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Electrochemical detection of hydroquinone based on MoS_2/reduced graphene oxide nanocomposites

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ABSTRACT

Layered molybdenum disulfide/reduced graphene oxide (MoS_2/RGO) nanocomposites were synthesized by solvothermal method, and were characterized by high-resolution transmission electron microscopy (HRTEM), field-emission scanning electron microscopy (FE-SEM), X-ray diffraction (XRD), X-rayphotoelectron spectroscopy (XPS), and Raman spectroscopy. The electrochemical properties of the nanocomposites were studied by cyclic voltammetry and electrochemical impedance spectroscopy. Hydroquinone was selected as model molecular to investigate the electrochemical responses of the modified electrode. The results found that the synergetic effect of nanomaterials endowed the nanocomposite excellent electrocatalytic behavior towards the electrochemical reaction of hydroquinone. Under the optimal condition, hydroquinone can be sensitively detected in the range of 1–9 nM with the detection limit of 0.3 nM (S/N = 3). The obtained results revealed MoS_2/GRO composites exhibited superior electrochemical performance in the detection of hydroquinone, and it may have promising potential for electrochemical sensors.

1. Introduction

In the past decade, graphene has become the subject of a lot of experimental and theoretical investigation because of its attractive and exceptional physical and chemical properties [1–3]. Graphene based material has been developed as an advanced nanoelectrocatalyst for constructing electrochemical sensors [4–7]. Driven by the outstanding properties of graphene, other kinds of layered two-dimensional nanomaterials such as metal dichalcogenides have aroused increasing attention, which have been used for catalysis, batteries, light harvesting and solid lubricants [8]. Among these 2D nanomaterials, molybdenum disulfide (MoS_2) and its nanocomposites have been investigated mostly. Various applications of MoS_2-based nanomaterials have been focused in the fields like energy storage, electronic devices, and biomedical engineering [9–11]. However, few attentions have been put into its application as an electrode material for sensor because the electrochemical performance of few-layer MoS_2 nanosheets is often impeded by their inherent limitations. For example, the exfoliated MoS_2 nanosheets often suffer from poor cycling stability and rate capability, which are attributed to the poor electronic conductivity of MoS_2 as well as large volume change and restacking of MoS_2 nanosheets during the potential cycling [12,13]. The inherent stacking feature among MoS_2 layers severely decreases the amount of exposed active sites [14]. The combination of MoS_2 and other conducting materials may overcome this deficiency. Recently, several groups have reported that the integration of MoS_2 with conventional materials, such as metal nanoparticles, carbon materials, conductive polymers, and graphene, exhibited remarkable electrocatalytic performance and electrochemical energy conversion properties [15–20]. Due to their analogous microstructure and morphology, graphene can be used as an ideal substrate for MoS_2 sheets to grow on. The incorporation of graphene not only greatly improves the conductivity, but also facilitates the formation of MoS_2 nanosheets on the graphene. The MoS_2/graphene hybrids prepared by different methods have been demonstrated to exhibit excellent electron conductivity and electrochemical performance for lithium ion battery, electrochemical sensor, and electrocatalytic hydrogen evolution reaction [21–25]. Previous work revealed that MoS_2-graphene composite can be used to fabricate electrochemical sensor to sensitively determine acetaminophen, ascorbic acid, and dopamine [26]. However, the detection of hydroquinone with MoS_2/graphene modified electrode has not been reported. Herein, layered MoS_2/reduced graphene oxide (MoS_2/RGO) composites were synthesized by solvothermal reaction. The MoS_2/RGO composite was used to construct electrochemical platform. Hydroquinone was selected as a model molecular to evaluate the electrochemical properties of the layered MoS_2/RGO composites. The modified electrode exhibited remarkable electrochemical responses

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compared with MoS_2 and RGO modified electrodes, demonstrating that MoS_2/RGO nanocomposites were promising for fabrication of electrochemical sensors.

2. Experimental

2.1. Materials

All chemical used in this work were of analytical grade. $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$, hydroquinone, hydrazine solution (50 wt%), ammonia solution (28 wt%) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Graphene oxide (GO) were purchased from Energy Chemical Company. $(NH_4)_2MoS_4$ was synthesized according to the reported method [27]. Phosphate buffer solutions (PBS, 0.1 mol L^{-1}) with various pH values were prepared with Na_2HPO_4 and NaH_2PO_4 and adjusted by 0.1 mol L^{-1} H_3PO_4 and 0.1 mol L^{-1} NaOH solutions. Double distilled water was used throughout.

2.2. Preparation and characterization of MoS_2/RGO composite

$(NH_4)_2MoS_4$ was prepared according to previously reported literature [27]. In a typically procedure, 5 g $(NH_4)_6Mo_7O_{24}$ was dissolved in 15 mL double distilled water. Then, 50 mL concentrated ammonium hydroxide solution was added. H_2S was passed through the above solution to change the color of solution from yellow to deep red, and large amount of crystalline $(NH_4)_2MoS_4$ was obtained. The product was washed successively with cold water and methanol, and dried in a vacuum. The MoS_2/RGO nanocomposites were prepared by solvothermal reaction of $(NH_4)_2MoS_4$, $NH_2OH{\cdot}HCl$ and GO in aqueous solution according to the literature method [28]. In the reaction, the $(NH_4)_2MoS_4$ precursor was reduced to MoS_2 on GO film, and the GO was transformed to RGO by hydroxylamine hydrochloride reduction. In a typical process, 10 mg of GO was dispersed in the solution containing 20 mg of $(NH_4)_2MoS_4$ and 10 mL water. The mixture was sonicated for approximately 10 min before 0.1 mL of hydrazine solution (50 wt%) was added. The reaction solution was further sonicated for 30 min. Then, the mixture was transferred into a 30 mL Teflon-lined autoclave and heated at 200 °C for 12 h. After cooling to room temperature, the product was collected by centrifugation at 8000 rpm for 5 min, washed with DI water and re-collected by centrifugation. MoS_2 nanosheet was prepared by the similar method of MoS2/RGO except the absence of GO.

Scanning electron microscopy (SEM) image was obtained on a field-emission scanning electron microscopy (Zeiss Sigma 500). Transmission electron microscopy (TEM) images were obtained on a transmission electron microscopy (TEM, JEM-2100). The crystallinities of as-synthesized samples were characterized by powder X-ray diffraction (XRD) on a Bruker D-8 Advance diffractometer using Cu Kα (λ = 1.5406 Å) radiation at a scanning rate of 6°/min. X-ray photoelectron spectroscopy (XPS) was carried out on a Thermo ESCALAB 250XI multifunctional imaging electron spectrometer using the binding energy of C as the internal standard. Raman spectra were collected with a Horiba JY H800 Raman spectrometer using a 532 nm laser source.

2.3. Preparation of MoS_2/RGO modified electrode

A glassy carbon electrode (GCE, 3 mm in diameter) was polished with 0.05 μm Al_2O_3 power, and cleaned in an ultrasonic cleaner with alcohol and double-distilled water sequentially. The cleaned electrode was dried by nitrogen. The MoS_2/RGO suspension was prepared by dispersing 10 mg of MoS_2/RGO power in 10 mL of double-distilled water under sonication for 20 min, giving a quite stable black suspension. Then, 10 μL of the suspension was spread on the working area of cleaned bare GCE using a micropipette to prepare MoS_2/RGO modified GCE (denoted as MoS_2/RGO/GCE). MoS_2 and RGO modified electrodes were prepared by the same method for the comparison (denoted as MoS_2/GCE and RGO/GCE).

2.4. Electrochemical measurement and sample analysis

A conventional three-electrode cell configuration was employed for the voltammetric measurements. A modified electrode was used as the working electrode, with a saturated calomel reference electrode (SCE) and a platinum wire electrode for the reference and the counter electrode, respectively. Differential pulse voltammogram (DPV) was performed by potential scan from −0.15 V to 0.30 V with amplitude of 50 mV, pulse width of 50 ms and potential step of 4 mV vs SCE. Electrochemical impedance spectroscopy (EIS) was carried out at open circuit potential in 0.1 M KCl solution containing $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ (5 mM, 1:1). The frequency range was selected as 0.01 Hz–100 kHz, and potential amplitude was 5 mV. For the chromatography experiments, a detailed treatment was required for the tap water sample. The sample was cleaned by filtration through a filter paper, followed by filter membrane of 0.45 μm porosity and subsequent injection into the chromatographic system. The parameters utilized for HQ analysis was: injection volume of 20 μL, mobile phase comprising methanol (A) and water (B) in isocratic mode (25%), running of 7.5 min at a flow rate of 1.0 mL min^{-1} and DAD monitoring at 291 nm.

3. Results and discussion

3.1. Characterization of MoS_2/RGO nanocomposites

The morphologies of MoS_2/RGO were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), and Raman spectroscopy as shown in Fig. 1. For comparison, the characterization results of pure MoS_2 and RGO were listed in the Supporting materials as Figs. S1 and S2.

Fig. 1A showed SEM images of MoS_2/RGO, in which MoS_2 thin sheet formed flower-like shape. The TEM image (Fig. 1B) showed that MoS_2 nanosheet layered on the reduced graphene oxide. High-resolution TEM (HRTEM) image revealed that the typical layers MoS_2 with a few layers and the lattice distance of 0.62 nm corresponds with the (003) plane (Fig. 1C), and the lattice distance of 0.27 nm corresponds with the (101) plane (Fig. 1D) of MoS_2 hexagonal atomic lattices. The MoS_2/RGO hybrid was characterized by X-ray diffraction (XRD), and the broad diffraction peaks (Fig. 1E) indicated nano-sized MoS_2 crystal domains with hexagonal structure [powder diffraction file (PDF) no. 75-1539]. In order to further confirm MoS_2/RGO composite, Raman spectroscopic investigation was conducted. The Raman spectrum MoS_2/RGO (Fig. 1F) showed the characteristic peaks of MoS_2 at 378 and 407 cm^{-1} and the D and G bands of graphene oxide at 1340 and 1585 cm^{-1}, respectively [29].

Fig. 2A showed the XPS curves of MoS_2/RGO. The curve presented O 1s peaks, Mo 3d peaks, S 2p peaks and C 1s peaks in one spectrum. In the high-resolution XPS spectrum of the C 1s region (Fig. 2B), the strong peak of C=C indicated the present of graphene, and the weak C−O peak suggested the present of oxygen atoms on RGO. The XPS spectrum at the Mo 3d region (Fig. 2C) can be deconvoluted into four peaks, and the peak at 226.4 eV corresponds to the S 2s of MoS_2 [30]. Two characteristic peaks at 229.6 eV and 232.7 eV corresponded to Mo $3d_{5/2}$ and Mo $3d_{3/2}$ of MoS_2, respectively. The high binding energy peak at 235.9 eV corresponded to the presence of Mo−O bonds, which should be attributed to the good coupling between Mo and oxygen function groups of RGO, indicating the formation of MoS_2/RGO composite [29]. The peaks at 162.0 and 163.1 eV at the S 2p region (Fig. 2D) corresponded to S $2p_{1/2}$and S $2p_{3/2}$ lines of MoS_2, respectively [30]. Meanwhile the binding energies at 164.4 and 168.8 eV can be ascribed to the S_2^{2-} species and S^{4+} species on the surface or edges of MoS_2 nanosheet, respectively [30–32]. XPS analysis indicated that the interaction of electrons structure between MoS_2 and RGO could dramatically enhance the conductivity [33].