Strategies to improve electrocatalytic performance of MoS$_2$-based catalysts for hydrogen evolution reactions

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Electrocatalytic hydrogen evolution reactions (HERs) are a key process for hydrogen production for clean energy applications. HERs have unique advantages in terms of energy efficiency and product separation compared to other methods. Molybdenum disulfide (MoS$_2$) has attracted extensive attention as a potential HER catalyst because of its high electrocatalytic activity. However, the HER performance of MoS$_2$ needs to be improved to make it competitive with conventional Pt-based catalysts. Herein, we summarize three typical strategies for promoting the HER performance, i.e., defect engineering, heterostructure formation, and heteroatom doping. We also summarize the computational density functional theory (DFT) methods used to obtain insight that can guide the construction of MoS$_2$-based materials. Additionally, the challenges and prospects of MoS$_2$-based catalysts for the HER have also been discussed.

1. Introduction

With the rapid growth of the economy, the traditional, polluting sources of energy are being consumed heavily, resulting in environmental degradation; thus, developing sustainable and clean energy has become urgent. Among all the alternative energies, hydrogen has significant advantages due to its high energy density and environmental friendliness.$^*$ Currently, mass H$_2$ production mainly comes from steam reforming of hydrocarbons, which is highly energy-consuming and relies on the polluting petroleum industry.$^5–^7$ To promote the adoption of the H$_2$ economy, in the past several decades, new H$_2$ production technologies, like photocatalytic and electrocatalytic water splitting, have been developed.$^{8–12}$ Compared with photocatalytic water splitting, the electrochemical approach has more advantages in terms of energy efficiency and achieving effective product separation. Electrochemical water splitting consists of two half-reactions, which are named as the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER).$^{13}$ The OER is hard to occur, because it involves four-electron transfer.$^{14}$ The reaction mechanism is as follows:

Total reaction:

\[ \text{H}_2\text{O}(l) \rightarrow \text{H}_2(g) + \frac{1}{2}\text{O}_2(g) \quad (1) \]

In acidic solution:

\[ \text{Cathode: } 2\text{H}^+(aq) + 2e^- \rightarrow \text{H}_2(g) \quad (2) \]
\[ \text{Anode: } \text{H}_2\text{O}(l) \rightarrow 2\text{H}^+(aq) + \frac{1}{2}\text{O}_2(g) + 2e^- \quad (3) \]

In neutral and alkaline solution:

\[ \text{Cathode: } 2\text{H}_2\text{O}(l) + 2e^- \rightarrow \text{H}_2(g) + 2\text{OH}^- (aq) \quad (4) \]
\[ \text{Anode: } 2\text{OH}^- (aq) \rightarrow \text{H}_2\text{O}(l) + \frac{1}{2}\text{O}_2(g) + 2e^- \quad (5) \]

Generally, the HER consists of the three following steps:

Volmer step: \( \text{H}^+ + e^- \rightarrow \text{H}^* \quad (6) \)

Heyrovsky step: \( \text{H}^* + \text{H}^+ + e^- \rightarrow \text{H}_2 \quad (7) \)

Tafel step: \( 2\text{H}^* \rightarrow \text{H}_2 + 2^* \quad (8) \)

In acidic electrolytes, the HER occurs when protons are adsorbed at the surface of the MoS$_2$ and consequently, step (6) takes place, which is then followed by step (7) or (8). The overall reaction rate relies on the Gibbs free energy of H$_2$ adsorption ($\Delta G_{\text{H}}^\ddagger$). In theory, the closer this value is to zero, the greater is the HER activity. The reactions (7) or (8) are inhibited when the binding of H to the catalyst surface is weak. Therefore, catalysts...
with excellent HER performance tend to exhibit good adsorption of H atoms, which is conducive to charge transfer and bond breakage, resulting in the formation of $H_2$.\textsuperscript{9,15–18}

Under standard conditions, initiating HER requires a dynamic overpotential, which essentially involves additional energy consumption; thus, electrocatalysts are integral to abate the overpotential. As of today, Pt-based materials are the most widely used electrocatalysts; however, Pt is scarce and costly, making it essential to develop cost-effective electrocatalysts. Currently, a wide range of materials, including transition metal alloys,\textsuperscript{19–27} transition metal carbides,\textsuperscript{28–36} transition metal dichalcogenides,\textsuperscript{37–45} transition metal phosphides,\textsuperscript{46–50} and so on, are being studied as possible alternative HER electrocatalysts. Among them, MoS\textsubscript{2} has attracted wide attention due to its unique two-dimensional layered structure and adjustable band gap width, which makes MoS\textsubscript{2} has a property of ease incorporation into the lattice (heteroatoms and vacancies) and adjustability of electron transport. However, experimental and theoretical studies reveal that the HER activity of MoS\textsubscript{2} remains unsatisfactory due to three main issues. First, the HER activity of MoS\textsubscript{2} correlates with the active edge sites rather than basal planes, but the edge sites just account for a small part of the surface area of MoS\textsubscript{2}. Second, the semiconducting basal plane of MoS\textsubscript{2} has a low intrinsic electronic conductivity, which leads to poor charge transfer. Third, the aggregation and restacking of MoS\textsubscript{2} hinders the availability of edge sites. Herein, we discuss three important approaches that have been demonstrated to improve the intrinsic catalytic activity and HER performance of MoS\textsubscript{2} effectively, \textit{i.e.}, defect engineering, formation of the heterostructure, and heteroatom doping (Fig. 1).

### 2. Properties of MoS\textsubscript{2}

MoS\textsubscript{2} is a typical layered transition metal dichalcogenides composed of stacking S–Mo–S layers by van der Waals interactions, leading to a sandwich-like layered structure.\textsuperscript{51,52} The basal plane of MoS\textsubscript{2} is generally believed to be inert toward HER, while the edge sites of MoS\textsubscript{2} layers possess much higher chemical reactivity than the basal plane.\textsuperscript{13} Based on the arrangement of the S atoms, three phases of MoS\textsubscript{2} can be obtained, \textit{i.e.}, 1T, 2H and 3R.\textsuperscript{53} The 2H phase MoS\textsubscript{2} is thermodynamically stable, but the conductivity of 2H phase MoS\textsubscript{2} is poor.\textsuperscript{54,55} Compared to 2H MoS\textsubscript{2}, 1T MoS\textsubscript{2} is metallic and is 10\textsuperscript{7} times more conductive than 2H MoS\textsubscript{2}.\textsuperscript{56} Nevertheless, 1T MoS\textsubscript{2} is thermodynamically unstable and does not exist in nature\textsuperscript{57} (Fig. 2). Under some specific conditions, 1T MoS\textsubscript{2} can also exist and phase transformation is one of the most effective methods to improve the catalytic performance of MoS\textsubscript{2}.\textsuperscript{58,59} Zhao \textit{et al.}\textsuperscript{60} investigated the HER dynamics in the MoS\textsubscript{2} basal plane of the 1T and 2H phases. They calculated the absorbed H free energies on the 2H/1T structural interfaces and their work offered a new way to increase the number of MoS\textsubscript{2} active sites on the basal plane. DFT calculations demonstrated that MoS\textsubscript{2} had a similar H binding energy as that of Pt.\textsuperscript{61} In theory, MoS\textsubscript{2} should exhibit outstanding HER performance; however, bulk MoS\textsubscript{2} displays poor performance due to the following reasons. (i) The active sites of bulk MoS\textsubscript{2} cannot be fully exposed.\textsuperscript{62} (ii) The superimposition of the van der Waals force in the interior of the bulk MoS\textsubscript{2} leads to an incongruous effect of the active sites.\textsuperscript{63} (iii) The covalently bonded atoms in the layers lead to poor HER performance.\textsuperscript{64} (iv) The electronic conductivity of bulk MoS\textsubscript{2} is low.\textsuperscript{65} Thus, many efforts have been devoted to designing
a reasonable MoS$_2$ nanostructure and modulating the MoS$_2$ electronic structure. Furthermore, many engineering methods such as phase transformation engineering, vacancy engineering, and stretching have been developed to overcome the disadvantages of bulk MoS$_2$. Cao et al. demonstrated that S vacancies could provide another type of active site for the HER besides the Mo and S active edge sites. They also found that the HER activity of grain boundaries was much lower than that of the S vacancy and S edge sites. Based on the structure determining properties, many efforts have been devoted to constructing specific MoS$_2$ nanostructures, including nanoparticles, nanoflakes, nanowires, and...
3. Synthetic methods for MoS₂

In order to synthesize MoS₂, many strategies have been developed, including mechanical exfoliation, solution exfoliation, chemical vapor deposition (CVD), hydrothermal synthesis, electrodeposition methods, and molecular beam epitaxy (MBE). These methods can be classified as top-down methods (including mechanical exfoliation and solution exfoliation) and bottom-up methods (including hydrothermal synthesis, CVD, MOCVD, and MBE). In the top-down methods, the morphology of MoS₂ can be well controlled since the structure of the final product is inherited from the original materials. However, top-down methods have intrinsic shortcomings; for instance, the nanoscale morphology of the final product is hard to adjust since it is difficult to change the distance between ions and atoms in top-down methods. In bottom-up methods, a large and complicated system is formed by atoms, molecules, and nanoparticles through self-assembly or weak interactions, and the usage of materials is more efficient. The specific surface area and thickness of MoS₂ can be better controlled than in top-down methods. For example, in hydrothermal method, the thickness and size of MoS₂ can be modulated by simply tuning the hydrothermal time, temperature and growth parameters of solution concentration. The main disadvantage of bottom-up methods is the difficulty of large-scale synthesis. In the rest of this section, we try to list out the general methods of synthesizing MoS₂ for the electrochemical HER (Table 1).

| Synthetic method                  | Advantages                                                                 | Disadvantages                                                                 | Reference |
|----------------------------------|---------------------------------------------------------------------------|------------------------------------------------------------------------------|-----------|
| Hydrothermal synthesis           | Easy to operate, high purity, good dispersibility, complete crystal form, uniform particle size | Easy to agglomerate, unclear reaction mechanisms, unsuitable for water sensitive materials, poor repeatability | 90-92     |
| Chemical vapor deposition        | Simple film-forming device, easy to control the product composition, good repeatability, good uniformity | May produce corrosive, toxic or explosive reaction gas, low film forming rate, easy to introduce impurities | 87-89     |
| Mechanical exfoliation           | Few defects, smooth surface, high mobility                                | Difficult to control the thickness, random position on substrate, small output | 81-83     |
| Solution exfoliation             | Low cost, high controllability, easy to realize large-scale preparation    | Small product size, low yield                                                | 84-86     |
| Electrodeposition methods        | Adjustable grain size, easy to operate, low cost, high efficiency         | Difficult to control growth rate, low crystallinity of product                | 93-95     |
| Metal-organic chemical vapor deposition | Low reaction temperature, wide application range, suitable for mass production | May produce toxic and flammable vapor, difficult to in situ monitor the growth process | 96-98     |
| Molecular beam epitaxy           | Atomic-level controlled film thickness, composition and dopants            | High requirements for equipment conditions                                   | 99-101    |

3.1. Hydrothermal synthesis

Hydrothermal method is to seal the reactants in the reactor, and the reaction process is completed through chemical transmission. Liquid or gaseous water is the pressure transmission medium under high temperature and high pressure, and most of the reactants can be dissolved in water, so that the reaction can be carried out in the critical state of gas phase and liquid phase solvent. Compared with other powder preparation methods, the powder prepared by hydrothermal methods has the advantages of complete grain development, small particle size, uniform distribution, light particle agglomeration, cheaper raw materials, and appropriate stoichiometry and crystal shape are easily obtained. Typically, the ceramic powder prepared by hydrothermal methods does not need high-temperature calcination treatment, which prevents grain growth, defect formation and introduction of impurities in the calcination process, so the prepared powder has high sintering activity.

Liu et al. prepared ultrathin MoS₂ nanosheets grown on an in situ-formed polysaccharide matrix derived from glucose condensation via a hydrothermal method. 0.80 g of glucose with a varied amount of ammonium heptamolybdate tetrahydrate [(NH₄)₆Mo₇O₂₄-4H₂O] and thiourea (CS[NH₂]₂) was dissolved in 15.0 mL of distilled water, and then the solution was turned to a Teflon-lined stainless-steel autoclave, with a hydrothermal treatment at 240 °C for 48 h. After centrifugation, washing and annealing, the MoS₂/C nanospheres was successfully synthesized. Wang et al. prepared 1T/2H MoS₂ via a facile hydrothermal method with the addition of ammonium bicarbonate. During the hydrothermal process, ammonium bicarbonate was decomposed into small molecules and ions as guests, including NH₄⁺, H₂O and CO₂, which were inserted into the lamellar structures of MoS₂, inducing the formation of multiphasic 1T/
2H MoS$_2$. Zhang et al.$^{118}$ used the hydrothermal method to construct MoS$_2$/NiCoS nanosheets with ultrathin NiCo bimetal–organic framework (NiCo-MOF) nanosheets and (NH$_4$)$_2$MoS$_4$ as precursors. The hydrothermal process was controlled at 200 °C for 24 h. In this reaction, (NH$_4$)$_2$MoS$_4$ not only acts as a precursor for the synthesis of MoS$_2$, but also provides a source of sulfur for in situ conversion of NiCo-MOF nanosheets to NiCoS. Li et al.$^{119}$ prepared V-doped 1T MoS$_2$ nanosheets as a highly efficient HER electrocatalyst in both acidic and alkaline solutions through a hydrothermal method. Typically, 0.2 g sulfur was put into 4 beakers with different molar quantity of ammonium heptamolybdate ([NH$_4$]$_7$Mo$_7$O$_{24}$·4H$_2$O). Then, 4 mL of hydrazine monohydrate (N$_2$H$_4$·H$_2$O) was dissolved in each beaker. Then, 36 mL of DI water was added into the beakers to make the mixture 80% of autoclave volume, and different molar quantity of ammonium metavanadate (NH$_4$VO$_3$) were added into the beakers as the V source. Then the precursors were transferred to 50 mL stainless steel autoclaves. The whole set was sealed and put into the oven at 200 °C for 48 h. Xiao et al.$^{120}$ synthesized 1T/2H MoS$_2$@graphene via a hydrothermal method. The introduction of metallic 1T-MoS$_2$ endues the as-prepared materials with remarkably electrocatalytic activity and favorable kinetics, highly efficient and stable HER performance.

### 3.2. Chemical vapor deposition

Chemical vapor deposition (CVD) is a method of synthesizing coatings and nanomaterials deposited on a substrate surface by chemical gas or vapor reaction. It is the most widely used technology for depositing a variety of materials in the semiconductor industry, including a wide range of insulating materials, most metal materials and metal alloy materials.$^{121-123}$ Theoretically, the CVD process is very simple: two or more gaseous raw materials are introduced into a reaction chamber, which then react with each other to form a new material that is deposited on the wafer surface. However, experimentally, the reaction that takes place in the reaction chamber is very complex, and there are many factors that must be considered. The deposition parameters, which can vary over a wide range, include the pressure in the reaction chamber, the temperature of the wafer, the flow rate of the gas, the distance of the gas through the wafer, the chemical composition of the gas, the ratio of one gas to another, the role of the intermediate product of the reaction, and whether other reactions are needed.$^{124-128}$ Pumera et al.$^{129}$ synthesized MoS$_2$ films via powderless gas deposition. The CVD fabrication method they used is suitable for industry because this powderless and one-step process eliminates the deviations of MoS$_2$ growth which are likely to arise from the usage of a powder precursor. Yu et al.$^{130}$ hybridized MoS$_2$ micro-flowers on VS$_2$ by a one-pot CVD method and their catalyst exhibited excellent HER performance. Atomic layer deposition (ALD) is a method in which substances can be deposited on the surface of the substrate, layer by layer, in the form of a monoatomic film.$^{131}$ ALD has similarities with ordinary chemical deposition, except that the chemical reaction of the new layer of atomic film is directly dependent on the previous layer. In this way, only one layer of atoms is deposited per reaction. Due to its highly controllable deposition parameters (thickness, composition, and structure), atomic layer deposition technology, excellent deposition uniformity and consistency, it has wide application potential in the field of micro-nanoelectronics and nanomaterials. Tan et al.$^{132}$ successfully synthesized layered MoS$_2$ via the ALD method. Typically, MoS$_2$ films were prepared by alternating exposure to molybdenum chloride (MoCl$_5$) and hydrogen disulfide (H$_2$S) vapors. Due to the self-limiting reactions of the vapors, the number of MoS$_2$ film layers can be precisely controlled by the number of deposition cycles.

### 3.3. Exfoliation method

At present, the most effective preparation methods of single- or few-layer MoS$_2$ are exfoliation methods, which can be divided into mechanical exfoliation, lithium-ion intercalation exfoliation and liquid phase ultrasonic exfoliation. The mechanical exfoliation method, MoS$_2$ powder is directly stripped to form a thin layer of MoS$_2$ nanoflakes with a special gummy tape. This is the most original and traditional preparation method. The thickness of MoS$_2$ that was first peeled off in 1965 ranged from a few layers to dozens of layers.$^{133}$ After the improvement of this stripping process, monolayer MoS$_2$ was successfully obtained.$^{134}$ The most obvious advantage of the mechanical exfoliation method is that the process is simple, can be obtained manually, and the stripping efficiency is high. However, this method has obvious disadvantages, such as low yield and poor repeatability. The lithium-ion intercalation-based exfoliation method can be used, for instance the Li$_x$MoS$_2$ ($x \geq 1$) intercalation compound is obtained by the reaction of the lithium-ion intercalation agent (such as n-butyl lithium) and MoS$_2$ powder (intercalation process). Then the intercalation compound reacts violently in water and other protonic solvents, and the stripping process occurs. Thus, multilayer and monolayer MoS$_2$ can be obtained by ultrasonic extraction. In 1986, Morrison et al.$^{135}$ prepared monolayer MoS$_2$ by this method. The efficiency of the Li ion intercalation stripping was found to be very high, with a yield close to 100%. The quality of the prepared nanosheets was very good, making it suitable for mass-production, and the method could be used to peel many other inorganic layered compounds. However, this preparation method is complex, the intercalation agent is sensitive to the environment, leading to a high production cost, and long preparation time. Moreover, it is difficult to control the degree of intercalation, which makes the post-treatment difficult. For this reason, Zeng et al.$^{136}$ used an electrochemical lithium battery device to control the lithium ion insertion and stripping process, so as to prepare a variety of monolayer materials such as MoS$_2$. This electrochemical lithium-ion intercalation exfoliation method can effectively avoid many of the abovementioned problems and obtain high yield monolayer MoS$_2$. The basic principle of the liquid-phase ultrasonic exfoliation method is to put MoS$_2$ and other layered materials into a suitable solvent,
use the ultrasonic wave to vibrate and peel off the lower layer of materials from the block, and then centrifuge to obtain thin MoS$_2$ nanosheets. In 2011, Coleman et al.\textsuperscript{137} prepared monolayer and multilayer nanosheets such as MoS$_2$, BN and WS$_2$. The solvent selected by the liquid phase ultrasonic exfoliation method is generally a polar solvent with good dispersity.
and solubility for layered materials and similar surface energy. Coleman et al.\textsuperscript{138} prepared thin MoS\textsubscript{2} material by adding a sodium cholate surfactant and stripping it in an aqueous phase. However, Zhou et al.\textsuperscript{139} used ethanol/water mixed low-boiling solvents to successfully peel off nanosheets such as MoS\textsubscript{2}, making the peeling method cheaper and environmentally friendly, and peeling MoS\textsubscript{2} under water phase conditions has become a new choice for people. The liquid-phase ultrasonic peeling method is simple and fast, and can be suitable for large-scale production, but generally the peeling degree is not high, the concentration of the obtained nanosheet solution is small, and the dependence on the ultrasonic conditions is high, and the ultrasonic power is too large or too small, which is not conducive to the formation of nanosheets.

3.4. Electrodeposition method

Electrodeposition method is an attractive way to synthesize MoS\textsubscript{2} thin film in large scale because it uses cheap equipment, enables the deposition in large area and easy control of growth parameters through applied potential, current, pH and temperature of the bath.\textsuperscript{140} Many researchers have studied the mechanism of an electrochemical deposition of MoS\textsubscript{2} from aqueous and little from non-aqueous solutions. A variety of electrodeposition techniques have been reported for the preparation of MoS\textsubscript{2} films using anodic oxidation or cathodic reduction.

Ping et al.\textsuperscript{141} developed an edge-guided electrodeposition approach for the construction of high quality edge contacted metal-2D MoS\textsubscript{2} and further demonstrated the potential of this approach in the fabrication of high performance electrocatalyst. Hwang et al.\textsuperscript{142} developed a novel MoS\textsubscript{2} electrode with a nanocarbon (NC) coating as a catalytic cathode for hydrogen production in a microbial electrolysis cells (MEC), while treating simulated urine. The MEC performance of HER using the MoS\textsubscript{2}-NC cathode was characterized and evaluated under different applied voltages and various dilution factors for adjusting conductivity. Lyndi et al.\textsuperscript{143} prepared MoS\textsubscript{2} films via an electrodeposition method. Electrodeposition of molybdenum disulfide films was carried out with a 10 mM (NH\textsubscript{4})\textsubscript{2}MoS\textsubscript{4} (ammonium tetrathiomolybdate) with 0.1 M LiClO\textsubscript{4} adjusted to pH 10 with NH\textsubscript{4}OH using chronoamperometric deposition. Jiang et al.\textsuperscript{144} prepared the MoS\textsubscript{2}–Co\textsubscript{3}S\textsubscript{4}/NF heterostructure layer by Co-MOF vulcanization and cyclic voltammetry (CV) method, which showed better electrochemical performance than the single-layer Co\textsubscript{3}S\textsubscript{4}/NF. The as-prepared MoS\textsubscript{2}–Co\textsubscript{3}S\textsubscript{4} heterostructure layer was decorated by ZnCo-LDH, the hydrogen evolution performance was further improved.

Though the above synthetic methods have been demonstrated to be an effective way to synthesize bulk MoS\textsubscript{2}, the HER performance of bulk MoS\textsubscript{2} is still not satisfactory. In the following part, we summarize three main strategies to promote the HER performance of MoS\textsubscript{2} (Fig. 3).

4. Main strategies to promote the HER performance of MoS\textsubscript{2}

4.1. Defect engineering

Many physical and chemical properties of materials are closely related to the existence of defects.\textsuperscript{145–147} Generally, defects can be classified as vacancies, grain boundaries and disorders.\textsuperscript{148–150} Furthermore, vacancies can consist of, for instance, Mo vacancies, S vacancies, O vacancies, N vacancies and C vacancies.\textsuperscript{151–155} Thermodynamically, it’s unavoidable to introduce vacancies in the process of synthesizing MoS\textsubscript{2}.\textsuperscript{156} Many studies
have examined the impact of vacancies on the HER performance of MoS2.\textsuperscript{167-167} Theoretically, the rational design of defects on the basal plane of MoS2 can enhance the HER performance of MoS2 because the basal plane of MoS2 is inert while the edge sites are significantly more active.

Li et al.\textsuperscript{168} designed vertically aligned MoS2 with a selectively cleaved Mo–S bond. Their work showed a new way to synthesize MoS2 with a vacancy and their synthesis route is shown in Fig. 4(a). Fig. 4(b) shows that the scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images confirm the existence of micro-cubic c-MoS2–C morphology. Aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (AC HAADF-STEM) images show the existence of the vacancy. This unique defect is beneficial to a thermoneutral H-adsorption energy, which leads to accelerate HER kinetics. The energy-dispersive X-ray spectroscopy (EDS) elemental mapping results further confirm the formation of MoS2 nanosheets with Mo and S defects. The electrocatalytic performance of the defect-rich MoS2 is shown in Fig. 5. Further DFT calculations reveal that the newly generated interior edge sites break the periodic electronic structure of the MoS2 basal plane, leading to an optimized surface charge configuration for H adsorption and desorption.

Li et al.\textsuperscript{174} conducted a study of the catalytic activities of all potential reaction sites, such as edge sites, S vacancies and grain boundaries. For the first time, they demonstrated that S vacancies provide another active site for HER in addition to the well-known active edge sites (Fig. 6(a)). In order to identify the influence of S vacancy states and concentration on catalysis, Wang et al.\textsuperscript{169} synthesized MoS2 with homo-vacancies, with an H2O2 chemical etching strategy (Fig. 6(b)). They performed DFT calculations of ΔG\textsubscript{H*} to explore the effect of S vacancy concentration and distribution on the HER performance. The results showed that 12.50% of the single S-vacancies yielded the optimal HER performance. They synthesized a vertically aligned MoS2 nanosheet guided by these theoretical DFT calculations. The X-ray diffraction (XRD) results in Fig. 7(a) demonstrate that the sample phase was firm and did not change after H2O2 etching. To determine the S-vacancy concentration as a function of the etching process, three X-ray photoelectron spectroscopy (XPS) spectra of P-MoS2 and MoS2\textsubscript{–x} are shown in Fig. 7(a). The S : Mo ratio in each spectrum was calculated and it was
converted to the corresponding S-vacancy concentration. The electrochemical results are shown in Fig. 7(b) indicate that MoS$_2$ with 12.11% S-vacancy exhibited the best HER performance and the ratio of S-vacancy was very close to the theoretically predicted optimal value of 12.50%. Furthermore, the superiority of single S-vacancies over agglomerate S-vacancies was found to originate from more effective engineering of the surface electronic structure. The synergistic modulation of catalytic performance from both vacancy concentration and distribution broadens the vacancy design field and can be further extended to other types of TMDs and for other catalytic reactions.
Forming pits on MoS$_2$ monolayers has been found to be desirable for promoting HER performance. Park et al. investigated the effect of adventitious C on the pit formation in the MoS$_2$ layers. They used an aperture type in situ ETEM to study the reaction between MoS$_2$ monolayers and O$_2$. The HER activity of MoS$_2$ was enhanced in the presence of pits, which can be ascribed to the increase of active edge sites (Fig. 8(b)). They also conducted DFT calculations and found that the presence of C nanoparticles on monolayer MoS$_2$ was favorable for progressive oxidation (Fig. 8(a)).
Although the existence of defects can significantly improve the HER performance of MoS$_2$, the key is the ability to detect the existence of defects. Thus, we need to study the relationship between defect types and electronic modes. Up till now, the existence of defects was observed indirectly because the concentration of defects is typically very low. One of the
Fig. 9  (a) SEM images of bulk MoS$_2$ and CoS$_2$@MoS$_2$ nanoparticles. (b) HER performance of CoS$_2$@MoS$_2$. Reproduced with permission from ref. 182, Copyright 2020 Elsevier B.V. (c) The HER performance of PCN, PCN@MoS$_2$, PCN@MoS$_2$@C and Pt/C. Reproduced with permission from ref. 183, Copyright 2020 the Royal Society of Chemistry.
detecting methods is Raman spectroscopy, which can effectively detect edge defects and show distinct electronic structure. The vital task of defect engineering is to enhance the electrochemical activity of the MoS$_2$ basal plane.

4.2. Formation of heterostructure

The construction of heterostructured composites is an effective way to enhance the activity of MoS$_2$.$^{173-181}$ Wei et al.$^{182}$ synthesized core–shell structured CoS$_2$@MoS$_2$ by a hydrothermal method. As shown in Fig. 9(a), the CoS$_2$@MoS$_2$ nanoparticles had a uniform size distribution, ranging from 20–30 nm. The HER performance of CoS$_2$@MoS$_2$ in Fig. 9(b) shows that the overpotential of HER was only 276 mV and the Tafel slope was 60 mV dec$^{-1}$. Mei et al.$^{183}$ constructed a PCN@MoS$_2$@C sandwich-like heterostructure by a facile hydrothermal method. The PCN@MoS$_2$@C exhibited excellent HER performance within a wide pH range (Fig. 9(c)).

Constructing heterostructures with multiple electrocatalytically active components simultaneously to improve HER performance is regarded as an effective strategy. He et al.$^{184}$ synthesized CoS$_2$/SnO$_2$@MoS$_2$ (denoted as CSM) nanotubes by a fast template-engaged hydrothermal treatment. The SEM and TEM images of the obtained CSM are shown in Fig. 10(a) and (b). These images revealed a porous structure, which enlarged the surface area of the material and boosted the mass transport process, leading to excellent HER performance (Fig. 10(c)). Huang et al.$^{185}$ designed an exfoliated few-layer FePS$_3$ decorated with vertical MoS$_2$ nanosheets through a facile hydrothermal reaction. The synergistic effect between the FePS$_3$ and MoS$_2$ led to excellent HER performance. This effect can regulate the electronic structure and improve the electron conductivity. As

![Image](https://example.com/image.png)
shown in Fig. 10(d). The overpotentials of FeS$_3$@MoS$_2$ were 175 mV and 168 mV in alkaline and acidic media, respectively. Furthermore, the heterostructure could prevent agglomeration during electrocatalytic cycling, which led to high stability.

Tahira et al.$^{186}$ reported a stable electrocatalyst composed of TiO$_2$ nanorods decorated with MoS$_2$ nanosheets by a two-step hydrothermal method. This electrocatalyst showed an enhanced HER performance compared with bulk MoS$_2$ (Fig. 11(a)). Cao et al.$^{187}$ prepared cobalt molybdenum nitride with a nanoscale morphology using a two-step solid-state reaction. This compound did not belong to any layered structural family prepared for HER; however, it exhibited HER activity comparable to MoS$_2$ (Fig. 11(b)).

Theoretically, heterostructure engineering of MoS$_2$ with graphene is an effective and facile method and the enhanced catalytic performance can be attributed to two factors. First, the induced graphene substrate prevents the agglomeration of MoS$_2$ nanosheets; thus, creating sufficient edge sites for HER. Second, the excellent electronic conductivity of graphene encourages rapid electron transfer, which is beneficial for the absorption of the H atom and reduces the Gibbs free energy. Furthermore, the heterojunction of the MoS$_2$@graphene hybrid provides new chemical properties and may be beneficial for an enhanced HER performance. Wang et al.$^{189}$ constructed a MoS$_2$@rGO hybrid catalyst by growing MoS$_2$ arrays on the rGO surface via a one-step hydrothermal method. The MoS$_2$@rGO presented a three-dimensional flower-like morphology, with plentiful active edge sites exposed, which contributed to good HER performance. Yan et al.$^{186}$ reported a bottom-up method for the large-scale synthesis of 3D hybrid architectures constructed from graphene, MoS$_2$ and graphitic carbon nitride nanosheets by self-assembly. Due to the distinct architectural features such as 3D interconnected porous networks and low charge-transfer resistance, the MoS$_2$-CN/G exhibited superior HER performance with low overpotential, small Tafel slope and long-term durability. Wu et al.$^{191}$ designed MoS$_2$/MoN heterostructures with tuned components and the catalyst showed excellent HER performance in acid and alkaline electrocatalyst. DFT calculations suggested that the MoS$_2$/MoN interface could optimize the H atom adsorption kinetic energy, accelerating the HER process. Liu et al.$^{192}$ reported a hierarchical ZnS@C@MoS$_2$ core–shell nanostructure in a bottom-up strategy combined with a selective etching method. The co-existence of ZnS and porous carbon shell not only improved the electrical conductivity but also separated and loaded the MoS$_2$ nanosheets, which effectively exposed active edge sites. This catalyst showed an excellent HER performance with an overpotential of 118 mV and a Tafel slope of 55.4 mV dec$^{-1}$. Li et al.$^{193}$ reported a 1T-MoS$_2$/CoS$_2$ heterostructure via a self-sacrificing template method. In this work, they compared the cohesive energy of in-

![Fig. 11](image-url) 

(a) HER performance of TiO$_2$/MoS$_2$, TiO$_2$, MoS$_2$, Pt/C. Reproduced with permission from ref. 188, Copyright 2019 American Chemical Society. (b) HER performance of Co$_{0.6}$Mo$_{1.4}$N$_2$. Reproduced with permission from ref. 187, Copyright 2013 American Chemical Society.
4.3. Heteroatom-doping method

4.3.1. Metal-doping method. Metal doping is an effective method to promote the HER activity of MoS2. Transition metals (Fe, Co, Ni, etc.) can significantly enhance the conductivity of MoS2 and modulate the electronic structure of MoS2. Co doping can enhance the conductivity of MoS2, which can decrease the H atom adsorption energy of MoS2 for HER, and also add new active catalytic sites for HER.

Xiong et al.194 reported Co-doped MoS2 nanosheets via a facile one-step hydrothermal method. As shown in Fig. 12(a), the obtained Co-MoS2 exhibited superior HER activity with an overpotential of 60 mV/90 mV at a current density of 10mA cm⁻² for HER in 0.5 M H₂SO₄ and 1.0 M KOH, respectively. They conducted DFT calculations (Fig. 12(b)) and revealed that the ΔGₜᵣ value of pristine MoS2 was about ~2.06 eV while the ΔGₜᵣ value decreased to ~0.20 eV after Co doping, demonstrating that Co doping is an effective method for enhancing HER activity of MoS₂. They also studied the OER activity origin of Co-doped MoS₂ by recording the ex situ Co and Mo K-edge EXAFS spectra of Co-MoS₂.

Iron is a typical nonprecious and earth-abundant element, and Fe-containing materials are more effective in adsorbing hydroxyl, which leads to its unique conductivity to water splitting.13 Previous studies195,196 have verified these observations through XPS characterizations. Xue et al.197 synthesized a series of Fe-doped MoS₂ nanomaterials via a facile one-pot solvothermal method. The Fe-MoS₂ displayed high cycling stability and high HER activity with a small overpotential of 173 mV at a current density of 10 mA cm⁻² (Fig. 12(c)). As shown in Fig. 12(d), the XPS full spectrum confirmed the existence of Fe, S, Mo and O.

Ni doping has a significant impact on surface topography and valence state of Mo in MoS₂, which can accelerate the HER reaction kinetics. Wang et al.198 prepared Ni-doped MoS₂ via a hydrothermal method. The layer number of MoS₂ can be
Fig. 13  (a) HER performance of Pd–MoS2/CP and its comparison. Reproduced with permission from ref. 203, Copyright 2020 Elsevier Ltd. (b) HER performance of MoS2–rGO–Cu and its comparison. Reproduced with permission from ref. 202, Copyright 2020 Elsevier. (c) HER performance of V–MoS2 and its comparison. Reproduced with permission from ref. 204, Copyright 2014 The Royal Society of Chemistry. (d) HER performance of Ni–Co–MoS2 and its comparison. Reproduced with permission from ref. 206, Copyright 2016 WILEY.
estimated by the difference in frequency between two characteristic Raman peaks. The results indicate that Ni doping decreases the vibration frequency of MoS2 and increases the number of layers of MoS2. Fig. 12(e) shows that the Ni-MoS2 displayed enhanced HER performance with an overpotential of 164 mV to reach a current density of 10 mA cm$^{-2}$ in acidic media and a small charge transfer resistance ($R_\text{ct}$) of 89 Ω.

In addition to Co, Fe, Ni doping, some other transition metals can also promote the HER activity of MoS2. Huang et al.\textsuperscript{202} prepared a self-supporting electrode composed of Cu mesh-supported graphene and MoS2 by electroplating zinc, followed by a hydrothermal reaction. The self-supporting catalytic electrode has the advantages of avoiding complex pretreatment of the active substance and the usage of binders. As shown in Fig. 13(b), the MoS2–rGO–Cu exhibited excellent HER performance with a low Tafel slope of 54 mV dec$^{-1}$ and a small overpotential of $-300$ mV at a current density of 400 mA cm$^{-2}$. The excellent HER performance can be ascribed to the good electron transport capability of the Cu mesh, and specifically, the self-supporting electrode can be fabricated into any desired shape, which is well maintained while the HER takes place. Luo et al.\textsuperscript{203} designed Pd-doped MoS2 via a spontaneous interfacial redox technique. The Pd doping converted 2H phase MoS2 into a stabilized 1T structure. Furthermore, Pd atoms occurred at the Mo site, which simultaneously introduced an S vacancy. As shown in Fig. 13(a), the Pd-doped MoS2 exhibited good cycling stability and excellent HER activity with an overpotential of 78 mV at a current density of 10 mA cm$^{-2}$. The DFT calculations demonstrated that the S atom next to the Pd sites had a low H atom adsorption energy of $-0.02$ eV. Sun et al.\textsuperscript{204} designed a novel intralayer V-doping method to synthesize semi-metallic V-doped MoS2 nanosheets. The introduction of V atoms regulated the intrinsic electrical properties of MoS2, leading to an enhanced in-plane conductivity and shortened electron transfer paths. The V-doped MoS2 showed excellent catalytic activity with an overpotential of 130 mV and a small Tafel slope (Fig. 13(c)). Zhang et al.\textsuperscript{205} reported a single Ru atom-doped MoS2 electrocatalyst for HER. As shown in Fig. 14(b) and (c), the DFT calculations revealed that the synergistic effects of the single Ru atom doping, S vacancies and phase transition of MoS2 modulated the electronic structure of MoS2 and significantly reduced the energy barrier of the Volmer step, leading to enhanced HER performance of Ru-MoS2 (Fig. 14(a)). Multidoping methods are also a promising way to enhance the HER activity of MoS2. Yu et al.\textsuperscript{206} reported a typical MOF-engaged synthetic method to prepare Ni and Co incorporated MoS2 nano-boxes. The ultrathin nanosheets obtained exhibited enhanced electrochemical activity for HER (Fig. 13(d)). In recent years, materials with single-atom structure have been recognized as promising HER catalysts due to the maximized atom efficiency and tunable electronic properties. Ni et al.\textsuperscript{207} reported that Ru-based single-atom catalysts are promising HER catalysts due to its excellent HER performance, which is comparable to commercial Pt/C catalysts. However, Ru-based single atom catalysts have problems such as large amount of Ru and unsatisfactory stability. Ge et al.\textsuperscript{208} synthesized dual-metallic Ru and Ni atoms decorated MoS2, which resolve the above problems well. The introduction of Ni has two key roles. On the one hand

![Fig. 14](image_url) (a) HER performance of Ru–MoS2 and its comparison. (b) Free energy diagrams of the different MoS2 model catalysts under alkaline solution. (c) Contour maps of the electron localization function (ELF) in 2H/1T–Ru–MoS2–Sv. Reproduced with permission from ref. 205, Copyright 2019 WILEY.
hand, the introduction of highly electronegative heteroatom Ni could regulate the electronic structure of Ru and optimize the H* adsorption during the water splitting process, thus vastly enhancing the HER property. On the other hand, the incorporation of highly electronegative heteroatom Ni in the substrate exposes abundant active sites and improves electron transfer of the catalyst, and further anchors the single atom Ru and reduces the consumption of precious metal Ru atoms.

4.3.2. Nonmetal-doping method. Nonmetal doping can enhance the electrocatalytic activity of MoS2. Wang et al. synthesized amorphous P-doped MoS2 nanoparticles hydrothermally. The P-doping promoted the amorphization of MoS2; thus, affecting the HER performance of MoS2. Deng et al. prepared O-doped MoS2 via an electrochemical anodic activation method. The HER activity of O-doped MoS2 significantly improved at an overpotential of 50 mV, at a current density of 1 mA cm\(^{-2}\) (Fig. 15(a)). As shown in Fig. 15(b), the XPS images confirmed the strong electron interactions after O doping, which indicated the existence of Mo–O bonds and demonstrated that the O doping was successful. Liu et al. reported O and P dual-doped MoS2 nanosheets, which have a porous structure and conductive network via a one-pot hydrothermal approach. As shown in Fig. 15(c), the O, P multi-doped MoS2 showed superior electrocatalytic performances compared with O-doped MoS2 nanosheets. Wang et al. prepared MoS2 decorated Ni-Fe–N-doped carbon nanotubes via a hydrothermal method. According to the SEM results shown in Fig. 15(d), the catalysts were hierarchically structured. Due to the synergistic effect of the NiFe alloy and N-doped carbon nanotubes, the catalysts exhibited excellent HER performance with a cell voltage of 1.6 V at a current density of 10 mA cm\(^{-2}\). Tian et al. synthesized N, P dual-doped MoS2 on hollow carbon spheres by a template and hydrothermal process. The synergistic effect of N, P dual-doped carbon and MoS2 led to the enhanced electrocatalytic performance of MoS2 with an overpotential of 147 mV, at a current density of 10 mA cm\(^{-2}\) and Tafel slope of 72 mV dec\(^{-1}\). As shown in Fig. 15(e), the XPS spectra confirmed the co-existence of N and P atoms.

Metal-doping and nonmetal-doping can be synergistically used to improve the HER performance of MoS2. Meng et al. reported a 3D mesoporous hybrid structure of Co-doped MoS2 and graphene. The Co-doping enhanced the intrinsic

![Fig. 15](a) HER performance of O-doped MoS2. (b) Mo 3d XPS spectra of O, P-MoS2 (R = 10%) and O-MoS2. Reproduced with permission from ref. 210, Copyright Elsevier Ltd. (c) HER performance of O, P dual-doped MoS2 and its comparison. Reproduced with permission from ref. 211, Copyright 2019 WILEY. (d) SEM images and elemental mapping of NiFe–NCNT–MoS2. Reproduced with permission from ref. 212, Copyright 2019 The Royal Society of Chemistry. (e) XPS survey spectra and high-resolution scans of B, C 1s, C, N 1s, D, P 2p, E, S 2p, and F, Mo 3d electrons of the P-MoS2@NCs-2. Reproduced with permission from ref. 213, Copyright 2021 John Wiley & Sons Ltd.
electrocatalytic activity of the in-plane S sites. The graphene network was found to be electronically conductive and robust, which improved the conductivity of electrons and enhanced the stability of the hybrid structure. The catalysts showed good cycling stability and an excellent HER performance, with an overpotential of 143 mV at a current density of 10 mA cm\(^{-2}\). Wu et al.\(^{215}\) designed Co, Se dual-doped electrocatalysts via a solvothermal and post-low-temperature selenylation process. Due to the abundance of interfaces, the electrocatalysts exhibited excellent HER performance, with a low overpotential of 58 mV at a current density of 10 mA cm\(^{-2}\) and a small Tafel slope of 84 mV dec\(^{-1}\). Sun et al.\(^{216}\) reported plasma-induced N, Pt-doping and phase modulation of MoS\(_2\) nanosheets. The synergetic doping of N and Pt heteroatoms regulates the electronic and coordinated structures of MoS\(_2\) and further facilitates water adsorption and dissociation during the HER. Notably, this plasma bombardment method is highly feasible for the large-area fabrication of MoS\(_2\)-derived HER active electrodes.

4.4. Theoretical study of the HER

The studies of electronic structures of MoS\(_2\) offer theoretical guidance for designing efficient catalysts. For MoS\(_2\), a typical 2D material, the theoretical calculation of the basal plane positions, Mo edge and S edge is quite significant. Furthermore, it is also beneficial to investigate the adsorption energy of intermediates. Jacob et al.\(^{217}\) proposed an H-binding mechanism for S atoms in the basal plane of MoS\(_2\). This model was tested and verified by DFT calculations; herein, the energy barrier can be

![Fig. 16](image-url)
tuned by introducing metal dopants and defects. Their study revealed the electronic structure mechanism which tends to influence the basal plane S atoms activation (Fig. 16(a) and (b)). Xian et al. synthesized the monodisperse single-crystal Pt nanoparticles decorated on 2H phase MoS2 nanosheets via a wet chemical method. They construct the atomic model of Pt truncated octahedron loaded on MoS2, and choose four Pt sites (Fig. 16(c)). The charge-density difference is showed in Fig. 16(d), indicating the variations of the charge distributions for Pt and S at the interface of Pt-MoS2 atomic model from those for pure Pt and S. The results reveal that the Pt–S bonds are formed. Then, they calculate the free energy of adsorbed atomic hydrogen ($\Delta G_{H^*}$), including MoS2 (001), Pt (100), Pt (100) interface, Pt (1–11) and Pt (1–11) interface (Fig. 16(e)). The results indicate that the Pt (100) interface owns the smallest $\Delta G_{H^*}$ as well as the best HER activity. Further, they found that with the studied Pt atoms changing to the interface, the D-band center move away from the Fermi level (Fig. 14(f)), indicating the decrease of $\Delta G_{H^*}$, which confirms the superiority for Pt (100) interface in HER performance. In published DFT studies, the electronic structures of MoS2-based materials are usually computed by VASP and the electron–ion interactions are described by the projector-augmented wave method. All calculations are typically implemented with PBE exchange–correlation functional on periodically repeated slabs. The details of the molecular model-building, HER mechanism and free-energy calculations are provided in the relevant ref. 219–222.

5. Conclusions and outlook

With the depletion of traditional fossil energy, the development of green energy such as hydrogen energy has become urgent. Electrocatalytic water splitting to produce hydrogen offers a means to develop new energy sources. Up to now, significant progress has been made in achieving effecting hydrogen evolution reactions (HERs) using promising electrocatalysts such as transition metal sulfides (TMDs), transition metal carbides (TMCs), transition metal phosphides (TMPs) and transition metal nitrides (TMNs). As a typical electrocatalyst, MoS2 has been widely studied and much progress has been made. In this review, we summarize the synthetic methods of MoS2 and the effective strategies adopted to optimize the HER performance of MoS2. The introduction of defects significantly enhanced the HER activity of the MoS2-based materials, which was also verified theoretically. The formation of heterostructures is another effective way to enhance the HER activity of MoS2, which can modulate the electronic structure. Furthermore, doping metal atoms (Fe, Co, Ni, Cu, Mn, V, Ru etc.) or nonmetal atoms (C, N, F, P, S, Se etc.) into MoS2 can also improve its electrocatalytic HER performance.

However, there are still some challenges for the commercial application of MoS2-based materials. Firstly, even though ultrathin MoS2-based materials can be synthesized by CVD and hydrothermal methods, the large-scale production of MoS2 is still a challenge. Secondly, the standards for evaluating electrocatalytic stability have not yet been developed. Thirdly, while DFT calculations can provide a detailed theoretical insight into the reaction mechanism of a single active center, research involving the existence of multiple active centers is still lacking. Fourthly, the catalytic influence of H2O on the MoS2 surface and interlayers is still not completely understood because of the difficulty to develop bifunctional electrocatalysts for all electrolytes. Lastly, vacancies, doping atoms, and heterojunctions usually have a positive effect on the electrocatalytic process. However, the reaction mechanism needs to be further explored.

While there is still a long way to go for the development of MoS2-based electrocatalytic materials, the research interest in this area is increasing. Moreover, with the rapid development of computational tools, it is possible to make advances in many experimental areas, including MoS2-based materials. From this point of view, we can foresee that MoS2-based materials will be very promising for hydrogen production applications.

Conflicts of interest

The authors declare no competing financial interest.

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