Highly sensitive determination of lead(II) and cadmium(II) by a large surface area mesoporous alumina modified carbon paste electrode

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Nanosized mesoporous γ-alumina (M-γ-Al2O3) was first prepared and then modified into a carbon paste to fabricate a novel modified carbon paste electrode. The prepared alumina has pores with an amorphous wall and large surface area. The electrochemical behavior of the modified carbon paste electrode was investigated using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) methods. The modified carbon paste electrode was employed to determine Pb2+ and Cd2+ simultaneously by a differential pulse voltammetry (DPV) method. Amperometric determination was carried out in 0.1 mol L−1 NaAc–HAc buffer solution (pH 6.0) after enriching for 360 s at −1.0 V. The oxidation peak currents of Pb2+ and Cd2+ were proportional to their concentration in the range of 0.001–10 μmol L−1 and 0.01–10 μmol L−1, respectively. The detection limits of Pb2+ and Cd2+ were 0.20 nmol L−1 and 2.0 nmol L−1 (S/N = 3), respectively. The modified carbon paste electrode shows good stability, repeatability and sensitivity. The proposed method was applied to the determination of Pb2+ and Cd2+ in water samples with satisfactory results.

1. Introduction

Lead and cadmium are both toxic heavy metal elements. Because of their toxicity and non-biodegradability, they can not only be accumulated in the body and endanger human health, but also cause serious pollution to the environment. Consequently, knowledge of the quantities of Pb2+ and Cd2+ in environmental samples has important practical significance. At present, various analytical techniques have been reported for the determination of Pb2+ and Cd2+ at low concentrations, such as atomic fluorescence spectrometry, atomic absorption spectroscopy, inductively coupled plasma mass spectrometry, and high performance liquid chromatography. Although these techniques have good selectivity and high sensitivity, most of the above techniques require relatively ponderous and complicated instruments and are time-consuming, in particular for the in situ analysis of metal ions. In contrast, electrochemical voltammetry is widely used for trace heavy metal ion analysis and on-site testing because of its low-cost instruments and equipment, high sensitivity, wide detection range, rapid performance and high portability.

The carbon paste electrodes have the advantages of simple preparation, non-toxicity, chemical inertness, very stable electrochemical response, easy updating the surface, long operational lifetime and low background current. Owing to these advantages, carbon paste electrodes have become one of the most popular electrode materials. The selectivity and sensitivity of the carbon paste electrodes may be improved by adding special modifiers to the carbon paste. However, it is still a challenging requirement to design or synthesize a new type of modifier for higher selectivity and sensitivity.

Mesoporous materials, such as Ni-ZSM-5, Ni-SBA-15, Cu-zeolite and Pb-zeolite, were widely applied in catalysts, sensors and energy storage due to their high specific surface area, large pore volume, narrow pore size distribution, tunable pore size and favorable stability. Research indicates that M-γ-Al2O3 can raise the electrode conductivity, the electron transfer and can also enhance the analytical sensitivity due to their large surface areas. Up to now, many electrochemical sensors have been reported based on M-γ-Al2O3 with ordinary structure for the determination of sodium aerosol, nicotinamide adenine dinucleotide, amitriptyline, captopril, ascorbic acid, dopamine and uric acid, and so on.

Many approaches have been used to synthesize large surface area mesoporous alumina with the P123 as a structure-directing agent. The high surface area alumina are prepared via mainly controlled the Al3+ hydrolysis speed by regulating pH value and reducing the concentrations of anions in the reaction system to disturb the self-assembly process. In process of the synthesis, the added aniline could not only regulate the pH value of the reaction system to control the Al3+...
hydrolysis speed, but also could protect the aluminum ions at the organic–inorganic interface from being affected by the chloride ions of the reaction system. So in present work, aniline was chosen as an interface protective agent to prepare large surface area mesoporous alumina which was employed to modify the carbon paste. The as-prepared large surface area mesoporous alumina modified carbon paste was used to prepare modified carbon paste electrode. The prepared M-\(\gamma\)-Al\(_2\)O\(_3\) was characterized by powder X-ray diffraction (PXRD), transmission electron microscopy (TEM) and Brunauer–Emmett–Teller (BET) analysis. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) methods were utilized to study the electrochemical behavior of the novel working electrode. A DPV method was developed for the simultaneous determination of Pb\(^{2+}\) and Cd\(^{2+}\). The results show that the modified carbon paste electrode has excellent sensitivity, wide linear range, low detection limit, favorable stability and reproducibility. Finally, the modified carbon paste electrode was successfully applied to the determination of Pb\(^{2+}\) and Cd\(^{2+}\) in water samples.

2. Experimental

2.1. Apparatus

The CHI660D Electrochemical Workstation (Shanghai Chenhua Instruments, Shanghai, China) was used to perform the electrochemical measurements. The three electrodes electrochemical cell contain an unmodified or modified carbon paste electrode with a diameter of 3.0 mm and 5.0–6.0 mm in depth (working electrode), a platinum electrode (auxiliary electrode) and Ag/AgCl/sat. KCl electrode (reference electrode). Powder X-ray diffraction (PXRD) analysis was conducted by a PANalytical X’pert diffractometer with Cu Ka (1.5418 Å) radiation generated at 40 kV and 40 mA. The surface area (calculated by...
buffer solution. Distilled water was used for the preparation of all solutions and for washing. Both standard solution and buffer solutions were kept in a 4 °C refrigerator.

2.3. Preparation of large surface area M-γ-Al₂O₃

In order to prepare the large surface area M-γ-Al₂O₃, a delicate procedure should be designed. Firstly, 1 g of Pluronic P123 was dissolved in 20 mL of the absolute ethanol to form a solution. Then quantitative aluminum isopropoxide, HCl and aniline were added successively to the solution. This mixture was stirred at room temperature until the entire solid was dissolved completely. Consequently, a homogeneous sol was obtained. Secondly, the homogeneous sol was transferred to an oven. The solvent was evaporated with a temperature at 40 °C for 48 h to prepare a gel product. After that, the gel product was dried at 100 °C for 24 h. Finally, the as-prepared sample was calcined at 400 °C in a muffle furnace with a heating rate of 10 °C min⁻¹ and held for 3 h at the maximum calcination temperature. The large surface area M-γ-Al₂O₃ was synthesized successfully after the above steps.

2.4. Preparation of modified carbon paste electrode

The modified carbon paste electrode was prepared as following process. M-γ-Al₂O₃, graphite powder and liquid paraffin were mixed together in definite proportions. The mixture was grinded for about 10 minutes to get a homogenous carbon paste. Small amount of the obtained carbon paste was taken to pack tightly into the tip cavity of a carbon paste electrode. This electrode is defined as M-γ-Al₂O₃-CPE. For comparison purpose, bare carbon paste electrode (BCPE) can be manufactured by the similar way without adding M-γ-Al₂O₃. Smooth surfaces of M-γ-Al₂O₃-CPE and BCPE can be obtained by polishing the electrodes on a weighting paper.

2.5. Electrochemical measurements

DPV method was carried out in a 10 mL volume of electrochemical cell containing 0.1 mol L⁻¹ NaAc–HAc buffer solution (pH 6.0) as supporting electrolyte medium. The accumulation potential of Pb²⁺ and Cd²⁺ is −1.0 V with an accumulation time of 360 s. The optimum conditions of DPV method were determined. The potential ranges from −1.2 to 0 V. The pulse amplitude, the pulse width and the scan rate are 50 mV, 50 ms and 100 mV s⁻¹, respectively. The calibration curves were obtained by plotting the peak current versus the Pb²⁺ and Cd²⁺ concentration. All electroanalytical measurements were conducted at room temperature.

3. Results and discussion

3.1. Characterization of M-γ-Al₂O₃

The PXRD pattern of large surface area M-γ-Al₂O₃ is shown in Fig. 1. Only one flat peak can be found at 24°, which demonstrates the crystallinity of M-γ-Al₂O₃ is low and the M-γ-Al₂O₃ has pores with amorphous wall according to Yang et al.²⁸ Fig. 2 shows the nitrogen adsorption-desorption isotherms and pore size distribution curve of the M-γ-Al₂O₃. The synthetic M-γ-Al₂O₃
shows type IV curve with hysteresis loop at high pressure, which implies the existence of mesoporous pores. The isotherms exhibit distinct capillary condensation steps, indicating uniform mesoporosity. The synthetic Mg-Al2O3 possesses a large surface area of 522 m² g⁻¹, a pore volume of 0.38 cm³ g⁻¹, and a narrow pore-size distribution centered at 4.9 nm. The TEM image of large surface area Mg-Al2O3 is shown in Fig. 3. The image reveals that the sample has lath-like appearance without significant order of pore arrangement. The grain diameters of sample are in the range of 10–20 nm. Hence, the very weak intensity of these diffraction peaks in the PXRD patterns for the sample could be attributed to their nanosized structure.

The improved surface area and comparable narrow pore size distribution were obtained compared with the prior literatures²¹,²⁷,²⁸ which used the P123 as a structure-directing agent for synthesizing the M-γ-Al₂O₃. In the synthesis system of mesoporous alumina synthesized by sol–gel method, the Cl⁻ from the acidity adjustment will be coordinated with Al³⁺, and the charge balance between the organic template and inorganic aluminum will be destroyed, thus interfere the self-assembly process. The addition of aniline can coordinate with Al³⁺ and inhibit the coordination between them, thus promoting mesoporous structure formation. Therefore, it is considered that aniline is an interfacial protective agent for forming mesoporous alumina.²⁹–³¹ So aniline was chosen as interface protective agent to prepare the mesoporous alumina with large surface area. The synthetic M-γ-Al₂O₃ promise its potential application in the field of modified electrode.

3.2. The modified proportion of mesoporous alumina
The mass ratio of the solid mixture (graphite powder and M-γ-Al₂O₃) to liquid paraffin was fixed as 3 : 1. Influences of different
Table 1 Analytical parameters for simultaneous determination of Pb²⁺ and Cd²⁺

| Analyte | Linear range (µmol L⁻¹) | Regression equation \( i_p,^a, C^b \) | \( R^2 \) | Detection limit (nmol L⁻¹) |
|---------|--------------------------|------------------------------------------|--------|--------------------------|
| Pb²⁺    | 0.001–10                 | \( i_p = 11.349C + 0.1034 \)             | 0.9988 | 0.20                     |
| Cd²⁺    | 0.01–10                  | \( i_p = 3.4627C + 0.0006 \)             | 0.9971 | 2.0                      |

\( a \) \( i_p \) (µA) is the peak current. \( b \) \( C \) (µmol L⁻¹) is the concentration of the analyte. Electrochemical conditions are the same as Fig. 9.
to two metal ions and meanwhile the large surface areas of M-γ-Al2O3 can accelerate the electron transfer.

3.6. Optimization of detection parameters

3.6.1 The supporting electrolyte and pH. Three kinds of buffer solution namely NaAc–HAc, Britton–robinson and Na2HPO4-NaH2PO4 were tried to be used as the supporting electrolyte of detection system. The results show that better peak shape, resolution and sensitivity were achieved by using buffer solution of NaAc–HAc than that of Britton–robinson and Na2HPO4-NaH2PO4. So NaAc–HAc buffer solution was selected as the supporting electrolyte for subsequent experiments.

The effects of pH values (NaAc–HAc buffer solution, pH 4.5–7.0) on the peak potential and peak currents of two metal ions are shown in Fig. 7. The peak potentials of two metal ions shift negatively with the increasing of pH values. Good linear relationships between the peak potentials of two metal ions and pH values are obtained. The linear equations are 

\[ E_{pa} (V) = -0.4252 - 0.0149 \text{pH} (R^2 = 0.9922) \]  

and 

\[ E_{pa} (V) = -0.6532 - 0.0184 \text{pH} (R^2 = 0.9914) \]  

inset B), respectively. The peak currents of Pb2+ and Cd2+ firstly increases and then decreases with the increase of pH values (inset A). They achieve the maximum at pH 6.0. Therefore, pH 6.0 was selected for further study.

3.6.2 The accumulation potential and accumulation time. The accumulation potential is an important parameter which can affect greatly on the sensitivity of determination for heavy metal ions. Fig. 8 shows the effect of accumulation potential on the peak current of Pb2+ and Cd2+ with accumulation potential ranging from −0.7 V to −1.2 V. The peak currents of Pb2+ and Cd2+ can improve obviously with negative shifting of the accumulation potential. When the accumulation potential exceed to −1.0 V, the peak current of two metal ions begin to stabilize. Hence, the accumulation potential is fixed as −1.0 V.

| Table 2 | Comparison of the response characteristics of different modified electrodes |
|-----------------|-----------------|------------------|-----------------|------------------|
| Electrode materials | Pb2+ (μmol L−1) | Cd2+ (μmol L−1) | Pb2+ (μmol L−1) | Cd2+ (μmol L−1) | Reference |
| Bi-xerogel/GCE | 0.0097–0.082 | 0.0044–0.080 | 6.3 | 3.3 | 32 |
| SNAC/GCE | 0.09–5.70 | 0.09–4.8 | 5.7 | 24.0 | 33 |
| (C–Bi) nanocomposite/CPE | 0.0048–0.48 | 0.0089–0.89 | 2.9 | 5.3 | 34 |
| RGO/Bi/CPE | 0.097–0.58 | 0.18–1.07 | 2.7 | 25.0 | 35 |
| Mo5S4–1 NWs/GCE | 0.0072–2.17 | 0.0045–1.33 | 2.2 | 0.9 | 36 |
| SnNP/MWCNT/CPE | 0.048–0.29 | 0.089–0.53 | 3.1 | 6.9 | 37 |
| CB-15-crown-5/GCE | 0.053–0.9 | 0.14–1.7 | 16.0 | 42.0 | 38 |
| BiOCl/MWCNT/GCE | 0.024–0.24 | 0.044–0.44 | 2.8 | 11.0 | 39 |
| c-GS/GR-CS/GCE | 0.05–0.30 | 0.005–0.60 | 2.2 | 1.1 | 40 |
| BiF/CPE | 0.097–0.48 | 0.18–0.89 | 5.8 | 87.0 | 41 |
| ERGNO/Bi/SPE | 0.0048–0.29 | 0.089–0.53 | 3.8 | 4.5 | 42 |
| Bi/NGF-Nafion/GCE | 0.0024–0.53 | 0.018–0.62 | 0.48 | 4.5 | 43 |
| Sparked Bi graphite SPE | 0.0024–0.058 | 0.005–0.11 | 0.97 | 1.8 | 44 |
| M-γ-Al2O3-CPE | 0.001–10 | 0.01–10 | 0.2 | 2.0 | This work |

| a Bismuth-dispersed xerogel-based composite films modified glassy carbon electrode.  
| b Spherical carbon nanoparticle decorated activated carbon modified glassy carbon electrode.  
| c Bismuth–carbon nanocomposites/carbon paste electrode.  
| d Reduced graphene oxide/Bismuth/carbon paste electrode.  
| e Mo5S4–1 nanowires modified glassy carbon electrode.  
| f Antimony nanoparticle-multiwalled carbon nanotubes composite immobilized at carbon paste electrode.  
| g 4-Carboxybenzo-15-crown-5 modified glassy carbon electrode.  
| h Bismuth-oxychloride particle-multiwalled carbon nanotube composite modified glassy carbon electrode.  
| i L-cysteine/graphene modified glassy carbon electrode.  
| j Ammonium tetrafluorobismuthate modified carbon paste electrode.  
| k Electrochemically reduced graphene oxide film modified screen-printed electrode.  
| l Three-dimensionally interconnected mesoporous graphene framework modified glassy carbon electrode.  
| m Bi2O3-modified graphite screen printed electrode.  

Table 3 Results of the proposed method for the determination of Pb2+ and Cd2+ in various water samples (n = 3)

| Sample | Analytes | Added (nmol L−1) | Found (nmol L−1) | Recovery (%) |
|--------|----------|-----------------|-----------------|--------------|
| Tap water | Pb2+ | 0 | 21.67 ± 0.15 | 97.24 |
| | | 20 | 40.52 ± 0.66 | 97.46 |
| | Cd2+ | 0 | 8.17 ± 0.13 | 101.2 |
| | | 50 | 59.51 ± 0.79 | 102.3 |
| Lake water | Pb2+ | 0 | 41.22 ± 0.86 | 103.94 |
| | | 20 | 63.63 ± 1.09 | 103.94 |
| | Cd2+ | 0 | 37.01 ± 0.54 | 103.94 |
| | | 50 | 85.72 ± 1.18 | 98.52 |

* Electrochemical conditions are the same as Fig. 9.
The accumulation time is also another parameter which can apparently influence the detection sensitivities of Pb²⁺ and Cd²⁺. With the increase of accumulation time, the peak currents of Pb²⁺ and Cd²⁺ noticeably increase at first and then decrease gradually after reaching the peak value. In addition, the accumulation time beyond 360 s might result in the distortions of signals for these two metal ions. These results might be explained that the adsorptions of Pb²⁺ and Cd²⁺ on the surface of M-γ-Al₂O₃-CPE attain a saturation level. So 360 s is considered to be the accumulation time in this work.

3.7. Analytical performances of Pb²⁺ and Cd²⁺

Under the optimum conditions, the determinations of Pb²⁺ and Cd²⁺ were conducted at M-γ-Al₂O₃-CPE using DPV method. As described in Fig. 9 and 10, good linear correlation could be found between the peak currents and the concentrations of Pb²⁺ and Cd²⁺. The regression equations, linear response ranges and detection limits are summarized in Table 1. Compared with previous literatures (Table 2), improved or comparable performances have been achieved for the determinations of Pb²⁺ and Cd²⁺ using M-γ-Al₂O₃-CPE.

In order to verify the reproducibility, stability and anti-interference performance of M-γ-Al₂O₃-CPE, the measurements were carried out in a NaAc–HAc buffer solution (pH 6.0) containing 1.0 μmol L⁻¹ Pb²⁺ and 1.0 μmol L⁻¹ Cd²⁺. The reproducibility was evaluated by 8 continuous measurements of peak currents for Pb²⁺ and Cd²⁺. RSDs of the peak currents are 3.5% and 4.3%, respectively. At the same time, five modified carbon paste electrodes were prepared and examined in the same conditions, RSDs of the peak currents are 3.2% and 4.8%, respectively. The M-γ-Al₂O₃-CPE was polished by a weighting paper and then eluted by distilled water. The treated electrode was dried and stored in a 4 °C refrigerator. After 7 days, the stripping peak currents for 1.0 μmol L⁻¹ Pb²⁺ and 1.0 μmol L⁻¹ Cd²⁺ decrease by 6.2% and 7.4%, respectively. These experimental results indicate that the M-γ-Al₂O₃-CPE exhibit good reproducibility and stability. Interference experiment was also investigated by adding general coexistence ions to a solution containing 1.0 μmol L⁻¹ Pb²⁺ and 1.0 μmol L⁻¹ Cd²⁺ in a NaAc–HAc buffer solution (pH 6.0). No evident interference can be found for the determinations of Pb²⁺ and Cd²⁺ in the presence of Na⁺ (1000 μmol L⁻¹), K⁺ (1000 μmol L⁻¹), Cl⁻ (1000 μmol L⁻¹), Br⁻ (1000 μmol L⁻¹), F⁻ (1000 μmol L⁻¹), Al³⁺ (500 μmol L⁻¹), Mg²⁺ (500 μmol L⁻¹), Ca²⁺ (500 μmol L⁻¹), Zn²⁺ (500 μmol L⁻¹) and Mn²⁺ (500 μmol L⁻¹) and Fe³⁺ (50 μmol L⁻¹) with a maximum allowable error of 5.0%. In addition, Cu²⁺ can interfere with the detection of Cd²⁺, which can compete with Cd²⁺ to reduce on the electrode surface.

3.8. Application

To evaluate the application of the proposed M-γ-Al₂O₃-CPE, it was used to analyze the concentrations of Pb²⁺ and Cd²⁺ in artificial lake water and tap water samples. The supernatant liquid of artificial lake water and the tap water were collected and diluted 5 times by 0.1 mol L⁻¹ NaAc–HAc buffer solution (pH 6.0). The treated water samples were determined by M-γ-Al₂O₃-CPE under the optimal experimental conditions. The results are listed in Table 3. The recoveries for these two metal ions are between 97.24% and 103.94%. The water samples were also detected by conventional atomic absorption spectrometry (AAS, WFX-130A, Beijing Rayleigh Analytical Instrument Corp. Ltd.) method. The concentrations of Pb²⁺ and Cd²⁺ were 21.58 ± 0.19 and 8.23 ± 0.11 nmol L⁻¹ in tap water, respectively; while those of lake water are 41.67 ± 0.52 and 37.32 ± 0.61 nmol L⁻¹, respectively. The measuring results obtained by these two methods are basically the same, indicating a good reliability of the proposed methods.

4. Conclusion

In present work, aniline was chosen as an interface protective agent to prepare large surface area M-γ-Al₂O₃ which possess a large surface area and a narrow pore-size distribution. The M-γ-Al₂O₃ was modified into the carbon paste to fabricate a novel M-γ-Al₂O₃-CPE. The proposed electrode has a high sensitivity, stability and reproducibility in the presence of M-γ-Al₂O₃. The electrode exhibits excellent performance for the detections of Pb²⁺ and Cd²⁺ in artificial lake water and tap water samples. The developed method will have extensive potential in the field of environmental monitoring.

Conflicts of interest

There are no conflicts to declare.

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