Boosting Hydrogen Evolution Performance of MoS$_2$ by Band Structure Engineering

Jing Li, Jiahao Kang, Qian Cai, Wenting Hong, Chuanyong Jian, Wei Liu,* and Kaustav Banerjee

Molybdenum sulfide (MoS$_2$) 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 MoS$_2$. In this work, a simple method of fabricating polycrystalline multilayer MoS$_2$ 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 ($\Delta G_{\text{H}}$). For the first time, theoretical and experimental results show that the HER performance of synthesized MoS$_2$ 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 MoS$_2$ 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 (MoS$_2$), 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 MoS$_2$. Except improving the charge transport of MoS$_2$ films$^{[17,18]}$ the most popular method is to create more edges and defects on MoS$_2$ films.$^{[19-26]}$ It is well known that the edges of MoS$_2$ are more active than the inert basal plane for HER.$^{[22]}$ Various post-treatment methods and vertical MoS$_2$ 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–MoS$_2$ grown by chemical vapor deposition (CVD) could be improved by introducing excess S vacancies and strain.$^{[28]}$ The S vacancies and strain the basal plane of MoS$_2$ can tune the band structure of MoS$_2$, allowing the reduction of the $\Delta G_{\text{H}}$. Wang et al. demonstrated an approach to intercalate Li$^+$ into the 2D MoS$_2$, which can tune the band structure of MoS$_2$, therefore enhancing the HER activity notably.$^{[29]}$ Nguyen et al. employed thiol functionalization to manipulate the electronic structure of MoS$_2$ flakes, which can be utilized to tune the band alignment of MoS$_2$ 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 MoS$_2$ in HER due to the complicated process and high costs. Growing large area monolayer MoS$_2$ films with defects is still a challenge.$^{[31-33]}$ Therefore, there is a need of a simple method which can produce MoS$_2$ with excess S vacancy concentration.

Herein, we report a systematic study of the high-performance HER using multilayered MoS$_2$, which is synthesized by a simple hydrothermal reaction. Our experimental results show that MoS$_2$ 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 MoS$_2$ and the Mo substrate. Our previous work reported that Mo is an excellent contact metal, which can
form a seamless contact with MoS$_2$.[14] 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 MoS$_2$ can be modified by depositing metal nanoparticles on the surface.[15] To further enhance the HER performance of synthesized MoS$_2$, very small amount of Pt is decorated on the surface or fill the vacancies, which can introduce new gap states, thereby lowering the $\Delta G_{\text{H}}$ and more catalytic sites in real space with suitable free energy (Figure 1). Pt nanoparticle decorated MoS$_2$ synthesized on the Mo foil (Pt/MoS$_2$/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 MoS$_2$ 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 MoS$_2$. The detailed DFT calculation method is provided in Section S1 in the Supporting Information. The band structure of pristine MoS$_2$ is shown in Figure 2a. When an S vacancy is introduced into the MoS$_2$ crystal structure ($3 \times 3$ 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.[16] 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 $\Delta G_{\text{H}}$ (Figure 1b). Therefore, by depositing a slight amount of Pt onto MoS$_2$ surface, the HER performance of MoS$_2$ 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 MoS$_2$. 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 MoS$_2$ is improved and charges transport more efficiently, thereby enhancing the HER performance.

In this work, MoS$_2$ with S vacancy is directly grown on Mo foil using the hydrothermal method at 200 °C, which is provided in the "Experimental Section." After MoS$_2$ 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 MoS$_2$ is further investigated by a transmission electron microscope (TEM). The low-magnification TEM image shows that the synthesized MoS$_2$ films have the porous structure (Figure 4b). The selected area electron diffraction pattern of MoS$_2$ confirms the polycrystalline nature of synthesized MoS$_2$. After loading of Pt nanoparticles onto MoS$_2$/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 MoS$_2$ 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 MoS$_2$. 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 MoS$_2$.[16] The peak at 226.2 eV belongs to S 2s orbital of MoS$_2$. In addition, in the S 2p region of the spectra, two peaks are found at around 162 and 163.2 eV, which correspond to S$^{2-}$ 2p$_{3/2}$ and S$^{2-}$ 2p$_{1/2}$ components, respectively.[17] For the synthesized MoS$_2$, 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 MoS$_2$. 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.[18] Raman spectra of synthesized MoS$_2$ (black line) and CVD-grown MoS$_2$ on Mo foil at 700 °C (red line) are shown in Figure 4f. For MoS$_2$ synthesized by the

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**Figure 1.** Schematic of HER process on a) MoS$_2$ with S vacancy and b) MoS$_2$ with S vacancy and Pt. H* represents H free radical. The HER process has two steps: absorption (H$^+$ + e$^-$$\rightarrow$ H*) on catalytic sites and release (2H$^+$ $\rightarrow$ 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^+.
hydrothermal method at 200 °C, peaks at 382.7 and 409.6 cm$^{-1}$ corresponds to the $E_{12g}$ 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. While for the CVD-grown MoS$_2$ at 700 °C, the peak at 410 cm$^{-1}$ is much sharper and narrower compared with hydrothermal MoS$_2$ films, indicating that the CVD-grown MoS$_2$ has a high degree of crystalline order. Additionally, the position of $A_{1g}$ mode of hydrothermal synthesized MoS$_2$ blueshifts about 11.4 cm$^{-1}$, while $E_{12g}$ 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 MoS$_2$.

The HER performance of the synthesized samples is measured in 0.5 mol L$^{-1}$ H$_2$SO$_4$ 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 MoS$_2$ and Pt, as well as the sketch of the cathodic current direction in the HER process. The representative polarization curves for the Mo foil, MoS$_2$/Mo, and Pt/MoS$_2$/Mo are shown in Figure 5a. Apparently, Mo foil has weak HER activity, while MoS$_2$/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 MoS$_2$/Mo electrode to achieve a cathodic current density of 10 mA cm$^{-2}$. The significantly improved HER activity of MoS$_2$/Mo indicates the intrinsically high catalytic activity of MoS$_2$.

Pt nanoparticles are deposited by the cyclic voltammetry method. After electrodeposition of Pt nanoparticles on the surface of MoS$_2$, the Pt/MoS$_2$/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 MoS$_2$, 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/MoS$_2$/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 Pt/MoS$_2$/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/MoS$_2$/Mo electrocatalyst displays the largest current density of 216 mA cm$^{-2}$ at the same potential of 300 mV when compared with MoS$_2$/Mo and Mo foils. The corresponding Tafel plots (Figure 5b) show that MoS$_2$ with S vacancy has a Tafel slope of 68 mV dec$^{-1}$, which is lower than that of MoS$_2$ with S vacancy created by Ar plasma etching. After depositing Pt to create more gap states and form additional active centers on MoS$_2$ 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/MoS$_2$/Mo validates the theoretical calculations mentioned above. The fabricated hybrid material exhibits significantly
high HER electrocatalytic activity compared to other works as shown in Table S2 (Supporting Information).

The interaction between Pt and MoS$_2$ can be reflected by the electrochemical impedance spectroscopy (EIS) Nyquist plots of MoS$_2$/Mo foil and Pt/MoS$_2$/Mo foil shown in Figure 5c. Pt/MoS$_2$/Mo has better HER performance than that of MoS$_2$/Mo. Pt/MoS$_2$/Mo should have a smaller resistance than MoS$_2$/Mo. However, the Pt/MoS$_2$/Mo electrocatalyst has a larger resistance than MoS$_2$/Mo, indicating that electrons flow from MoS$_2$ to Pt due to the difference of the work function between Pt and MoS$_2$. Hence, the HER activity of Pt/MoS$_2$/Mo is mainly from the MoS$_2$. The EIS measurements indicate that Pt-induced gap states play the key role in enhancing the HER performance of MoS$_2$. 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$^{-1}$ H$_2$SO$_4$ solution, cyclic voltammetry measurements are carried out on MoS$_2$/Mo and Pt/MoS$_2$/Mo to determine the $C_{dl}$. $C_{dl}$ can be extracted from the positive and negative current density differences ($A_j = j_a - j_c$) 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 MoS$_2$/Mo (53 mF cm$^{-2}$) and Pt/MoS$_2$/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/MoS$_2$/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 MoS$_2$ 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
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 $\Delta G_{\text{H}}$. 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]

**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