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Direct formation of (Co, Mn)$_3O_4$ nanowires/Ni composite foam for electrochemical detection

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ABSTRACT

The three dimensional (Co, Mn)$_3O_4$ nanowire array grown on Ni foam (3D (Co, Mn)$_3O_4$ nanowires/Ni composite foam) were successfully synthesized through a one-step hydrothermal approach and then directly applied as the electrode for heavy metal sensor. The structure of (Co, Mn)$_3O_4$ nanowires/Ni composite foam was characterized by the X-ray power diffraction (XRD), Scanning electronic microscopy (SEM) and Raman spectrum. Additionally, serving as a Hg(II) sensor, the (Co, Mn)$_3O_4$ nanowires/Ni composite foam electrode exhibited remarkable electrocatalytic activity towards Hg(II) oxidation with high limit of detection and sensitivity of 0.013 μM and 6.91 μA/μM, respectively. Furthermore, the (Co, Mn)$_3O_4$ nanowires/Ni composite foam electrode for sensor exhibited high cycling stability and long-term durability. These results are attributed to the unique features of the (Co, Mn)$_3O_4$ nanowires/Ni composite foam electrode, which enables the surface of (Co, Mn)$_3O_4$ nanowires grown on Ni foam to become highly accessible to the metal ion and provides more void volume for the reaction with metal ion. This work suggests that there is great potential in employing the 3D (Co, Mn)$_3O_4$/Ni composite foam as heavy metal ions sensors.

1. Introduction

Heavy metals are considered as low density chemical components, which are highly toxic [1]. Among various heavy metals, lead (Pb), cadmium (Cd), mercury(Hg), arsenic (As) and chromium (Cr) are the most probable causes for most of the heavy metal-related diseases [2,3]. Therefore, sensitive and selective determination of toxic heavy metals with a cost-effective and convenient procedure is paramount important. Various techniques have been developed for the detection of heavy metal ions, including electrochemical [4], mass spectrometric [5] and optical methods [6]. Due to the capability of short analytical time, low power cost, high sensitivity and easy adaptability for in-situ measurement [7], electrochemical detection methods have attracted great interest in the detection of heavy metal ions. Among various materials, nanostructured metal oxides such as ZnO, Fe_3O_4, NiO, SnO_2, ZrO_4, TiO_2, MgO and MnO_2 have also been widely used in the detection of heavy metals due to their interesting nanomorphological, functional biocompatible and non-toxicandcatalytic properties [1–7]. Unfortunately, in most cases, the metal oxides products generated by the most methods were often in powder type, which were further coated on the glass carbon electrode for electrochemical detection [1,2]. Therefore, the further electrode preparation leaded to additional cost and time. Furthermore, the low interaction and high contact resistance between metal oxide powder and glass carbon electrode would greatly decrease sensitivity and cycle stability of electrode, which greatly precluded their practical application in electrochemical detection [8]. Therefore, there is still a need for further study to explore and develop the performance of metal oxide by effective routes in order to achieve high performance for electrochemical detection application. Recently, the electrocatalytic active materials could be directly grown on Ni foam substrate as working electrode for electrochemical detection application [9–13]. For example, single layer of nickel hydroxide nanoparticles were covered on a porous Ni foam, which was applied in highly sensitive non-enzymatic glucose sensor [10]. Antibody-functionalized 3D Ni foam substrate as the trapping platform was detection of

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sulforhodamine B using impedimetric technique [11]. 3D porous Ni foam as a novel electrochemical sensing platform for nonenzymatic glucose detection was reported [12]. Ni_3S_2 nanosheet array grown on Ni foam as electrode was applied in highly sensitive non-enzymatic glucose sensor [13]. The electrode based on Ni foam has many advantages over other glass carbon electrode when used for electrochemical detection application. Firstly, Ni foam not only acts as a working electrode, but also functions as an effective electrocatalyst. What'more, the 3D porous surface electrode based on Ni foam leads to the enhanced electrocatalytic characteristics [9]. Secondly, it is a convenient way of preparing electrode of sensor for electrochemical detection by one-step synthesis method. Thirdly, the key advantage is its low cost and its ability to create sensing system with fast electron transport, revisable, selective and sensitive recognition over a wide range of concentrations and with the low detection limit in real-life samples [10]. In a word, the electrocatalytic active materials directly grown on Ni foam as electrode is applied in a novel and excellent sensor for electrochemical detection. However, there were few works reporting the metal oxide/Ni composite foam electrode for application in electrochemical detection, especially, detection of heavy metal ion. In addition to this, the $(Co, Mn)_3O_4$ array has been reported to be catalytically active for lithium–oxygen batteries in recent years due to be nanomorphological, functional biocompatible, non-toxicandcatalytic properties and low cost [14,15]. However, little research has so far been carried out on the use of $(Co, Mn)_3O_4$ array for electrochemical detection sensors.

Based on the above considerations, we developed a facile one-step hydrothermal approach to grow 3D $(Co, Mn)_3O_4$ nanowire array on Ni foam and then directly used them as the electrode for heavy metal sensors. Owing to the unique porous morphology, the $(Co,Mn)_3O_4$ nanowires/Ni composite foam electrode delivers significant electrochemical activity and cycling stability.

2. Experimental

2.1. Materials

Ni foam (110PPI, 320 g/m^2, Shanghai Ltd. China). CH_3COCH_3, HCl, $Co(NO_3)_2{\cdot}6H_2O$, $MnSO_4{\cdot}H_2O$, $CO(NH_2)_2$ and so on were analytically pure and purchased from Shanghai Reagents Company.

2.2. Preparations of $(Co, Mn)_3O_4$ nanowires/Ni composite foam electrode

The $(Co, Mn)_3O_4$ nanowires/Ni composite foam electrode was prepared by one-step hydrothermal method as shown in Scheme 1. 0.01mol $Co(NO_3)_2{\cdot}6H_2O$, 0.02mol $CO(NH_2)_2$ and 0.01mol $MnSO_4{\cdot}H_2O$ were dispersed in deionized water under prolonged magnetic stirring to form a homogeneous solution. Subsequently, the above solution was transferred into a Teflon-lined stainless steel autoclave with a volume of 100 ml. Meanwhile, a piece of Ni foam was put into above uniformity of mixture solution and heated at 90 °C for 10 h. After that, the composite foam was picked out, which was repeatedly washed with deionized water for three times. Finally, the composite foam was transferred into the crucible and calcined at 300 °C for 4 h in the air.

2.3. Characterization

The morphology and phase structure of sample was investigated by a field emission scanning electron microscope (FESEM, Hitachi S-4700).

Raman spectrum was collected on a Jobin-Yvon Lab Ram HR800 Raman spectroscope equipped with a 514.5 nm laser source.

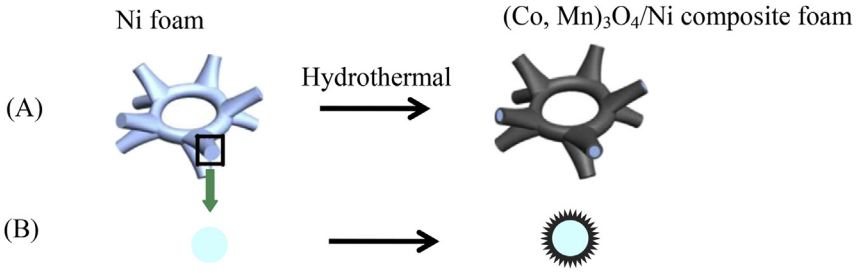
Structures of the as-prepared electrode were characterized by a Bruker D8 Avance X-ray diffractometer using Cu Ka radiation at a scan rate of 5°/min.

2.4. Electrochemical characterization

The electrochemical measurements (cyclic voltammetry) were conducted in a 3-electrode single-cell system in the electrolyte (0.1 M HCl) containing the target analyte (Hg^{2+}) with various concentration. The $(Co, Mn)_3O_4$/Ni composite foam electrode with 1.0 cm × 2.0 cm, Pt-wire and Ag/AgCl electrodes were used as working, counter and reference electrodes, respectively with CHI1140A electrochemical workstation (CHI110, Austin, TX). All electrochemical measurements were carried out at room temperature. To eliminate the effect of dissolved oxygen, the electrolyte was purged with nitrogen gas for half an hour.

3. Result and discussion

The XRD analysis of $(Co, Mn)_3O_4$ nanowires/Ni composite foam was carried out for the structure identification as shown in Fig. 1A. It clearly showed two sharp peaks at 44.4° and 51.8°, corresponding to the diffractions of (111) and (200) planes of Ni (JCPDS card No. 04-0850), respectively [16]. In addition, excluding the diffraction peaks of Ni foam, the small diffraction peaks at around 36.4° and 64.8° corresponded to (311) and (440) planes of $(Co, Mn)_3O_4$, which agreed well with the literature values (JCPDS Card no. 18–0408) [17]. These results indicated the formation of $(Co, Mn)_3O_4$ nanowires/Ni composite foam. These peaks were broad and weak, demonstrating that the crystallinity of the $(Co, Mn)_3O_4$ obtained from hydrothermal method at low temperature was relatively poor [18]. The formation of $(Co, Mn)_3O_4$ nanowires/Ni composite foam was further confirmed by the Raman spectrum as shown in Fig. 1B. It clearly showed two strong peaks at around 571.0 cm^{-1} and 681.0 cm^{-1}, corresponding to characteristic of ν (Co–O) and ν (Mn–O) modes of $(Co, Mn)_3O_4$, respectively [19]. The result further suggested that the $(Co, Mn)_3O_4$/Ni composite foam could be



Scheme 1. (A) Schematic illustration of the fabrication procedures of the $(Co, Mn)_3O_4$ nanowires/Ni composite foam electrode by the hydrothermal method. (B) Cross-section view of a Ni foam and composite foam branch.