochemical stripping method. The resulting BFEs showed satisfactory stripping performance for Pb^{2+} and Cd^{2+} ions. Compared with traditional bulk modifiers, BiOCl is easy to synthesize with better stability and low cost.

2. EXPERIMENTAL

2.1 Chemicals and Reagents

Graphite power (spectrum grade, size < 20 μm), hydrochloric acid (37% w/v), nitric acid (67% w/v), hydrofluoric acid (40% w/v), and paraffin oil were obtained from Sinopham Chemical Reagent Co., Ltd. (Shanghai, China). A 0.1 $\text{mol}\cdot\text{L}^{-1}$ NaCl solution (pH value controlled by 0.5 $\text{mol}\cdot\text{L}^{-1}$ hydrochloric acid) served as the supporting electrolyte. All solutions were prepared with deionized water (18.2 $\text{M}\Omega$) obtained from a Ultra Pure Water system (Millipore-Q). A 1.0 g/L stock solution of Pb^{2+} or Cd^{2+} was prepared by dissolving $\text{Pb}(\text{NO}_3)_2$ or $\text{Cd}(\text{NO}_3)_2$ (Kemiou Chemical Reagent Co., Tianjin, China) in deionized water. All the chemicals were of analytical reagent grade.

2.2. Preparation of BiOCl modifier

BiOCl samples were prepared by a simple solvothermal route. The preparation procedure was as follows: 1.0 mmol of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was dissolved in 30 ml dilute nitric acid (1 mol/L); then, the resulting solution was added to 20 ml deionized water containing 1.0 mmol of KCl under vigorous stirring. After 30 minutes, the mixture was transferred into a 100 mL Teflon-lined stainless-steel autoclave. The autoclave was sealed and heated at the desired temperature and time, then cooled to room temperature. The resultant products were gathered and washed thoroughly by repeated alternate cleaning with deionized water and ethanol. Finally, the obtained dried products were collected for further use without additional treatment.

2.3 Real soil sample analysis

Soil samples were taken from farmlands near a cement plant (Dalian Cement Group CO., LTD.). The treatment of soil samples was as follows: first, the soil sample was dried in an oven at 80°C for 4 h. Then, the sample was ground with a mortar and pestle and further sieved by a 200 μm sieve. Approximately 1.0 g of soil sample was accurately weighed in a vessel, and then 2 ml of HNO_3 and 6 ml of HCl were added and heated under reflux at 120°C for 4 h. Then, the mixture was centrifuged and filtered with a filter (0.22 μm pore size). The resulting solutions were quantitatively transferred into a 50 ml flask and brought to volume with deionized water. The heavy metal concentration of the soluble fraction in soil was determined by atomic absorption spectrometry (AAS, Shimadzu AA-7000) or the proposed voltammetric procedure. For each set of measurements, a blank sample containing the same amount of acid was also analyzed.

2.4. Preparation of carbon paste electrode

Carbon paste was prepared by mixing 2 g of graphite powder with 0.6 ml of paraffin oil and the desired amount of modifier until a homogenous paste was obtained. The as-obtained carbon paste was packed into the hole of the electrode body. A Teflon holder (8 cm length) with a hole at one end (3.5 mm diameter) served as the electrode body. A copper rod was inserted through the center of the holder to produce electrical contact. This copper rod could be moved up and down by screwing to press the paste down, and the carbon paste electrode was smoothed with weighing paper to renew the electrode surface.

2.5 Apparatus

Electrochemical experiments were recorded using a CHI 660E potentiostat/galvanostat (ChenHua Instruments Co., Shanghai, China) with a standard three-electrode system. A platinum plate and saturated silver chloride were used as the counter electrode and reference electrode. The morphologies of the electrodes were measured using a JSM-6460 scanning electron microscope

(JEOL, Japan). The products were characterized by X-ray powder diffraction on a Shimadzu XRD-6100 X-ray diffractometer with graphite monochromatized CuK α radiation ($\lambda = 1.5418 \text{ \AA}$).

2.6. Test methods

Square-wave anodic stripping voltammetry (SWASV) measurements were performed for the detection of Pb²⁺ and Cd²⁺. A deposition potential of -1.2 V was first applied to the working electrode for the desired time under stirring conditions. Then, stirring was stopped, and after a 10 s equilibration period, a SWASV potential scan was carried out from -1.2 V to $+0.2 \text{ V}$ (square-wave amplitude, 25 mV; potential step, 5 mV; frequency, 25 Hz). Prior to the next measurement, a cleaning step at a potential of $+0.3 \text{ V}$ was applied for 30 s. All experimental procedures were carried out in the presence of dissolved oxygen at room temperature.

3. RESULTS AND DISCUSSION

3.1 SEM and XRD analysis

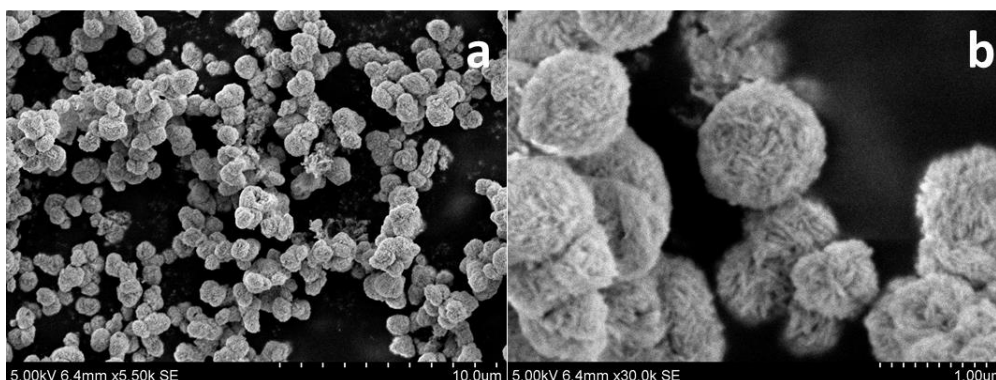
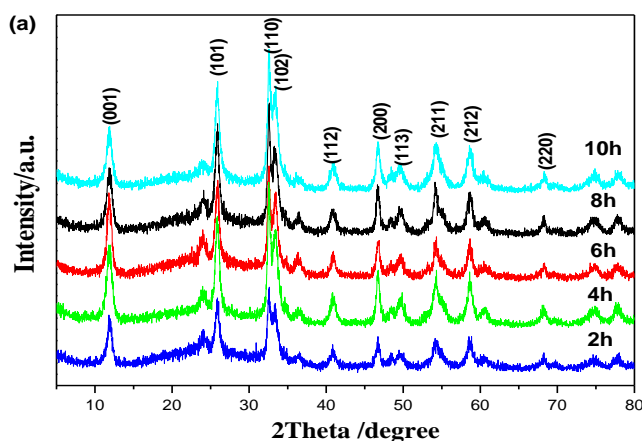


Figure 1. SEM images of a BiOCl sample under low and high magnification



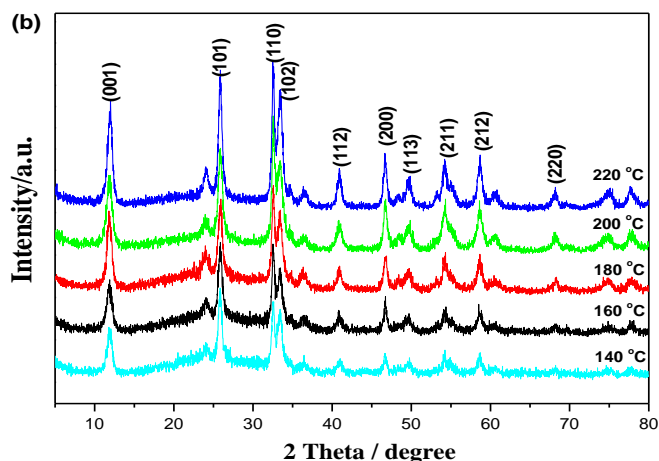


Figure 2. XRD patterns of BiOCl samples prepared under different hydrothermal conditions

The typical morphology of the as-obtained BiOCl sample was revealed by SEM and is shown in Fig. 1. Fig. 1a shows that the as-obtained BiOCl material exhibited sphere-like structures with an average diameter of 1.0 μm . The high-magnification SEM image (Fig. 1b) clearly shows that the surface of the BiOCl microspheres is loose and porous and these porous microspheres are self-assembled by numerous nanosheets. Clearly, the porous structure of BiOCl microspheres is beneficial for the transportation of ions and can improve the electroanalytical performance. The XRD patterns of BiOCl samples obtained under different hydrothermal conditions are shown in Fig. 2 (Fig. 2a for hydrothermal time and Fig. 2b for hydrothermal temperature). As shown in Fig. 2, all the diffraction peaks of the as-prepared BiOCl samples can be indexed to the tetragonal phase of BiOCl. No diffraction peaks of other impurities were detected, which implies that the as-prepared BiOCl samples have high purity. Nevertheless, the crystallographic structure of the as-prepared samples was strongly influenced by hydrothermal temperature and time. The diffraction peaks of the as-prepared samples are gradually narrowed and the intensity of the peaks becomes stronger with increasing hydrothermal temperature and time.

3.2 Comparison of the stripping response of bare CPEs and BiOCl-modified CPEs

Fig. 3 shows a comparison of the stripping voltammetric responses of Pb^{2+} and Cd^{2+} ($500 \mu\text{g L}^{-1}$) at a bare CPE and BiOCl-modified CPE. As shown in Fig. 3, the stripping voltammetric peaks of Pb^{2+} and Cd^{2+} ions at the bare CPE appeared at -0.60 and -0.87 V (vs. Ag/AgCl), respectively. For the BiOCl-modified CPE, a stronger stripping response and broader potential separation between stripping signals for Pb^{2+} and Cd^{2+} ions can be observed. Additionally, the stripping voltammograms of the BiOCl-modified CPE showed an obvious current response at more positive potentials than -0.25 V and more negative potentials than -1.0 V.

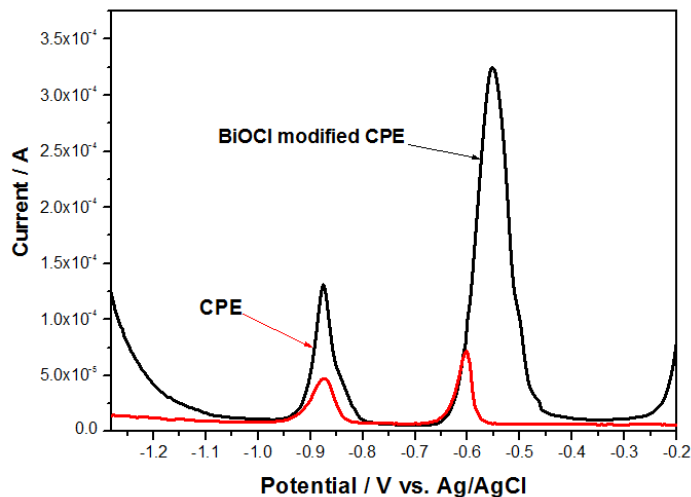
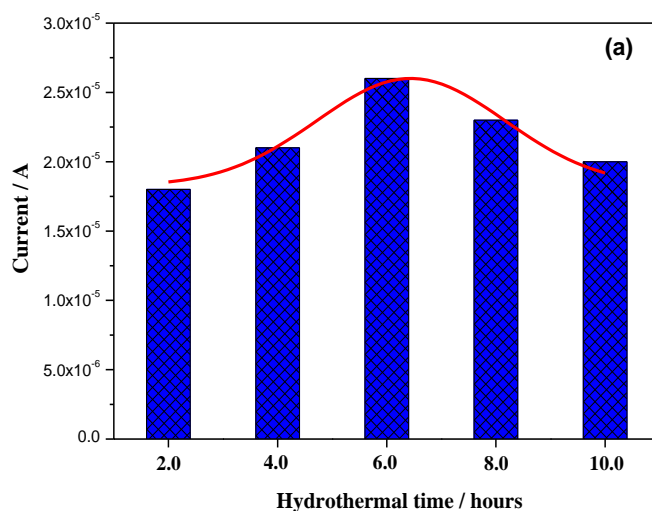


Figure 3. Comparison of the stripping voltammetric responses for Cd²⁺ and Pb²⁺ over the bare CPE and BiOCl-modified CPE.

The signal response at approximately -1.0 V can be ascribed to the electrochemical reduction of Bi compounds [12]. In contrast, the signal response at more positive potentials than -0.25 V can be attributed to the reoxidation of the deposited metallic Bi [8]. Based on the above results, we considered that the stronger stripping response could be ascribed to the bismuth (reduced from BiOCl) strongly interacting with target metal ions, which facilitated the enrichment and reduction of heavy metals [26]. Therefore, in this experiment, BiOCl was recommended as a modifier to prepare the CPE.

3.3 Effect of preparation conditions of BiOCl



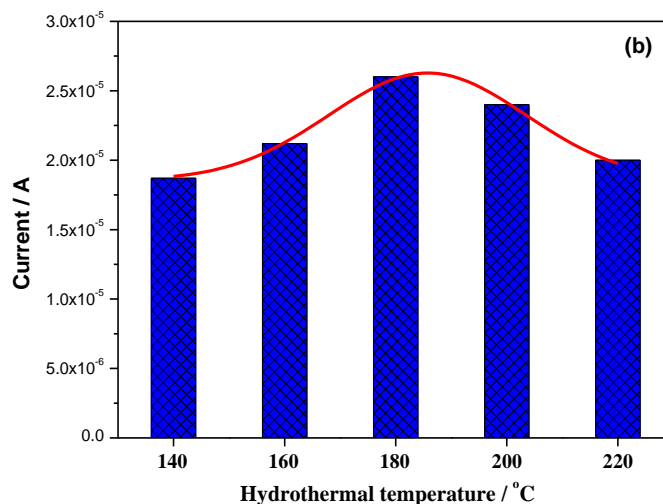


Figure 4. Effects of (a) hydrothermal temperature and (b) hydrothermal time on the stripping peak current for $400 \mu\text{g L}^{-1} \text{Pb}^{2+}$ in $0.1 \text{ mol}^{-1} \text{NaCl}$ solution ($\text{pH}=2.0$)

It is well known that the crystallographic structure of the modifier strongly influences the electroanalytical performance of CPEs [27]. Thus, the relationship between the preparation conditions of BiOCl and the sensing of heavy metal ions (Pb^{2+} is used as an example) was investigated and is shown in Fig. 4. As shown in Fig. 4a, the peak current first increased and then decreased with an increase in hydrothermal temperature during the preparation of BiOCl. The highest peak current was found when the hydrothermal temperature was 180°C . A similar trend was obtained for the effect of hydrothermal time on the peak current of CPEs. It can be seen from Fig. 4b that the BiOCl-modified CPE showed the highest peak current when using a hydrothermal time of 6.0 h. On the basis of this result, we considered the relationship between the preparation conditions of BiOCl and the sensing of heavy metal ions can be attributed to the fact that the affinity towards heavy metal ions and the conductivity of modifiers depends on their crystallographic structure [28].

3.4 Optimization of the content of modifier

The content of the modifier is one of the most important parameters in the fabrication of CPEs. **Fig. 5** indicates the effect of the amount of BiOCl on the stripping signals of heavy metal ions (Pb^{2+} is used as a model metal ion). As shown in Fig. 5, increasing the amount of BiOCl modifier can enhance the peak current response owing to “the formation of Bi films on the surface of the electrode”. However, a further increase in BiOCl caused a decrease in the peak current response because an excessive amount of BiOCl can decrease the conductivity of the CPE [13]. Thus, the optimized content of BiOCl in the CPE is approximately 10 wt% (mass ratio of BiOCl to graphite power).

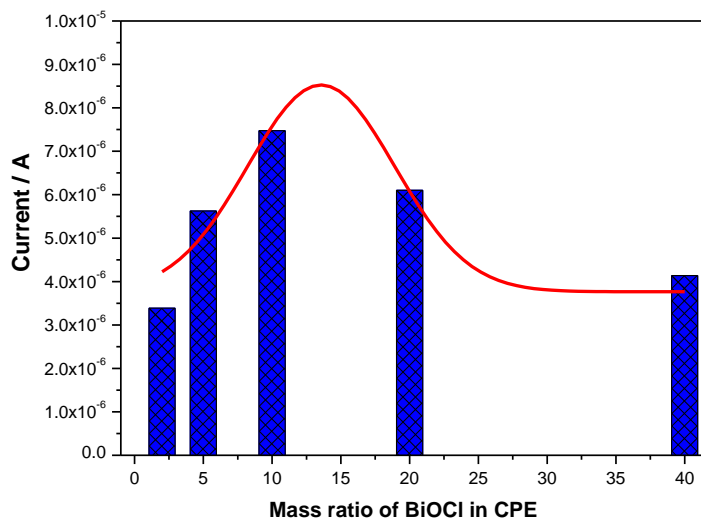


Figure 5. The effect of the content of the modifier on the stripping peak current for $400 \mu\text{g L}^{-1} \text{Pb}^{2+}$ in $0.1 \text{ mol}\cdot\text{L}^{-1} \text{NaCl}$ solution ($\text{pH}=2.0$)

3.5 Effect of experimental parameters

To further optimize the performance of the BiOCl-modified CPE, the main parameters influencing the detection sensitivity towards the target metal ions, including the content of the modifier, the pH value of the supporting electrolyte, the deposition potential and time, were diligently investigated.

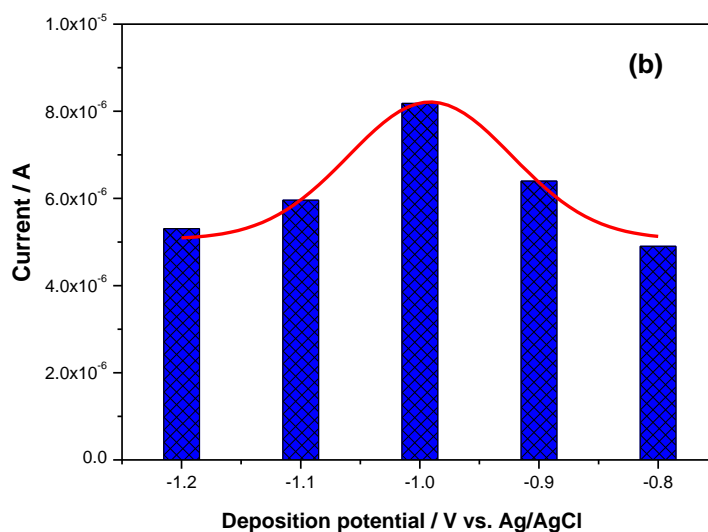
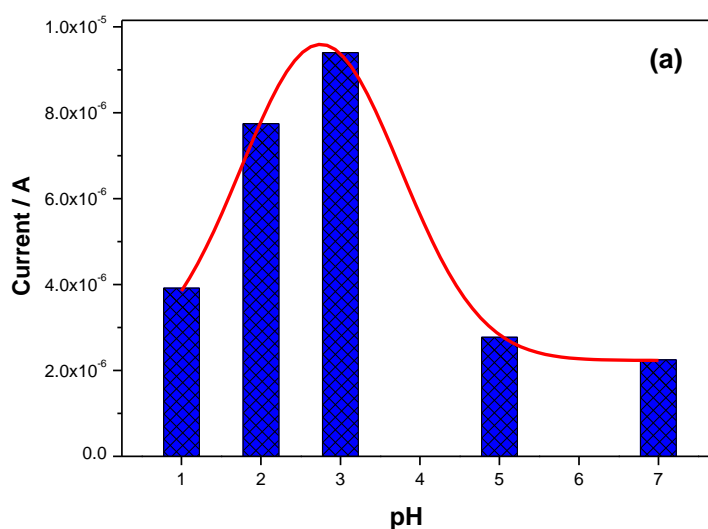
3.5.1 pH of supporting electrolyte

Fig. 6a shows the influence of the pH of the electrolyte solution on the stripping response. As shown in Fig. 6a, the stripping peak current is strongly dependent on the pH of the electrolyte solution. The optimum pH value is approximately 3.0, where a maximum peak current can be obtained. At lower pH values, the lower responses of the anodic peak current can be ascribed to competition from H^+ (i.e., hydrogen evolution can interfere with the deposition process) [29]. However, when the pH of the electrolyte solution was higher than 3.0, the sharp decrease in the stripping peak current might be ascribed to the hydrolysis of Pb^{2+} to form metal hydroxide complexes, which caused a significant decrease in the metal ion amount in the solution phase [30]. Therefore, all further experiments were carried out in electrolyte solution with a pH value of 3.0.

3.5.2 Deposition potential and time

Fig. 6b-c demonstrates the effect of deposition potential and time on the stripping response. Fig. 6b shows that the influence of deposition potential in the range of -1.2 to -0.8 V on the stripping response of $400 \mu\text{g L}^{-1} \text{Pb}^{2+}$ varied. When applying deposition potentials more positive than -0.8 V , the

stripping peak current continued to increase and reached the maximum value at -1.0 V. The increase in stripping current may be attributed to the negative potential facilitating the deposition of target ions (enrichment) and the formation of a Bi film. However, the decrease in stripping signals at more negative potentials than -1.0 V was probably attributed to hydrogen evolution and the reduction of some other chemicals, which interfered with the determination of target ions [6]. The influence of deposition time on the stripping peak current of Pb^{2+} ions is illustrated in Fig. 6c. As shown in Fig. 6c, the peak current increased almost linearly with deposition time with increasing deposition time from 15 to 300 s. When the deposition time exceeded 300 s, the stripping signal began to drop due to the saturation loading of the bismuth film on the electrode surface [31]. Therefore, a deposition potential of -1.0 V and a deposition time of 300 s were selected to achieve a high sensitivity of detection.



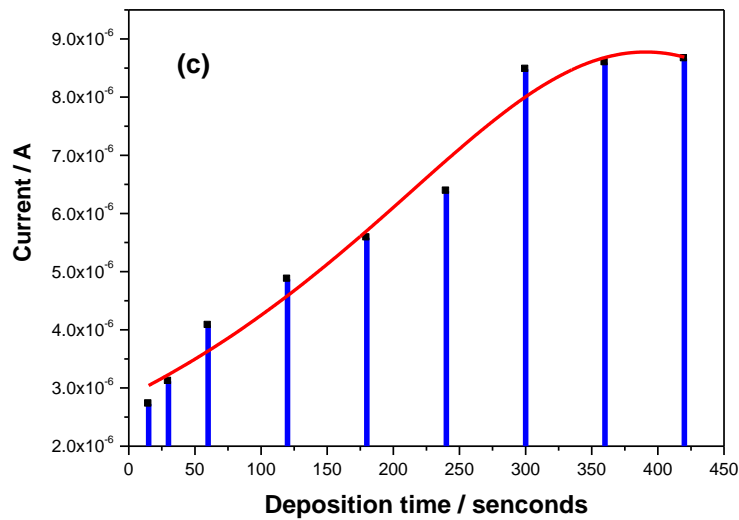
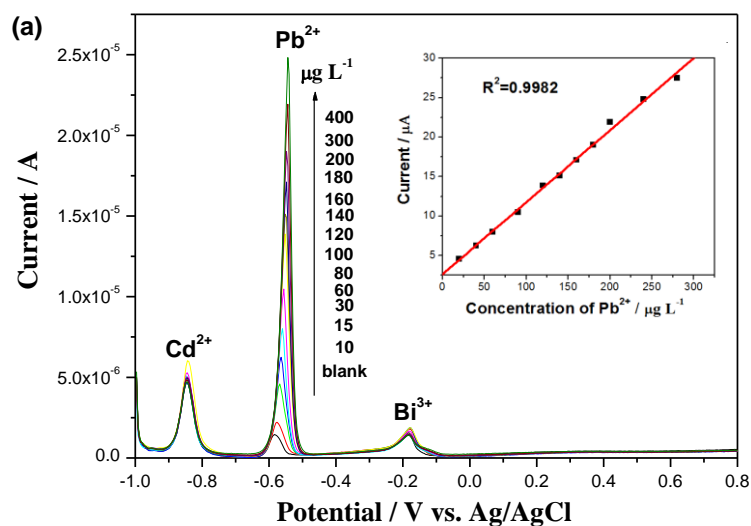


Figure 6. Effect of experimental parameters on the stripping peak current for $400 \mu\text{g L}^{-1} \text{Pb}^{2+}$ in $0.1 \text{ mol}\cdot\text{L}^{-1} \text{NaCl}$ solution

3.5 Analytical performance

Fig. 7a-b illustrates a series of stripping voltammetric responses with different concentrations of Pb^{2+} and Cd^{2+} and their corresponding calibration curves under the optimized parameters. In the measurement process, the concentration of Cd^{2+} (or Pb^{2+}) is constant when the concentration of Pb^{2+} (or Cd^{2+}) varies. There is a good linear relationship between the peak current and the concentration of target ions in the range from 10.0 to $400.0 \mu\text{g L}^{-1}$ for Pb^{2+} and from 10.0 to $450.0 \mu\text{g L}^{-1}$ for Cd^{2+} . The calibration curves for Pb^{2+} and Cd^{2+} exhibited desirable correlation coefficients (R^2) of 0.9982 and 0.9975 , respectively. According to the $3S/N$ criterion, the limits of detection for Pb^{2+} and Cd^{2+} were estimated to be $0.42 \mu\text{g L}^{-1}$ and $0.76 \mu\text{g L}^{-1}$, respectively.



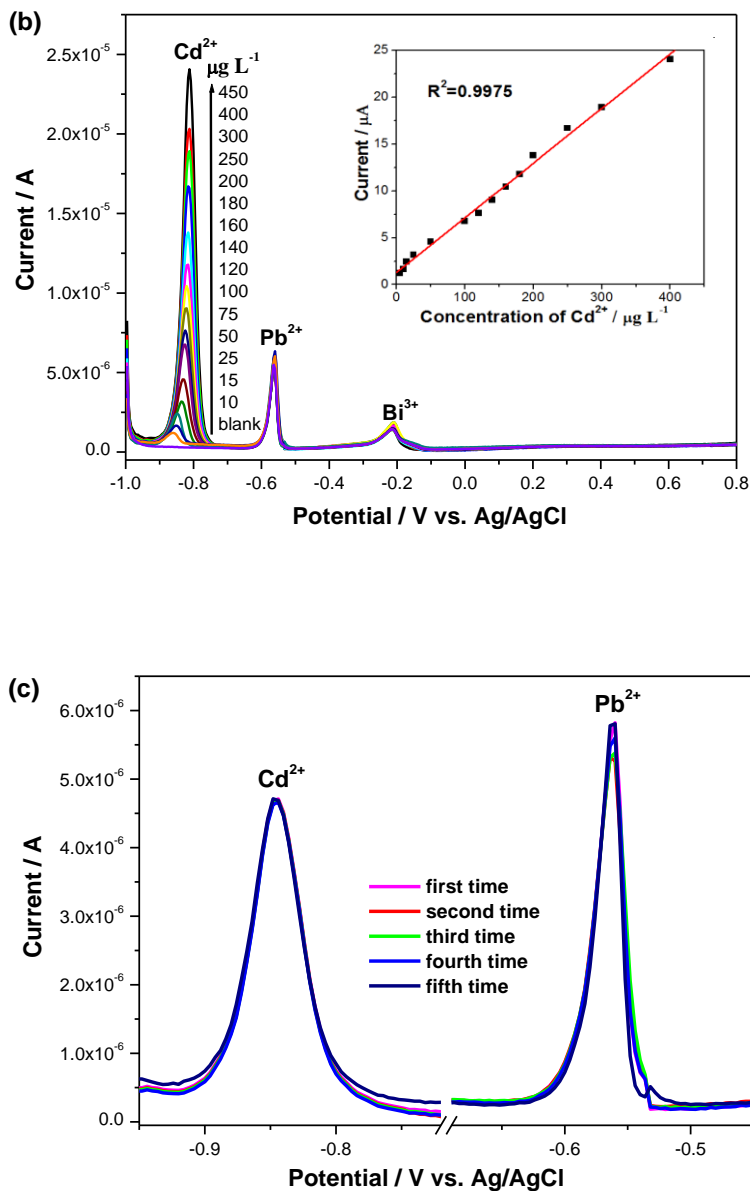


Figure 7. Stripping voltammetric responses for Pb²⁺ (a) and Cd²⁺ (b) at various concentrations over a BiOCl-modified CPE under optimized parameters (inset: the calibration curves of Cd²⁺ and Pb²⁺); (c) The evaluation of the reproducibility of the BiOCl-modified CPE using an electrolyte solution containing 60 µg L⁻¹ of Pb²⁺ or Cd²⁺.

The reproducibility of the BiOCl-modified CPE was evaluated using an electrolyte solution containing 60 µg L⁻¹ of Pb²⁺ or Cd²⁺. As shown in Fig. 7c, the BiOCl-modified CPE showed good reproducibility, with relative standard deviations (RSDs) of 5.62% for Pb²⁺ and 0.72% for Cd²⁺, respectively, in five repeated measurements. Furthermore, the coexistence of both model metal ions did not reveal any cross-interference. Nevertheless, the peak current of Cd was lower than that of Pb when their concentrations were the same. This phenomenon is probably attributed to the stronger interaction between Pb and bismuth or bismuth compounds [30, 32-34].

Concerning the practical reliability of the BiOCl-modified CPE, the determination of heavy metals (Cd^{2+} and Pb^{2+}) in a real soil sample (as specified in the Experimental Section) was performed. The contents of Pb^{2+} and Cd^{2+} in the real soil sample were $40.2 \pm 2.9 \text{ mg kg}^{-1}$ and $0.81 \pm 0.3 \text{ mg kg}^{-1}$, respectively. Moreover, the experimental results obtained by the voltammetric method were also compared with those of the AAS method to evaluate the analytical accuracy of the voltammetric method. The AAS (atomic absorption spectrometry) results showed that the concentrations of Pb^{2+} and Cd^{2+} were $41.6 \pm 0.2 \text{ mg kg}^{-1}$ and $0.79 \pm 0.12 \text{ mg kg}^{-1}$, respectively. The results showed that the proposed voltammetric method has comparable performance to that of the AAS method for the determination of heavy metal ions. To further verify the viability of the proposed voltammetric procedure, recovery experiments were performed, and the average recovery was estimated as 97.6% for Pb^{2+} and 101.3% for Cd^{2+} .

Furthermore, the BiOCl-modified CPE was compared with similar sensors/methods published in the literature for the detection of Pb^{2+} and Cd^{2+} (see Table 1). The BiOCl-modified CPE exhibited improved analytical characteristics compared with those of other sensors. This suggests that the BiOCl-modified CPE can be used as a working electrode for the practical voltammetric determination of heavy metal ions.

Table 1. Analytical performance of some composite electrodes with bulk-modified Sb or Bi precursors.

Technique	Sensor	Analyte	LOD ($\mu\text{g L}^{-1}$)	DT (s)	Ref.
SWASV	Bi powder in CPE	Pb^{2+}	0.9	300	[23]
		Cd^{2+}	1.2	300	
SWASV	Bi_2O_3 powder in GCE	Pb^{2+}	1.25	60	[24]
		Cd^{2+}	0.62	60	
SWASV	$(\text{BiO})_2\text{CO}_3$ powder in GCE	Pb^{2+}	3.25	60	[24]
		Cd^{2+}	1.58	60	
SWASV	Sb_2O_3 powder in CPE	Pb^{2+}	0.7	90	[30]
		Cd^{2+}	1.0	90	
SWASV	Bi needle	Pb^{2+}	0.093	180	[35]
		Cd^{2+}	0.054	180	
SWASV	Bi_2O_3 printed on SPE	Pb^{2+}	2.3	300	[36]
		Cd^{2+}	1.5	300	
SWASV	BiOCl powder in CPE	Pb^{2+}	0.42	300	This work
		Cd^{2+}	0.76	300	

Note: SWASV: square-wave anodic stripping voltammetry; DT: deposition time; CPE: carbon paste electrode; GEC: graphite-epoxy composite; SPE: screen-printed electrode;

4. CONCLUSIONS

In summary, BiOCl can be used as a bulk modifier to decorate CPE for the sensitive detection of heavy metal ions (e.g., Pb^{2+} and Cd^{2+}). The crystallographic structure of the BiOCl modifier strongly influences the stripping voltammetric performance. Optimized hydrothermal conditions (hydrothermal temperature of 180°C and hydrothermal time of 6 h) for preparation of the BiOCl

modifier were determined. Furthermore, some influencing factors, including the mass ratio of the modifier, electrolyte pH, and preconcentration conditions (deposition potential and time), were also optimized. Under the selected conditions, the BiOCl-modified CPE showed higher sensitivity, a wider linear working range, and good reproducibility, which demonstrated that it is an acceptable electrochemical analyzer for detecting heavy metal ions (e.g., Pb^{2+} and Cd^{2+}).

ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (21875026, 21878031), Program for Liaoning Excellent Talents in University (LR2014013), and Science and Technology Foundation of Liaoning Province (No.201602052).

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