

Modification and Reduced Graphene Oxide (rGO) Composites Based on MoS₂: Improvement of Electrocatalytic Hydrogen Evolution Performance

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Abstract. Designing an electrocatalyst for hydrogen evolution reaction (HER) with low cost, high performance and strong stability is crucial for improving the development of electrocatalytic water splitting hydrogen production technology. Besides, 2D flaky molybdenum disulfide (MoS₂) is expected to replace platinum-based electrocatalysts due to its excellent HER catalytic performance. MoS₂ nanosheets (MoS₂/rGO) supported on reduced graphene oxide (rGO) were synthesized by a simple one-step hydrothermal method, which presents highly efficient catalytic activity in line with expectations, that is, an overpotential of 148 mV and a Tafel slope of 56 mV·dec⁻¹ in a medium of 10 mA·cm⁻² and 0.5 M Na₂SO₄. The results show that the synergistic effect between MoS₂ nanosheets and rGO loading enhances the performance of the hydrogen evolution reaction. The increase of MoS₂ layer spacing avoids the re-aggregation of nanosheets, making more active sites exposed, and the rGO loading reduces the charge transfer resistance of the materia.

Keywords: Molybdenum disulfide; Reduced graphene oxide; Hydrogen evolution reaction; Electrocatalysis; Modifying.

1. Introduction

With the increasingly prominent environmental problems caused by fossil energy combustion and the continuous growth of global energy demand, the development of clean, efficient and sustainable energy conversion and storage technologies has become more and more urgent [1]. Hydrogen (H₂), a carbon-free and sustainable clean energy with a high energy density [2], is expected to transform energy structure in the future. Hence, the hydrogen production technology with characteristics of low cost, high efficiency and high stability has become an urgent breakthrough technology. Electrocatalytic water splitting is considered to be the most promising method for hydrogen production, because it can use renewable electric energy such as solar energy and wind energy to convert water into hydrogen fuel with high energy density [3]. However, there are many problems limiting the large-scale application of this technology, such as the high cost of existing platinum-based electrocatalysts, the low efficiency as well as the poor conductivity and anisotropy of noble metal electrocatalysts [4]. Especially for HER, efficient and stable electrocatalysts are needed to reduce the hydrogen evolution overpotential and increase the current density.

In recent years, two-dimensional nanosheets have become a popular research topic due to their unique physical and chemical properties, especially transition metal dichalcogenides (TMDCs), whose general formula is MS₂ (M=Mo, W, Fe, Co or Ni). MoS₂ has attracted researchers for its unique structural characteristics, high density of active centers at edge sites, and low cost. It is considered to be a promising non-noble metal HER electrocatalyst [5]. MoS₂ tends to form a two-dimensional (2D) nanosheet morphology, probably due to its intrinsic anisotropic structure [6]. Meanwhile, its hydrogen adsorption free energy ΔG_{H}^* is about 0.08 eV [7], which is close to 0 and similar to platinum group metals. Thus, it shows excellent HER catalytic performance^[8]. However, traditional MoS₂ materials as semiconductors have two major defects including fewer edge exposure sites and lower conductivity, which hinder the effective transfer of electrons and HER dynamics. The flaky

MoS₂ catalyst synthesized by Li et al. [9] by hydrothermal method has a hydrogen evolution overpotential of 351 mV (at 10 mA • cm⁻²) and a Tafel slope of 155.9 mV • dec⁻¹, with its electrocatalytic efficiency far lower than that of platinum-based catalysts, which confirms the above point of view.

Existing research mainly overcomes the above defects through two approaches. One is to build nanostructures or expand layer spacing and other methods to expose more edge active sites [10]. For example, Liu et al. [11] synthesized monolayer MoS₂ quantum dots (3.6 nm) by one-step hydrothermal method, which shows an overpotential of 160 mV and a Tafel slope of 59 mV • dec⁻¹ during the HER process, proving that the hydrogen evolution performance of nanostructure is far better than that of bulk MoS₂ crystal materials. Huang et al. [12] assembled MoS₂ nanosheets into three-dimensional structures to expose more interfaces and active sites, exhibiting a lower hydrogen evolution onset overpotential (160 mV).

The other is to combine MoS₂ with conductive materials to form heterostructures to enhance conductivity, thereby optimizing electrocatalytic performance [13]. Graphene derivatives have outstanding performance among many conductive support materials, including carbon nanotubes (CNTs) and reduced graphene oxide (rGO) [14]. In addition, their excellent electronic conductivity, high specific surface area and good chemical stability can effectively reduce HER overpotential [15, 16], thus being applied to various electrocatalyst substrate materials. For example, the MoS₂/CNT nanocomposite prepared by Yan et al. [17], which has a large number of edge exposed sites and a reticular structure with low crystallinity, exhibits a hydrogen evolution onset overpotential of about 90 mV and a Tafel slope of 44.6 mV • dec⁻¹. With comparable electrical conductivity and better hydrophilicity than ordinary graphene [18], rGO carriers can accelerate the electrochemical reaction kinetics by building heterostructures with electroactive materials to generate more active centers, while maintaining their chemical stability [19]. For example, Wang et al. [15] synthesized Fe_{0.39}Co_{0.61}S₂ ternary catalyst supported on rGO material for the HER process in acidic solution exhibits a low overpotential of 198 mV (if the current density is 10 mA • cm⁻²) and a Tafel slope of 94 mV • dec⁻¹, which has a small Gibbs free energy for hydrogen adsorption. Therefore, it is foreseeable that dispersing MoS₂ nanosheets on the surface of rGO to form composite materials can effectively avoid re-stacking and aggregation of MoS₂ nanosheets and maintain maximum active site exposure. At the same time, it can improve the conductivity of the material and effectively reduce the HER overpotential.

In this study, MoS₂-modified rGO composites (denoted as MoS₂/rGO) were prepared by a simple one-step hydrothermal method, and the synergistic effect between MoS₂ nanosheets and rGO with extended layer spacing was systematically investigated. Meanwhile, the application potential of this material in HER is also evaluated. Through detailed physicochemical characterization and electrochemical testing, it is found that the obtained MoS₂/rGO (1:5) shows better HER properties, including lower overpotential and lower Tafel slope, compared to pure MoS₂ or rGO materials.

2. Experimental Section

2.1 Materials

NaNO₃, H₂O₂ (30%), H₂SO₄ (98%), thiourea, hydrazine hydrate (50% aqueous solution), and graphite powder were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). KMnO₄, ethanol (99.5%), and (NH₄)₆Mo₇O₂₄ • 4H₂O were obtained from Aladdin Ltd. (Shanghai, China). All chemicals were analytical grade and directly utilized without any purification.

2.2 Characteristics and Electrochemical Measurements

X-ray diffraction (XRD) analysis was performed on a Model XD-3 X-ray diffractometer (Puxi General Instrument, Beijing, China) with a Cu K α radiation source ($\lambda=1.5406$ Å) and a scanning

range of 5° to 70°. Raman spectra were collected on an inVia Qontor type Raman spectrometer (Renishaw, Britain) with a scanning range of 700 to 2,000 cm⁻¹.

Electrocatalytic performance measurements were performed using a three-electrode system with a CHI 660E electrochemical workstation (CH Instruments, Shanghai, China). Platinum electrodes and saturated calomel electrodes (SCE) were used as reference electrodes and reference electrodes, respectively (Ada Hengsheng Technology, Tianjin, China). Linear sweep voltammetry (LSV) was performed in 0.5 mol · L⁻¹ Na₂SO₄ solution at a scanning rate of 1 mV · s⁻¹. In this study, the electrode potential of SCE to reversible hydrogen electrode (RHE) is calibrated by the Nernst equation (Equation 1).

$$E_{\text{RHE}} = E_{\text{appl.}} + 0.059 \times \text{pH} + E_{\text{Hg}_2\text{Cl}_2/\text{Hg}}^\circ (0.2412 \text{ V}) \quad (1)$$

2.3 Preparation of MoS₂/rGO Composite Materials

The GO in this study was prepared from graphite powder by the Hummers method [20]; MoS₂ was synthesized by the one-step hydrothermal method. The specific method is as follows. 0.406 g thiourea and 0.412 g (NH₄)₆Mo₇O₂₄ · 4H₂O were weighed and dissolved in 40 mL deionized water. After ultrasonic dispersion for 1 hour, the solution was transferred to a polytetrafluoroethylene-lined 50 mL reactor. Reaction at 240°C lasted for 24 hours. After the reaction, it was naturally cooled to room temperature, the product black powder was washed three times with anhydrous ethanol and deionized water, and finally dried at 80°C for 12 hours to obtain the product MoS₂ [21].

The prepared GO was uniformly dispersed in deionized water, and the mass ratios of MoS₂ to GO were 1:1, 1:3, 1:5 and 1:7 respectively, by adding different masses of MoS₂ powder into the suspension. Hydrazine hydrate was added to the mixed solution and ultrasound dispersed for 1 hour. After that, the solution was transferred to a reaction kettle for 24 hours at 240°C. After cooling to room temperature at the end of the reaction, it was washed to neutral using deionized water and absolute ethanol and dried. Besides, the resulting black samples were denoted MoS₂/rGO (1:1), MoS₂/rGO (1:3), MoS₂/rGO (1:5) and MoS₂/rGO (1:7), respectively. While conducting the above experimental process, hydrazine hydrate was added to the GO suspension for reduction to prepare a pure rGO carrier for control [22].

3. Results and Discussion

3.1 XRD and Raman Characterization of rGO and MoS₂/rGO

Figure 1 (a) is the X-ray diffraction (XRD) pattern of pure rGO with MoS₂/rGO (1:5) powder sample. It is observed that rGO exhibits a broad characteristic diffraction peak with the 2θ at 11.4°, corresponding to the (001) crystal plane of graphene. Compared with the characteristic diffraction peak where the 2θ of graphite is located at 26.5°, the smaller diffraction angle of rGO indicates its characteristics of expanding layer spacing, which is conducive to the application of rGO in the preparation of electrocatalytic materials [23]. The XRD patterns of MoS₂/rGO (1:5) material show characteristic diffraction peaks of MoS₂, with 2θ at 14.38°, 32.68°, 39.54° and 58.34° corresponding to the (002), (100), (103) and (110) crystal faces of MoS₂ crystal respectively (against standard card JCPDS No. 37-1492). The presence of these peaks indicates the successful synthesis of MoS₂ and the construction of a heterostructure of MoS₂/rGO.

Figure 1 (b) shows the Raman spectrum of the rGO and MoS₂/rGO (1:5) structures. The spikes at 1350 cm⁻¹ and 1580 cm⁻¹ are the D band gap and G band gap unique to rGO respectively. The D band gap intensity reflects the defect and disorder structure of the rGO crystal, and the G band gap reflects the tensile motion intensity of sp² hybrid carbon atoms. I_D/I_G of the ratio of the two band gap peak strengths represents the disorder degree of the internal crystalline form of carbon materials [16]. The larger the value, the more defects in the internal crystalline form and the lower the order degree [24]. Compared with the I_D/I_G of 0.97 obtained by direct reduction of GO by hydrazine hydrate, the peak

value after doping MoS₂ is higher than 1.10, which may be due to the construction of the heterostructure of MoS₂ and rGO, causing defects in the graphene lattice and disordered structure. For the MoS₂/rGO composites, the characteristic activity peak of MoS₂ can also be observed, but the results are not obvious due to the narrow scanning range and the low mass proportion of MoS₂.

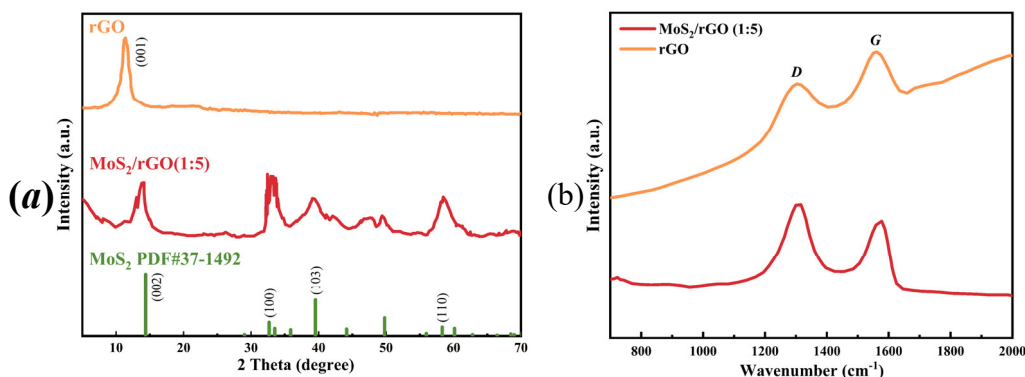


Figure. 1 (a) XRD Patterns and (b) Raman Spectrum of rGO and MoS₂/rGO (1: 5) Materials

3.2 HER Activity of MoS₂/rGO Electrocatalysts

To explore the HER electrochemical activity of MoS₂/rGO composites with various mass ratios in 0.5 mol · L⁻¹ Na₂SO₄ solution, the HER electrochemical data were measured using the conventional three-electrode system, which is compared with the results of rGO directly synthesized by hydrazine hydrate. Figure 2 shows the overpotential comparison of different electrocatalysts when the current density is 10 mA · cm⁻². According to the results, when the mass ratio of MoS₂ to rGO is 1:5, the overpotential of the composite material is only 148 mV, which shows better HER electrocatalytic efficiency than that of rGO and other mass ratios of composites. Further data analysis and performance comparison of MoS₂/rGO (1:5) composites were carried out.

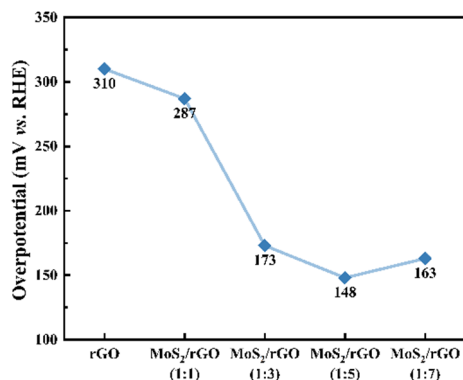


Figure. 2 Overpotentials at 10 mA·cm⁻² for Different Electrocatalysts

According to the linear sweep voltammetry (LSV) curve in Figure 3 (a), the starting potential of the modified MoS₂/rGO (1:5) material is only 115 mV, which is significantly lower than the starting potential of 221 mV of pure rGO. It indicates that the doping of MoS₂ and the construction of MoS₂/rGO heterostructure have a significant effect on the HER activity of the rGO electrocatalyst. Figure 3 (b) shows the Tafel slope of rGO versus MoS₂/rGO materials. The LSV curves of the two electrocatalysts combined with the Tafel equation ($\eta = a + b \lg |j|$, in which η is the overpotential, b is the Tafel slope, and j is the current density) fit the Tafel slope of the HER process. When the current density is constant, the smaller the Tafel slope, the lower the overpotential required for the HER process. The MoS₂/rGO (1:5) electrocatalyst exhibits an extremely low Tafel slope of only 56 mV dec⁻¹, while the pure rGO had a Tafel slope of 127 mV dec⁻¹.

The results of LSV curve overpotential and Tafel slope show that with the increase of overpotential, the precipitation rate of H₂ catalyzed by MoS₂-doped rGO material increases significantly faster, which indicates its better catalytic reaction kinetic performance [25]. This may be due to the

heterostructure formed by the dispersion of MoS₂ active centers on the surface of monolayer rGO. This synergistic effect enables the composite to significantly increase its HER activity while maintaining the advantages of high surface area and low charge transfer resistance of rGO, thus showing excellent electrocatalytic hydrogen evolution performance. These findings are of great significance for the understanding and design of high-efficiency HER electrocatalysts, which contribute to the development of new energy conversion technologies, especially for the production of green hydrogen energy.

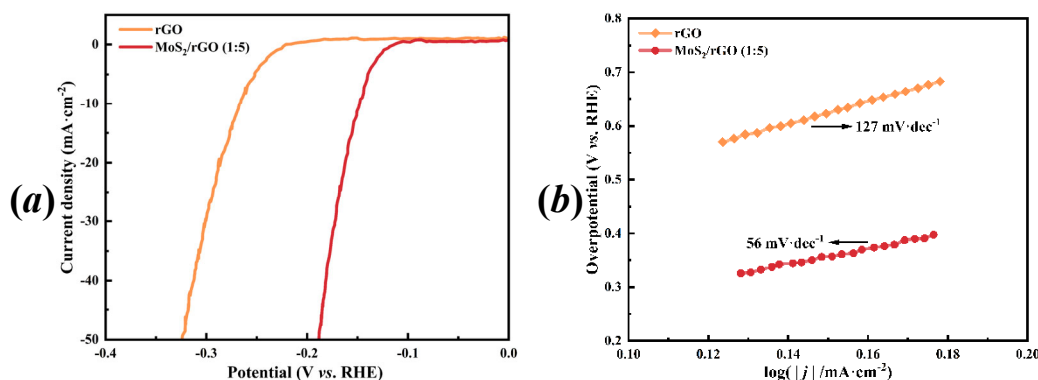


Figure. 3 Characterization of HER Performance of Different Electrocatalysts. (a) Polarization Curves for HER with rGO and MoS₂/rGO (1:5) Materials. (b) Tafel Slope of rGO and MoS₂/rGO (1:5) Electrocatalysts

Table 1 compares some of the recently reported studies on other modified rGO or MoS₂ nanostructural composites as electrocatalysts for HER reactions. It can be found that the MoS₂/rGO (1:5) heterostructural materials proposed in this study have excellent electrical properties and hydrogen evolution. It has broad application prospects in this field.

Table 1 Comparison of the Performance of HER Electrocatalysts Modified with rGO or MoS₂ Materials Reported Recently

Electrocatalyst	Substrate	Modified Materials	Onset Potential/mV	Overpotential at 10 mA · cm ⁻² /mV	Tafel Slope/ (mV · dec ⁻¹)	Reference
MoS ₂ /rGO (1:5)	rGO	MoS ₂	115	148	56	This Work
Ni _{0.85} Se/rGO	rGO	Ni _{0.85} Se	–	182	62	[16]
Sb ₂ Se ₃ /rGO	rGO	Sb ₂ Se ₃	320	630	109	[26]
MTC-1	MoS ₂	Ti ₃ C ₂ Tx	–	280	84	[5]
CS-MoS ₂ -2	MoS ₂	CdSe/CdS	–	171	122	[27]
MoS ₂ /MoP	MoP	MoS ₂	–	113	62	[28]

4. Conclusions

In conclusion, MoS₂ nanosheets were synthesized through a simple one-step hydrothermal reaction and combined with rGO support to form MoS₂/rGO composites, which show better HER electrocatalytic performance than pure MoS₂ or rGO. The performance improvement may be due to the synergistic effect between the two materials. The high conductivity of rGO reduces the charge transfer resistance of the material and improves its intrinsic conductivity. Meanwhile, the high surface

area of rGO contributes to the adhesion of MoS₂ nanosheet materials, which increases the exposure of active sites, thereby improving the electrochemically active area of the composite materials.

Given the reinforced HER properties of the composite, it can be considered a promising high-performance noble metal-free catalyst for future electrocatalytic water splitting technologies. Finally, this study suggests further research to optimize the synthesis method of MoS₂/rGO composites, to explore the influence of different ratios of MoS₂ to rGO on the HER properties of materials, and to probe into the application of hydrogen production under large-scale production conditions.

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