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RESEARCH PAPER

Preparation of Zinc Oxide-Graphene Composite Modified Electrodes for Detection of Trace Pb(II)

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Abstract: ZnO nanotubes were prepared via electrospinning $Zn(Ac)_2$-polyacrylonitrile-polyvinyl pyrrolidone precursor, followed by thermal decomposition of the above polymers from the precursor fibers. Scanning electron microscopy (SEM) and X-ray diffraction (XRD) characterization confirmed that the as-prepared ZnO nanofibers presented the hollow nanotube form, which was composed of ZnO nanoparticles with the size of about 40 nm in wurtzite crystal structure. By mixing with reduced grapheme oxide (RGO), the obtained ZnO-RGO composite modified glassy carbon electrode (ZnO-RGO/GCE) was successfully constructed by drop-coating, and used for the determination of Pb^{2+} in water. The sensitive response of the ZnO-RGO/GC electrode to Pb^{2+} in solution was demonstrated by square wave stripping voltammetry, with the response potential at –0.4 V. Under the optimized conditions, a good linear relationship between peak current and Pb^{2+} concentration was obtained in the range of 2.4×10^{-9}–4.8×10^{-7} M (R = 0.9970) by 10 min preconcentration at –1.0 V in 0.1 M HAc-NaAc buffer solution (pH 4.6). The detection limit was 4.8×10^{-10} M ($S/N \geq 3$). The ZnO-RGO/GC electrode had good stability. The practical analytical application of the ZnO-RGO modified electrode was assessed by the measurement of the actual water sample and the result was consistent with that obtained by ICP-MS.

Key Words: Electrospinning technique; Zinc oxide-graphene-glassy carbon electrode; Lead; Square wave stripping voltammetry

1 Introduction

ZnO is a very promising material for semiconductor[1]. One-dimensional ZnO nanomaterials, due to its unique catalytic, electrical characteristics[2] and low cost, were widely applied in various fields[3] such as chemically modified electrode[4,5] and molecular imprinted electrochemical sensor[6]. ZnO nanomaterials could be prepared through precipitation method[7], hydrothermal synthesis method[8], electrochemical deposition method[9] and so on.

Electrospinning is a facile technique to process nanofibers with controllable diameters and porosities[10] via selecting a suitable precursor. Moreover, the obtained fibers possess good homogeneity and fiber-origination[11]. Compared with ZnO nanofibers, ZnO nanotubes have larger specific surface area and higher porosity[12]. It is known that there are many hydroxy groups on the surface of ZnO nanotubes[13], resulting in coordination interaction between heavy metal ions and hydroxy groups, so ZnO nanotubes can be used as the adsorbents of heavy metal ions[4]. However, the poor conductivity of ZnO limited its application in electrochemistry[14]. The conductivity of ZnO could be improved by addition of RGO[15] to attain the ZnO/RGO composite, which extended the application of ZnO nanomaterials in electrochemistry.

Lead is a kind of heavy metal with high toxicity. Many analytical methods were developed for detection of Pb^{2+}, including atom absorption spectrophotometry (AAS)[16], atomic emission spectroscopy (AES)[17], inductively coupled plasma mass spectrometry (ICP-MS)[18] etc. However, the practical applications suffered from complication of operation and high cost. Square wave stripping voltammetry (SWSV)

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was employed to sensitively detect Pb^{2+} due to its inherent features, such as simple apparatus and high sensitivity[19].

In this work, ZnO nanotubes with high specific surface area were prepared via electrospinning $Zn(Ac)_2$-PAN-PVP precursor, followed by thermal decomposition of the above polymers from the precursor fibers. A ZnO-RGO modified GC electrode was constructed by mixing ZnO nanotubes with conductive RGO for the sensitive detection of Pb^{2+}.

2 Experimental

2.1 Chemicals and instruments

Polyacrylonitrile (PAN, M_w 150000), *N*,*N*-dimethylformamide (DMF) and Nafion (5%,) were purchased from Aldrich. Polyvinyl pyrrolidone (PVP, M_w 1300000) was from Acros, Belgium. Pb^{2+} standard solution (1.0 g L^{-1}), Zinc acetate ($Zn(CH_3COO)_2 \cdot 2H_2O$), $K_3[Fe(CN)_6]$ and all other reagents were purchased from Sinopharm Chemical Reagent Co., Ltd. Reduced grapheme oxide (RGO) was purchased from The Sixth Element Materials Technology Co., Ltd. (China); All the experiments were done using ultra-pure water (18. 2 MΩ cm, Thermo).

Electrospinning equipment was assembled by High voltage DC power (Tianjin Dongwen High-voltage Power Supply Co., Ltd.) and constant current syringe pump (Baoding Longer Precision Pump Co.,Ltd.). JSM-5600LV scanning electron microscope (SEM, JEOL Co., Ltd.) was used to observe the morphology of the sample. The electrochemical experiments were carried out by CHI 660 Electrochemical apparatus (Shanghai Chenhua instruments Co., Ltd.) in three electrode system with glassy carbon electrode as working electrode (d = 3 mm), Ag/AgCl (3 M NaCl) as reference electrode and platinum wire as auxiliary electrode.

2.2 Preparation of ZnO nanotubes

ZnO hollow nanofibers were prepared according to the literatures[10]. First, PVP and $Zn(Ac)_2$ (mass ratio of PVP/$Zn(Ac)_2$ = 2:0.25) were dissolved into 17% PAN-DMF solution, and the light yellow precursor solution of $Zn(Ac)_2$/PAN/PVP was obtained by heating at 60 °C with vigorous stirring for some time. Subsequently, the above precursor solution was drawn into a 5 mL syringe. The positive terminal of a variable high-voltage power supply was connected to the needle tip of the syringe while the other terminal was connected to the collector plate. 10 kV of positive voltage was applied to the tip, and the distance between the needle tip and the collector was 10 cm at a jet velocity of 1 mL h^{-1}, resulting in a dense web of electrospun composite nanofibers of $Zn(Ac)_2$/PAN/PVP being collected on the aluminum foil. Afterward, the above composite nanofibers were calcined by heating in air at a rate of 25 °C h^{-1} till 650 °C and held at this temperature for 2 h. After cooling down, the ZnO nanotubes were obtained.

2.3 Preparation of ZnO-RGO/GCE

ZnO nanotubes and RGO (in certain ratio) were mixed and dispersed in 0.005% Nafion-ethanol by ultrasonic agitation for 90 min to obtain ZnO-RGO suspension. Prior to the surface modification, the bare GC electrode was polished carefully with 1.0 and 0.3 μm alumina powder, respectively, and ultrasonic-cleaned with ultra-pure water and ethanol. ZnO-RGO composite modified glassy carbon electrode was obtained by drop-coating a certain amount of ZnO-RGO suspension above on clean GC surface and drying naturally.

As a control, ZnO modified glassy carbon electrode (ZnO/GCE) was obtained by similar method as above without RGO addition.

2.4 Procedure for detection of Pb^{2+}

The freshly prepared ZnO-RGO/GCE was dipped into 0.1 M HAc-NaAc buffer solution (pH 4.6) containing Pb^{2+} and kept at –1.0 V (*vs*. Ag/AgCl) for 10 min for preconcentration under stirring. The voltammogram of Pb^{2+} was recorded from –0.8 V to –0.1 V. After measurement, the electrode was regenerated by immersing the electrode into blank buffer solution and holding at +0.6 V (*vs*. Ag/AgCl) for 2 min to ensure that no peak appears within the potential range.

3 Results and discussion

3.1 SEM of ZnO nanotubes

Figure 1A illustrates the SEM image of the $Zn(Ac)_2$-PAN-PVP composite nanofibers. The nanofibers were uniform with the diameter of about 350 nm. After oxidation, the nanofibers became nanotubes with the form of "string-of-beads" (Fig.1B). Figure 1C shows the high magnified SEM image of ZnO nanotubes. It is clear that the nanotube was composed of compact ZnO nanoparticles with the size of about 40 nm, so that the nanotubes with hexagon-like wall were obtained. The spaces between the particles enlarged the specific surface area of nanotubes, increased active sites and made the diffusion of adsorbate easier. The inner and outer diameters of nanotubes were about 80 nm and 160 nm, respectively. The growth of ZnO nanoparticles along the fiber was mainly due to the stability of PAN in the fiber even at 400 °C. At this temperature, the ZnO was formed, and PAN could support the growth of ZnO nanoparticles.

3.2 XRD analysis of ZnO nanotubes

Figure 2 illustrates the X-ray diffraction pattern of ZnO