Well-Arranged Porous Co$_3$O$_4$ Microsheets and Its Electroanalysis toward Pb (II)

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Abstract—Well-arranged porous Co$_3$O$_4$ microsheets has been successfully synthesized via a hydrothermal process and subsequent thermal decomposition. The characterization of the as-prepared product is identified with scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM) and X-ray diffraction (XRD). The results show that the as-prepared porous Co$_3$O$_4$ possesses the face-centered cubic phase structure and well single-crystallized phase. Its electrochemical performance was characterized with square wave anodic stripping voltammetry (SWASV) for the detection of Pb(II) at the porous Co$_3$O$_4$/nafion modified electrode with the good sensitivity of 48.5 μA·µM$^{-1}$ and detection limited of 30 nM (3σ method). In addition, the stability measurement is investigated under the optimized conditions.

Index Terms—Porous Co$_3$O$_4$ microsheets, hydrothermal process, heavy metal ions, electroanalysis.

I. INTRODUCTION

In recent years, the pollution of heavy metal ions in drinking-water has attracted the increasing concern because of their toxicity in direct adverse impact on human health and the environment even at trace amount [1]. Take Pb (II) for example, it can be widely found in drinking-water and known to cause health problems at very low concentrations, such as digestive, neurological, cardiac, and mental troubles [2]. In recent years, there are already many mature methods to analyze heavy metal ions, such as flame atomic absorption spectrometry [3], electrothermal atomic absorption spectrometry [4], [5] and inductively coupled plasma spectrometry [6].

Alternatively, opportunity for electrochemical techniques has been accepted with advantages of highly sensitive, easy to perform, and low-cost [7]-[9]. In particular, great efforts have been devoted to studying the sensing materials for developing the electrochemical methods which can remarkably improve the efficiency of electrochemical technique and has developed to be the important part for the determination of heavy metal ions. For instance, CNTs [10]-[12], metal nanomaterials [13]-[15], graphene [8], [16], [17] are common materials used for modifying electrode, whereas porous metal oxide nanomaterials are rarely reported. Considering the porous metal oxide that can provide a high surface area, a high hydrothermal stability, and surface active sites which can interact with micropollutants, e.g., heavy metal ions and organic micropollutants, a study on developing porous metal oxides as chemical sensing materials for detection heavy metal ions is of much interest and significance.

Co$_3$O$_4$ is one of the most intriguing p-type semiconductors and has been widely applied in a wide range of fields, including lithium-ion batteries [18]-[21], supercapacitors [22]-[24], catalysts [25], and gas sensors [26], [27]. Inspired by the unique porous nature and special surface active sites of Co$_3$O$_4$, we would expect that the porous Co$_3$O$_4$ as sensing material to modify electrode for ultratrace metal ions detection with high sensitivity. In this study, we prepared the porous Co$_3$O$_4$ microsheets with highly uniform porosity morphology by calcining the layered precursor Co$_3$(OH)$_2$CO$_3$. A case study with Pb (II) was developed to evaluate its electrochemical performance with square wave anodic stripping voltammetry (SWASV).

II. MATERIAL AND METHODS

A. Chemical Reagents

All reagents were purchased from Sinopharm Chemical Reagent Co., Ltd. (China) and were of analytical grade. 0.1 M acetate buffer (NaAc-HAc, pH 5.0) solution was prepared using NaAc and HAc. Ultrapure fresh water was obtained from a Millipore water purification system (MilliQ, specific resistivity >18 MΩ cm, S.A., Molsheim, France) and used in all runs.

B. Synthesis of porous Co$_3$O$_4$ Microsheets

Porous Co$_3$O$_4$ was synthesized using a modified strategy that has been used previously [23]. In brief, 1.455 g Co(NO$_3$)$_2$·6H$_2$O (5 mM) was dissolved in 25 mL deionized water, which was dropped into 25 mL of 0.025 mM polyvinyl pyrroldione (PVP, K-30) aqueous solution. After stirring for 1 h, 10 mM urea was added to the solution under stirring for additional 3 h. The resulting solution was then sealed in a 60 mL Teflon-lined autoclave, followed by hydrothermal treatment at 120°C for 24 h. After treatment, a light pink, solid precipitate was collected by centrifugation, washed repeatedly with deionized water and absolute ethanol, and dried at 60°C in a vacuum. Finally, the precipucer was heated to 600°C for 2 h in air. Layered Co$_3$O$_2$ was prepared by calcination of the precursor at 300°C for 2 h as a comparison.

C. Apparatus

Electrochemical experiments were recorded using a CHI
660D computer-controlled potentiostat (ChenHua Instruments Co., Shanghai, China). A conventional three-electrode system consisted of a glassy carbon working electrode (GCE, 3 mm diameter), an Ag/AgCl reference electrode, and a platinum wire counter electrode. The scanning electron microscopy (SEM) images were taken by a FEI Quanta 200 FEG field emission scanning electron microscope.

**D. Preparation of Modified Electrode**

Before each modification, the bare glassy carbon electrode was sequentially polished with 0.3 µm and 0.05 µm alumina power slurries to a mirror-shiny surface and then sonicated with HNO₃ solution (v:v 1:1), absolute ethanol and deionized water, respectively. The porous Co₃O₄/nafion film on the surface of glassy carbon electrode was performed in the following manner: 2.0 µL of Co₃O₄ ethanol (0.1 mM) solution was dripped onto the surface of a freshly polished glassy carbon electrode. The electrode was allowed to dry, and then 2.0 µL of 0.5% w/w nafion solution was pipetted onto it. The electrode was then allowed to air-dry at room temperature. Layered Co₃O₄/nafion electrode was prepared in the same way.

**E. Electrochemical Measurements**

Square wave anodic stripping voltammetry (SWASV) was used for Pb(II) detection in 0.1 M NaAc-HAc solution under optimized conditions. A deposition potential of -1.2 V was applied for 180 s to the working electrode with stirring. SWASV responses were recorded between -1.0 and -0.2 V with a step potential of 5 mV, amplitude of 20 mV, and frequency of 25 Hz. A desorption potential of 0 V for 210 s was performed to remove the residual metal ions under stirring conditions. All experiments were performed at room temperature under air atmosphere.

**III. RESULTS AND DISCUSSIONS**

**A. Morphology Characteristics of Porous Co₃O₄ Microsheets**

Fig. 1a-Fig. 1b show SEM images of the porous Co₃O₄ microsheets (in different magnifications) with calcination of the precursor at 600ºC. It can be clearly seen that the product exhibits well-arranged multilayered structure composed of many microsheets. The further insight of the porous Co₃O₄ microsheets was characterized with HRTEM. It is observed that the sample not only has highly apparent porous morphology with pore size approximately 200 nm (Fig. 1c), but also clearly shows that the lattice fringes with a lattice spacing of about 0.468 nm corresponding to the (111) plane [28], [29]. Furthermore, it appears that the integrated porous architecture is fabricated by small nanocrystals growing in an oriented manner (Fig. 2d). The selected area electron diffraction (SAED) (Inset in Fig. 2d) also clearly shows the highly single-crystalline structure.

Generally, the porous Co₃O₄ obtained involved two process, formation of Co₂(OH)₂CO₃ in hydrothermal conditions and subsequent thermal decomposition in air ambient. In aqueous solution, the reactant urea can generate OH⁻ and CO₃²⁻ after decomposition and hydrolyzation, which can in situ combine with Co²⁺ to form cobalt hydroxide carbonate precipitation. More information on the formed structures can be observed with a series of SEM images (Fig. 2). Fig. 2a shows the SEM image of precursor Co₂(OH)₂CO₃, which is multilayered morphology with well-arranged two-dimension microsheets. The hypothesis of the formation mechanism is proposed. As we know, the solvent, inorganic additives and surfactant can have a significant influence on the crystal growth of nanomaterials by modifying the surface energies, which can regulate or control certain crystallographic planes. In addition, it can make the nanoparticles growth into different shapes by the selective adsorption of ions onto different crystal planes [23]. Herein, the PVP we introduced is a common and typical neutral surfactant, which can efficiently modulate the OH⁻ and CO₃²⁻ combining with Co²⁺. It can further induce the nanocrystals growth in certain direction and generate the layered structure under hydrothermal conditions that can provide better advantage in controlling the structure and crystallization. Fig. 2a shows the SEM image of precursor Co₂(OH)₂CO₃, which is multilayered morphology with well-arranged two-dimension microsheets. Fig. 2a-Fig. 2e show the SEM images of precursor after thermal decomposition in different
temperature. No remarkable change with the layered structure after calcinations could be observed. As increasing the temperature, the surface of the layered structure gradually becomes rougher and the pores become much larger and more apparent, which may lead to the aggregation and re-crystallization of the nanoparticles during the calcination process. Fig. 2f depicts the typical XRD patterns of the precursor, layered Co$_3$O$_4$ and porous Co$_3$O$_4$. The precursor as the monoclinic Co$_2$(OH)$_2$CO$_3$ (JCPDS Card no. 29-1416) can be well indexed. The XRD patterns of Co$_3$O$_4$ at 300ºC and 600ºC have identical peaks, which can be perfectly indexed to face-centered cubic phase (JCPDS Card no. 43-1003 space group: Fd3m). The peaks represent the Bragg reflections of the (111), (220), (311), (222), (400), (422), (511), and (440) planes and no peaks from other phase have been dedicated, revealing the high purity of the synthesized sample. As expected, with increasing calcining temperature, the peak intensity increases, indicating the significantly improvement of the crystallinity.

B. Optimization of Electrochemical Experimental Conditions

In order to gain the high sensitive electrochemical performance with the porous Co$_3$O$_4$/nafion modified electrode to heavy metal ions, the effect of experimental parameters (deposition potential, deposition time, pH, etc.) were first discussed.

It is known that the application of appropriate deposition potential is very important to achieve the best sensitivity. Therefore, the effect of the deposition potential was investigated after 180 s accumulation in 0.1 M NaAc-HAc solution at pH 5.0. Fig. 3a depicts the peak currents of 0.15 µM Pb(II) with deposition potential ranged from -0.8 V to -1.4 V. When the potential shifts negatively from -0.8 V to -1.2 V, the peak currents increase significantly, which is the fact that Pb(II) can be more easily reduced at more negative deposition potential because of enhanced kinetics. The peak current reaches a maximum at deposition potential of -1.2 V. However, the peak currents decrease when the deposition potential is beyond -1.2 V, which is due to the interference of the hydrogen evolution. Therefore, deposition potential of -1.2 V is selected as the optimum.

The dependence of the deposition time was also investigated from 30 s to 210 s. Fig. 3b shows the relationship between the peak currents and deposition time for 0.15 µM Pb(II) at -1.2 V in 0.1 M NaAc-HAc solution at pH 5.0. As depicted in Fig. 3b, the peak currents increase with the increase of the deposition time. Note that the adsorption equilibrium of Pb(II) and Co$_3$O$_4$ is strongly related to interaction time. In order to detect Pb(II) more sensitively, longer deposition time could be applied. But considering that the upper detection may be limited due to the surface saturation at high Pb(II) concentrations. Therefore, to achieve lower detection limit and wider response range, a deposition time of 180 s is chosen.

The effect of pH ranged of 4.0-7.0 was investigated in 0.1 M NaAc-HAc solution containing 0.15 µM Pb(II). As displayed in Fig. 3c, the peak currents firstly increase versus pH and the maximum current is observed at 5, which may be ascribed to the leakage of the modifier at rather acid condition. However, peak currents reduce significantly when pH exceeds 5, due to the formation of metal hydroxide complexes (Pb(OH)$_2$, Pb(OH)$_2$) that may be partially soluble. As a result, a pH of 5.0 is selected for further measurements.

C. Electrochemical Determination of Pb(II) at Co$_3$O$_4$ Modified Electrode

In comparison with other different electrodes (bare GCE, nafion/GCE, layered Co$_3$O$_4$/nafion), the performance of porous Co$_3$O$_4$/nafion modified electrode toward Pb(II) was evaluated by the square wave stripping voltammograms (SWASV) response in the presence of 0.20 µM Pb(II) in 0.1 M NaAc-HAc solution containing 0.15 µM Pb(II). There is no obvious peak at bare GCE and a small stripping peak for nafion/GCE is observed under the same conditions. However, a strong and well-defined
response at -0.55 V can be clearly obtained for porous Co$_3$O$_4$/nafion modified GCE. The peak current is increased by nearly 5-fold than that of at nafion/GCE, 12-fold than that of bare-GCE. For layered Co$_3$O$_4$/nafion modified GCE, the response performance is not comparable with the porous Co$_3$O$_4$/nafion. The results demonstrate that porous Co$_3$O$_4$ is of great benefit to electrochemical sensing Pb(II) due to its adsorption behavior.

Subsequently, the electrochemical measurement toward Pb(II) on porous Co$_3$O$_4$/nafion modified electrode was analyzed with SWASV under the optimal experimental conditions. The stripping voltammograms for Pb(II) at concentrations of 0.05-0.675 µM are illustrated in Fig. 4a. As seen, the peak currents increase linearly versus the Pb(II) concentrations and the linearization equation is \(i/\mu A = -2.29 + 48.5c/\mu M\) (Fig. 4b) with the limit of detection (LOD) is 30 nM (3σ method). These results suggest that the modifier of porous Co$_3$O$_4$ has the excellent performance to heavy metal ion (Pb(II)) with high sensitivity. The comparative data of the modified electrode to the common electrode modified with Hg, Bi, or Sb and the conditional methods are summarized in Table I. These results suggest that the modified porous Co$_3$O$_4$ is highly sensitive to heavy metal ions (Pb(II)).

In addition, the stability study was investigated with the porous Co$_3$O$_4$/nafion modified GCE to characterize the reproducibility of the electrode performance. Fig. 5 illustrates the peak currents after successive cycling for 16 times in 0.1 M NaAc-HAc (pH 5.0) solution containing 0.3 µM Pb(II). No obvious change with the peak currents is observed with the relative standard deviation (RSD) 9.2 %, indicating that the porous Co$_3$O$_4$/nafion modified electrode exhibits favorable stability for repetitive deposition-stripping in the experimental conditions.

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**REFERENCES**


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