

The rise of two-dimensional MoS₂ for catalysis

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Two-dimensional (2D) MoS₂ is used as a catalyst or support and has received increased research interest because of its superior structural and electronic properties compared with those of bulk structures. In this article, we illustrate the active sites of 2D MoS₂ and various strategies for enhancing its intrinsic catalytic activity. The recent advances in the use of 2D MoS₂-based materials for applications such as thermocatalysis, electrocatalysis, and photocatalysis are discussed. We also discuss the future opportunities and challenges for 2D MoS₂-based materials, in both fundamental research and industrial applications.

Keywords catalysis, 2D materials, MoS₂, non-precious metal, electronic properties

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tural and electronic properties, such as graphene, hexagonal boron nitride (h-BN), layered oxides, and other 2D layered transition metal dichalcogenides (TMDCs), have attracted great research interest in heterogeneous catalysis [4–9].

MoS₂ is a prototypical 2D layered TMDC material (Fig. 1) composed of three atomic layers, S-Mo-S, which are stacked through van der Waals forces. It has three phases: 1T, 2H, and 3R [10–12]. In the layered structure, each plane typically has a thickness of 6–7 Å, and consists of a hexagonally packed layer of metal atoms sandwiched between two layers of sulfur atoms. The intralayer Mo-S bonds are predominantly covalent in nature, whereas the sandwich layers are held by weak van der Waals forces, allowing the crystal surface layer to be readily cleaved. Despite this specific physical structure, 2D layered MoS₂ material with unique electronic, optical, and mechanical properties has been used in catalytic reactions, such as conventional heterogeneous catalysis [13–17], electrocatalysis [12, 18–21], and photocatalysis [22–24]. However, pure 2D MoS₂ has a poor intrinsic activity, limiting its application in heterogeneous catalysis [25–29]. Therefore, new strategies to enhance the intrinsic activity of 2D MoS₂ are of great interest. Recently, many researchers have sought to improve the intrinsic activity of MoS₂ through various strategies that mainly focused on the tuning of its electronic structure, including self-structure changing and the modulation of hybrid

1 Introduction

Catalysis, particularly heterogeneous catalysis, is an important domain in chemistry because most industrial chemical processes (e.g., energy, pharmaceutical, food, or material production industries) are based on it [1–3]. For heterogeneous catalysis, it is important to explore catalytic materials with excellent properties, such as high activity, selectivity, and stability. Recently, various novel two-dimensional (2D) materials with unique struc-

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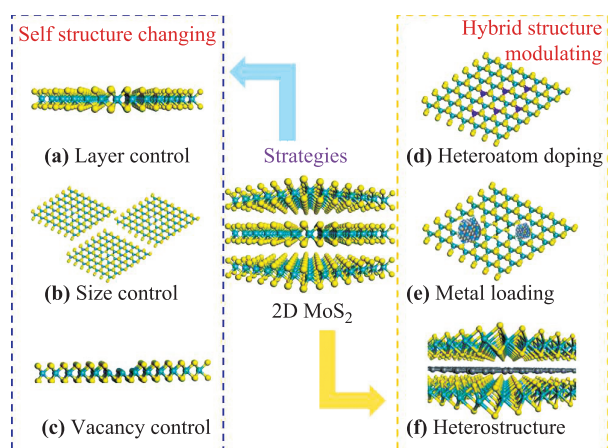


Fig. 1 The strategies for tuning the electronic state of 2D MoS₂. Self structure changing (Left): (a) Layer control; (b) Size control; (c) Vacancy control. Hybrid structure modulating (Right): (d) Heteroatom doping; (e) Metal loading; (f) Heterostructure.

structure (Fig. 1). As shown in Figs. 1(a)–(c), the layer thickness, plane size, and defects of MoS₂ can be regulated to efficiently promote an increase in the number of active sites and to modulate the electronic structure of MoS₂. Reducing the bulk or multi-layered MoS₂ to a single layer [Fig. 1(a)] can offer higher surface area and more active sites. Using single-layered MoS₂ with a direct-gap conductor allows easy transfer of electrons from the valence band to the conduction band, which can promote electrical conductivity and enhance the electrocatalytic activity. Furthermore, the fast charge-transfer may also be used in photocatalytic applications to accelerate the reaction rate. Moreover, reducing the plane size of layered 2D MoS₂ can expose more edge sites, thereby increasing the number of active sites [Fig. 1(b)]. In addition, the number of active sites can be increased by constructing a disordered structure [30–32]. Defects [12, 17] [Fig. 1(c)] as a new generated active sites break the traditional views that edge sulfur or molybdenum atoms are the only active sites. The formation of vacancies not only can induce the modulation of electronic structure, but also to some extent increases the number of active sites.

In addition to the strategy for changing the structure of MoS₂, the electronic structure of MoS₂ can be tuned through the modulation of the hybrid structure. As shown in Figs. 1(d)–(f), composite materials offer even greater control over the structural and electronic properties of MoS₂ in combination with other materials such as single atoms, metal clusters or nanoparticles, and bulk materials. Heteroatom doping [Fig. 1(d)] can tune the electronic structure and activate the in-plane inert sulfur atoms, facilitating molecular adsorption. Further-

more, 2D MoS₂ with unique electronic structure can also tune the heteroatom dopants and make it as active sites for enhancing the catalytic activity. Metal loading [Fig. 1(e)] by different metal-support interactions can tune the electronic state of the metal or support for improving the catalytic activity; this may be attributed to newly generated metal active sites. MoS₂ [Fig. 1(f)] can couple with bulk materials or even form a heterojunction to change the band structure to a suitable band gap for harvesting light in photocatalysis. Furthermore, these composite materials with enhanced electrical conductivity can promote the transfer of electrons and accelerate the reaction rate in electrocatalytic reaction systems.

In this review article, we first briefly introduce the active sites of MoS₂ that are applied in specific catalytic reactions. Thereafter, the recent strategies for enhancing the catalytic performance in thermocatalysis, electrocatalysis, and photocatalysis are overviewed; we simultaneously illustrate the “structure-activity relationship” of 2D MoS₂-based materials in catalysis. Finally, we go beyond the fundamental properties of these structures and discuss the potential for using such materials in heterogeneous catalysis.

2 Recognition of active sites

Recently, molybdenum sulfide catalysts have been widely used for heterogeneous catalysis due to their unique structure (Table 1). In the early days, MoS₂ as a catalyst was mainly used industrially for hydrotreating petroleum fractions. By the 1980s, at least three structural models [33, 34] had been proposed for the catalytic active sites of binary sulfide systems. In all the models, coordinatively unsaturated sites (CUS) of MoS₂ with a layered structure act as the active center for hydrodesulfurization (HDS) or hydrogenation (HYD). Then, promoters such as Co and Ni could significantly enhance the catalytic activity of the MoS₂ catalyst. Subsequently, the “Co(Ni)MoS” phase [35] has been widely accepted as the active site for binary sulfide systems. In the “Co(Ni)MoS” phase, Co or Ni atoms are located at the edges of the MoS₂ sheets. In addition, the active edges will change when the number of layers of MoS₂ is reduced. The stacked layers of MoS₂ could catalyze the HDS, with all the edges having coordinatively unsaturated sites, whereas only the top and bottom layers could provide catalytic active sites for HYD because of steric hindrance [36–38]. η^6 adsorption of π bonding cannot occur on the edge sites except in the top and bottom layers. MoS₂ was also used for hydrodeoxygenation (HDO) cleaving of the C–O bond in biomass, similar to hydrodesulfurization. For HDO, the sulfur vacancies of MoS₂ were primarily the active sites [14, 15, 17].

In electrocatalysis, MoS₂ has attracted great attention because it is prone to form a two-dimensional (2D) morphology that offers large surface areas and 2D permeable channels for ion adsorption and transport [39–41]. During the past few years, enormous effort has been made to explain the mechanism of the electrocatalytic hydrogen evolution reaction (HER). Both theoretical [42] and experimental [43] studies concluded that the HER activity mainly arises from the sites located along the edges of the 2D MoS₂ layers, while the basal surfaces are catalytically inert. However, with the development of characterization technology, the understanding of active sites has also changed. In-plane sulfur atoms can also be activated by transition metals doped into the MoS₂ [44]. Likewise, sulfur vacancies [17] generated during chemical doping can also act as active sites for HER.

For catalysis, activity, selectivity, and stability are very important parameters for evaluating a catalyst. Thus, how to improve the performance of the material is crucial. Although most active site of MoS₂ are coordinatively unsaturated sulfur atoms, there are also other active sites in specific reactions. Based on experiments and calculations, specific strategies for modifying 2D MoS₂ materials have been proposed for generating new active sites like sulfur vacancies, which noticeably enhance the performance. However, due to the complexity of the reaction mechanisms, it is too difficult to accurately recog-

nize the active sites. Therefore, it is necessary to study the active sites through the means of *in situ* characterizations and theoretical simulations, which may further guide us to design an efficient catalyst for specific reactions.

The recent development of *in situ* characterizations and theoretical simulations provides new insight into the active sites for some simple reactions. The in-plane sulfur of MoS₂ can be activated as active sites for producing hydrogen from water. The Deng group demonstrated that if a single atom of Pt replaces a Mo atom, it can activate the adjacent S atom due to the formation of a Pt-S bond [44], which results in a platinum oxidation state [Fig. 2(a)]. Density functional theory calculations (DFT) also demonstrated that the in-plane sulfur is responsible for the hydrogen evolution [Fig. 2(b)]. The transition metal doping process can not only activate the basal sulfur for the electrocatalytic hydrogen evolution reaction, but it can also be applied in the thermal catalytic hydrogenation reaction. As shown in Fig. 2(c), DFT indicated that neighboring Pt monomers worked in synergy to activate the adjacent sulfur atoms as active sites for further activation of hydrogen and intermediates [45]. Besides basal sulfur active sites, sulfur vacancies can act as active sites for water splitting. The Zheng group [46, 47] discovered that strained S-vacancies in the basal plane of 2H-phase monolayer MoS₂ act as a new, highly active, and tunable

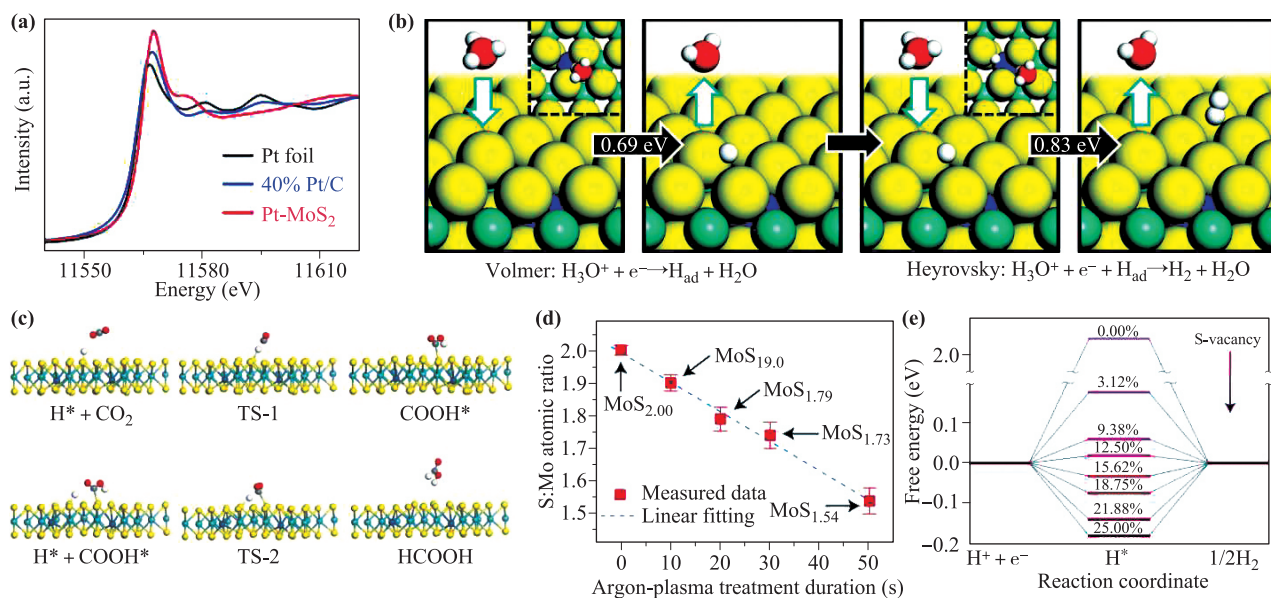


Fig. 2 Characterizations and theoretical simulations for the recognition of active sites. (a) The normalized Pt L₃-edge XANES spectra of Pt-MoS₂, Pt foil, and commercial 40% Pt/C [44]; (b) HER process on a Pt-MoS₂ catalyst. The top views are shown in the insets. The reaction barriers are shown by the black arrows. The green, yellow, blue, red and white balls represent Mo, S, Pt, O, and H atoms, respectively [44]; (c) Intermediates and transient states over neighboring Pt monomers MoS₂ during CO₂ hydrogenation [45]; (d) The S:Mo atomic ratio decreases with increasing duration of Ar-plasma treatment, as obtained from XPS measurements [46]; (e) Free energy versus the reaction coordinate of HER for the S-vacancy range of 0–25% [46].

catalytic site for the HER via argon-plasma treatment duration experiments [Fig. 2(d)] and the theoretical calculations [Fig. 2(e)].

3 Application

Two-dimensional MoS₂ materials with unique physical structures and electronic properties have become efficient catalysts. Theoretical research may guide the design or optimization of the MoS₂-based catalysts because 2D MoS₂ has a well-defined structure, which is an ideal theoretical model. Thus, many research groups have constructed various specific strategies for tuning the electronic structure of 2D MoS₂ and to further understand the mechanisms or the “structure-activity-relationship” of 2D MoS₂-based materials when used in catalytic reactions. The applications of these specific strategies for improving the catalytic performance are summarized in Fig. 3, including thermocatalysis, electrocatalysis, and photocatalysis.

3.1 Thermocatalysis

Thirty years ago, MoS₂ was mainly used for hydrodesulfurization (HDS) in the petroleum chemical industry [48]. With the increasing demands for energy, MoS₂ has been widely applied in various kinds of hydrogenation reactions (Table 1), such as hydrodeoxygenation (HDO) of biomass for chemicals or fuels, syngas to alcohols, nitrobenzene hydrogenation, and so on. Recently, the conversion of biomass into high-added value chemicals and

fuels (HDO) has attracted much attention, Tsang *et al.* [49] reported that the synthesis of 2D MoS₂ monolayer sheets decorated with isolated Co atoms via a chemical (Li) intercalation method that creates covalent bonds to sulfur vacancies on the basal planes exhibits superior activity, selectivity, and stability for the hydrodeoxygenation of 4-methylphenol to toluene under harsher conditions compared to conventionally prepared bulk or few layer MoS₂ samples. X-ray absorption fine structure spectroscopy (EXAFS) [Fig. 4(a)] showed that there were no first shell Co-Co bonds in Co-single layer MoS₂ (Co-^SMoS₂) sample compared to Co foil and Co(thiourea)₄ acetate samples, suggesting that Co species was not form into particles or clusters. HAADF-STEM [Fig. 4(b)] also showed that Co species inhabited surrounding Mo and sulfur sites. The DFT optimized structure [Fig. 4(c)] indicates that Co was situated on top of Mo sites. The simulated image also showed good agreement with the experimental image in Fig. 4(d). The specific structures exhibited superior activity for hydrodeoxygenation of 4-methylphenol to toluene. As shown in Fig. 4(e), a small amount of Co doped monolayer MoS₂ sheets could noticeably improve the conversion rate of 4-methylphenol to toluene over other samples, which illustrated that the immobilized Co on the basal sites of ^SMoS₂ facilitated the formation of more closely spaced catalytic sites for cascade catalysis at higher temperature. A Co-^SMoS₂ sample also exhibited remarkable activity for converting the 4-methylphenol (Conversion >90%) to toluene (Selectivity = 98.5%) at a lower temperature (180°, 3 MPa), and simultaneously showed significant stability for 7 cycles [Fig. 4(f)]. In conclusion, previous authors first presented a method for synthesizing monolayer MoS₂ with Co doping via high-temperature treatment in H₂ (300°) for creating basal sulfur vacancies, which formed a Co-S-Mo structure that could act as active sites for the hydrodeoxygenation reaction at a lower temperature (180°). It exhibited excellent properties and opened the possibility of using this novel type of catalyst for biomass conversion without sulfur loss. Aside from the non-noble Co atom, it is necessary to synthesize MoS₂ using other transition metal atom-doped catalysts for the hydrodeoxygenation reaction of 4-methylphenol or for applications in other reaction systems.

Wang *et al.* [50] reported a novel two-step oxidation-hydrogenation strategy for cleaving the C-O bonds in lignin. In the oxidation step, the O₂/NaNO₂/DDQ/NHPI system selectively oxidized C_α H-OH to C_α=O within the β-O-4 structure. In the hydrogenation step, the α-O-4 and the preoxidized β-O-4 structures were further hydrogenated over the 2D Ni-MoS₂ catalyst, leading to the cleavage of C_β-OPh and C_α-OPh bonds for the high yield production of phenolic monomers [Fig. 5(a)]. Figure 5(b) shows that MoS₂ and NiS phase peaks exist

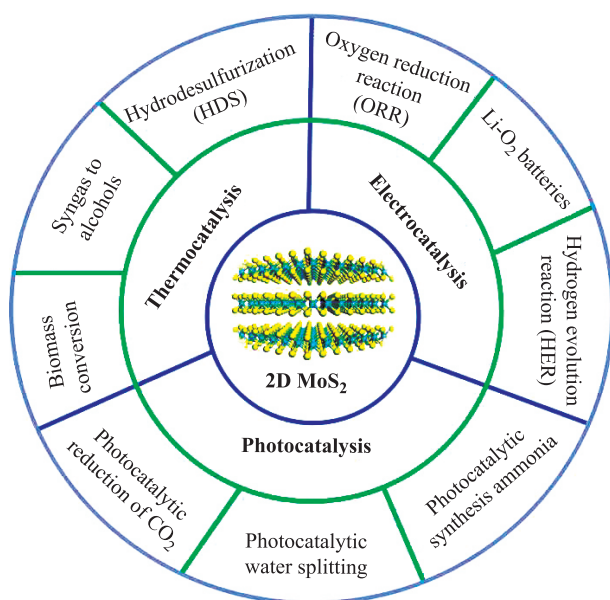


Fig. 3 Two dimensional MoS₂-based materials for application in various kinds of catalytic reaction.

Table 1 Summary of 2D MoS₂ for application in heterogeneous catalysis.

Catalysts	Catalytic systems	Performance or parameter	Activity origin or mechanism
Thermocatalysis			
MoS ₂ microflowers	Hydrogenation of nitrobenzene [103]	MoS ₂ microflowers show 100% conversion at 6 h than the bulk MoS ₂	Coordinative unsaturated Mo sites are the active sites
NiMo/ γ -Al ₂ O ₃	Hydrodesulfurization of dibenzothiophene and 4, 6-dimethyldibenzothiophene [104]	The NiMo/ γ -363 catalyst presented the highest activity	The superior catalytic performance from appropriate acidity and moderate dispersion degree
Pure MoS ₂	Influence of sulfur vacancy on thiophene hydrodesulfurization [105] Hydrodeoxygenation of p-cresol [106]	The sulfur vacancy was beneficial for the formation of intermediates Water has a positive effect on the deoxygenation degree but a negative effect on catalyst stability	The sulfur vacancy at Mo-edge is the active site Sulfur vacancies generated in reaction conditions are the main active sites
Unsupported MoS ₂ , MoO ₂ , Mo ₂ C and WS ₂	Hydrodeoxygenation of solvolysed lignocellulosic biomass [107]	Unsupported MoS ₂ catalysts show the high gross calorific value of 38 MJ·kg ⁻¹	Unsupported MoS ₂ catalysts with different morphology can clearly affect react rate
K promotion on MoS ₂	The synthesis of higher alcohols from syngas [13]	The presence of K not only changes the electronic properties for promoting the formation of higher alcohols	The electronic properties of MoS ₂ change upon promotion lead to the formation of higher alcohols via CO insertion
Pt-MoS ₂	Carbon dioxide hydrogenation [45]	CO ₂ can be converted into methanol without forming formic acid over isolated Pt monomers. But the formic acid could form and then convert to methanol over neighboring Pt monomers	Every Pt atom and its corresponding activated S atoms comprised an "active center"
Electrocatalysis			
MoS ₂ -based materials	Electrocatalytic hydrogen evolution reaction (HER): Activating the inert S edges via doping [108, 109] Increase the number of active sites [23, 56, 110–118] Improving the electrical conductivity [57, 118–129] Optimizing the electronic structure of MoS ₂ [40, 46, 118, 130–134] Construct heterostructures [135] Electrocatalytic oxygen reduction reaction (ORR) [58, 59]	Strategies for improving the HER activity of MoS ₂ Nanocomposites exhibited improved electrocatalytic activity for ORR with dominant 4 electron pathway in alkaline solutions [59] DFT revealed that N doping renders MoS ₂ monolayer better catalytic performance than P doping due to its moderate binding strength with ORR species [58]	The edge of MoS ₂ is active site and the modulating of electronic state can enhance the performance The resistance connection charge transfer from NG to the active sites is reduced and more active sites are exposed [59] The improved performance of MoS ₂ monolayer mainly originates from the induced suitable spin density due to N and P doping [58]
	Electrocatalytic carbon dioxide reduction reaction (CO ₂ RR) [60, 61]	MoS ₂ shows superior CO ₂ RR performance compared with the noble metals with a high current density and low overpotential in an ionic liquid [60] The onset overpotential is 31 mV, which is the lowest onset potential for CO ₂ RR reported so far [61]	The molybdenum-terminated edges of MoS ₂ are mainly responsible for its catalytic performance [60] Nb dopants can enhance the catalytic performance by modifying their electronic properties [61]
	Electrocatalytic nitride reduction reaction (NRR) [136]	The single Mo atom embedded into the MoS ₂ nanosheet was found to be the most active catalyst for NRR	Single transition metal atoms embedded into a MoS ₂ nanosheet with an S-vacancy as electrocatalysts for NRR
Photocatalysis			
MoS ₂ -based materials	Photocatalytic water splitting [137–139]	Non-precious metal could also show high activity	MoS ₂ in the form of nanosheets exhibits particularly good activity in its metallic form
Ultrathin MoS ₂	Photocatalytic reduction of dinitrogen to ammonia [93]	The pure ultrathin MoS ₂ exhibits high ammonia synthesis rate [325 $\mu\text{mol}/(\text{g}\cdot\text{h})$]	Photocatalytic N ₂ reduction is six-electron reduction process

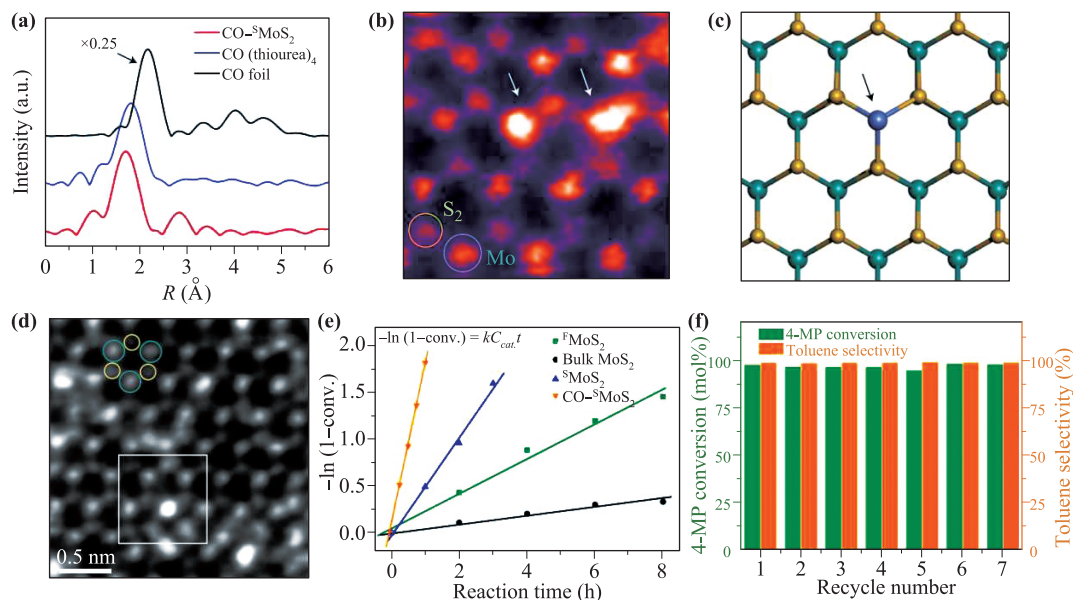


Fig. 4 Structural and catalytic performance of MoS₂-based catalysts. (a–d) the structure of Co-SMoS₂ [49]; (a) EXAFS spectra of three samples; (b) HAADF-STEM image of Co-SMoS₂, showing two bright contrast sites in the MoS₂ monolayer (arrows); (c) Geometry optimized DFT of a single Co on Mo atop site, showing good agreement with b; (d) HAADF-STEM image of Co-SMoS₂; (e) A kinetic study of 4-methylphenol to toluene [49]; (f) Stability test of Co-SMoS₂ for HDO of 4-methylphenol [49].

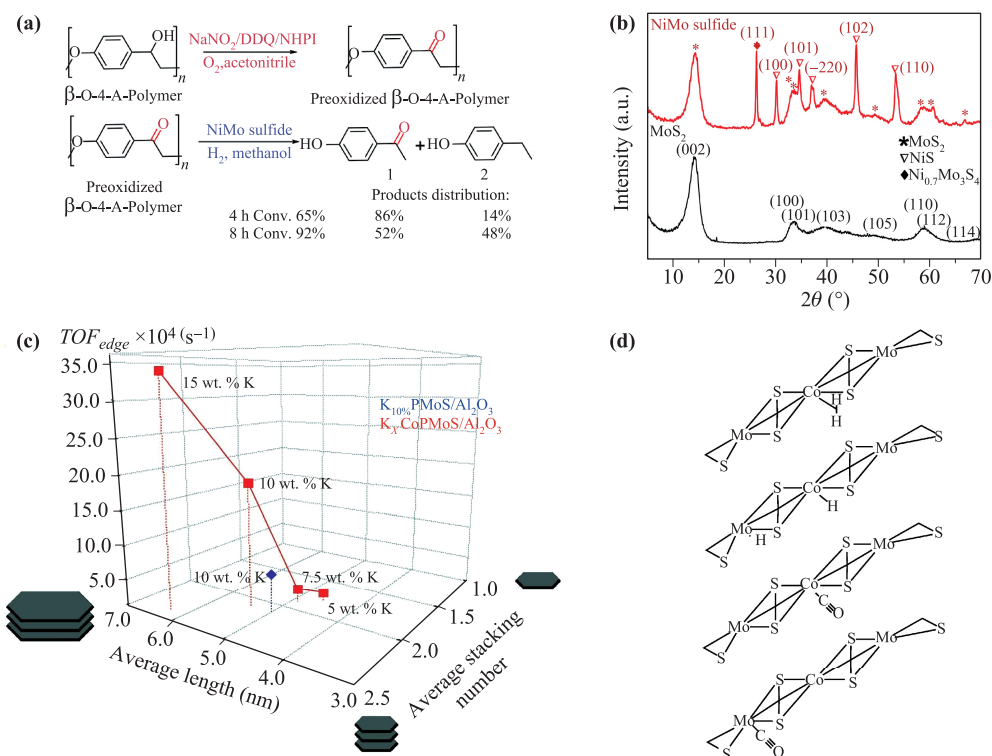


Fig. 5 Specific structures with high performance. (a) Two-step oxidation-hydrogenation strategy for high activity and selectivity; (b) XRD patterns of the NiMo sulfide and MoS₂ catalysts [50]; (c) Dependence of TOF of the edge sites in alcohol synthesis on particle sizes and layer numbers of the K_xCoPMoS/Al₂O₃ and K_{10%}PMoS/Al₂O₃ catalyst active phases; (d) Four models for H₂ molecular adsorption and CO molecular adsorption on the Co or Mo site [51].

in the XRD pattern of the NiMo sulfide catalyst. There are also peaks attributed to $\text{Ni}_{0.7}\text{Mo}_3\text{S}_4$, which is one of the Ni-doped heterometallic cubane-type Mo clusters. Kogan *et al.* [51] synthesized $\text{KCoMoS/C/Al}_2\text{O}_3$ for use in the production of alcohol from syngas. The addition of potassium to $\text{CoMoS/C/Al}_2\text{O}_3$ could substantially affect both the morphology of molybdenum disulfide crystallites and catalyst activity in the synthesis of alcohols. As shown in Fig. 5(c), the turnover frequency (TOF) in alcohol production over the K-CoMoS slab edges is approximately three times greater than that over unpromoted K-MoS edges. Thus, promotion of the $\text{KMoS/Al}_2\text{O}_3$ catalyst by Co atoms was beneficial for selective formation of alcohols. In addition, the average stacking number and particle length of the $\text{K}_x\text{-CoPMo/Al}_2\text{O}_3$ active phase also affected the TOF in alcohol formation, and the increasing number of active phase components could significantly enhance the catalytic activity. DFT and models of H_2 and CO molecule adsorption [Fig. 5(d)] showed that the CO molecule was likely to adsorb on Co atoms by a single K atom doping. In conclusion, potassium on the CoMoS phase active sites demonstrated that electron-density transfer from the potassium atom to transition metal atoms (predominantly to Co) improves the activity and selectivity.

3.2 Electrocatalysis

Two-dimensional (2D) materials with a substantial number of exposed active sites appear to be beneficial for fast interfacial charge-transfer and facile electrochemical catalysis. Very promising results have already been realized in developing nanosheets for clean energy conversion (involving water, hydrogen, and oxygen), competitive with noble metal electrocatalysts [52].

Hydrogen has been considered to be the most promising, sustainable, clean, and renewable energy carrier. It can be produced from electrochemical water splitting through the hydrogen evolution reaction (HER). This method has attracted much attention because it is efficient, clean, and sustainable for large-scale hydrogen production compared to the burning of fossil resources [53]. Recently, pure, novel two-dimensional electrocatalysts with unique structures and electronic properties, such as 2D MoS_2 material, showed high HER catalytic activity and has attracted the interest of many scientists. Both theoretical [42] and experimental [43] studies demonstrated that the unsaturated sulfur atoms on the edges of the pure MoS_2 nanocatalyst is the active site for the electrocatalytic HER, while the basal surfaces are catalytically inert. Different from its multilayer structure, 2D MoS_2 has more edge active sites, and the band gap transfers from an indirect-gap semiconductor to a direct-gap semiconductor when the number of layers is reduced

to a single layer, exhibiting high activity for the HER. In addition, the tunable intrinsic electronic properties of 2D MoS_2 by chemical doping or other routes brings new opportunities for the electrocatalytic HER compared to the pure 2D structure. Due to the unique electronic properties on the surface of MoS_2 , it lowers the kinetic barrier and promotes the HER rate. Deng *et al.* [44] first successfully introduced single metal atoms into the in-plane domain of few-layer MoS_2 nanosheets via a direct chemical synthesis method. According to the experimental results, Pt atoms are predicted to be the most effective for modulating the adsorption behavior of H atoms on neighboring sulfur sites. A one-pot solvothermal method was successfully used to synthesize the Pt atom doped 2D MoS_2 material (Pt- MoS_2). The transmission electron microscopy (TEM) images [Fig. 6(a)] and HAADF-STEM images [Figs. 6(b), (c)] show that Pt- MoS_2 consists of flower-like 2D nanosheets with a layer distance of 0.62 nm, corresponding to the (002) plane of MoS_2 , and single Pt atoms are highly uniformly dispersed in-plane of 2D MoS_2 . This is also demonstrated by the EXAFS spectra in Fig. 6(e) without the obvious appearance of Pt-Pt bonds in Pt- MoS_2 . As shown in Fig. 6(f), Pt metal atoms could be better than other metals when doped into the 2D MoS_2 material. As shown in Fig. 6(g), Pt-doped 2D MoS_2 (Pt- MoS_2) showed significantly higher HER activity with a much lower overpotential than pure few-layer MoS_2 (FL- MoS_2), indicating that a single Pt atom can trigger the 2D MoS_2 activity. The Tafel slope calculations further confirmed that the doped Pt atoms only tune the electronic properties of 2D MoS_2 , rather than directly catalyzing the H^+ to H_2 like the 40% Pt/C catalyst. In addition, Pt-doped 2D MoS_2 also showed better catalytic stability with 5000 cycles and poisoning resistance than Pt directly supported on 2D MoS_2 . From the above results, two-dimensional MoS_2 doped with transition metal heteroatoms can tune the electronic properties of the surface sulfur sites to noticeably enhance the HER activity, which offers the new ideas for future research.

We found that the Co atom can also be a better candidate for triggering the intrinsic activity of the MoS_2 surface [Fig. 6(f)]. However, the HER performance is greatly inferior to the Pt-doped 2D MoS_2 . To improve the intrinsic activity of such non-noble metal doped catalysts, Deng *et al.* [54] developed a multi-scale control strategy for constructing a 3D MoS_2 -confined single Co atom composite. Figure 7(a) shows that the composite has a uniform mesoporous structure at the macroscale, which facilitated the transport of H_3O^+ and H_2 and increased the accessibility of the MoS_2 surface. At the nanoscale, oriented vertical growth of MoS_2 nanosheets around the mesoporous structure increases the number of edges, which are active sites. At the atomic scale, chemical doping with single Co atoms of mesoporous

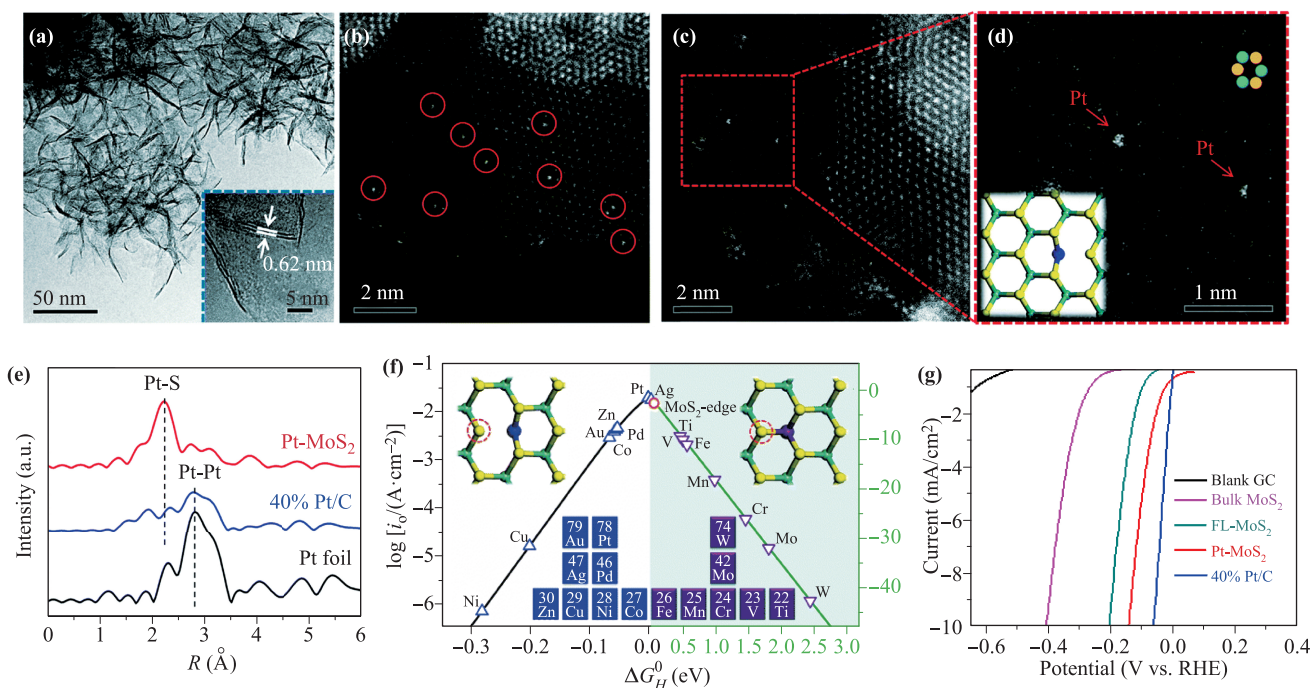


Fig. 6 Characterizations and the performance of Pt-MoS₂ catalysts. (a–e) The single atom structure of Pt-MoS₂ [44]; (a) TEM image of Pt-MoS₂; (b, c) HAADF-STEM images of Pt-MoS₂; (d) Magnified domain with red dashed rectangle in (c) showing a honeycomb arrangement of MoS₂, the bottom inset shows the simulated configuration of Pt-MoS₂; The blue balls represent Pt; (e) The k^2 -weighted EXAFS spectra of various samples; (f) Relationship between current (\log_{10}) and difference in Gibbs free energy (ΔG_H^0) represented by volcano curve when 2D MoS₂ doped with single metal atoms [44]; (g) HER polarization curves for various catalysts [44].

MoS₂ foam (mPF-MoS₂) can further enhance the intrinsic HER activity by triggering the activity of neighboring S atoms. The authors also found that the optimum Co content in the Co-doped mesoporous MoS₂ foam (mPF-Co-MoS₂) for high-performance HER activity was 16.7% [Fig. 7(b)]. This material showed long-term durability over more than 5000 cycles and an overpotential of only 156 mV at a current density of 10 mA/cm², comparable to those of Pt-MoS₂ [Fig. 6(g)] and many other excellent MoS₂-based electrocatalysts. DFT calculations confirmed that moderate Co doping could modulate H adsorption on MoS₂ to a suitable degree and simultaneously maintain the structural stability, enabling the HER activity to reach the optimum value [Fig. 7(c)].

Surprisingly, Gao's group [55] discovered that non-metal P-doped MoS₂ nanosheets exhibited excellent HER activity with a small Tafel slope of 34 mV/decade, an extremely low overpotential of 43 mV at a benchmark current density of 10 mA/cm², and good stability, superior to pure MoS₂. Both the experimental and theoretical studies indicate that the high performance is attributed to the quantity of intrinsic basal-plane S active sites and newly generated dopant P atoms. In addition, the improved conductivity of materials with P-doping and the

enlarged interlayer spacing enabled fast proton/electron adsorption and hydrogen release processes. Likewise, Xie *et al.* [56] demonstrated the successfully synergistic regulation of both structural and electronic benefits by controllable disorder engineering and simultaneous oxygen incorporation in 2D MoS₂ catalysts, leading to dramatically enhanced HER activity. HRTEM images and corresponding FFT patterns [Figs. 8(a)–(d)] reveal controllable disorder engineering with an obvious evolution of the degree of disorder, illustrating that oxygen incorporation can reduce the crystallinity of MoS₂, increasing the number of unsaturated sulfur atoms [30, 31] and boosting the HER intrinsic activity. The calculated density of states (DOS) shown in Fig. 8(e) indicates that the bandgap of oxygen incorporated in the MoS₂ slab (1.30 eV) is lower than the pristine 2H-MoS₂ slab (1.75 eV). As shown in Fig. 8(f), the incorporated oxygen atom significantly contributes to the charge density for both the valence and conduction bands, which is in sharp contrast to that of the pristine 2H-MoS₂, confirming the effect of oxygen incorporation on the electronic properties. Previous research suggested that the decrease of bandgap can improve the conductivity of the material and further efficiently enhance its intrinsic activity in the HER

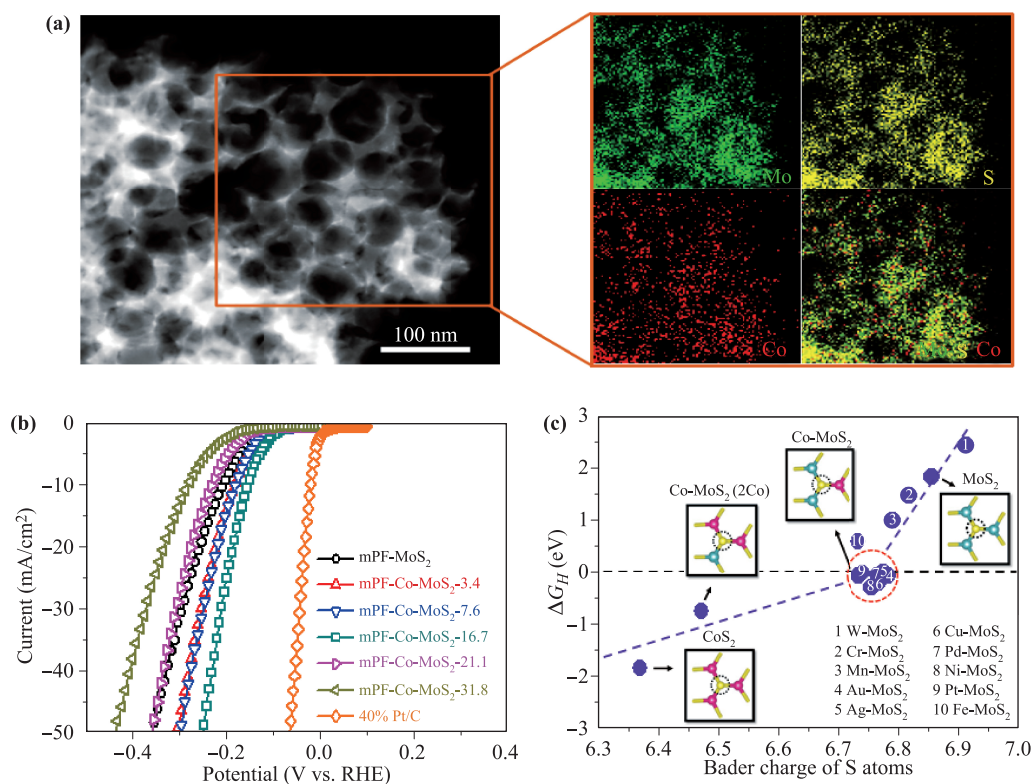


Fig. 7 Structural and performance of MoS₂-based catalysts. (a) HAADF-STEM image of mPF-Co-MoS₂ and corresponding energy-dispersive X-ray maps [54]; (b) HER polarization curves form various of samples [54]; (c) ΔG_H of S atoms versus Bader charge of S atoms for different structures with different atomic ratios of Co to Mo [54].

[57]. Figures 8(g) and (h) also show that the disordered structure provides a number of unsaturated sulfur atoms as active sites for the electrocatalytic HER and that the oxygen incorporation reduces the bandgap for enhancing the conductivity, facilitating the combination of positive protons and the surface of catalyst. In conclusion, previous authors mainly increased the HER activity by regulating the 2D MoS₂ material via two strategies: increasing the number of active sites and electrical conductivity.

In addition, 2D MoS₂-based materials with a unique structure and tunable electronic properties can also be applied in the oxygen reduction reaction (ORR) [58, 59], the carbon dioxide reduction reaction (CO₂RR) [60, 61], Li-oxygen batteries [62], Li-S batteries [63, 64], and other electrocatalytic reactions.

3.3 Photocatalysis

With the increasing energy shortage and environmental pollution issues, semiconductor photocatalysis has been widely studied in recent decades since only solar irradiation is required to drive the photocatalytic reaction via a suitable semiconductor [65]. Atomically-thin 2D MoS₂ materials with an ultrahigh specific surface area, ultrathin thickness, strong quantum confinement

of electrons, and a suitable band structure have been widely applied in photocatalysis [18]. In comparison to its bulk counterparts, atomically-thin 2D MoS₂ with a unique structure and tunable electronic properties can promote the photocatalytic efficiency via three crucial photocatalytic processes: light harvesting, charge separation, and interfacial catalytic reactions. 2D MoS₂ with few layers or even a single layer expose more active sites, not only facilitating the adsorption of ultraviolet-visible light [66], but also accelerating the migration of photo-generated electron-holes from the semiconductor inside to the surface-active sites. Moreover, 2D MoS₂ material can also be decorated by chemical doping, defect engineering, and other semiconductor materials, which can controllably modulate its electronic states for promoting molecular adsorption, improving the photocatalytic activity. The strategies for enhancing the photocatalytic performance of 2D MoS₂, such as using a hybrid structure, have made it suitable for applications in water splitting, CO₂ reduction, and other fields.

3.3.1 Photocatalytic water splitting

Photocatalytic water splitting into H₂ fuel has been a research focus for its key role in solving the energy

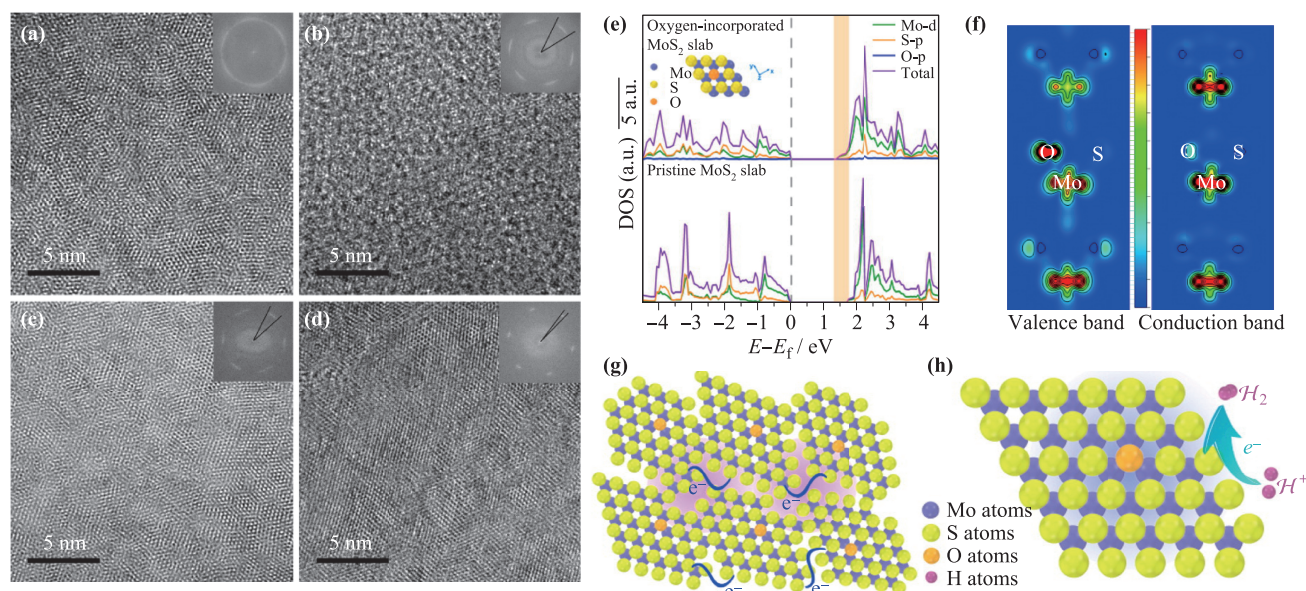


Fig. 8 Structural and electronic structure of oxygen-incorporated MoS₂. (a–d) HRTEM images and corresponding FFT via different synthesis temperature [56]; (a) 140 °C; (b) 160 °C; (c) 180 °C; (d) 200 °C; (e) Calculated density of states (DOS) of the oxygen-incorporated MoS₂ slab (top) and the pristine 2H-MoS₂ slab (bottom) [56]; (f) The charge density distributions of valence band (left) and conduction band (right) near the oxygen atom, respectively [56]; (g) The disordered structure in oxygen-incorporated MoS₂ ultrathin nanosheets provide more active sites and enhancing the intrinsic electrical conductivity [56]; (h) Constructed model of an individual oxygen-incorporated MoS₂ nanodomain and the illustration of the HER process at the active sites [56].

crisis and environmental problems [67, 68]. Thus, excellent electrocatalysts have been widely developed for the water splitting process. MoS₂-type earth-abundant layered transition-metal dichalcogenides have recently been studied extensively as photocatalysts as well as co-catalysts for photocatalytic H₂ production because of their structures and suitable band gap [69–71]. As previously discussed, 2D MoS₂ material, with its high number of edges active sites, has been widely applied in the electrocatalytic HER because the surface-binding free energy of MoS₂ with atomic hydrogen is analogous to that of Pt, which is close to zero [42]. To further enlarge the quantities of active sites for boosting the photocatalytic efficiency, several groups [72, 73] have reduced the number of layers of MoS₂ to a few layers or even a single layer. The activity is noticeably enhanced when the number of layers is reduced, which may be attributed to the greater number of exposed active sites. Moreover, it was found that single layer MoS₂ with a direct band gap, is more beneficial for the migration and separation of electrons from the valence band to conduction band than few layer MoS₂ with an indirect band gap. However, the low in-plane conductivity of pure MoS₂ nanosheets limits its application. Constructing composite materials or heterojunction structures can promote its application overcome this limitation. Recently, many

researchers have focused on the study of MoS₂ combined with other conductive materials, such as TiO₂ [74–76], ZnO [77, 78], and ZnS [79], which may significantly improve the photocatalytic activity for water splitting. 2D MoS₂ nanosheets form an intimate heterojunction with ZnO, which favors charge-transfer. Recombination of the photogenerated electron-hole pairs is suppressed, resulting in a significantly enhanced photocatalytic activity for hydrogen evolution. Moreover, the rate of H₂ evolution by CdS under visible light ($\lambda > 420$ nm) can be significantly enhanced by MoS₂ as co-catalyst [80–82]. He *et al.* [83] reported the highest H₂ production (95 mmol·h⁻¹·g⁻¹), which was obtained under artificial visible light irradiation using ultrathin MoS₂ decorated CdS nanowire composites. Kim *et al.* [84] also reported that highly dispersed ultrathin MoS₂ nanosheet decorated CdS nanorods were an efficient photocatalyst for spectacular hydrogen evolution under solar light irradiation. A simple ultrasonic method for the preparation of ultrathin MoS₂/CdS composite materials showed a high rate of H₂ production (174 mmol·h⁻¹·g⁻¹) under solar light irradiation. TEM showed that ultrathin 2D MoS₂ nanosheets were highly dispersed on the 1D CdS₂ nanorods, shown in Figs. 9(a)–(c). The synthesized material was evaluated for H₂ production via photocatalysis, as shown in Fig. 9(d), suggesting that the ultrathin MoS₂

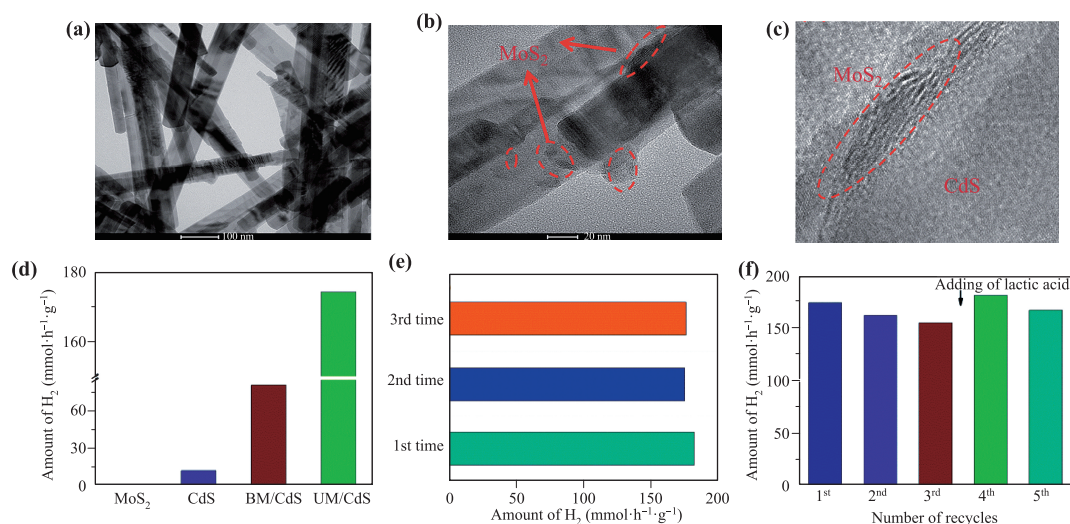


Fig. 9 Structural and photocatalytic performance of CdS decorated catalysts. (a–c) TEM analysis of UM/CdS composite [84]; (d) Hydrogen production rate with different photocatalysts [84]; (e) Reproducibility test for 6 wt% UM/CdS [84]; (f) Recyclability test of 6 wt% UM/CdS [84].

decorated CdS nanorods could better facilitate the rate of H₂ production compared to the pure CdS material. In addition, in combination with the bulk MoS₂ decorated CdS nanorods, ultrathin MoS₂ with its unique structural and electronic properties showed high activity for H₂ generation. Furthermore, it displayed high reproducibility in three experiments and better stability after five cycles [Figs. 9(e), (f)]. The ultrathin MoS₂ nanosheets with a high specific surface area and abundant active edge sites effectively separated the photo-generated charge carriers and reduced the probability of recombination of electron-hole pairs.

Carbon nitride, C₃N₄, is a promising candidate for a metal-free catalyst, but it suffers from low activity due to the high recombination rate. However, this semiconductor can be coupled with 2D MoS₂ material, which efficiently promoted the separation of charge carriers and boosted the hydrogen evolution activity under the visible light region [85–87]. MoS₂-g-C₃N₄ (0.5 wt.%) showed high catalytic activity (0.23 mmol·h⁻¹·g⁻¹), which was 11.3 times greater than the unmodified g-C₃N₄ (0.020 mmol·h⁻¹·g⁻¹) [86]. Similarly, a heterojunction with layered mesoporous C₃N₄ and MoS₂ showed an improvement of nearly 200 times with an activity of 1.030 mmol·h⁻¹·g⁻¹ compared to the mesoporous C₃N₄, ~0.05 mmol·h⁻¹·g⁻¹. Planar nanojunctions between layered MoS₂ and graphitic C₃N₄ (g-C₃N₄) allow fast charge separation across the interfaces, which facilitate hydrogen production. Karimi *et al.* [88] presented a facile approach for the preparation of MoS₂ nanosheets decorated by porous titanium dioxide with effective photocatalytic activity. Mesoporous titanium

dioxide nanostructures were first synthesized by a hydrothermal process using titanium (III) chloride, and then the MoS₂/TiO₂ were prepared through mixing of MoS₂ nanosheets with mesoporous titanium dioxide under ultrasonic irradiation. The as-prepared MoS₂/TiO₂ nanocomposites exhibited outstanding photocatalytic activity for dye degradation under sunlight irradiation, which could be attributed to a synergistic effect between the molybdenum disulfide nanosheet and mesoporous titanium dioxide. Cui *et al.* [89] constructed a three-dimensional double-heterostructured photocatalyst by connecting TiO₂-MoS₂ core-shell nanosheets assembled on a graphite fiber (GF) via a facile two-step hydrothermal method. As shown in Figs. 10(a)–(c), transmission electron microscopy (TEM) suggested that MoS₂@TiO₂ nanosheets scrapped from the surface of the GFs and the thin MoS₂ are intimately deposited on the surface of TiO₂ nanosheets with a few layers. The schematic diagram [Figs. 10(d), (e)] illustrates the energy band structure and the principle of the separation of charge carriers in GF@MoS₂-TiO₂ composites. The presence of MoS₂ nanosheets can modify the band gap for harvesting UV-visible light adsorption. The photocatalytic activity can be significantly enhanced under UV and visible irradiation when the loading of MoS₂ reaches 50% [Figs. 10(f), (g)], which is mainly attributed to the high interfacial charge-transfer and separation ability suppressing the recombination of electron-hole pairs. It was demonstrated that the heterostructures formed by the combination of 2D MoS₂ can efficiently tune the band gap for higher light energy utilization, and can promote the separation of photogenerated carriers and accelerate the

carrier-transfer of the ternary heterostructure.

3.3.2 Other reactions

2D MoS₂-based materials with the advantages of strong light harvesting behavior, high charge separation and transfer efficiency, and fast interfacial reaction rates can be applied in photocatalytic water splitting. It can also be used in other reaction systems, such as photocatalytic CO₂ reduction [90], pollutant removal [91, 92], ammonia synthesis [93], organic synthesis [94], and environment catalysis [95–101]. In a recent study, Xie *et al.* [102] reported the first visible-light-driven dehydrogenative coupling of methanol into ethylene glycol, an important chemical material. Ethylene glycol (EG) is formed with 90% selectivity and high efficiency together with hydrogen over a molybdenum disulfide nanofoam-modified cadmium sulfide nanorod catalyst. As shown in Figs. 11(a)–(d), HRTEM and HAADF-STEM studies revealed that the MoS₂ foam located on the CdS rod had more edge sites and more intimate contact with CdS than the MoS₂ sheet on CdS. EXAFS studies clarified that the MoS₂-foam/CdS sample has more edge sites due to having less Mo-Mo coordination than the corresponding MoS₂ sheet. The presence of MoS₂ would accelerate the separation and transfer of photogenerated excitons, in particular, MoS₂ foam [Fig. 11(e)]. Therefore, MoS₂ accelerates the photocatalytic activity for EG formation by both providing H₂ evolution active sites and enhancing the transfer of photogenerated electrons and holes [Fig. 11(f)]. In conclusion, this work not only offers an alter-

native non-petroleum route for the synthesis of EG, but also presents a unique visible-light-driven catalytic C-H activation with hydroxyl groups in the same molecule, keeping it intact. In this reaction system, MoS₂ plays a role in accelerating the rate of hydrogen production. Composite materials with enhanced photocatalytic performance offer new ideas for how to rationally design catalysts. Furthermore, heterostructures with greater control over the structural and electronic properties may lead to new directions in catalytic research and application of these materials.

For example, methane and carbon dioxide are the main greenhouse gases, which can be directly utilized for producing liquid fuels and chemicals. Due to the high energy consumption, photocatalytic methane or carbon dioxide activation through C-C coupling oxidation to ethylene glycol or high value-added products, may be important chemical processes. It not only solves the problem of high energy consumption and demand for chemicals, but also reduces the emission of greenhouse gases. New methods for designing composite materials would contribute to the catalysis field.

4 Conclusions and perspectives

Two dimensional MoS₂ material with unique structural and electronic properties is a promising candidate for the application in heterogeneous catalysis, including thermocatalysis, electrocatalysis, and photocatalysis. The mod-

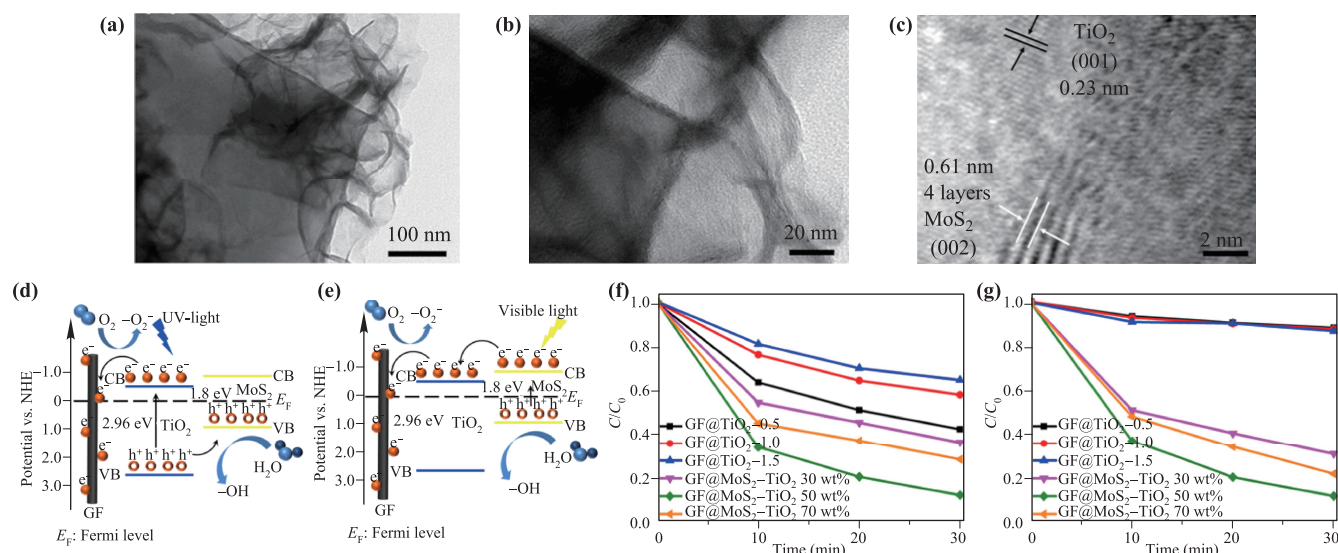


Fig. 10 Structural and photocatalytic performance of GF@MoS₂-TiO₂ composites. (a–c) TEM images of GF@MoS₂-TiO₂ composites (50wt% MoS₂) [89]; (d, e) Schematic diagram of electron-hole separation mechanism upon UV-vis excitation for 3D GF@MoS₂-TiO₂ composites [89]; Photocatalytic performance over GF, GF@TiO₂, and GF@MoS₂-TiO₂ composites under (f) UV and (g) visible light irradiation [89].

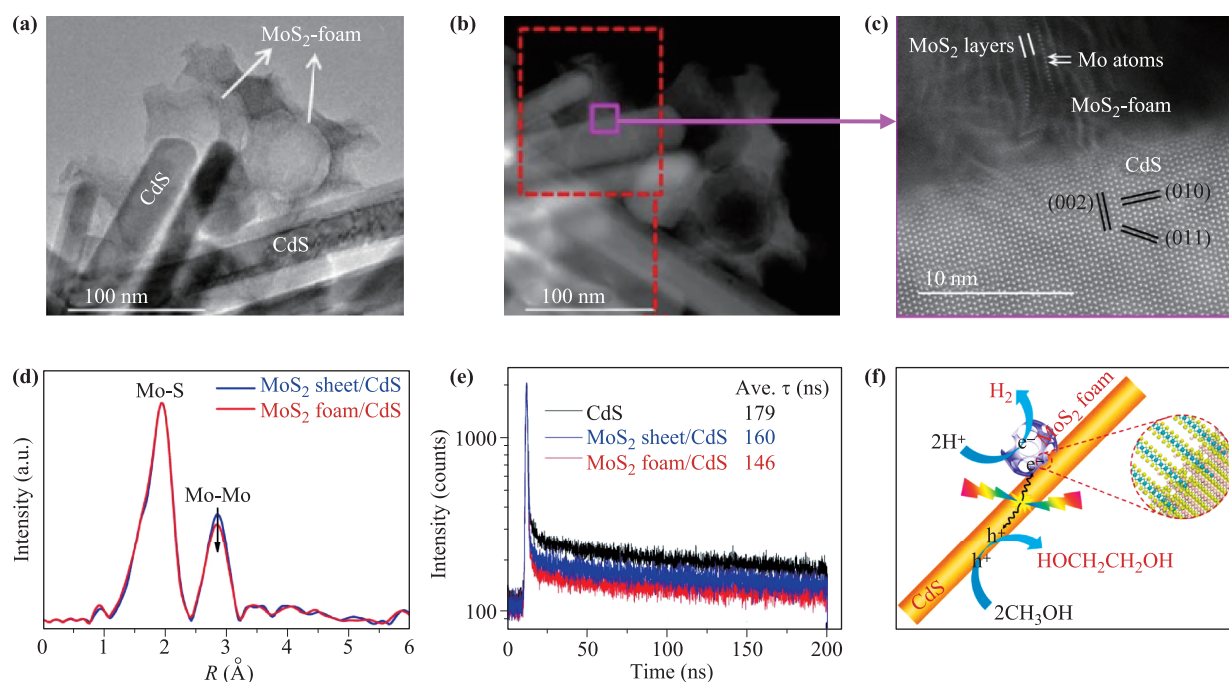


Fig. 11 Structural and physicochemical properties of the MoS₂-foam/CdS catalyst. (a–d) The structure of MoS₂-foam/CdS [102]; (a) HRTEM; (b) HAADF-STEM; (c) High-resolution HAADF-STEM; (d) The k^2 -weighted EXAFS spectrum of two samples; (e, f) Physicochemical properties of the MoS₂-foam/CdS [102]; (e) Time-resolved photoluminescence (TRPL) spectra of three samples; (f) Schematic illustration of MoS₂-foam/CdS for photocatalytic synthesis of EG and H₂ from CH₃OH.

ulation in electronic states via different routes, such as reducing the number of layers or plane size, introducing metal or non-metal heteroatoms, and combining with other materials, is crucial for enhancing the catalytic activity.

Active sites play a role in catalytic reactions. They not only efficiently convert reactants to one specific product, but also can help us to understand the reaction process in depth. Thus, it is also very important to develop efficient *in situ* characterizations and theoretical simulations to reveal the catalytic reaction mechanisms at molecular and atomic levels. Theoretical research may guide the design or optimization of MoS₂-based catalysts because 2D MoS₂ has a well-defined structure, which is an ideal theoretical model. Consequently, a clear understanding of the reaction mechanisms will not only promote understanding of the catalysts, but also can help to guide the design of efficient catalysts and achieve a huge leap from trial-and-error to rational design of materials.

Though 2D MoS₂-based catalysts have been widely investigated for real industrial applications, there are still a number of unsolved technological problems. For example, achieving mass production and controllable preparation of these 2D MoS₂-based catalysts, which is key to downstream applications.

In addition to the above strategies that have been re-

ported, there are other possible methods for regulating the electronic structure in 2D MoS₂ materials. As reported before, the in-plane sulfur is inert for the hydrogen evolution reaction. However, some research has demonstrated that the Mo substituted by other metals can activate the basal sulfur atoms via tuning their electronic structures [44]. Co single atoms can be anchored on the surface of 2D MoS₂, which can also enhance the catalytic activity [49]. Thus, the electronic structure of basal sulfur might be modulated by the decoration of organic ligands or ionic liquids. Ideally, active sites can be constructed for selectively activating the reactant molecule, which may apply to some specific catalytic reactions. Furthermore, according to the concept “electron penetration” that was reported previously [140], electrons may also transfer from the metal to the MoS₂ layer for regulating the electronic structures when the metal is encapsulated by a 2D MoS₂ nanosheet. In addition, reducing the size of 2D MoS₂ and dispersing it to a support may also change the electronic properties for facilitating the catalytic performance. In conclusion, the strategies for the regulation of the electronic structure can be summarized in three parts. First, the MoS₂ self-structure changing can adjust the size of the band gap when reducing the layers to single layer, which is attributed to the quantum confinement effect. Second, the electronic

state of molybdenum or sulfur atoms can be tuned by a heteroatom doping process, mainly due to a difference in electronegativity. Third, the electronic properties of MoS₂ might be tuned by other supports or heterostructure materials. The interaction between MoS₂ and its support can regulate the electronic state of MoS₂ for adapting to the specific reactions.

Finally, two-dimensional MoS₂, with its unique electronic structure, has received increasing research interest for catalysis. In addition to these properties, other characteristics being developed for applications in other fields, such as charge density waves, magnetism, lubricating property, and band gap vary with the number of layers.

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