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Novel molybdenum disulfide nanosheets–decorated polyaniline: Preparation, characterization and enhanced electrocatalytic activity for hydrogen evolution reaction

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ABSTRACT

Novel molybdenum disulfide nanosheets–decorated polyaniline (MoS_2/PANI) was synthesized and investigated as an efficient catalyst for hydrogen evolution reaction (HER). Compared with MoS_2, MoS_2/PANI nanocomposites exhibited higher catalytic activity and lower Tafel slope for HER in H_2SO_4 solution. The amount of 19 wt% PANI for coupling with MoS_2 resulted in a high current density of 80 mA cm^{-2} at 400 mV (vs. RHE). In addition, the optimal MoS_2/PANI nanocomposite showed impressive long-term stability even after 500 cycles. The enhanced catalytic activity of MoS_2/PANI nanocomposites was primarily ascribed to the effective electron transport channels of PANI and the increase of electrochemically accessible surface area in composite materials, which was advantageous to facilitate the charge transfer at catalyst/electrolyte interface.

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1. Introduction

Hydrogen is one of the most promising energy sources for sustainable energy applications because of its numerous advantages, such as recycling, pollution-free and fuel efficient [1–4]. Electrochemical reduction of water is considered to be a simple and economical way to produce hydrogen in high purity and large quantity [1]. An efficient catalyst for hydrogen evolution reaction (HER) is usually required to reduce the overpotential in HER process and achieve large exchange current density [5]. At present, Pt-based catalysts are considered to be the most efficient HER catalysts due to their superior electrocatalytic property and robust stability [6]. Unfortunately, Pt is an extremely scarce resource, making it expensive to use on a large scale for hydrogen production technologies, which push forward the intensive study on the cost-effective alternative to Pt catalyst [7].

Recent years have witnessed the wide development of cheap layered transition-metal sulfides with high catalytic activity, including NiS_2, CoS_2, MoS_2 and WS_x [8–12]. Among these alternatives, MoS_2 has received tremendous attention owing to its earth-abundant composition and high activity. Both theoretical and experimental studies have demonstrated that the electrocatalytic activity of MoS_2 increases substantially when the surface active sites grow in number or quantity and, however, the bulk material is relatively inert owing to the fewer surface active sites [13]. Therefore, different methods have been developed to reduce the size of MoS_2 to the nanoscale, such as hydrothermal method, gas phase synthesis and electrochemical method [14–16]. Besides the aspect of active sites, the conductivity of catalyst is another crucial factor which can affect the electrocatalytic activity because high conductivity can ensure fast electron transport during the HER catalytic process [17]. On the basis of the above two key factors, enormous attempts have been made to focus on the improvement of either the number of active sites or the conductivity of MoS_2 electrocatalyst [18,19].

Normally, MoS_2 is a semiconductor which contains a mixed metallic 1T phase and a semiconducting 2H phase, and the latter constrains the conduction of the material [20]. In order to attain a faster charge transport of MoS_x-based catalysts, carbon-based materials have been used as conductive networks or supporting templates [21–23]. For instance, Cai et al. developed MoS_2/SWCNT composites, and in which SWCNT served as a conductive solid support to load MoS_2 catalyst [21]. Ma et al. utilized the reduced graphene oxide paper as a flexible direct substrate to absorb the

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MoS_2, which effectively compensated the poor conductivity of nanosized MoS_2 [22]. Significantly, the conductive templates or supports are proposed to be an effective way to mediate the aggregation of MoS_2, which may improve the catalytic activity of the host materials.

As a member of electro-conductive polymers, polyaniline (PANI) is a promising candidate for use as a conductive substrate due to the high electrical conductivity, environmental durability and easiness of preparation. The combination of PANI with MoS_2 appears to be a promising way to increase the conductivity and mediate the aggregation of MoS_2. However, to the best of our knowledge, the nanocomposite of MoS_2 nanosheets–decorated PANI with similar structures has not previously been applied in the field of HER.

In this work, we presented a simple hydrothermal method to fabricate MoS_2/PANI nanocomposites using PANI as conductive substrate in aqueous solution containing $Na_2MoO_4 \cdot 2H_2O$ and $CS(NH_2)_2$ precursors. The as-obtained products evenly integrated MoS_2 ultrathin nanosheets with PANI into the primary architecture, resulting in the novel polymer-hybrid nanocomposites. Such nanostructures of MoS_2/PANI are expected to exhibit enhanced HER electrocatalytic activity and fulfill the advantages of both high electrocatalytic activity of MoS_2 and superior conductivity of PANI.

2. Experimental

2.1. Reagents and materials

Aniline monomer (ANI), ammonium persulfate (APS), cetyltrimethylammonium bromide (CTAB), methylbenzene, ethanol, H_2SO_4 (98 wt%), hydrazine monohydrate ($N_2H_4 \cdot H_2O$, 80 wt%), Nafion solution (5 wt%) and HCl were analytical grade and purchased from Aldrich Chemical Reagent Co., Ltd. $Na_2MoO_4 \cdot 2H_2O$ and $CS(NH_2)_2$ were purchased from Chengdu Chemical Reagent Co., Ltd. (Chengdu, China). ANI was purified through distillation under reduced pressure and stored at low temperature before use. All chemicals were analytically pure grade. Distilled water was used throughout the whole experiments.

2.2. Sample preparation and characterization

PANI was prepared by chemical polymerization of aniline. A homogeneous mixture was formed by adding 5.0 mmol CTAB into 200 mL 0.20 M HCl solution (0 °C) and the mixture was stirring for 10 min. Then, 20.0 mmol APS was added into the mixture, and the resulting solution immediately turned milky white and viscous. The solution was transferred slowly to the beaker containing 20.0 mmol ANI and 50 mL methylbenzene (0 °C), and a static organic/aqueous interface was formed. Subsequently, the reaction system was placed in an ice-bath for 24 h. The obtained precipitate was washed successively with deionized water and ethanol and then collected by filtration and dried at 60 °C under vacuum.

MoS_2/PANI nanocomposites were prepared as follows. 4.50 mmol $Na_2MoO_4 \cdot 2H_2O$ was dissolved in 10 mL distilled water, and 0.11 mL $N_2H_4 \cdot H_2O$ as reducing agent was added. The mixture solution was stirred for 30 min, and then 22.5 mmol $CS(NH_2)_2$ as sulfur precursor was added and stirred for another 10 min, followed by the addition of as-prepared PANI with different weight percentages and ultrasonication. The final mixture was transferred into a 100 mL Teflon-lined stainless steel autoclave and heated at 185 °C for 16 h. After cooling naturally, the black precipitate was collected by centrifugation, washed with deionized water and ethanol several times and then dried at 60 °C for 24 h to obtain MoS_2/PANI nanocomposites. MoS_2/PANI samples prepared in the presence of PANI with different weight percentages (0, 5, 10, 15, 17, 19, 20, 21 and 25 wt%) were marked as MoS_2, MoS_2/PANI-1, MoS_2/PANI-2, MoS_2/PANI-3, MoS_2/PANI-4, MoS_2/PANI-5, MoS_2/PANI-6, MoS_2/PANI-7 and MoS_2/PANI-8, respectively.

The crystallographic structures of as-prepared samples were characterized by X-ray diffraction analyzer (XRD, X' Pert PRO, Netherlands) with Cu K_α radiation ($\lambda = 0.154060$ nm) and recorded from 3.0° to 80° at a speed of 2.0° per minute. The chemical states of catalyst samples were examined on Perkin-Elmer PHI-5702 multifunctional X-ray photoelectron spectroscope (XPS, Physical Electronics, USA) using Al K_α radiation of 1486.6 eV as excitation source. All XPS spectra were calibrated using C 1s peak at 284.6 eV. Fourier transform infrared spectra were obtained with a Fourier transform infrared spectrometer (FTIR, Nicolet 5700, USA) in wavelength range of 4000 ~ 400 cm^{-1} with KBr pellet method. The morphologies of as-prepared samples were investigated using a scanning electron microscope (SEM, Ultra 55, Germany).

2.3. Electrode preparation and electrochemical measurements

To prepare the working electrode, 5.0 mg MoS_2/PANI nanocomposites and 10 μL 5 wt% Nafion solution were dispersed in 1.0 mL water/ethanol (50:50 v/v) mixed solvent, followed by ultrasonication for 30 min. And 5.0 μL obtained mixture was dropped onto polished glassy carbon electrode (GCE, 3 mm in diameter) surface. Then, the GCE was dried at room temperature to yield a catalyst loading of 0.36 mg cm^{-2}.

Electrochemical measurements were performed with a PARSTAT 2273 electrochemical workstation (Princeton Applied Research, USA) with MoS_2/PANI nanocomposites modified above GCE as working electrode, a saturated calomel electrode (SCE) as reference electrode and a platinum electrode as counter electrode. Steady-state polarization curves were performed in 0.50 M H_2SO_4 at a scan rate of 5 mV s^{-1}. Tafel slopes were obtained by linear fitting the plot of overpotential versus log current density (η vs. log j). Electrochemical impedance spectroscopy (EIS) measurements were examined in the frequency range of 10^5 to 10^{-2} Hz at open circuit potential and the perturbation amplitude was 5 mV. Durability in 0.50 M H_2SO_4 was tested by cyclic voltammetry (CV) with a scan rate of 50 mV s^{-1} for 500 cycles.

Before the electrochemical measurements, the electrolyte was purged with N_2 for 1 h to remove oxygen completely. All of the potentials reported were calibrated to the reversible hydrogen electrode (RHE).

3. Results and discussion

It was found in the latter part of this work that the structures and morphologies of MoS_2/PANI-1, MoS_2/PANI-2, MoS_2/PANI-3, MoS_2/PANI-4, MoS_2/PANI-5, MoS_2/PANI-6, MoS_2/PANI-7 and MoS_2/PANI-8 were similar. So, only MoS_2/PANI-5 sample was selected to represent the results of XRD, XPS, FTIR and SEM.

3.1. Structural and morphological characterization of as-prepared samples

Shown in Fig. 1 were XRD patterns of MoS_2, PANI and MoS_2/PANI-5 nanocomposite, respectively. Clearly, MoS_2 showed diffraction peaks at 13.9°, 32.9°, 40.0° and 60.0° corresponding to (002), (100), (103) and (110) faces, respectively, which could be assigned to the hexagonal MoS_2 (2H-MoS_2, JCPDS no. 37-1492). The peaks of PANI at 15.5°, 20.4° and 25.4° corresponded to the primary diffraction of (011), (020) and (200) planes [24]. It was noted that the weak peak at 20.4° of as-prepared MoS_2/PANI-5 nanocomposite revealed the perfect combination of MoS_2 and

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