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Constructed 3D hierarchical porous wool-ball-like NiO-loaded AlOOH electrode materials for the determination of toxic metal ions

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ABSTRACT

The novel 3D hierarchical porous wool-ball-like NiO-loaded AlOOH hybrid (NiO/AlOOH-WB) was successfully fabricated through a facile hydrothermal approach followed in-situ growth of NiO nanoparticles (NPs) on AlOOH-WB support. Due to NiO NPs incorporated onto 3D AlOOH-WB surface, which not only increased electroactive area of the electrode but also showed the improved electron transfer rate examined by cyclic voltammetry (CV) and impedance analysis (EIS). NiO/AlOOH-WB/GCE displayed excellent electrochemical performance toward the simultaneous detection of thallium (Tl^{+}), lead (Pb^{2+}) and copper (Cu^{2+}) ions. More importantly, compared with nano AlOOH wire clusters (WC) and nano leafs (LF), 3D hierarchical architecture AlOOH-WB showed excellent electrochemical activity toward targets due to the desirable structural properties. As-fabricated NiO/AlOOH-WB/GCE electrode revealed a higher selectivity and sensitivity towards Tl^{+}, Pb^{2+} and Cu^{2+} with a low detection limit (S/N = 3) of 0.028, 0.025 and 0.030 μg/L and a broad linear range (0.1−100.0 μg/L). Furthermore, the fabricated sensor exhibited good stability, satisfactory reproducibility and good application prospect for the electrochemical detection of toxic metal ions individually and simultaneously.

1. Introduction

Recently, the release of toxic metal ions into the environment has aroused wide concern because of their high toxicity and non-biodegradable [1,2]. They are ubiquitous and can enter living organism through food chain and have a serious negative impact on human health [3,4]. Therefore, the development of rapid, sensitive and reliable strategies for the determination of trace metal ions is becoming increasingly important to environment and human health.

Electrochemical analysis, especially stripping voltammetry technique, has been widely recognized as a promising method for the determination of trace metals owing to its fast analysis speed, easy operation, low cost and good portability [5,6]. As the core component of the electrochemical sensor, the modified electrode material should have the ability to accumulate metal ions and provide fast electron transfer on the electrode surface. As a result, numerous attempts have been poured into designing advanced materials with excellent sensing properties to improve sensitivity, selectivity and stability.

Recently, AlOOH, which is an aluminum oxide hydroxide, has attracted considerable attention for its promising properties like high thermal and chemical stability, environmental friendliness, low cost and low toxicity, which has significant applications in many fields including adsorbents, composite materials and catalysts [7,8]. In addition, AlOOH was found to be inclined to interact with foreign molecules or metal ions [9], which can help to accumulate the targets onto the electrode surface. However, the use of AlOOH as a novel electrode material is still greatly inhibited due to its inherent low electron conductivity [10]. As reported previously, the surface of AlOOH contains abundance of hydroxyl groups [11] which can increase the number of anchoring sites, making it easy to construct AlOOH-based composites for exploiting its electrochemical sensing properties. In this regard, coupling AlOOH with noble metal nanoparticles (NPs) and carbon-based materials has been proven to be an effective method to improve conductive performance of the AlOOH. For example, Ag/AlOOH composite was prepared for the construction of non-enzymatic H_2O_2 sensor by employing AlOOH as the support [12]. Gao's group [13] developed a AlOOH-RGO nanocomposite for electrochemical simultaneous determination of Cd^{2+} and Pb^{2+} in drinking water. Although these methods can provide satisfying results, the high cost and

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complicated synthesis process restrict their competitive in wider practical applications. Therefore, developing inexpensive and easy-to-fabricate electrode materials with high electrochemical performance remains the focus.

In addition to the properties of the material, morphology is another very important factor that greatly affects electrode performance. It has been found that 3D hierarchical architectures have attracted increasing interest due to their unique structures, which can integrate the advantages of the single building block [14]. Up to now, various hierarchically structured AlOOH, such as hollow microspheres [15], spindle [16], cantaloupe [17] and flower-like [18] morphology have been prepared. These complex structures can not only endow materials with large accessible surface area, rich pores and the rapid path ways for ionic and electronic transport [19], but also serve as supports for loading other active materials [20,21], which may be present great potential applications in electrochemical reactions. Hence, it is of great importance to rationally design and fabricate electroactive materials with surface functionality and unique morphology, which make them promising electrode materials for electrochemical sensing.

In this work, 3D hierarchical porous wool-ball-like NiO/AlOOH composites (NiO/AlOOH-WB) were synthesized through a simple strategy, which were used as an effective sensing platform for the sensitive determination of Tl^{+}, Pb^{2+} and Cu^{2+}. Due to the unique structure and the abundance of hydroxyl groups, AlOOH-WB can act as the support for NiO NPs deposition and further improved the conductivity of the electrode material. The as-synthesized NiO/AlOOH-WB can effectively provide more electroactive sites and favorable paths for targets transport. Hence, the NiO/AlOOH-WB/GCE exhibited excellent electrochemical responses towards three metal ions, and revealed high sensitivity, good repeatability and stability. Finally, the proposed electrochemical sensor showed satisfactory results in the simultaneous determination of toxic metals in environmental samples.

2. Experimental

2.1. Reagents

$NaAlO_2$, $Al(NO_3)_3 \cdot 9H_2O$, nickel acetate and urea were bought from Sinopharm Chemical Reagent Co., Ltd. (Shenyang, China). Stock standard metal ion solutions (1.0 mg/mL) were prepared by dissolving Tl_2SO_4, $Pb(NO_3)_2$ and $Cu(NO_3)_2$ with ultrapure water and stored in a refrigerator when they were not used. The supporting electrolyte solution with different pHs were prepared by adjusting stock solutions of 0.1 M NaAc by adding 0.1 M HAc. All reagents were of analytical grade.

2.2. Apparatus

A CHI660D electrochemical workstation (Chenhua Instrument Co., Shanghai, China) was used for voltammetric measurements with a typical three-electrode system consisting of an Ag/AgCl reference electrode, a Pt wire auxiliary electrode and a modified or bare glassy carbon electrode (GCE) as working electrode. The morphologies and sizes of the samples were observed on transmission electron microscopy (TEM, JEM-2010, Japan) and a scanning electron microscopy (SEM, Hitachi SU8000, Japan, equipped with an energy-dispersive X-ray spectroscopy (EDS)). FT-IR spectroscopic measurements were performed on Nicolet-330 spectrometer using KBr pellet technique. X-ray diffraction (XRD) analysis using Cu Kα radiation was performed on Siemens D5000 Diffractometer (Germany). The load quality of NiO was analyzed by the inductively coupled plasma-atomic emission spectroscopy (ICP-AES, Perkin–Elmer).

2.3. Synthesis of electrode materials

2.3.1. Synthesis different morphology of AlOOH

3D hierarchical porous AlOOH-WB was synthesized through a facile hydrothermal method. Typically, 0.51 g $NaAlO_2$ and 1.44 g urea were dissolved into 50.0 mL deionized water followed by stirring for 1 h. The resulted solution was poured into a Teflon-lined stainless autoclave and heated at 160 °C for 3 h. Then, the white solid powder was obtained by centrifuging, rinsing with deionized water several times and dried at 60 °C overnight.

For comparison, 1D AlOOH nano wire cluster (AlOOH-WC) and 2D AlOOH nano leaf (AlOOH-LF) were also synthesized by hydrothermal reaction. For the synthesis of AlOOH-WC, 13 mmol $Al(NO_3)_3 \cdot 9H_2O$ and 16 mmol urea were added to the Teflon-lined autoclave and heated at 180 °C for 12 h. AlOOH-LF was prepared similarly to AlOOH-WC, in this case, 13 mmol $Al(NO_3)_3 \cdot 9H_2O$ and 30 mmol urea were used.

2.3.2. Preparation of NiO/AlOOH-WB composite

In brief, 1.2 g AlOOH-WB were added to 100.0 mL 1.0 mM nickel acetate aqueous solution under stirring. The solution was continuously agitated by a magnetic stirrer for 12 h. After which, the samples were collected by centrifugation and washed, and then dried in a vacuum oven at 60 °C. Finally, the resulting precursor was further annealed in air at 350 °C for 1 h to decompose acetate compound to generate NiO NPs.

2.4. Electrode preparation

9.0 mg of NiO/AlOOH-WB was suspended in 3.0 mL of sodium dodecyl benzene sulfonate (SDBS) solution by ultrasonic 30 min to obtain a 3.0 mg/mL uniform suspension. Prior to modification, the bare GCE was mechanically polished with alumina power slurry (0.05, 0.3, and 1.0 μm) and subsequently cleaned with ethanol and deionized water by ultrasonication. After dried at room temperature, 8.0 μL of suspension was dropped onto the cleaned GCE surface carefully and dried under an infrared lamp. For comparison, AlOOH-WC/GCE, AlOOH-LF/GCE and AlOOH-WB/GCE were also prepared.

2.5. Analysis procedure

Square wave anodic stripping voltammetry (SWASV) method was performed in a electrochemical cell containing 5.0 mL 0.1 M HAc–NaAc solution (pH 4.5) and the certain amounts of Tl^{+}, Pb^{2+} and Cu^{2+} standard solutions. All target metal ions were deposited for 90 s at −1.1 V, and the electrochemical responses were recorded within a potential window of −1.3V–0.4 V. Before analysis, the HAc–NaAc solution was purged with highly purified N_2 thoroughly for 10 min. Electrochemical impendence spectroscopy (EIS) was also measured using a solution of 10.0 mM $[Fe(CN)_6]^{3-/4-}$ containing 0.1 M KCl with 5 mV amplitude in a frequency range from 0.1 to 10 kHz at the open circuit voltage. All the measurements were conducted at room temperature.

3. Results and discussion

3.1. Characterization of electrode materials

The morphology of as-prepared samples were observed using SEM analysis. Fig. 1A clearly showed the entangled straw-bundle-like structure, which was comprised by AlOOH nanowires with the length over about 1 μm. It can be found from Fig. 1B that several nano leaf-like AlOOH samples were closely stacked, and the thickness of the leaf was about 20 nm. As shown in Fig. 1C, a highly