



Research paper

The effect of reduced graphene oxide on MoS₂ for the hydrogen evolution reaction in acidic solutionLv Jinlong^{a,*}, Yang Meng^a, Liang Tongxiang^b, Ken Suzuki^a, Hideo Miura^a^a Fracture and Reliability Research Institute, School of Engineering, Tohoku University, Sendai 9808579, Japan^b School of Materials Science and Engineering, Jiangxi University of Science and Technology, Ganzhou, Jiangxi 341000, China

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ABSTRACT

The pure MoS₂ and MoS₂@reduced graphene oxide were synthesized on commercially available Ti plate by one-step hydrothermal method. The hole microspheres were successfully synthesized. The resulting MoS₂@reduced graphene oxide electrode on Ti plate exhibited higher catalytic activity than pure MoS₂ electrode on Ti plate for hydrogen evolution reaction. In addition, the excellent cycling stability was also obtained in MoS₂@reduced graphene oxide electrode on Ti plate. Such enhanced catalytic activity and excellent cycling stability occurred due to the abundance of catalytic edge sites, high specific surface area and the unique synergic effects between the MoS₂ and reduced graphene oxide.

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1. Introduction

The hydrogen has been regarded as a green and highly efficient energy resource for combustion [1]. Electrochemical water splitting technique could be an economic method to generate hydrogen [2]. Platinum has been considered as the most efficient electrocatalyst for hydrogen evolution reaction (HER) due to its low overpotential and small Tafel slope [3]. However, expensive price and scarcity hindered its large-scale commercial application. MoS₂ was regarded as promising candidate electrocatalysts for HER in acidic solution. Jaramillo et al. [4] suggested that the hydrogen evolution enhanced linearly with the number of edge sites on the MoS₂ catalyst by electrocatalytic activity measurements. Amorphous MoS₂ nanosheet arrays directly deposited on carbon cloth exhibited superior catalytic activity and stability for the HER in acidic solutions due to the abundant exposed edge sites [5]. MoS₂ nanostructures which consisted of many vertically aligned ultrathin MoS₂ nanosheets with preferentially exposed edges facilitated electron transfer and exhibited high electrocatalytic activities [6]. The molybdenum sulfide nanosheet arrays on Ti plate were obtained by hydrothermally process and exhibited 10 mA cm⁻² at overpotentials of 108 mV in acidic media due to its unique microstructures [7].

However, the low electrical conductivity ($\sigma = 2.09 \times 10^{-6} \text{ S cm}^{-1}$ at 298 K) of MoS₂ as a semiconductor material still inhibited its

commercial application for production H₂. Therefore, recently, highly conducting 1T phase MoS₂ nanosheets exhibited excellent catalytic activity for HER with a notably low Tafel slope of 40 mV/dec [8]. The investigator also found that the edges of the MoS₂ nanosheets are not the main active sites. MoS₂@carbon hybrid materials obtained by a one-step direct laser writing exhibited superior catalytic performance and stability for the HER in acidic solution [9]. The improved electrocatalysts for the HER could be attributed to small-sized MoS₂ particles and synergetic effect from the carbon matrix and the MoS₂ nanoparticles. Geng et al. [10] synthesized few-layer MoS₂ nanosheets on 3D graphene/nickel structure and found that as-prepared hybrid exhibited superior electrocatalytic activity towards HER due to a large number of edge sites, moreover, obtained backbone structure which facilitated charge transport during electrochemical reaction. MoS₂ nanoflowers coated on reduced graphene oxide (RGO) paper synthesized by one-pot solvothermal method exhibited a low overpotential of -0.19 V with a Tafel slope of 95 mV/dec [11]. The MoS₂@mesoporous graphene foams nanocomposites exhibited low Tafel slope of 42 mV/dec due to abundance of catalytic edge sites, high accessible surface area and the unique synergic effects between the mesoporous graphene foams and MoS₂ [12]. MoS₂ nanoparticles on reduced graphene oxide hybrid by selective solvothermal synthesis also exhibited superior electrocatalytic activity for HER with a Tafel slope of 41 mV/dec [13]. The significant improvement for the HER was attributed to a large amount of catalytic edge sites and excellent electrical coupling of MoS₂ nanoparticles with graphene network. CoP or CoSe₂ nanosheet

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arrays can be synthesized directly on Ti plate for electrochemical hydrogen evolution [14,15]. Ti plate was used as an excellent supporting substrate due to its good plasticity, superior electrical conductivity, high temperature tolerance and superior corrosion resistance [16]. The commercially available Ti plate can be used as the cheap current collector [17]. The direct growth of sulfides on a conducting Ti substrate which acts directly as electrode can be beneficial for catalytic performance.

Therefore, in this study, pure MoS₂ and MoS₂@RGO were formed on commercially available Ti plate by hydrothermal method. Then the efficiency of two electrodes for the HER in acid medium was evaluated by electrochemical technique.

2. Methods

2.1. Materials preparation

Before MoS₂ synthesis, a piece of Ti plate (1 cm × 1 cm in size) was mechanical polished for 2 h using a 0.02 μm colloidal silica suspension, then it was ultrasonically cleaned in acetone, ethanol and deionized water each for 30 min and dried at 60 °C in vacuum oven for preventing surface oxidation. Then, Ti plate was immersed into 12 M hydrochloric acid for 25 min at 60 °C for removing surface oxides. Finally, treated Ti plate was rinsed with deionized water and dried. The graphene oxide (GO) was synthesized from natural graphite (Nanjing Graphite Company) by a modified Hummers method according to previous report [18]. MoS₂ was synthesized based on a hydrothermal method. In brief, 3.7 mmol of ammonium molybdate tetrahydrate ((NH₄)₆Mo₇O₂₄·4H₂O), 32.4 mmol of thiourea and 5 mmol urea were dissolved in 70 ml of ultrapure water and the mixtures were vigorously stirred for 20 min. Then homogeneous solution and Ti plate were transferred to a 100 ml Teflon-lined stainless steel autoclave and maintained at 220 °C for 24 h. After the autoclave cooled down to room temperature, the Ti plate was taken out and rinsed with deionized water several times and dried at 60 °C in vacuum oven. In addition, the same synthesis process was adopted with the addition of 0.5 g RGO for comparison. The mass loading of the electrodes was determined by comparing the mass difference between the original Ti plate and the Ti plate with pure MoS₂ or MoS₂@RGO after hydrothermal test by high-precision analytical balance (model CPA225D, Sartorius, resolution is 0.01 mg). The obtained loading mass of on Ti plate was estimated to be about 5 mg cm⁻² and 5.2 mg cm⁻² for pure MoS₂ and MoS₂@RGO composites, respectively.

2.2. Materials characterizations

XRD (X-ray diffraction) patterns were recorded by a Rigaku Ultima IV diffractometer, using Cu-Kα radiation at 40 kV and 40 mA. The morphology of synthesized products was observed by scanning electron microscope (SEM JSM5800) instrument. The value of specific surface area was estimated using the Brunauer-Emmett-Teller (BET) method at 77 K. The pore size was achieved from the adsorption and desorption branch of the nitrogen isotherms by Barrett-Joyner-Halenda method. The detailed microstructures were also observed with transmission electron microscopy (TEM and HRTEM JEM-2010 FEF; 200 kV).

2.3. Electrochemical measurements

A three-electrode system was used to measure the response of the electrodes in 0.5 M H₂SO₄ aqueous solution. The electrochemical measurements were conducted with the CHI660E electrochemical station (Chenhua instrument Co. Shanghai, China). The

Ti plates loaded with MoS₂ or MoS₂@RGO were directly used as the working electrode, platinum mesh was used as counter electrode and saturated calomel electrode (SCE) was reference electrode. All the potentials measured in this study were calibrated with the reversible hydrogen electrode (RHE) according to the equation: E_{RHE} = E_{SCE} + 0.2412 + 0.05916 × pH.

3. Results and discussion

Fig. 1a shows a evident characteristic peak at 2θ angle of 12°. This indicates that there are oxygen functional groups between graphite layers for synthesized GO. The synthesized product was peeled off from Ti plate. The diffraction peaks agree with the standard pattern of 2H-MoS₂ (JCPDF 65-0160) in Fig. 1b [19]. This indicates that MoS₂ has been successfully synthesized by hydrothermal treatment. Moreover, evident diffraction peak at 23° corresponds to RGO in MoS₂@RGO composite coating. The result also elaborates that the GO can be reduced by hydrothermal process. In addition, in Fig. 1b, the peak of (002) plane for MoS₂ shows a shift left for MoS₂@RGO composite. This indicates interplanar spacing broadens due to adding to RGO according to Bragg's law. The typical Nitrogen adsorption-desorption tests results are showed in Fig. 1c. The specific surface area of MoS₂ or MoS₂@RGO composites is 105.3 m²/g and 212 m²/g, respectively, according to Nitrogen adsorption-desorption analysis. Moreover, the pore-size distribution curves of synthesized products were analyzed by the Barrett-Joyner-Halenda (BJH) method. The MoS₂ shows a more prominent pore size around 26 nm in Fig. 3d. While the same analysis exhibits a two peak distribution for pore size in MoS₂@RGO composites. This demonstrates that there are mesopores and macropores in MoS₂@RGO composites. Higher specific surface area and particular pore distribution could significantly improve the HER of the MoS₂@RGO composite electrode.

Figs. 2a and b show the SEM images of MoS₂ and MoS₂@RGO composite coating on Ti plate. The 'microspheres' like structures occur, regardless of addition to RGO. However, the size of MoS₂@RGO composite microspheres is more uniform than that of pure MoS₂. MoS₂@RGO composite microspheres are composed of petals, as shown in the insert of Figs. 2b. The obtained hollow MoS₂ and MoS₂@RGO composite microspheres will no doubt improve the HER electrocatalytic performance due to the presence of rich active sites and the validity of the synergistic structure [20].

The typical HRTEM images in Figs. 3a and b clearly show that most of synthesized products have a few layer MoS₂. The dispersed and curving MoS₂ bands are inserted into RGO in Fig. 3b. Insert in Fig. 3b shows that the band with an interlayer spacing of 0.63 nm is corresponding to the (002) plane of MoS₂. Insert also shows that RGO layers contain some very small pores after hydrothermal reaction. Comparing with MoS₂, larger pore size of MoS₂@RGO composite microspheres could indicate more defects. In addition, well dispersive MoS₂ bands also destroyed the strong self-stack of RGO and facilitated to induce more defects. More defects would result in higher activity for chemical reaction for HER. Xie et al. [21] suggested that improved electrochemical reaction of MoS₂ ultrathin nanosheets was attributed to the defect-rich microstructures. Therefore, the defect-rich MoS₂@RGO composite microspheres could induce excellent HER activity in this study.

As shown in Fig. 4a, MoS₂@RGO composite on Ti plate electrocatalyst reveals a lower onset overpotential than the bare MoS₂ on Ti plate. Pt/C electrode also was tested for comparing. These results clearly indicate that RGO on MoS₂@RGO composite electrode could facilitate the HER process. The corresponding Tafel plots of three electrodes are shown in Fig. 4b. It can be seen that MoS₂ and MoS₂@RGO composite electrodes on Ti plate show the Tafel slopes of 95.2 mV/dec and 52.2 mV/dec, respectively. Merki

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