

An Advanced Hierarchical MoS₂/Mn for High Performance Hydrogen Evolution Reaction

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Abstract. Recently, molybdenum disulfide (MoS₂) and other transition metal dichalcogenide (TMD) compounds represent a class of layered materials which have received tremendous attention due to their promising electronic, electrode material, catalytic, and mechanical properties. Currently, many researchers have investigated molybdenum disulfide (MoS₂) which represents one of the most promising catalysts among TMDs due to the semiconducting nature and enhanced photoluminescence properties for hydrogen evolution. In this work, a systematic study of the relationship between the hydrogen evolution reaction (HER) and the physiochemical properties of layered MoS₂ and doped derivatives has been performed. HER measurements with chemically modified MoS₂ nanosheets were carried out using a three-electrode cell with a 0.5 M sulfuric acid electrolyte. All of the modified MoS₂ nanosheets exhibit variation of overpotential catalytic activity towards the hydrogen evolution reaction. Taking into account this experimental result a configurational change will significantly enhance physical and chemical properties.

1. Introduction

Hydrogen as a future energy carrier has been intensively pursued due to its renewable and environmentally friendly properties compared to coal, gasoline, methane, etc. The sustainable hydrogen evolution reaction (HER) from the water splitting reaction is a clean and environmentally benign reaction pathway, which has been paid more attention by researchers all of the world [1, 2]. Pt and Pt-based materials are high efficient electrocatalysts for HER in both acidic and alkaline conditions. However, the high cost and scarcity of Pt are limited the widespread use as electrocatalysts for HER. Development of electrocatalysts that are lowly cost, highly active, and operable in benign conditions remains a challenging task [3]. Recently, metal sulfides (MoS₂, FeS₂, etc.), [4, 5] hybrid materials (carbon supported metal oxide, reduced graphene oxide supported metal sulfides, doped metal elements etc.) [5] or carbon-based (carbon nanotubes, graphitic carbon, etc.) [6, 7] have been intensively studied as substitutes for Pt-based electrocatalysts, which have high active HER activity and stability. Herein, we are reporting that MoS₂ serves as an active HER electrocatalyst with hybrid metals.

2. Experimental

2.1 Synthesis of the MoS₂/Mn heterostructure

All of the reagents were analytical grade and used without further purification. A 1.40g mixture of NH₂CSNH₂ and Na₂MoO₄ was added into 55 mL distilled water, and stirred until complete dissolved. The mass ratios of NH₂CSNH₂ and Na₂MoO₄ were controlled to be 3 : 4. Next, 0.016 g MnN₂O₆·XH₂O was added into the above mixture and a milky white suspension was formed after stirring for 2 h. Afterwards, the suspension was transferred to a 100 mL Teflonlined autoclave and the temperature was maintained at 240^oC for 24 h. The final products were rinsed three times with

distilled water and then ethanol, before being dried at 60°C for 10 h. Pure MoS₂ were prepared through the same procedure using individual Na₂MoO₄ and NH₂CSNH₂ precursors.

2.2 Characterization

The morphology was determined by scanning electron microscopy (SEM) using an FEI Nova Nano SEM 450. Samples were coated to decrease charging with an Au-Pt alloy with a Polaron model E5100 instrument. All the synthesized materials were ground to a fine powder in an agate mortar. The Powder X-ray diffraction (XRD) analysis was carried out at room temperature on a Rigaku Ultima IV diffractometer (CuK radiation, $\lambda = 1.5406\text{\AA}$). A beam voltage of 40 kV and a current of 44 mA were used.

2.3 Photoelectrochemical measurements

The electrocatalytic activities of the as-synthesized materials were examined in acidic aqueous (0.5M H₂SO₄, Figure 3) solutions.

3. Results and discussion

Figure 1(a-e) shows field-emission scanning electron microscopy (FESEM) images for the macroporous molybdenum (MoS₂/Mn) sample with various magnification scales. In terms of SEM results, the MoS₂/X sample is composed of ball-floc-like particles, which have sizes smaller than 4 μm . The porosity was formed by the aggregation of nanoparticles, and the pores are the connected lamellar structure. With lower magnification images (Figure 2c), it is easier to observe the good dispersion of the pores. For comparison, the SEM image of MoS₂ sample was also recorded (Figure 1a-c) which is composed of a giant square crystal structure (5–10 μm) with nanopore on the surface. Lamellar structure could be observed in this sample.

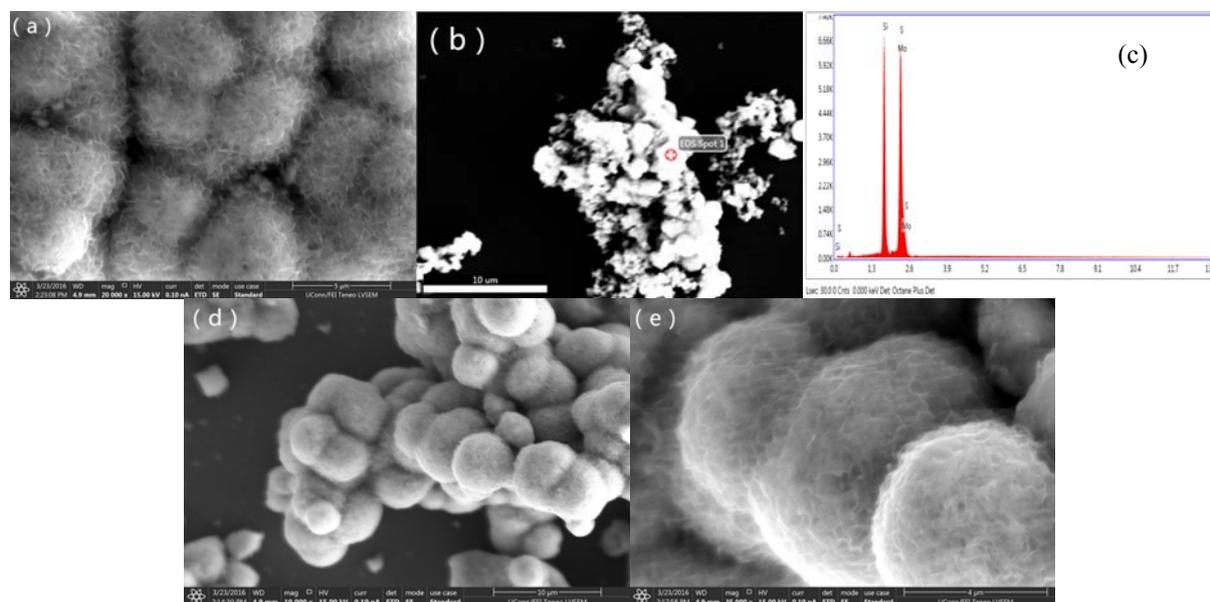


Fig. 1 Scanning electron microscopy (SEM) images for macroporous MoS₂/Mn and MoS₂ samples with different magnifications. Porosity could be observed with different scales.

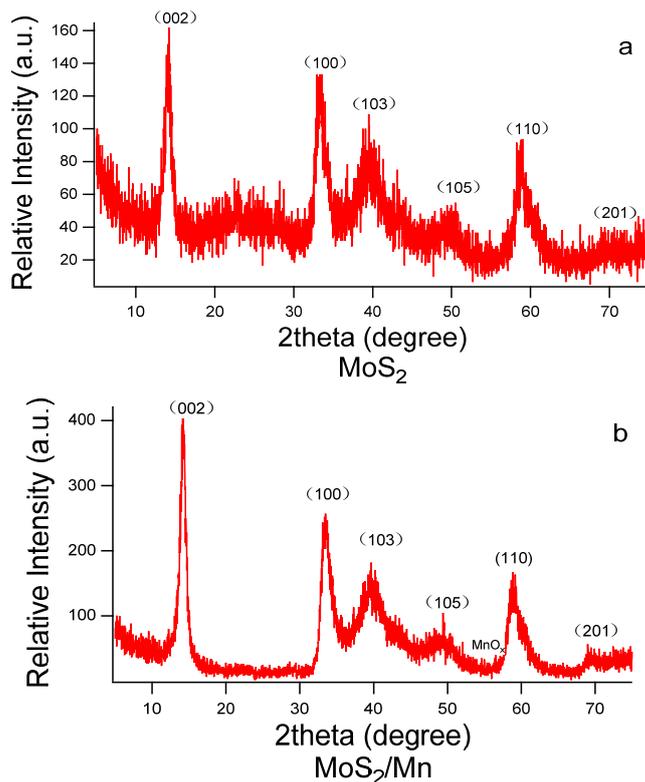


Fig. 2 (a) XRD patterns of MoS₂ and (b) the MoS₂/ Mn heterostructure

The XRD pattern in Fig. 2a indicates that there were polycrystalline corresponding to the hexagonal structure of MoS₂. The other six diffraction peaks were located at 14.3°, 33.6°, 40.1°, 49.1°, 59.0° and 69.4°, which correspond to the hexagonal crystallographic orientations structure. The diffraction peak is located at about 56.9° correspond to MnO_x.

The HER catalytic activity of the MoS₂/Mn catalyst was evaluated by using a rotating disc electrode (RDE) in a typical three-electrode cell in N₂-saturated 0.5 M H₂SO₄ solution. In contrast, the HER catalytic performance of the support-free MoS₂ was also measured. As shown in Fig. 3a, the MoS₂/Mn catalyst exhibited excellent activity for the HER.

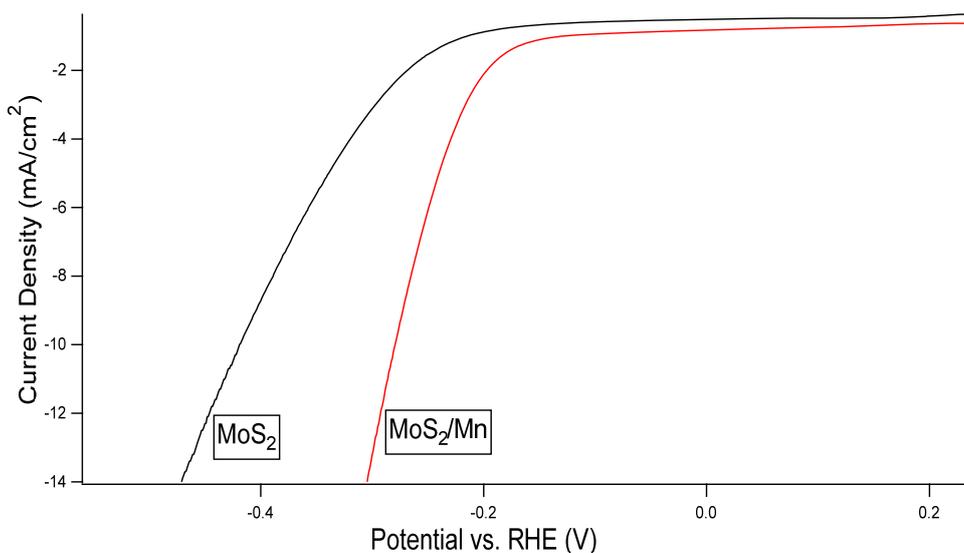


Figure 3. Polarization curves of MoS₂ and MoS₂/Mn materials in 0.5 M H₂SO₄ for comparison.

4. Conclusion

In this study, we have developed a one-pot hydrothermal synthesis of a MoS₂ and MoS₂/Mn heterostructure with a ball-floc-like morphology. The sheets have been found to have a dualfunction on both surface of MoS₂ and MoS₂/Mn. Given the highly exposed edges of ball-floc-like MoS₂ and the synergistic effects between the Mn and ball-floc-like MoS₂, which exhibited excellent electrocatalytic activity toward HER. Based on this study we can shows a new opinion for the development of ball-floc-like MoS₂/X hybrid as a promising support material for a variety of applications in synergistic catalysis.

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