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Recent progress and strategies of non-noble metal electrocatalysts based on MoS₂/MOF for the hydrogen evolution reaction in water electrolysis: an overview

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Abstract

Recently, hydrogen has emerged as a prominent energy source that can be used in various technologies. Molybdenum disulfide (MoS₂) is a typical catalyst material with two-dimensional groups that exhibit Pt-like hydrogen evolution reaction (HER) performance. In addition, metal-organic frameworks (MOFs) are a group of materials with ultrahigh porosity and enormous internal surface area, which are also highly beneficial for electrochemical processes. Therefore, catalysts based on MoS₂ and MOF materials have been extensively investigated for the production of hydrogen gases. Numerous studies have indicated that a combination of MoS₂ and MOF materials can dramatically boost the catalytic activity of these heterostructures. In this paper, the unique properties of MoS₂ and MOF materials and the progress and strategies to improve the HER efficiency of catalysts based on MoS₂/MOF hybrid materials are discussed. Furthermore, the challenges and future perspectives of these catalysts for HER are presented.

Keywords: Hydrogen energy, MoS₂, MOF, HER, MoS₂/MOF heterostructure



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INTRODUCTION

Over the last few decades, the overuse of fossil fuels, such as coal, oil, and petroleum products, has become a critical challenge due to numerous unexpected phenomena, including global warming, greenhouse effects, drought, and flooding^[1,2]. As technologies rapidly develop, many smart devices and materials have been employed to overcome the energy crisis, including green energy, energy-saving, and renewable energy technologies^[3-10]. Among them, hydrogen has various advantages such as environmental friendliness, earth abundance, high energy density, and renewability material^[11-14]. Therefore, hydrogen can be used in many fields such as fertilizers, transportation, green energy, hydrogen power stations, and energy storage. To date, numerous methods have been studied to improve the efficiency of the hydrogen evolution reaction (HER) process^[15,16]. In the last decade, conventional techniques, such as water electrolysis, have remained the most popular route for hydrogen production. Using low voltage, water molecules can be decomposed into oxygen and hydrogen. The efficiency of the process is highly dependent on the properties of the electrode materials where the gas can be released. Therefore, effective electrode materials that can boost the hydrolysis rate are desirable. In the past, noble metals, such as platinum group metals, have been used to produce hydrogen gas because of their fast kinetics, low hydrogen binding energy, and superb intrinsic conductivity^[17,18]. However, there are also drawbacks to these groups, including scarce and expensive materials, as well as poor stability of these materials on an industrial scale.

Researchers have been intensively investigating the preparation of other catalysts with superior stability that could be alternatives to noble metals^[18-20]. At the cutting edge of catalyst technologies, transition metal dichalcogenide (TMD) and metal-organic framework (MOF) materials have been intensively studied for the HER because of their unique properties and catalytic activity^[21-25]. Molybdenum disulfide (MoS₂) is one of the most typical TMD materials, exhibiting various advantages. MoS₂ is significantly cheaper and more abundant than Pt, making it a more economical choice for large-scale applications. Additionally, MoS₂ demonstrates excellent catalytic activity, especially in HER, and its properties can be further enhanced through methods such as doping or creating nanostructures, including low cost and remarkable catalytic stability^[26-28]. MOF can provide a large surface area for the absorption-desorption process, which is the main process in the water electrolysis reaction^[29,30]. The combination of MoS₂ and MOF materials used to prepare the heterostructure catalyst for the HER is illustrated in [Figure 1](#). These heterostructures provide numerous benefits for hydrogen technology and electrocatalytic applications. The properties, structural engineering, and HER performance of MoS₂, MOF, and hybrid catalysts based on MoS₂/MOF will be discussed in this paper. In addition, the challenges and future prospects of MoS₂/MOF catalysts are briefly presented.

HYDROGEN EVOLUTION REACTION

Mechanism

Water splitting occurs when a small potential is applied. Electrochemical hydrolysis is used to produce hydrogen gas. [Figure 2A](#) shows the mechanism of the water-splitting process using an electrochemical technique^[31]. Hydrolysis releases oxygen at the anode and hydrogen at the cathode. The theoretical free energy of water splitting is 1.23 eV at 25 °C and pressure of 1 atm. Because of the kinetic barrier for the reaction, the applied potential should be higher than 1.23 eV to overcome the kinetic barrier, and the process can proceed^[32].

In the electrochemical hydrolysis process, the reaction mechanism is complicated and highly dependent on the electrolyte and/or electrode materials. Various mechanisms have been proposed and discussed in the literature. As shown in [Figure 2B](#), different mechanisms of the HER can occur in acidic and alkaline

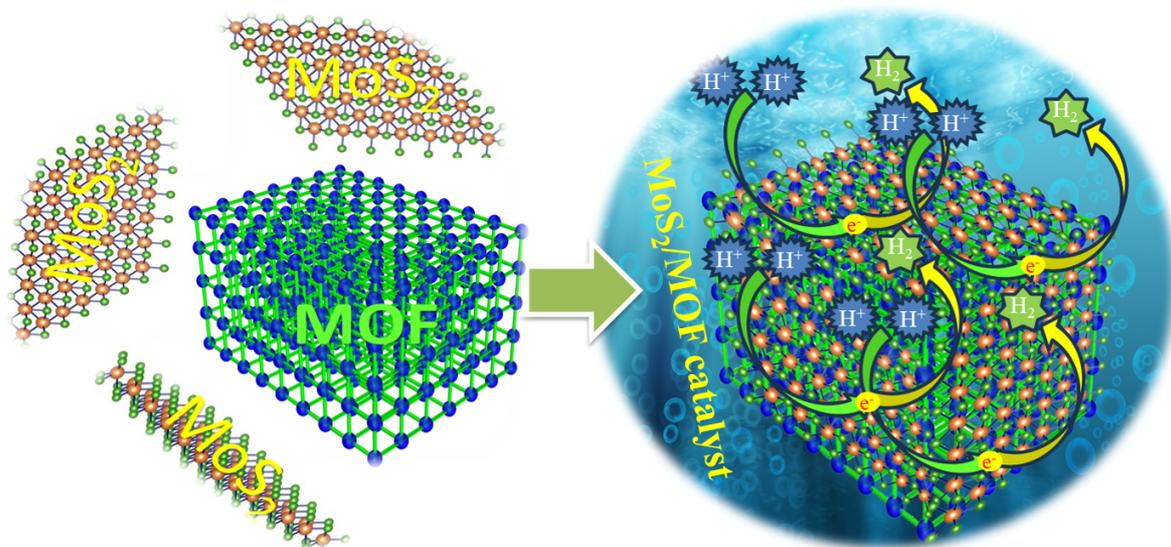


Figure 1. Electrocatalysts for HER application based on heterostructure MOF/MoS₂ materials.

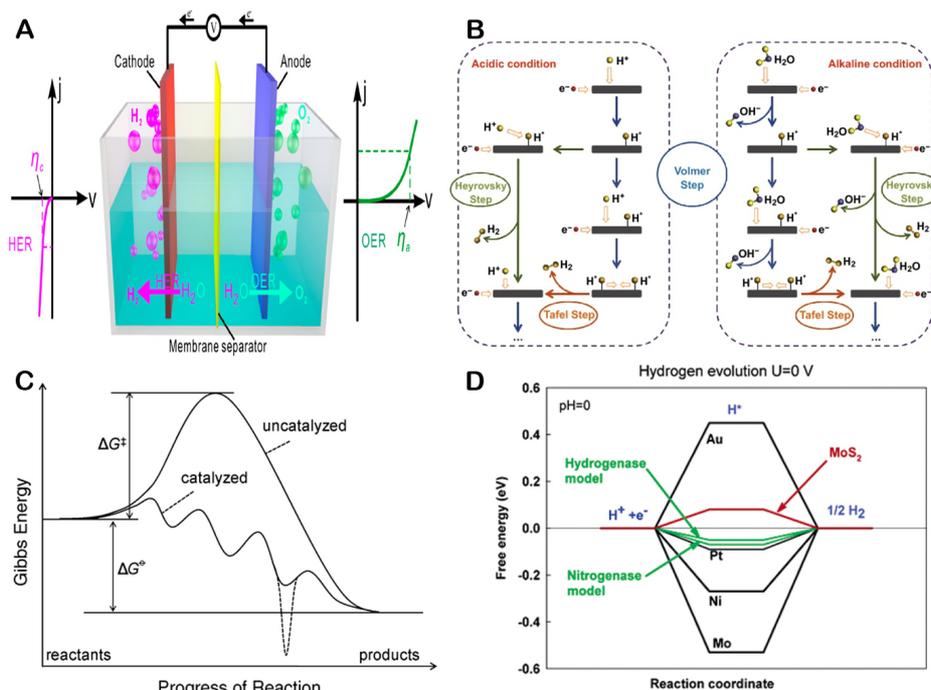


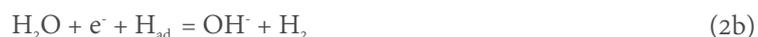
Figure 2. (A) Water splitting mechanism^[31]. Copyright 2020, American Chemical Society. (B) HER mechanism^[33]. Copyright 2018, Springer Nature. (C) Role of catalyst^[39]. Copyright 2012, American Chemical Society. (D) Hydrogen binding energy of various materials^[40]. Copyright 2005, American Chemical Society.

media^[33]. The mechanism of the HER is highly dependent on the media conditions in which the two-electron transfer process can occur at the cathode. The following three steps can be described for acidic media^[34,35]:



The first is the Volmer step (1a), which produces adsorbed hydrogen. The HER can then proceed via the Heyrovsky step (1b), Tafel step (1c), or both to produce H_2 .

In an alkaline environment, two steps can occur: the Volmer step (2a) and the Heyrovsky step (2b).



Catalysts play a critical role in chemical processes. By using catalysts, the energy consumed for chemical reactions can be dramatically decreased, and the rate of the reaction can be significantly boosted^[36-38]. Several studies have shown that the sluggish reaction kinetics of the HER, because of its high overpotential and small active surface area, are the main barriers to practical hydrogen production. The effects of the catalyst are illustrated in [Figure 2C](#)^[39]. Therefore, it is challenging to produce hydrogen from commercial materials. Among the numerous non-noble metal catalysts, MoS_2 is one of the most well-known two-dimensional catalysts, possessing numerous active sites and good catalytic activity. As shown in [Figure 2D](#), the free energy of MoS_2 is calculated and compared with different materials, which show a small free energy similar to that of Pt materials^[40].

HER parameters

Various parameters must be considered to evaluate the performance of catalysts. Four crucial factors are often calculated to evaluate and compare the catalytic activities, as shown in [Figure 3](#).

(1) Overpotential [[Figure 3A](#)]: In theory, for the HER, the required thermodynamic potential is 1.23 V. To overcome the intrinsic activation barriers caused by the anode and cathode, an overpotential must be added^[41]. The added overpotential of the catalysts is an important parameter for comparing their performance. The lower the overpotential, the better the catalytic material^[42].

(2) Tafel slope [[Figure 3B](#)]: The Tafel slope could unveil the mechanism of the HER process; the lower the Tafel slope, the faster the electrocatalytic reaction kinetics^[43]. This implied that catalysts with small Tafel slopes are desirable for HER applications^[44].

(3) Conductivity [[Figure 3C](#)]: The conductivity of the catalysts is another crucial parameter for evaluating the efficiency of the catalyst activities^[45]. The higher the conductivity of the catalysts, the easier the two-electron transfer. Therefore, hydrogen could be easily released^[46].

(4) Stability [[Figure 3D](#)]: Catalyst stability is a key factor in evaluating the prospects of materials for commercial products^[47]. High performance and superior stability of catalysts are the targets of research in the field of catalysis^[48,49].

MOS₂ CATALYSTS: STRUCTURE, PROPERTIES, AND HER PERFORMANCE

Structure and properties

MoS_2 is a typical material with two-dimensional dichalcogenide (TMD) groups, which can be formed using

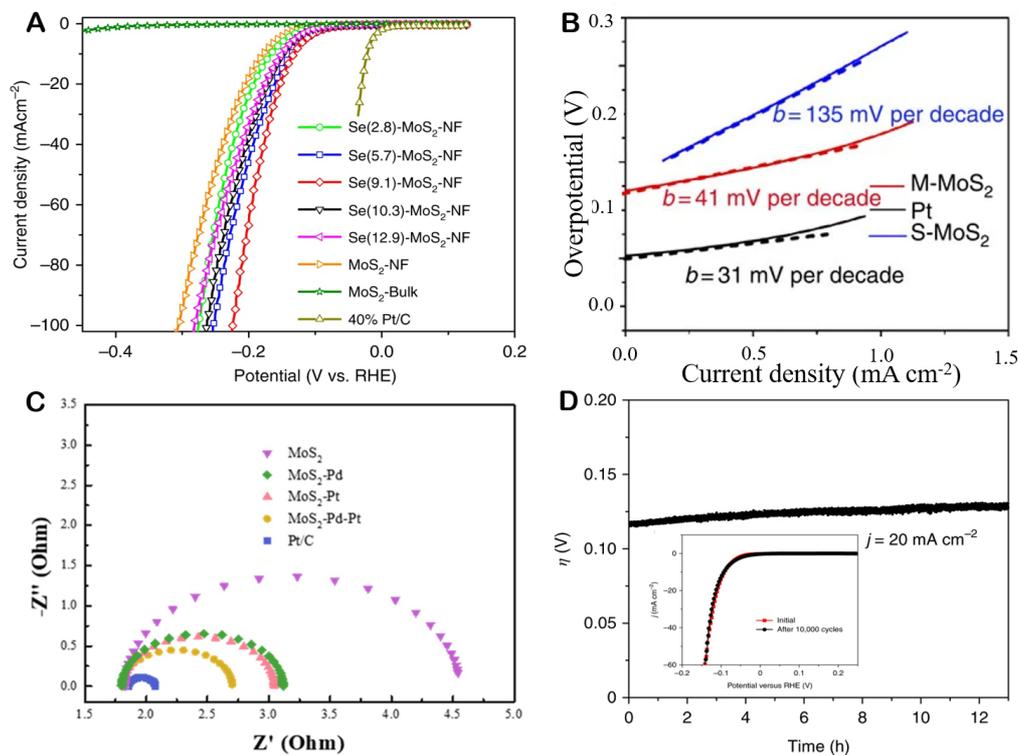


Figure 3. HER parameters, (A) LSV curves of various catalysts^[41]. Copyright 2020, Springer Nature. (B) Tafel slope of catalysts^[43]. Copyright 2016, Springer Nature. (C) Nyquist semicircle of catalyst^[45]. Copyright 2021, American Chemical Society. (D) Stability of catalysts^[47]. Copyright 2018, Springer Nature.

MX₂ (M = Transition metals; Ti, Zr, Hf, V, Nb, Ta, Mo, W, Tc, Re, Co, Rh, Ir, Ni, Pd, and Pt), X = Chalcogen (S, Se, and Te)^[50]. As a TMD material, MoS₂ can present different states, including semiconducting, metallic, and superconducting, which highly depend on the structure of the material. Figure 4A-C shows the detailed structure of MoS₂, which possesses a lamellar S-Mo-S structure^[51-53]. As shown in the single-layer MoS₂ films, the Mo⁴⁺ layer is sandwiched between two layers of S²⁻ by covalent bonds in a sequence of S-Mo-S. Weak van der Waals forces caused the interactions between the sandwiched layers. Monolayer of MoS₂ exhibits a thickness of 0.62-0.7 nm, and the space between each sandwiched layer is approximately 0.3 nm^[54,55]. In fact, MoS₂ exhibits three structures including tetragonal-1T MoS₂, hexagonal-2H MoS₂, and rhombohedral-3R MoS₂. Each TMD polymorph possesses unique structures and electronic properties from which different catalytic properties can emerge. Hence, it is imperative to compare different TMD polymorphs to understand the influence of the polymorphic structures on the catalytic properties of TMD materials^[56]. Additionally, layer-by-layer MoS₂, where individual monolayers are stacked vertically and held together by van der Waals forces, enables control over the thickness and orientation of the layers, optimizing properties such as surface area, charge carrier mobility, and bandgap crucial for applications in catalysis^[57]. Previous studies have reported a 2H → 1T phase transition when TMD materials are subjected to chemical exfoliation and a comparison of the catalytic properties of 1T- and 2H-TMDs has shown that the exfoliated, metallic 1T phase performs as better catalysts than their bulk, semiconducting 2H counterparts for HER. This can be attributed to the increased edge-exposed surface area, reduced sheet size, and enhanced electrical conductivity of the 1T phase. However, no previous study has been conducted and a lack of understanding exists on the catalytic properties of 3R-TMDs or comparison with their semiconducting 2H counterparts^[58]. As can be seen in Figure 4D, in bulk form or a few layers, MoS₂ exhibits the indirect bandgap while the direct bandgap could be found in monolayer MoS₂ (1.9 eV)^[59]. To evaluate the catalytic activity of MoS₂ toward HER application, the Gibbs free energy (ΔG) is an effective parameter.

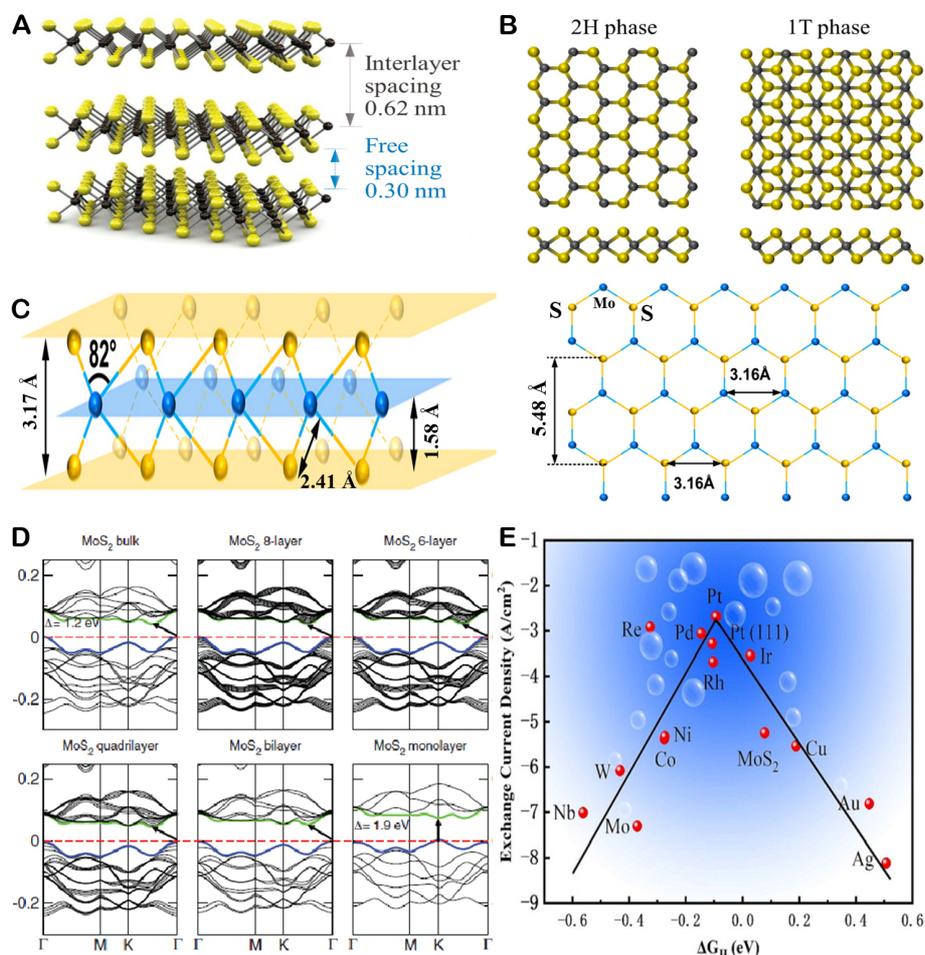


Figure 4. Structural features and properties of MoS₂. (A) 3D structure^[51]. Copyright 2011, Springer Nature. (B) Top view and side view of 2H and 1T MoS₂^[52]. Copyright 2017, American Chemical Society. (C) Lattice constant of MoS₂^[53]. Copyright 2016, Taylor & Francis. (D) Band structures of MoS₂^[59]. Copyright 2011, American Physical Society. (E) HER volcano plot of MoS₂ and metal^[61]. Copyright 2017, The American Association for the Advancement of Science.

$\Delta G_{\text{H}} > 0$ indicates that the hydrogen atom does not bind easily to the catalytic site, whereas $\Delta G_{\text{H}} < 0$ represents that the molecular hydrogen does not easily release from the catalytic site. The best value of ΔG_{H} for an ideal catalyst should be close to zero^[60]. The edge planes of MoS₂ with the Gibbs free energy of the adsorbed H (ΔG_{H}) of 0.06 eV are shown in Figure 4E^[61]. The basal planes of MoS₂ exhibit the ΔG_{H} of 1.92 eV, which implies the basal planes can hardly adsorb the H atom and are inactive toward HER, limiting the overall catalytic activity^[62]. Therefore, numerous efforts have been devoted to increasing the number of edge planes of MoS₂ by introducing different methods.

Synthesis process and HER performance of catalysts based on MoS₂

To prepare catalysts based on MoS₂ materials, various techniques and processes have been developed to optimize the efficiency of those materials.

Exfoliation

Exfoliation is the most conventional technique for preparing effective materials for catalytic, electrochemical storage, and sensor applications. Using the exfoliation process, bulk MoS₂ could be detached into a few layers, bilayers, or monolayers, which could exhibit a direct bandgap compared with the

indirect bandgap of bulk MoS₂^[63-65]. Layered MoS₂ is an ideal catalyst for electrochemical processes, such as the HER, because it can provide numerous active sites on the edge of the layers and the super intrinsic conductivity of the MoS₂ layer^[66,67]. **Figure 5A** presents the mechanism of the exfoliation process based on the MoS₂ material using sonication in n-butyllithium for 1.5 h^[68]. During sonication, lithium ions were intercalated into the bulk MoS₂, and the layered MoS₂ gradually detached to form a monolayer catalyst. The main advantages of this route include a simple process, low cost, and highly pure catalyst. However, several drawbacks limit the use of this method, such as time consumption, the danger of using lithium materials, and the restacking of exfoliated MoS₂. Another major challenge was to effectively transfer the exfoliated MoS₂ monolayer onto the surface of the cathode. This is because the catalyst coated on the electrode was unstable and nonuniform.

Chemical vapor deposition

To date, the chemical vapor deposition (CVD) process is preferred for the preparation of large-area and high-quality MoS₂ layers that can be used for various applications^[69-71]. **Figure 5B** shows the mechanism that could occur in a glass chamber at high temperatures^[72]. Using this technique, the number of MoS₂ layers can be controlled, which is beneficial for the HER. In the CVD process, there are several approaches for preparing MoS₂ thin films, such as sulfurization of the deposited molybdenum or molybdenum oxide, vapor-solid growth based on MoS₂ bulk materials, and sulfurization of coated thiomolybdate compounds. The main barriers to this technique are its complexity and high cost. Low product yield is another drawback of this technique.

Hydro/solvothermal process

To prepare catalytic materials, the hydro/solvothermal process is considered the most favorable strategy for synthesizing, doping, or even structure-engineering catalysts^[73-75]. The source materials, after pretreatment, could be put into a Teflon-lined stainless-steel autoclave at a high temperature (150-300 °C) for a long reaction time (10-30 h). The structure and morphology of the catalysts can be easily prepared or modified by changing the synthesis conditions, such as the temperature, time, and ratio of raw materials. Using this method, heterostructures of various catalysts can be easily prepared. The main disadvantage of this process is the elemental content of the products, which could affect the properties of the synthesized materials. **Figure 5C** presents the mechanism of the hydro/solvothermal process for preparing MoS₂ nanoflowers, which have been intensively investigated for HER with excellent catalytic activities^[76].

HER performance of catalysts based on MoS₂

Catalysts based on MoS₂ show excellent performance in HER applications. **Figure 6** shows the HER performance of various structures of MoS₂ prepared by different processes. **Figure 6A** demonstrates the performance of MoS₂ catalysts prepared by the exfoliation technique^[77]. As can be seen, after the exfoliation process, the 2H form of MoS₂ could be converted into 1T form which is metallic and more conductive compared with the initial form. Therefore, the catalytic activity of the material was drastically enhanced. The 1T MoS₂ exhibits great performance with the electrocatalytic current density of 10 mA cm⁻² at a low overpotential of -187 mV vs. the reversible hydrogen electrode (RHE) and a Tafel slope of 43 mV dec⁻¹ while the performance of 2H MoS₂ demonstrated the electrocatalytic current density of 10 mA cm⁻² at an overpotential of -320 mV vs. RHE and a Tafel slope of 110 mV dec⁻¹. This improvement can be attributed to the metallic MoS₂ polymorph form, which exhibits facile electrode kinetics and low-loss electrical transport and possesses a proliferated density of catalytically active sites. Another route, the hydro/thermal solution process, has been intensively used to synthesize and/or modify different catalyst structures based on MoS₂ materials.

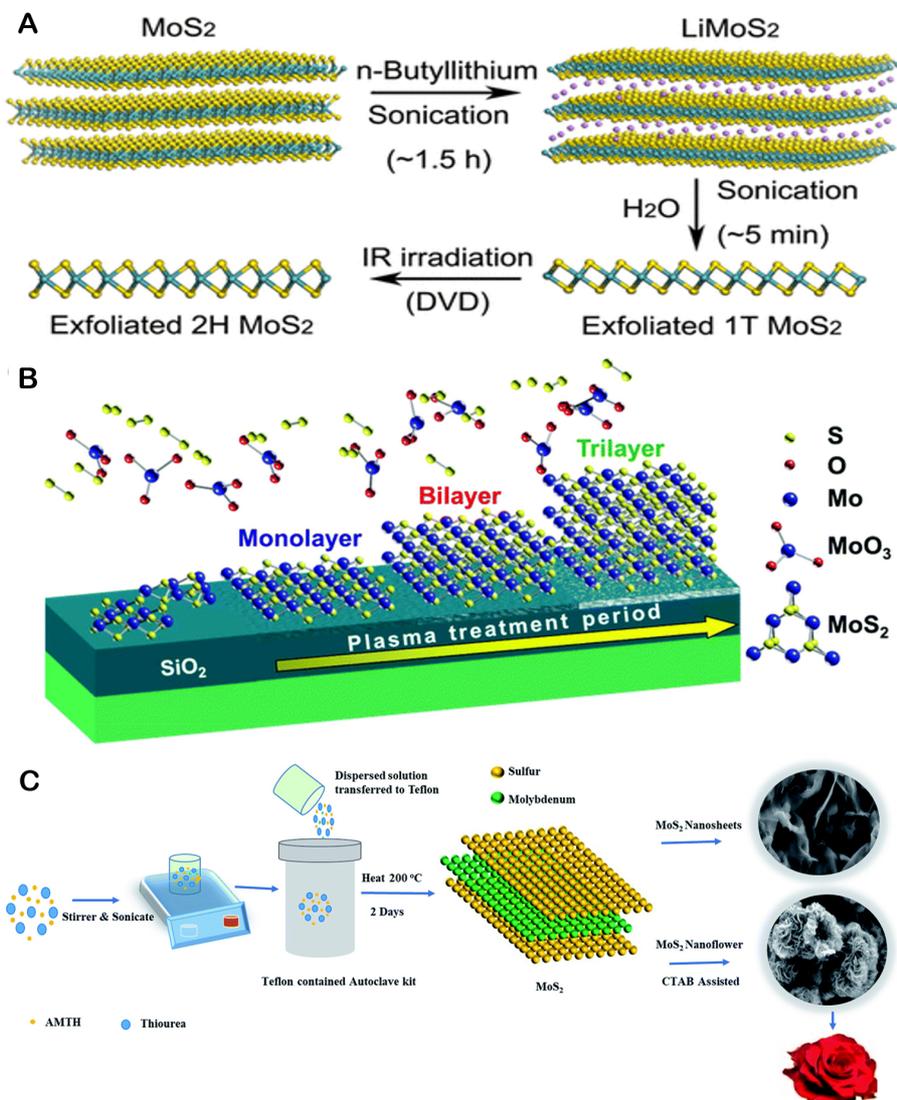


Figure 5. Synthesis process of catalysts based on MoS₂ by different processes. (A) Exfoliation^[68]. Copyright 2015, American Chemical Society. (B) CVD process^[72]. Copyright 2014, Royal Society of Chemistry. (C) Hydro/solvothermal process^[76]. Copyright 2018, Royal Society of Chemistry.

As shown in Figure 6B, Van Nguyen *et al.* reported a unique process to synthesize and modify the MoS₂ morphology by changing the pH and temperature; different morphologies of MoS₂ were successfully prepared^[78]. Among them, the small flower MoS₂ with dimensions of less than 100 nm presented a significant improvement compared to that of the normal nanoflower MoS₂ (900-1,500 nm). MoS₂ small flowers exhibit superior electrocatalytic activity toward HER with a low Tafel slope of 49 mV dec⁻¹ and an overpotential of 270 mV at a current density of 50 mA cm⁻². In this case, the catalytic improvement can be attributed to the large surface area, which was caused by the uniformity and small size of the flower catalysts.

The most effective technique for preparing a MoS₂-catalyst for the HER is the CVD process, as shown in Figure 6C. The CVD process can provide the most effective catalyst based on MoS₂ because monolayer or

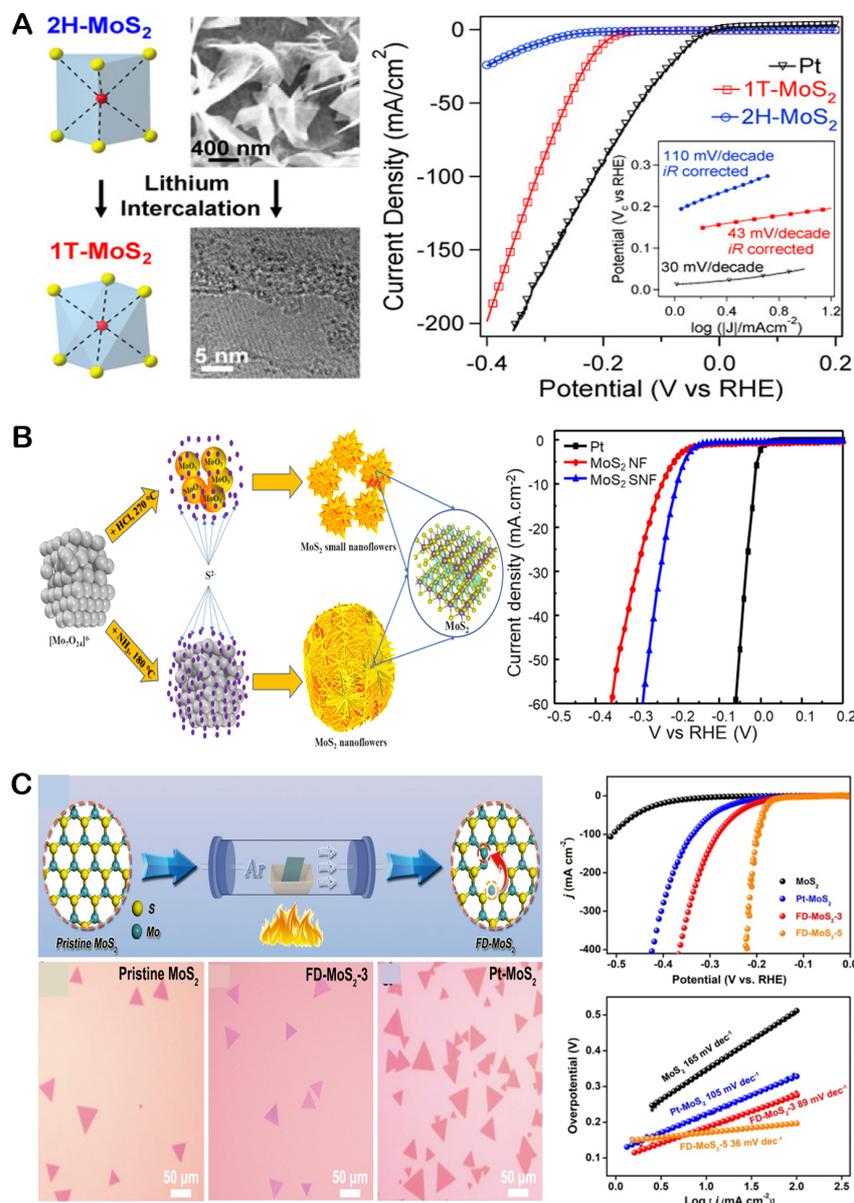


Figure 6. Performance of MoS₂ catalysts. (A) Exfoliation^[77]. Copyright 2013, American Chemical Society. (B) Hydro/solvothermal process^[78]. Copyright 2023, Elsevier. (C) CVD process^[79]. Copyright 2022, Springer Nature.

bilayer MoS₂ can be synthesized and/or modified. The super thin film MoS₂ exhibits superior catalytic activity for two-dimensional materials such as MoS₂. Xu *et al.* studied the performance of monolayer MoS₂ for HER applications based on the Frenkel defect: FD-MoS₂^[79]. At the current density of 10 mA cm⁻², the optimal Frenkel-defected monolayer MoS₂ exhibits a lower overpotential (164 mV) than either pristine monolayer MoS₂ surface plane (358 mV) or Pt-single-atom doped MoS₂ (211 mV). The FD-MoS₂ presented a low Tafel slope (36 mV dec⁻¹) which may be owing to the performance of Pt. The existence of Frenkel defects in MoS₂ could lead to a unique charge distribution that changes the H adsorption sites and provides moderate H⁺ adsorption energy for FD-MoS₂.

MOF MATERIALS: PROCESS AND PROPERTIES

Synthesis process and properties

MOF materials are a class of ultrahigh-porosity materials that can be formed between metal ions bonded by organic ligand linkers^[80,81]. MOF materials could provide up to 90% of the free volume with a large surface area, which could be extended to over 6,000 m²/g. The combination of organic and inorganic elements in super porous MOFs could be beneficial for many potential applications such as clean energy, hydrogen technology, and storage technology^[82-86].

MOFs are porous materials made up of metal centers and organic ligands with infinite lattice structures that enhance their catalytic performance through various methods^[87]. The specific surface area of MOFs enhances catalytic performance in HER processes due to their tailorable porous structures^[88]. MOFs bridge the gap between mesoporous materials and microporous zeolites, offering highly controllable pore sizes and large surface areas that facilitate selective catalysis and enhance molecule adsorption. In addition, the porous structure of MOFs allows electrolytes to penetrate and reach inner active sites, thus accelerating catalytic performance. Furthermore, modulating the electronic structure of active sites, including spin ordering and energy band structures, further improves intrinsic electrocatalytic properties^[89]. Techniques such as lattice strain engineering and pore partitioning further enhance catalytic efficiency by creating adaptive hetero-junctions and introducing novel heterometallic species. Moreover, embedding nanoparticles, such as Pt, Pd, or Ru, within MOFs introduces unique catalytic properties and synergistic effects, where the high surface area and stability of MOFs support the high catalytic activity of nanoparticles^[90]. The uniform dispersion of nanoparticles within the MOF matrix prevents aggregation and ensures stable catalytic performance. Additionally, the tailored pore environments of MOFs can preferentially allow specific reactants to access the nanoparticles, enhancing selectivity, while facilitating electron transfer processes that improve reactivity.

The mechanism of the MOF process is shown in [Figure 7A](#), in which the node-space arrangement is formed by organic linkers that can connect metal ions or clusters^[91]. Therefore, synthesized materials present various advantages such as high porosity and large surface area, which could be beneficial for different technologies, particularly electrochemical processes.

To synthesize and/or engineer the structure of MOF, in recent decades, researchers have investigated and developed numerous MOF types using different techniques, which are briefly discussed below. The synthesis method of MOFs can significantly influence their specific surface area and catalytic properties, which are crucial for their applications in gas storage, separation, and catalysis. Different synthesis conditions, such as temperature, solvent, and reaction time, can be adjusted to control the pore size and surface area of MOFs. The catalytic properties of MOFs can also be post-synthetically modified by incorporating different metal ions or functional groups, to enhance their catalytic activity and performance^[92,93].

Microwave-assisted methods

Microwave-assisted methods are usually employed with electromagnetic radiation (0.3-300 GHz). The advantages of microwave assistance include high yields, excellent control, and fast reaction times. Bu *et al.* reported the microwave-assisted synthesis of (FeNiP)/P-doped graphene^[94]. In this study, various MOFs (phosphide/graphene composites with adjustable heterostructures, including transition metal phosphide/P-doped graphene and core-shell transition metal phosphide@graphitized carbon/P-doped graphene) were quickly synthesized (approximately in 20 s). The synthesis materials show impressive HER performance with a low overpotential of approximately 173 mV at 10 mA cm⁻² in alkaline media and the

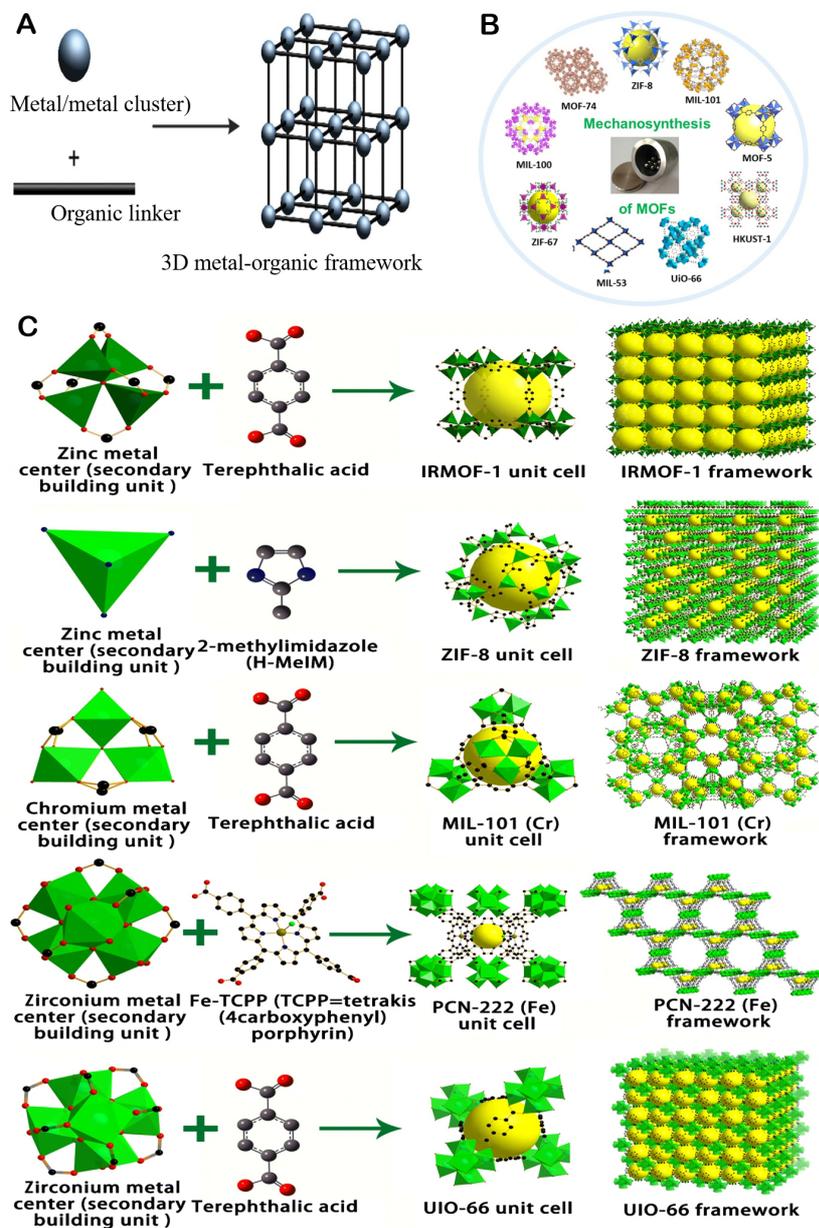


Figure 7. Synthesis process of MOF materials. (A) MOF synthesis mechanism^[91]. Copyright 2017, Elsevier. (B) Different MOF materials^[102]. Copyright 2021, Elsevier. (C) Synthesis process of MOF materials^[103]. Copyright 2021, Springer Nature.

Tafel slope of 50.3 mV dec^{-1} . The increased performance could be attributed to the large number of active sites of the MOF materials and the effect of P-doping. A fast, simple, and low-cost process is the main advantage of this method for synthesizing and/or modifying the structure of MOF for HER applications.

Electrochemical process

A thin film with controllable thickness based on MOF materials can be easily prepared using electrochemical techniques. The benefits of these routes are the high quality and homogeneity of thin-film materials. Alagar *et al.* developed a process for synthesizing CuZn-MOFs via controlled electrodeposition^[95]. In this study, CuZn-BTC-250 (BTC = 1,3,5-benzenetricarboxylate) was successfully

prepared, which shows a significant increase in HER application with the onset potential of 1.37 V, whereas the commercially available RuO₂/Pt/C exhibits 1.38 V in alkaline solutions during the overall water splitting.

Ultrasonic synthesis

This process can be performed using high energy unbound to a reaction mixture. The benefits of this process are its low cost, simplicity, and nonuse of toxic materials. Eliwa reported a process for producing a Pb-MOF catalyst via ultrasonication for 60-75 min. The synthesized catalyst was then investigated for HER application which showed good performance with the current density of 50 mA cm⁻² at an overpotential of -0.6 V (*vs.* RHE) and the obtained Tafel slope of 76 mV dec⁻¹.

Hydrothermal/solvothermal methods

The process could occur in closed systems, such as an autoclave, which could use different solvents at high temperatures (100-250 °C) and for a long time (10-30 h). This is the simplest, high-yield method for the preparation of MOF catalysts, which has been intensively investigated in previous studies^[96-100]. Ma *et al.* reported a MOF-derived flower-like MoS₂@TiO₂ nanohybrid, which benefited the HER process, using a simple hydrothermal method^[101]. Using this technique, the ratio of materials can be easily controlled. The authors concluded that at a ratio of 14.6% MoS₂, the synthesized material could show the significant performance of HER with an onset overpotential of -300 mV (*vs.* RHE) and a Tafel slope of ~81 mV dec⁻¹. The increased performance of the prepared catalyst could be attributed to the *in-situ* formation of active sites and uniform dispersion, as well as the strong connection between MoS₂ and TiO₂, which can facilitate electron transfer in the electrochemical process.

In general, as shown in [Figure 7B](#), various types of MOFs have been synthesized and reported to apply to energy storage and saving^[102]. The unit cells and frameworks of typical MOFs are shown in [Figure 7C](#)^[103].

MOF materials for HER application

Owing to their many advantageous properties that could benefit electrochemical processes, such as high porosity and large surface areas, MOF materials have recently been extensively applied in the HER. As seen in [Figure 8](#), the most effective way to utilize the benefits of MOF for HER applications is to dope highly catalytic metals, such as Ru and Pt, into the MOF framework. As shown in [Figure 8A](#), the Ru-doped MOF material based on Cu-BTC forms Ru-Cu@C^[104]. The optimized Ru-Cu@C-2 catalyst shows superior HER performance with an extremely low overpotential (20 mV at 10 mA cm⁻²), ultralow Tafel slope (37 mV dec⁻¹), small charge-transfer resistance (16.8 Ω), large electrochemical active surface area, and excellent stability. The large surface area and the synergy between Ru and Cu were the main reasons for the enhanced HER performance. Pt is a major catalytic metal. The combination of Pt and MOF for the HER was investigated by Wang *et al.*, and the results are shown in [Figure 8B](#)^[105]. The impressive catalytic activity of Pt/MOF materials could be even better than performance of commercial Pt. Pt/MOF materials show lower Tafel slopes of 24.4 and 101.6 mV dec⁻¹ in comparison with that of commercial Pt/C (32.9 and 131.1 mV dec⁻¹) in acidic and alkaline solutions, respectively. These results indicate that MOF catalysts could be modified or restructured to become excellent materials for HER applications.

MOF/MOS₂ HETEROSTRUCTURE: SYNTHESIS PROCESS AND HER ACTIVITIES

Synthesis strategies of catalysts based on MOF/MoS₂ materials

To exploit the advantages of both MoS₂ and MOF materials, heterostructure materials based on MoS₂ and MOF have been investigated. These hybrid catalysts show excellent catalytic activity toward HER applications. Therefore, different processes have been used to prepare these catalysts. There are two conventional processes for preparing heterostructure catalysts based on MOFs and MoS₂, as illustrated in

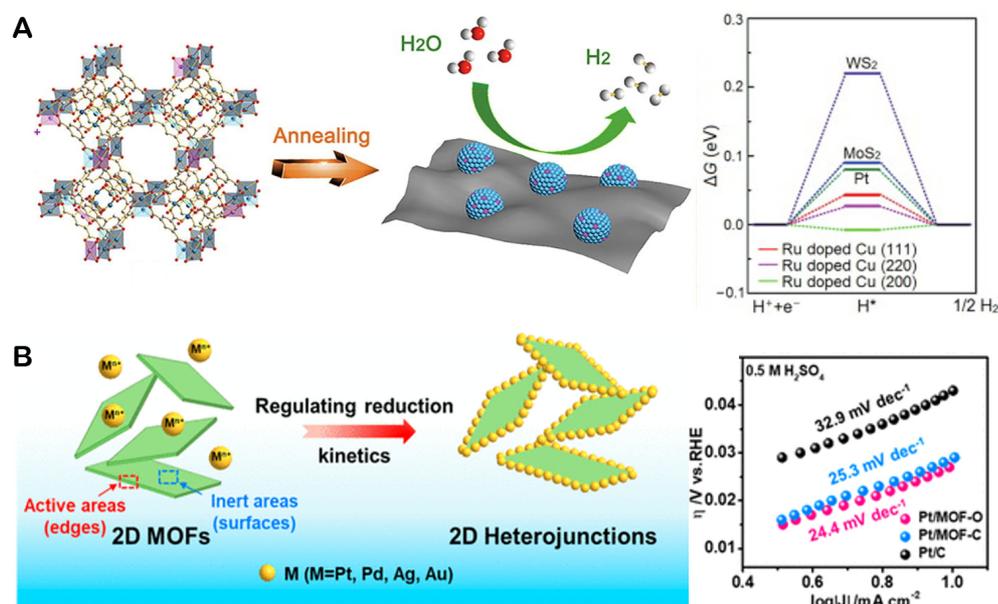


Figure 8. HER activities of catalysts based on MOF materials. (A) the catalytic activity (ΔG) of catalyst based on Ru doped MOF compared with WS_2 and MoS_2 ^[104]. Copyright 2021, Elsevier. (B) HER performance of catalysts based on Pt doped MOF^[105]. Copyright 2021, American Chemical Society.

Figure 9. As shown in **Figure 9A**, The MOF/ MoS_2 catalyst was effectively synthesized in one step by CVD^[106]. In addition, MOF and MoS_2 materials can be separately synthesized using various techniques, and the synthesized MOF or MoS_2 can be placed into the prepared solution to form a heterostructure of MOF/ MoS_2 catalyst via different processes, as shown in **Figure 9B**^[107].

HER activities of catalysts based on MOF/ MoS_2 materials

Catalysts based on MOF/ MoS_2 heterostructures show significant performance compared to other catalysts. As can be seen in **Figure 10**, for various heterostructures of MOF/ MoS_2 prepared by different routes, the performance of the synthesized heterostructures dramatically increased compared with that of the initial materials. The synthesis strategy used for formation of MoS_2 /MOF heterostructures significantly affects their properties and performance^[108-110]. Hydrothermal/solvothermal methods yield high crystallinity heterostructures with strong interactions but require high temperatures and long reaction times. Mechanical exfoliation and mixing are simple and cost-effective but may result in weaker interactions and less uniform distribution. CVD provides high-purity, well-controlled MoS_2 layers with excellent electronic properties but is complex and costly. Electrochemical deposition allows precise, uniform MoS_2 coverage and is cost-effective, though it may need optimization for consistent quality. Thus, the choice of method depends on the desired properties, scalability, and application requirements.

Figure 10A shows the one-step process for synthesizing the heterostructure of a catalyst based on MoS_2 /MOF materials [Co_9S_8 / MoS_2 embedded in N, S, O-doped carbon materials (Co_9S_8 / MoS_2 @NOSC)]. The utilized heterostructure of the Co_9S_8 / MoS_2 @NOSC catalyst presents significant improvement for HER in acidic environments with small overpotentials of 233 and 194 mV, respectively, at the current density of 10 mA cm^{-2} . The increased performance of the catalyst could be attributed to the synergistic effect of the two elements (Co_9S_8 and MoS_2) with intrinsic activity and the hierarchical porous carbon matrix doped with multiple heteroatoms. Furthermore, the heteroatom-doped carbon matrix could act as an outer shield for the Co_9S_8 / MoS_2 materials in the electrolyte, which resulted in the superior stability of the prepared materials.

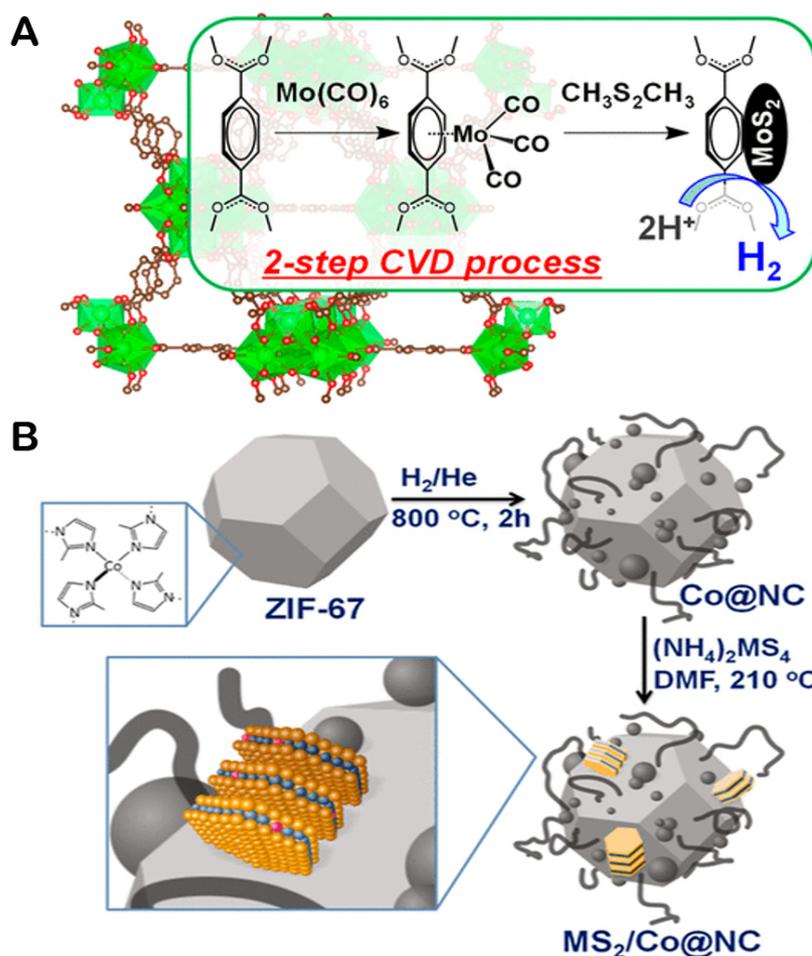


Figure 9. MOF/MoS₂ synthesis process. (A) CVD process^[106]. Copyright 2022, American Chemical Society. (B) Solution process^[107]. Copyright 2022, American Chemical Society.

As shown in [Figure 10B](#) and [C](#), heterostructure catalysts based on MoS₂/MOF were prepared by a multistep process. In these processes, MoS₂ could be separately synthesized in the first step and then combined with MOF source materials to form heterostructure materials. The heterostructure catalysts MoS₂ and MOF showed HER improvements similar to those of the pure MoS₂ and MOF materials. The main reason for this is the benefits of both MOF and MoS₂ and the synergistic effect between multiple elements in binary catalysts.

Strategies to increase HER performance of catalysts based on MoS₂/MOF materials

The outstanding properties of MoS₂ and MOF materials are discussed in detail. The performance improvement of MoS₂/MOF materials arises from several synergistic mechanisms. First, the high surface area and tunable porosity of MOFs enhance the dispersion of MoS₂, increasing the number of accessible active sites. This structural feature also facilitates efficient mass transport and diffusion of reactants to these active sites. Additionally, the electronic properties of MoS₂, such as high conductivity and catalytic activity, complement the stability and structural support provided by the MOFs. Thus, the intimate contact between MoS₂ and MOFs enhances electron transfer efficiency, reducing charge recombination and boosting overall catalytic performance^[111]. The results indicated that the combination of the two materials could be used as a catalyst for HER applications. However, the performance of the prepared products remains quite different from that of practical materials. Therefore, several strategies can be adopted to improve the efficiency of

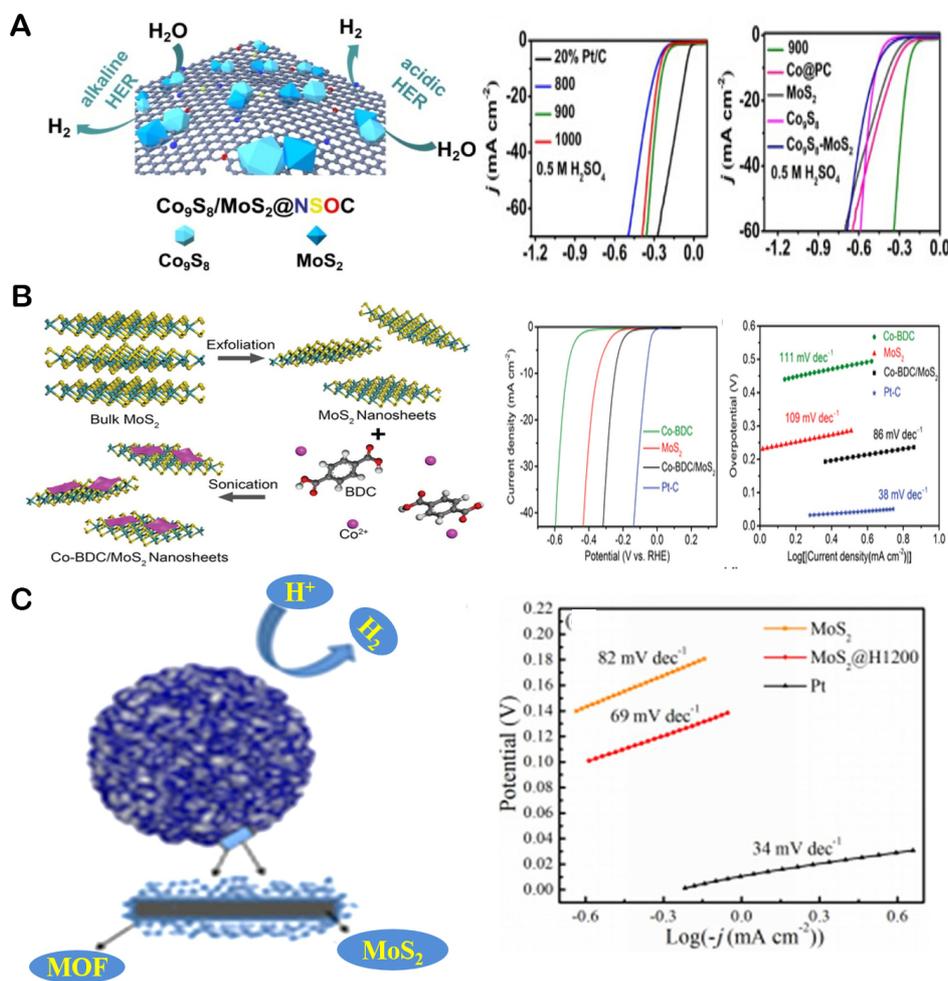


Figure 10. HER activities of catalysts based on MoS₂/MOF materials. (A) MOF/MoS₂ co-synthesis process^[108]. Copyright 2020, Elsevier. (B) Exfoliated MoS₂ for MOF/MoS₂ preparation^[109]. Copyright 2019, John Wiley & Sons. (C) Prepared MoS₂ for MOF/MoS₂ process^[110]. Copyright 2017, John Wiley & Sons.

catalysts based on MoS₂/MOF materials. Various strategies have been studied to increase the catalytic activity of MOF/MoS₂ materials [Figure 11]. Noble metal-Pt-doped MoS₂/MOF is the most effective for increasing the performance of catalysts based on the excellent characteristics of Pt. In this study, Rong *et al.* prepared a rose-like structured CuSNC@MoS₂-Pt electrocatalyst Figure 11A^[112]. Thus, the performance of the synthesized materials was significantly improved. The results indicated that the synergistic effects of Pt-doping, S, N-doped carbon substrate, and 3D open porous structural advantages allow CuSNC@MoS₂-Pt to achieve optimum alkaline HER activity with small overpotentials of 102.6, 165.6, and 199.0 mV at the current densities of 10, 50, and 100 mA cm⁻², respectively, and a small Tafel slope of 55.7 mV dec⁻¹. The improvement in these results can be attributed to the low kinetic energy barrier for water dissociation, hydrogen generation by the prepared catalyst, and the excellent hydrophilicity of CuSNC@MoS₂-Pt.

Nonmetal doping is another potential strategy for improving the performance of catalysts. Various processes have been reported to improve catalytic activity by adding small amounts of P, N, or S. As shown in Figure 11B, the HER performance of the P-doped catalyst was significantly better than that of the undoped MoS₂/MOF catalyst. The results indicated that the P-doped catalyst based on MoS₂/MOF shows increased HER activity with a low overpotential of 84 mV compared to those of NiCoC-MOF,

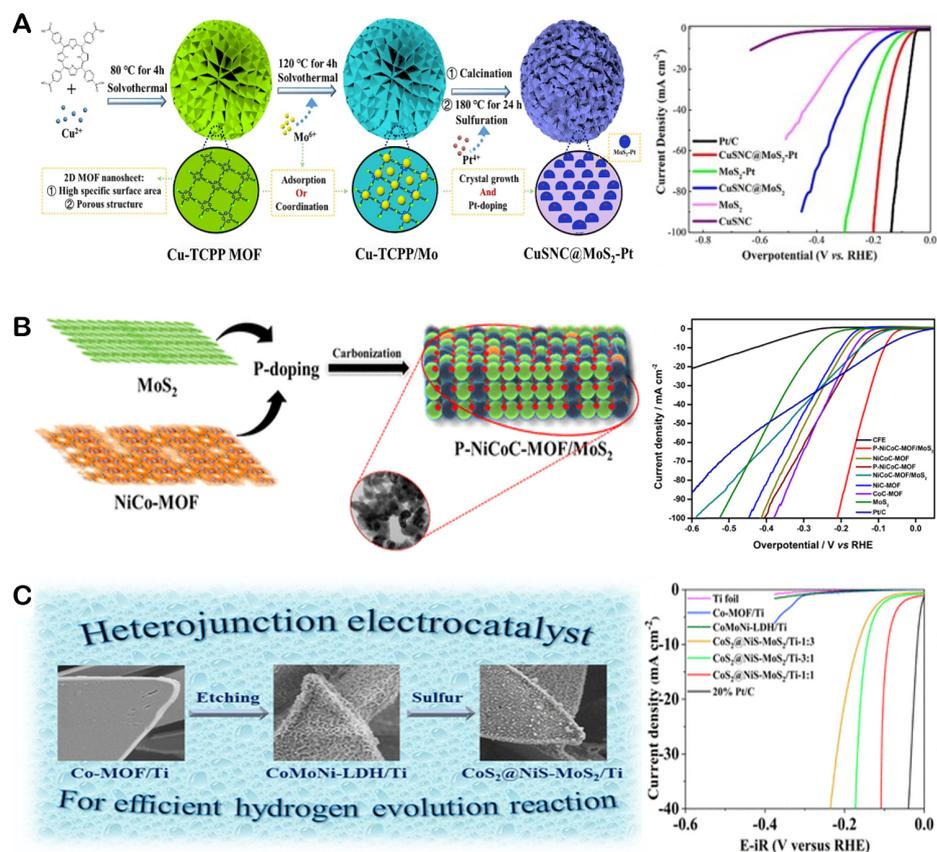


Figure 11. Improvement of the catalytic activities of MOF/MoS₂ by various methods. (A) Noble metal doping^[112]. Copyright 2021, Elsevier. (B) Nonmetal doping^[113]. Copyright 2021, American Chemical Society. (C) MOF/composite heterojunction MoS₂^[114]. Copyright 2022, American Chemical Society.

P-NiCoC-MOF, NiCoC-MOF/MoS₂, NiC-MOF, CoC-MOF, and MoS₂ which showed overpotentials of 220, 191, 200, 190, 160, and 260 mV to obtain the current density of 10 mA cm⁻², respectively.

Another effective technique that could be employed to improve the performance of catalysts based on MoS₂/MOF is to use ternary composite heterostructure materials. In Figure 11C, the catalysts based on the MOF and the ternary composite heterojunction CoS₂@NiS-MoS₂ are shown. To attain a current density of 10 mA cm⁻² for CoS₂@NiS-MoS₂/Ti-1:1, an overpotential of 91 mV was required compared to that of CoS₂@NiS-MoS₂/Ti-1:3 and CoS₂@NiS-MoS₂/Ti-3:1 (166 and 144 mV at 10 mA cm⁻², respectively). The research also reported that the Tafel slope of CoS₂@NiS-MoS₂/Ti-1:1 was as low as 53 mV dec⁻¹, which was significantly lower than those of CoS₂@NiS-MoS₂/Ti-1:3 (97 mV dec⁻¹), CoS₂@NiS-MoS₂/Ti-3:1 (69 mV dec⁻¹), Co-MOF/Ti (266 mV dec⁻¹), and CoMoNi-LDH (277 mV dec⁻¹). This could be attributed to the uniform leaf-like morphology and the disordered and defective regions caused by the ternary CoS₂-NiS-MoS₂. The abundant heterointerfaces of different structures and super porous MOF could create more edge-active sites and promote the HER reaction kinetics.

CONCLUSION AND PERSPECTIVE

Among several non-noble metal catalysts, MoS₂ is the most popular and has been intensively investigated for different applications because of its unique structure and special properties. For HER applications, MoS₂ is considered to be a prominent catalyst that could replace the Pt group in the electrochemical process because of its d-band electronic structure, analogous to that of noble metals. Many routes and techniques

have been used to synthesize and enhance the performance of catalysts based on MoS₂ to produce hydrogen gas. The application of catalysts based on MoS₂ for the HER is still being conducted in the laboratory. Some barriers exist to the commercial preparation of hydrogen gas using these catalysts because of the low efficiency and/or stability of the desired performance of practical materials.

Emerging as a unique material, the MOF group exhibits high porosity and possesses a superlarge surface area. High porosity and a large surface area are critical points in the electrochemical process for releasing gases. Recently, MOF-based catalysts have been extensively investigated for HER applications. However, the main drawbacks of these catalysts are their low conductivities and poor stability in strong electrolytes. Therefore, increasing the conductivity and lifetime of MOF catalysts is a key challenge in the preparation of practical materials for hydrogen technologies. Various methods, including structural modification, nonmetal and/or metal-doped catalysts, and heterostructures with other materials, have been thoroughly investigated.

The integration of the two most promising materials, MoS₂ and MOF, to prepare catalysts for the HER process is an outstanding strategy that utilizes the advantages of both materials. The stability and good catalytic activity of MoS₂ and the highly porous and large active sites of the MOF materials are important for the synthesis of effective catalysts for hydrogen production. Catalysts based on the MoS₂/MOF heterostructure present the benchmark HER performance and could be considered industrial-scale catalysts soon. However, some challenges need to be overcome, such as the conductivity and catalytic activities, which are still unworthy of practical application. Technological developments and various strategies, such as metal/nonmetal doping in heterostructure catalysts, could create a synergistic effect or increase the conductivity and improve the catalytic activities of MoS₂/MOF catalysts. After clearing these barriers, there is no doubt that, soon, catalysts based on MoS₂/MOF could play a crucial role as a promising technology for catalyst applications.

DECLARATIONS

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Availability of data and materials

Not applicable.

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Conflict of Interest

All authors declared that there are no conflicts of interest.

Ethical approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

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