



Synthesis and electrochemical performances of layered tungsten sulfide-graphene nanocomposite as a sensing platform for catechol, resorcinol and hydroquinone



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ARTICLE INFO

Article history:

Received 24 April 2013

Received in revised form 11 June 2013

Accepted 18 June 2013

Available online 26 June 2013

Keywords:

Layered tungsten sulfide-graphene nanocomposites

Catechol

Resorcinol

Hydroquinone

Simultaneous determination

ABSTRACT

The Layered tungsten sulfide (WS_2)-graphene (Gr) composites were prepared by a facile L-cysteine-assisted solution-phase method. Field emission scanning electron microscopy (SEM) and transmission electron microscopy (TEM) characterizations showed that layered WS_2 nanosheets were highly wrapped in the creasy Gr. The electrochemical properties of the nanocomposite film were investigated by electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV). The as-prepared WS_2 -Gr composite showed excellent electrochemical catalytic activities toward the oxidation of catechol (CT), resorcinol (RS) and hydroquinone (HQ). The superior electrochemical performances of the composites could be attributed to the robust composite structure and superior conductivity, large surface area and good flexibility of WS_2 -Gr composites. Some kinetic parameters, such as the electron transfer number (n), charge transfer coefficient (α) and the apparent heterogeneous electron transfer rate constant (k_s), were calculated. Differential pulse voltammetry was used for the simultaneous determination of CT, RS and HQ in their ternary mixture. The calibration curves for CT, RS and HQ were obtained in the range of 1×10^{-6} to 1×10^{-4} . The detection limits were $1 \times 10^{-7} \text{ mol L}^{-1}$ for RS and HQ, and $2 \times 10^{-7} \text{ mol L}^{-1}$ for CT ($S/N=3$). The developed sensor was used to detect CT, RS and HQ in environmental water samples with recoveries of 93.6–104.8%

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1. Introduction

In the recent years, there has been considerable interest in the study of transition metal dichalcogenide layered compounds, such as WS_2 and MoS_2 , a group of anisotropic materials with strong bonding within the layers and weak interlayer interactions [1,2]. As one of the representative members of this family, WS_2 has attracted considerable attention, due to its extensive applications as catalysts, lubricants, lithium battery, and so on [3–5]. It has an analogous structure to graphite, which are composed of three atom layers: a W layer sandwiched between two S layers, and the triple layers are stacked and held together by weak van der Waals interactions. Precisely because of this layered structure, atoms or molecules can be embedded by intercalation methods.

It is reported that the integration of carbon-based materials and metal or metal oxide nanoparticles usually shows synergistic effects in electrocatalytic applications [6,7]. Graphene (Gr) is a novel carbon material and has stimulated intense research interest because of its unique physical and chemical properties, such as high

surface area, high electrical conductivity, good chemical stability and strong mechanical strength [7,8]. However, many interesting and unique properties of Gr can be realized only after it is integrated into more complex assemblies. Some Gr-based hybrid materials show greater versatility when used as advanced electrode materials for the fabrication of electrochemical sensors and biosensors [9,10]. Most recently, we constructed a MoS_2 -Gr nanocomposite based electrochemical biosensor and used to sensitively determine acetaminophen, ascorbic acid and dopamine [11]. The MoS_2 -Gr based methods showed excellent analytical performance, such as high selectivity, broad dynamic range, and low detection limit.

Catechol (CT), resorcinol (RS) and hydroquinone (HQ) are three dihydroxybenzene isomers, which are widely used in cosmetics, tanning, pesticides, flavoring agents, medicines, and photography chemicals [12]. They are considered as environmental pollutants by the US Environmental Protection Agency (EPA) and the European Union (EU) due to their high toxicity and low degradability in the ecological environment [13]. These isomers are often coexisting in environmental samples [14]. Therefore, it is necessary to develop simple and rapid analytical method for simultaneous determination of dihydroxybenzene isomers. Some electrochemical methods have been developed for sensitive determination dihydroxybenzene isomers [15,16].

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In this paper, layered WS₂-Gr composites were synthesized by a modified L-cysteine-assisted solution-phase method and were firstly used to develop electrochemical sensor. The electrochemical behaviors of CT, RS and HQ at the modified electrodes were investigated by cyclic voltammetry. The performance of the sensor, such as linear range and detection of limit, was evaluated and discussed. The results demonstrated that WS₂-Gr nanocomposites were promising for fabrication of novel biosensors and electronic devices.

2. Experimental

2.1. Apparatus

Electrochemical measurements were performed on a CHI 660D Electrochemical Workstation (Shanghai CH Instruments, China). A conventional three-electrode system was used throughout the experiments. The working electrode was WS₂-Gr composites modified glassy carbon electrode (GCE) (3.0 mm in diameter); the auxiliary electrode was a platinum wire and the reference electrode was a saturated calomel electrode (SCE). The morphologies of the nanocomposite were recorded on a JEM 2100 transmission electron microscope (TEM) and a Hitachi S-4800 scanning electron microscope (SEM). The N₂ adsorption-desorption isotherms of the samples were measured using NOVA 2000 (Quantachrome, USA) in order to determine the specific surface areas. The specific surface area was calculated from the Brunauer-Emmett-Teller (BET) plot of the nitrogen adsorption isotherm.

2.2. Reagents

Na₂WO₄·2H₂O, L-cysteine, catechol (CT), resorcinol (RS), and hydroquinone (HQ) were purchased from Shanghai Chemical Reagent Corporation (analytical reagent grade, Shanghai, China). 0.1 mol L⁻¹ of three kinds of dihydroxybenzene stock solutions was prepared with double distilled deionized water and kept in darkness at 277.15 K. Working solutions were freshly prepared before use by diluting the stock solution. Phosphate buffer solutions (PBS, 0.1 M) with various pH values were prepared with Na₂HPO₄ and NaH₂PO₄ (analytical reagent grade, Sinopharm Chemical Reagent Co., Ltd., China) and adjusted by 0.1 M H₃PO₄ or 0.1 M NaOH solutions. All other chemicals not mentioned here were of analytical reagent grade and were used as received. Double distilled water was used throughout.

2.3. Synthesis of graphene oxide

Natural graphite powder was oxidized to graphite oxide by the modified Hummers method [17]. Specifically graphite powder (5.0 g) was dispersed in a solution containing 87.5 mL concentrated H₂SO₄ and fuming HNO₃ (45 mL) in an ice bath. 55 g KClO₃ was then added gradually. The mixture was stirred for 96 h and then diluted with deionized water. The graphite oxide (GO) prepared as such was re-dispersed in deionized water and then exfoliated to GO sheets by ultrasonication. A brown homogeneous supernatant was obtained by the repeated centrifuging and washing.

2.4. Synthesis of WS₂-graphene composite

WS₂-Gr composites were prepared by a modified L-cysteine-assisted solution-phase method [18]. 40 mL deionized water was added in the GO suspension prepared above and then 0.5 g of Na₂WO₄·2H₂O was added with stirring. After 30 min, the pH value of the mixture was adjusted to 6.5 with 0.1 M NaOH. 0.8 g L-cysteine was then added to the mixture followed by 80 mL deionized water.

After ultrasonication and stirring for 10 min, the mixture was transferred to a 100 mL Teflon-lined stainless steel autoclave, sealed tightly, and heated at 513.15 K for 24 h. After cooling to room temperature naturally, a black precipitate was collected by centrifugation, washed with deionized water and ethanol, and then dried in a vacuum oven at 353.15 K for 24 h.

2.5. Preparation of the modified electrode

A GCE was polished with 1, 0.3, and 0.05 μm alumina slurry sequentially, and then cleaned ultrasonically in absolute ethanol and water, respectively. The cleaned GCE was dried with nitrogen gas. The WS₂-Gr nanocomposites were dispersed in water with ultrasonication for 30 min to get a homogenous suspension (0.05 mg mL⁻¹). The WS₂-Gr modified electrode was prepared by casting 15 μL suspension onto the pretreated GCE using micropipet and dried in the air. For comparison, Gr modified GCE was prepared according to the same procedure.

3. Results and discussion

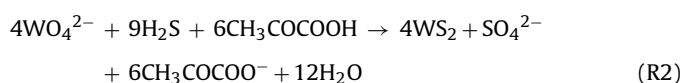
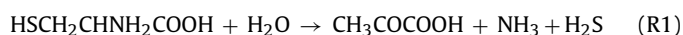
3.1. Characterization of WS₂-Gr composites

The morphology of the WS₂-Gr nanocomposite was examined by SEM and TEM. Fig. 1A showed the SEM image of Gr sheets, illustrating the flake-like shapes of Gr. Fig. 1B showed the SEM image of WS₂-Gr nanocomposite. It was clear that WS₂ distributed well on Gr sheets, evidencing the well-behaved assembly process. The cumulate layered sheets architecture would increase the contact area of WS₂-Gr with the analytes. The overlapping or coalescing of the Gr would form an interconnected conducting network, and facilitate rapid electronic transport in electrode reactions. Furthermore, this structure also enhances the stability of the WS₂-Gr composites due to superstrength of Gr. As shown in Fig. 1C, the synthesized Gr exhibit as ultrathin transparent nanosheets. It could be observed in TEM images that the nanosheets folded over on one edge with isolated fragments on its surface. The TEM image of WS₂-Gr composites in Fig. 1D shows that the typical layered WS₂ with a few layers are grown on the surface of Gr.

Gr and WS₂-Gr composite disperse in water by vigorous shaking, producing the homogenous black solution (Fig. 2A). However, Gr subsides to the bottom after left to stand for two days and WS₂-Gr still keep well disperse in the water (Fig. 2B), indicating good dispersibility of WS₂-Gr composite in water.

Fig. 2(C) shows the XRD patterns of Gr and WS₂-Gr composites. For Gr, the appearance of the (0 0 2) diffraction line in the XRD pattern give evidence that the graphite oxide was reduced to Gr. For WS₂-Gr composites, the presence of (0 0 2), (1 0 0) and (1 1 0) reflections suggests a few-layered structure for WS₂. The diffraction peaks display very weak, indicating the crystallinity of WS₂ is very poor. The poor crystallinity of WS₂ is attributed to the incorporation of the Gr inhibiting the growth of the layered WS₂ crystal during the hydrothermal process.

L-cysteine plays a role of reducing agent and sulfur donor during the whole hydrothermal process, in which L-cysteine released H₂S as a sulfide source as well as a reducing agent, resulting in the reduction of WO₄²⁻ precursors to WS₂ and reduction of GO to Gr. The reaction routes for the synthesis of WS₂ by L-cysteine could be expressed as follows [18]:



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