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Boosting Hydrogen Evolution Performance of MoS₂ by Band Structure Engineering

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Molybdenum sulfide (MoS₂) has emerged as a promising electrocatalyst for hydrogen evolution reaction (HER) owing to its high activity and stability during the reaction. However, the efficiency of hydrogen production is limited by the number of active sites in MoS₂. In this work, a simple method of fabricating polycrystalline multilayer MoS₂ on Mo foil for efficient hydrogen evolution is demonstrated by controlling the sulfur (S) vacancy concentration, which can introduce new bands and lower the hydrogen adsorption free energy (ΔG_H). For the first time, theoretical and experimental results show that the HER performance of synthesized MoS₂ with S vacancy can be further enhanced by the very small amount of platinum (Pt) decoration, which can introduce new gap states and more catalytic sites in real space with suitable free energy. The fabricated hybrid electrocatalyst exhibits significantly smaller Tafel slope of 38 mV dec⁻¹ and better HER electrocatalytic activity compared to previous works. This approach provides a simple pathway to design low-cost, efficient and sizable hydrogen-evolving electrode by simultaneously tuning the MoS₂ band structure and active sites.

Hydrogen has been widely considered as a promising alternative and renewable energy to replace fossil fuels.^[1–3] Toward this end, the direct and efficient approach for massive hydrogen production is to split water for electrocatalytic hydrogen evolution reaction (HER).^[4–6] The most active electrocatalyst for HER is Pt, which can drive the reaction with a near zero overpotential.^[7,8] However, the scarcity and high cost of Pt significantly

restrict its applications in large scale. It remains challenging to develop highly active HER catalysts based on the materials with more abundance and lower cost.^[9–11] Recently, molybdenum sulfide (MoS₂), as one of the transition metal dichalcogenides, has drawn considerable attention for HER applications due to the excellent stability and earth abundance.^[12–16] Numerous efforts have been made to improve the HER performance of MoS₂. Except improving the charge transport of MoS₂ films,^[17,18] the most popular method is to create more edges and defects on MoS₂ films.^[19–24] It is well known that the edges of MoS₂ are more active than the inert basal plane for HER.^[22] Various post-treatment methods and vertical MoS₂ structures have been developed to expose more edge sites for efficient HER.^[25–27] In addition to the above strategies, recently, Li et al.

reported that the HER performance of monolayer 2H-MoS₂ grown by chemical vapor deposition (CVD) could be improved by introducing excess S vacancies and strain.^[28] The S vacancies and straining the basal plane of MoS₂ can tune the band structure of MoS₂, allowing the reduction of the ΔG_H . Wang et al. demonstrated an approach to intercalate Li⁺ into the 2D MoS₂, which can tune the band structure of MoS₂, therefore enhancing the HER activity notably.^[29] Nguyen et al. employed thiol functionalization to manipulate the electronic structure of MoS₂ flakes, which can be utilized to tune the band alignment of MoS₂ at material interfaces to optimize the operation of catalytic systems.^[30] However, the post-treatment needed for nucleating activity sites and strain engineering are not practical for large-scale application of MoS₂ in HER due to the complicated process and high costs. Growing large area monolayer MoS₂ films with defects is still a challenge.^[31–33] Therefore, there is a need of a simple method which can produce MoS₂ with excess S vacancy concentration.

Herein, we report a systematic study of the high-performance HER using multilayered MoS₂, which is synthesized by a simple hydrothermal reaction. Our experimental results show that MoS₂ with adequate S vacancy concentration can be directly synthesized on the surface of Mo foil. The purpose of using Mo as the substrate and source is to form a seamless contact between MoS₂ and the Mo substrate. Our previous work reported that Mo is an excellent contact metal, which can

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form a seamless contact with MoS₂.^[34] This transparent contact is suitable for assisting charge transport to boost the HER performance eventually. Also, previous theoretical and experimental works have demonstrated that the band structure and electronic properties of MoS₂ can be modified by depositing metal nanoparticles on the surface.^[35] To further enhance the HER performance of synthesized MoS₂, very small amount of Pt is decorated on the surface or fill the vacancies, which can introduce new gap states, thereby lowering the ΔG_{H} and more catalytic sites in real space with suitable free energy (Figure 1). Pt nanoparticle decorated MoS₂ synthesized on the Mo foil (Pt/MoS₂/Mo) hybrid catalyst demonstrates high HER electrocatalytic activity with low overpotential and a small Tafel slope, which is much beyond the previously reported works using MoS₂ and is close to the upper limit values of HER achieved on the Pt electrode.

Density functional theory (DFT) calculation is employed to investigate the influence of the S vacancy and Pt atoms on the electronic structure of MoS₂. The detailed DFT calculation method is provided in Section S1 in the Supporting Information. The band structure of pristine MoS₂ is shown in Figure 2a. When an S vacancy is introduced into the MoS₂ crystal structure (3 × 3 cell), new bands appear in the gap near the Fermi level (red curves) as shown in Figure 2b. These new gap states are localized and responsible for hydrogen adsorption and release on the S vacancy.^[28] Hence, S vacancies are catalytic sites for HER. When a Pt atom is introduced (Figure 2c), more bands of localized states appear in the gap. This phenomenon can be observed no matter whether Pt fills the vacancies (Figure 2c) or stays on the surface (Figure 2d). The increase in the number of gap states results in the strengthening of hydrogen bonding. In addition, Pt nanoparticles themselves also serve as catalytic sites due to their suitable ΔG_{H} (Figure 1b). Therefore, by depositing a slight amount of Pt onto MoS₂ surface, the HER performance of MoS₂ can be further improved.

With the increase of S vacancy concentration, the bands move closer to the Fermi level due to the doping effect and the number of gap states increases (Figure 3). These gap states provide more free energy levels for H* on the catalytic sites, which are lower than that of the intrinsic MoS₂. When the S/Mo ratio is equal to 1.61, a significant number of gap states

appear in the gap, and hence many suitable energy levels can be exploited for HER (Figure 3c). Moreover, due to the doping effects of the S vacancy, the conductivity of MoS₂ is improved and charges transport more efficiently, thereby enhancing the HER performance.

In this work, MoS₂ with S vacancy is directly grown on Mo foil using the hydrothermal method at 200 °C, which is provided in the “Experimental Section.” After MoS₂ grown on Mo foil surface, the color of the Mo foil turns into black as shown in Figure 4a. The surface of Mo foil is covered by relatively flat films with some cracks (Figure S1, Supporting Information). The microstructure of MoS₂ is further investigated by a transmission electron microscope (TEM). The low-magnification TEM image shows that the synthesized MoS₂ films have the porous structure (Figure 4b). The selected area electron diffraction pattern of MoS₂ confirms the polycrystalline nature of synthesized MoS₂. After loading of Pt nanoparticles onto MoS₂/Mo by the electrodeposition method, the morphology of the grown films is not changed due to low dose of Pt (Figure S1, Supporting Information). The high-resolution TEM image indicates that the Pt nanoparticles have high quality with a crystal lattice with an interplanar spacing of 0.223 nm corresponding to the distances of (111) crystal plane of Pt shown in Figure 4c. The presence of Pt on MoS₂ surface is also confirmed by the X-ray photoelectron spectroscopy (XPS) of Pt 4f orbital, as shown in Figure S2 (Supporting Information).

XPS analysis is carried out to investigate the chemical states of MoS₂. As shown in Figure 4d, the Mo 3d spectrum consists of peaks around 229.2, 232.2, and 235.3 eV. Mo 3d_{5/2} peak at 229.2 eV and Mo 3d_{3/2} peak at 232.2 eV indicate the presence of MoS₂.^[36] The peak at 226.2 eV belongs to S 2s orbital of MoS₂. In addition, in the S 2p region of the spectra, two peaks are found at around 162 and 163.2 eV, which correspond to S²⁻ 2p_{3/2} and S²⁻ 2p_{1/2} components, respectively.^[37] For the synthesized MoS₂, the S/Mo ratio is around 1.61 which is extracted from the XPS spectra, indicating a large amount of S vacancies formed in the MoS₂. The S/Mo ratio (1.61) indicates a 19.5% concentration of S vacancies, which is close to the optimal value of S vacancy in Li et al.^[28] Raman spectra of synthesized MoS₂ (black line) and CVD-grown MoS₂ on Mo foil at 700 °C (red line) are shown in Figure 4f. For MoS₂ synthesized by the

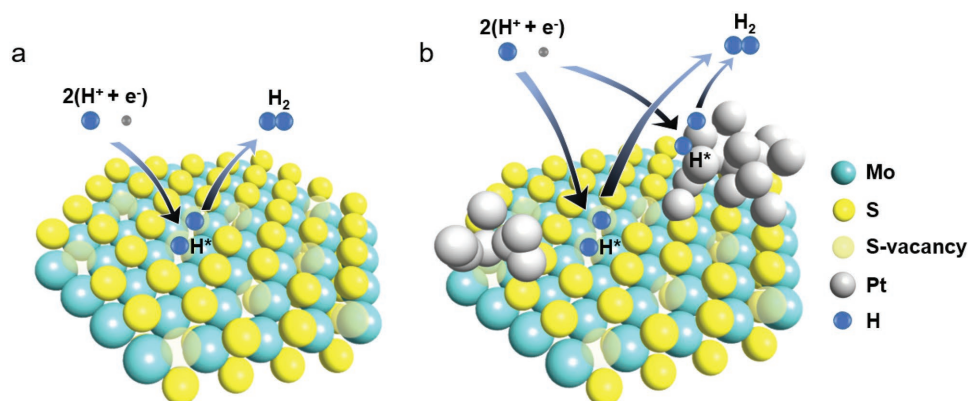


Figure 1. Schematic of HER process on a) MoS₂ with S vacancy and b) MoS₂ with S vacancy and Pt. H* represents H free radical. The HER process has two steps: absorption ($\text{H}^+ + \text{e}^- \rightarrow \text{H}^*$) on catalytic sites and release ($2\text{H}^* \rightarrow \text{H}_2$) from catalytic sites. Pt nanoparticles provide more catalytic sites for HER.

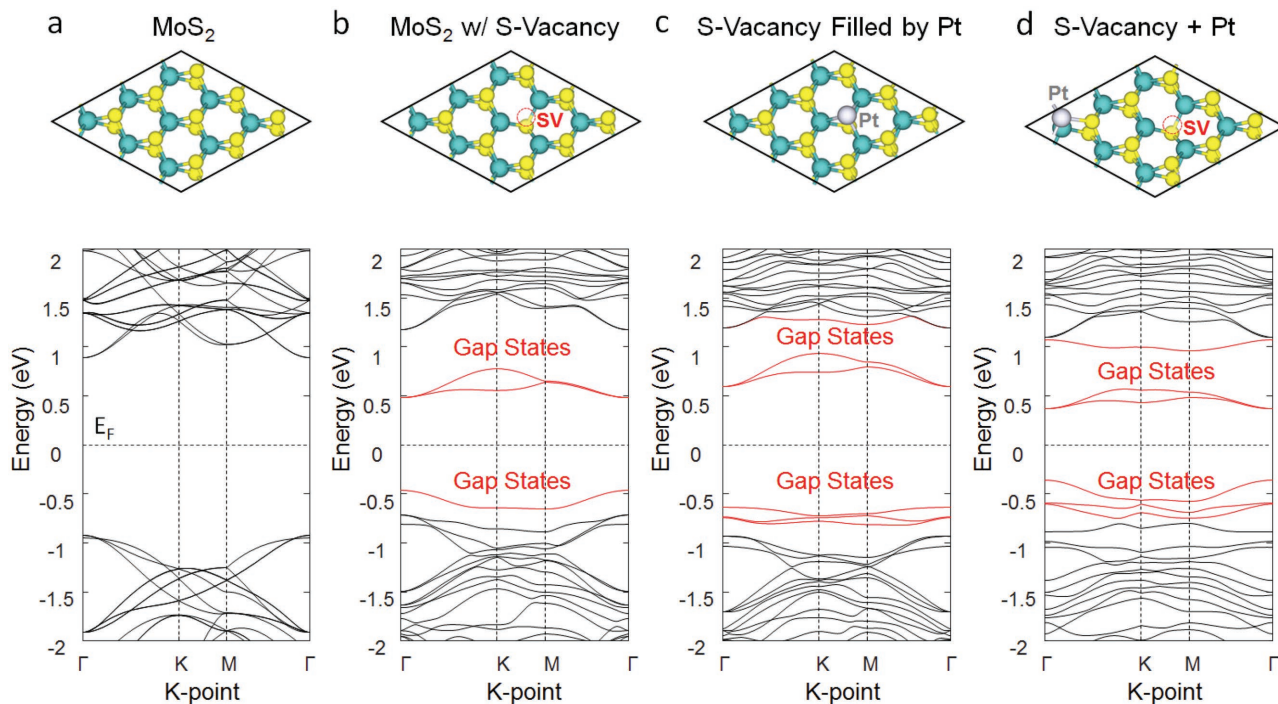


Figure 2. Theoretical calculations for the S vacancy and Pt atom influence on the band structure of MoS₂. Unit cells (top) and band structures (bottom) of a) pristine MoS₂, b) a 3 × 3 MoS₂ cell with one S vacancy, c) a 3 × 3 MoS₂ cell with a Pt atom sitting on S vacancy, and d) a 3 × 3 MoS₂ cell with one S vacancy and a Pt atom sitting on MoS₂ surface. Red curves indicate gap states induced by the S vacancy and Pt atoms.

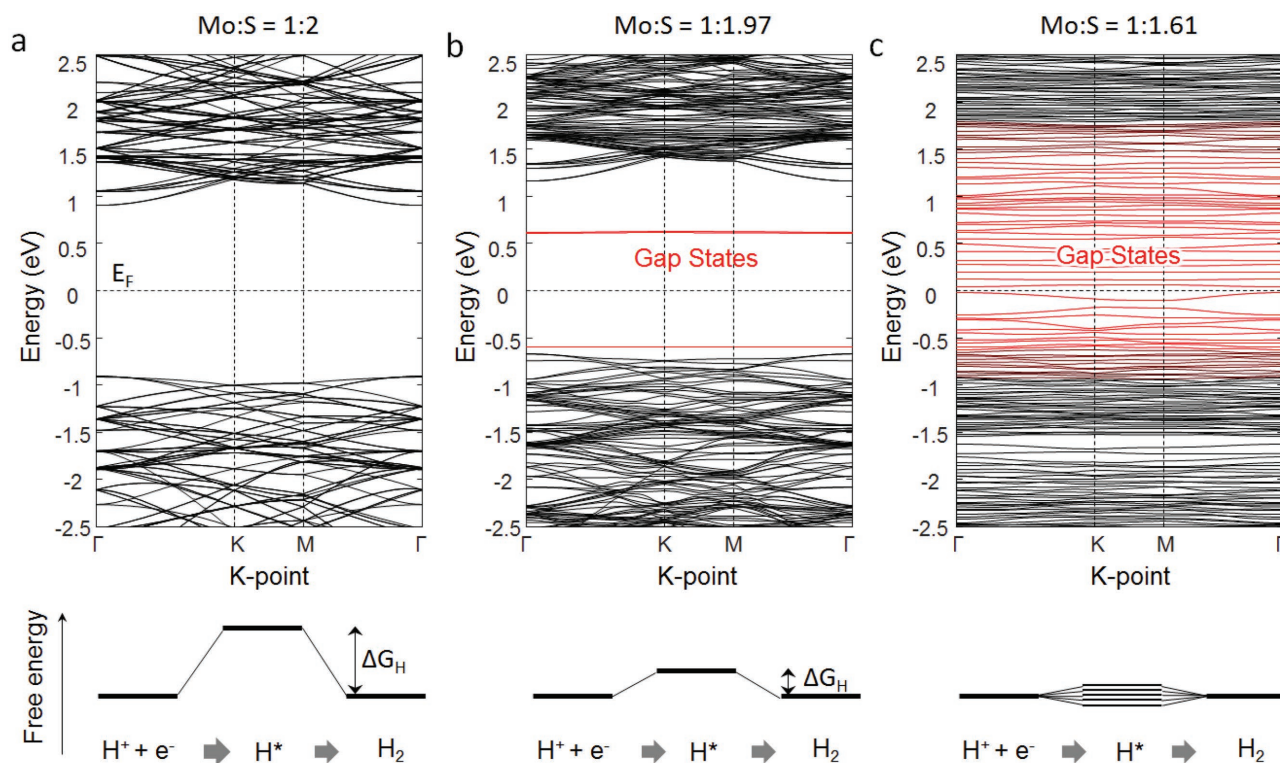


Figure 3. Impact of S vacancy concentration on the band structure of MoS₂ (upper) and hydrogen adsorption free energy (lower) for a) a 6 × 6 cell of pristine MoS₂, b) a 6 × 6 cell of MoS₂ with one S vacancy, which translates to an Mo:S ratio of 1:1.97, and c) a 6 × 6 cell of MoS₂ with 14 random S vacancies, which translates to an Mo:S ratio of 1:1.61. Higher vacancy density provides more catalytic sites with lower free energy levels for H*.

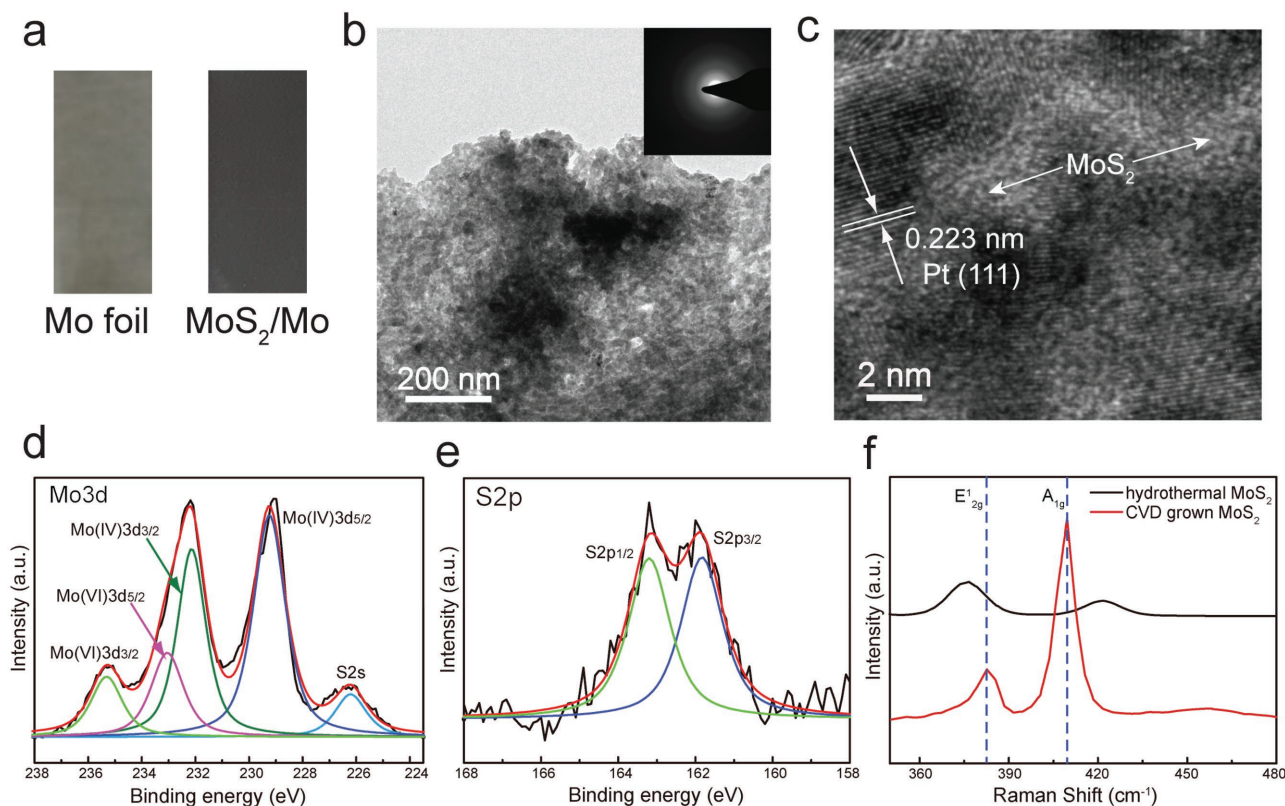


Figure 4. a) Optical images Mo foil (left) and Mo foil after MoS₂ growth (right). b) Low-magnification transmission electron microscope (TEM) images of MoS₂. Inset: Selected area electron diffraction pattern of MoS₂. c) High-resolution TEM image of MoS₂. d) X-ray photoelectron spectroscopy (XPS) of the Mo 3d orbital. e) XPS of S 2p orbital. f) Raman spectra of MoS₂ prepared by different methods. Raman laser wavelength: 532 nm.

hydrothermal method at 200 °C, peaks at 382.7 and 409.6 cm⁻¹ corresponds to the E₁^{2g} mode (the in-plane optical vibration mode of Mo–S bond) and A_{1g} mode (the out-of-plane optical vibration mode of S atoms), respectively.^[23,38] While for the CVD-grown MoS₂ at 700 °C, the peak at 410 cm⁻¹ is much sharper and narrower compared with hydrothermal MoS₂ films, indicating that the CVD-grown MoS₂ has a high degree of crystalline order. Additionally, the position of A_{1g} mode of hydrothermal synthesized MoS₂ blueshifts about 11.4 cm⁻¹, while E₁^{2g} mode redshifts about 6.6 cm⁻¹. Both the peaks have broader peak width, indicating the lattice distortion caused by the formation of defects (S vacancies) in MoS₂.

The HER performance of the synthesized samples is measured in 0.5 mol L⁻¹ H₂SO₄ solution using cyclic voltammetry (CV) method described in Section S2 in the Supporting Information. Figure S3 (Supporting Information) displays the schematic of the band alignment of MoS₂ and Pt, as well as the sketch of the cathodic current direction in the HER process. The representative polarization curves for the Mo foil, MoS₂/Mo, and Pt/MoS₂/Mo are shown in Figure 5a. Apparently, Mo foil has weak HER activity, while MoS₂/Mo shows significantly improved catalytic activity with an onset potential of 162 mV versus reversible hydrogen electrode (RHE). It only needs a potential of 198 mV for MoS₂/Mo electrode to achieve a cathodic current density of 10 mA cm⁻². The significantly improved HER activity of MoS₂/Mo indicates the intrinsically high catalytic activity of MoS₂.

Pt nanoparticles are deposited by the cyclic voltammetry method. After electrodepositing of Pt nanoparticles on the surface of MoS₂, the Pt/MoS₂/Mo electrocatalyst clearly shows better catalytic performance, as displayed in Figure S4 (Supporting Information). However, the HER activity starts to decrease if the amount of Pt is overloaded on the surface of MoS₂, indicating that the enhanced HER performance is not solely from the Pt nanoparticles. The comparison of the potential required to produce the current densities of 5 and 10 mA cm⁻² for different samples is presented in Table S1 (Supporting Information). It clearly shows that the Pt/MoS₂/Mo electrocatalyst has operating potentials of 36 and 58 mV at the cathodic current densities of 5 and 10 mA cm⁻², respectively, which is much lower than MoS₂/Mo (162 mV at 5 mA cm⁻² and 198 mV at 10 mA cm⁻²) and Mo foil (358 mV at 5 mA cm⁻² and 391 mV at 10 mA cm⁻²). In addition, the Pt/MoS₂/Mo electrocatalyst displays the largest current density of 216 mA cm⁻² at the same potential of 300 mV when compared with MoS₂/Mo and Mo foils. The corresponding Tafel plots (Figure 5b) show that MoS₂ with S vacancy has a Tafel slope of 68 mV dec⁻¹, which is lower than that of MoS₂ with S vacancy created by Ar plasma etching.^[28] After depositing Pt to create more gap states and form additional active centers on MoS₂ surface, the Tafel slope can be greatly reduced to 38 mV dec⁻¹, which is very close to that of Pt (30 mV dec⁻¹). The enhanced HER activity of Pt/MoS₂/Mo validates the theoretical calculations mentioned above. The fabricated hybrid material exhibits significantly

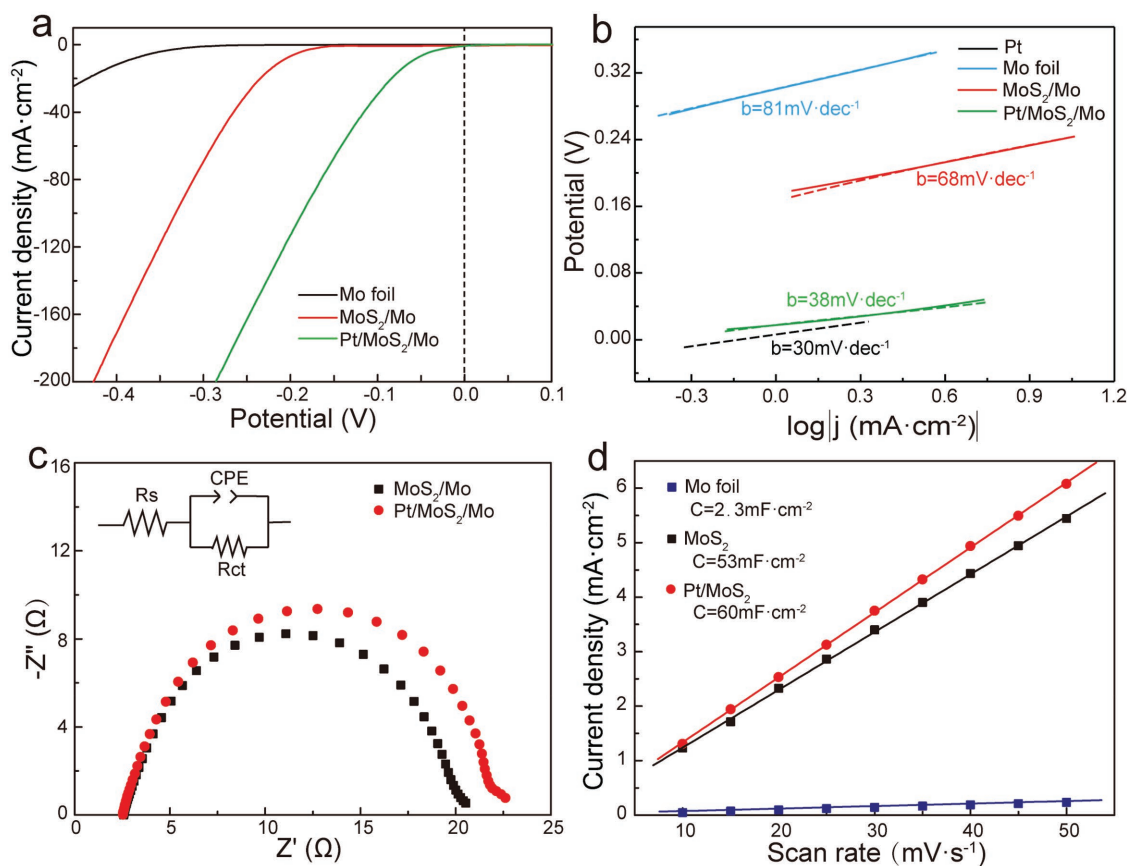


Figure 5. a) The polarization curves and b) corresponding Tafel plots of Mo foil, MoS₂/Mo foil, and Pt/MoS₂/Mo foil, reflecting the electrocatalytic performance of these samples. c) Electrochemical impedance spectroscopy (EIS) Nyquist plots of MoS₂/Mo foil and Pt/MoS₂/Mo foil. The inset circuit shows the corresponding equivalent circuit of the solid–liquid interface by a one-time constant. d) Current density variation at a given potential of 0.10 V versus RHE plotted against scan rate fitted to a linear regression enables the estimation of C_{dl} .

high HER electrocatalytic activity compared to other works as shown in Table S2 (Supporting Information).

The interaction between Pt and MoS₂ can be reflected by the electrochemical impedance spectroscopy (EIS) Nyquist plots of MoS₂/Mo foil and Pt/MoS₂/Mo foil shown in Figure 5c. Pt/MoS₂/Mo has better HER performance than that of MoS₂/Mo. Pt/MoS₂/Mo should have a smaller resistance than MoS₂/Mo. However, the Pt/MoS₂/Mo electrocatalyst has a larger resistance than MoS₂/Mo, indicating that electrons flow from MoS₂ to Pt due to the difference of the work function between Pt and MoS₂. Hence, the HER activity of Pt/MoS₂/Mo is mainly from the MoS₂. The EIS measurements indicate that Pt-induced gap states play the key role in enchaining the HER performance of MoS₂. The capacitance of the double layer (C_{dl}) is used to estimate the electrochemically effective surface area of different catalysts.^[39] In 0.5 mol L⁻¹ H₂SO₄ solution, cyclic voltammetry measurements are carried out on MoS₂/Mo and Pt/MoS₂/Mo to determine the C_{dl} . C_{dl} can be extracted from the positive and negative current density differences ($\Delta j = j_a - j_c$) at a potential of 0.10 V versus RHE against the CV scan rates (Figure S5, Supporting Information), which is equal to half the value of the linear slopes of the fitted lines in the plots. As shown in Figure 5d, Mo foil has a C_{dl} of only 2.3 mF cm⁻², which is much smaller than MoS₂/Mo (53 mF cm⁻²) and

Pt/MoS₂/Mo (60 mF cm⁻²). The latter exhibits larger C_{dl} indicating the higher electrochemically active surface area, which could contribute to its higher HER activity. Except the requirement for high HER activity, stability is another important criterion in evaluating the property of an electrocatalyst. In our work, a long-term CV test between 0.20 and -0.60 V versus RHE is conducted. Comparing with its initial activity, the Pt/MoS₂/Mo electrocatalyst shows almost no degradation of cathodic current densities after undergoing 1000 CV cycles (Figure S6, Supporting Information), reflecting the potential application of this catalyst in an electrochemical process.

To confirm that the S vacancy can contribute to the enhanced HER activity, samples are annealed at various temperatures (200, 300, 400, 500 and 600 °C in Ar, respectively) in the S vapor to repair the S vacancies. After annealing at 200 °C, the HER activity of MoS₂ is slightly improved. The Tafel slope also improves from 68 mV dec⁻¹ (without annealing) to 59 mV dec⁻¹ (200 °C) and 63 mV dec⁻¹ (300 °C). However, when the annealing temperature is above 300 °C, the cathodic currents are significantly reduced. At the same time, the Tafel slope of the sample annealed at high temperatures is also increased (Figure 6b). The S/Mo ratios of various samples are extracted from the XPS measurements (Figure S7, Supporting Information) and are shown in Figure 6c. After annealing at

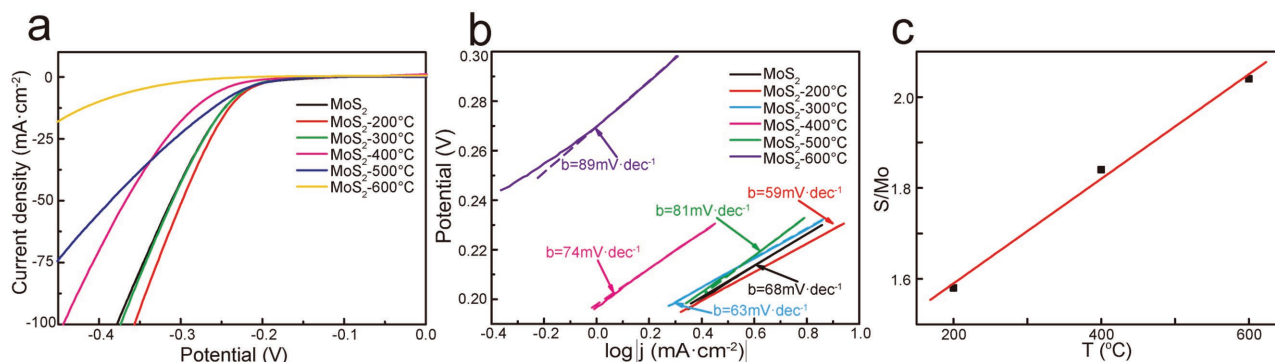


Figure 6. a) Polarization curves of MoS₂ films grown on Mo foil before and after annealing to repair defects (S hole) at different temperatures for 20 min. b) Tafel plots recorded on the catalysts of MoS₂ films grown on Mo foil and annealing at different temperatures. c) The linear fit of the S/Mo ratios with the change of temperature.

200 °C, the S/Mo ratio has slightly changed. The S/Mo ratio keeps increasing when the annealing temperature is above 300 °C. Once the S atoms fix the S vacancies after high-temperature annealing, the number of the gap states is reduced, resulting in the loss of HER activity. This is also consistent with the theoretical calculation shown in Figure 3.

In summary, we have successfully developed an in situ sulfuration process on Mo foil to fabricate polycrystalline MoS₂ with proper S vacancy concentration for HER. DFT calculation results show that S vacancy can introduce new bands, which can lower the ΔG_{H} . Theoretical and experimental results indicate that the HER performance of synthesized MoS₂ with S vacancy can be further enhanced by the slight addition of Pt decoration, which can introduce new gap states and more catalytic sites in real space with suitable free energy. A Pt/MoS₂/Mo hybrid electrocatalyst exhibits apparent and stable HER activity with an onset potential close to 0 V, a small Tafel slope of 38 mV dec⁻¹, and almost no change of the cathodic currents for up to 1000 CV cycles of continuous operation. The straightforward and efficient approach makes the polycrystalline MoS₂ films a promising candidate for electrochemical hydrolysis hydrogen production. In addition, the strategy demonstrated in this work can be further extended to the 2D transition metal oxides for the other half of water splitting to produce oxygen.^[40]

Experimental Section

Preparation of MoS₂/Mo Electrocatalyst: MoS₂ films on Mo foil were synthesized by a simple hydrothermal method. Before the hydrothermal reaction, the Mo foil was ultrasonically cleaned in acetone, ethanol, and water for 15 min, respectively. About 0.19 g of thiourea was dissolved in 30 mL deionized water to form a homogeneous solution. Then, the aqueous solution and the cleaned Mo foil were transferred into a 50 mL Teflon-lined stainless-steel autoclave, which was sealed and maintained at the temperature of 200 °C for 24 h. After hydrothermal reaction, the as-formed products were carefully rinsed by deionized water and ethanol.

Synthesis of Pt/MoS₂/Mo Hybrid Electrocatalyst: The Pt nanoparticles were deposited on MoS₂/Mo by use of the cyclic voltammetry method on a three-electrode system. The electrodeposition was conducted in 0.2 mmol L⁻¹ H₂PtCl₆ and 0.5 mol L⁻¹ H₂SO₄ solution with an Ag/AgCl (in 3.8 mol L⁻¹ KCl solution) reference electrode and a Pt wire counter

electrode. The deposition voltage ranged from 0 to -0.8 V versus Ag/AgCl with the scan rate of 100 mV s⁻¹.

Repair the Defects in MoS₂ Films: MoS₂/Mo foil was placed face down on a boat with 0.2 g of S powder which was loaded in the center of a 2 in. diameter quartz-tube furnace. The reactions were performed in the range of 200–600 °C for 15 min with the Ar flow of 30 sccm.

Growth of MoS₂ by the CVD Method: MoS₂ was grown by vapor transport synthesis from solid powder precursors. High-purity Mo foil as the growth substrate was placed in separate alumina boats and loaded in the center of a 2 in. diameter quartz-tube furnace. Sulfur (≥99.5%, 0.2 g) powder was placed 20 cm away from the center of the tube furnace. The center of the furnace was heated to 700 °C for 15 min with the flow of 50 sccm Ar. After growth, the system was cooled down to room temperature while flowing with 50 sccm Ar.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

band structure, hydrogen evolution reaction, molybdenum disulfide, vacancies

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