

Review

# Recent progress of MoS<sub>2</sub> for photocatalytic and electrocatalytic hydrogen generation—A review

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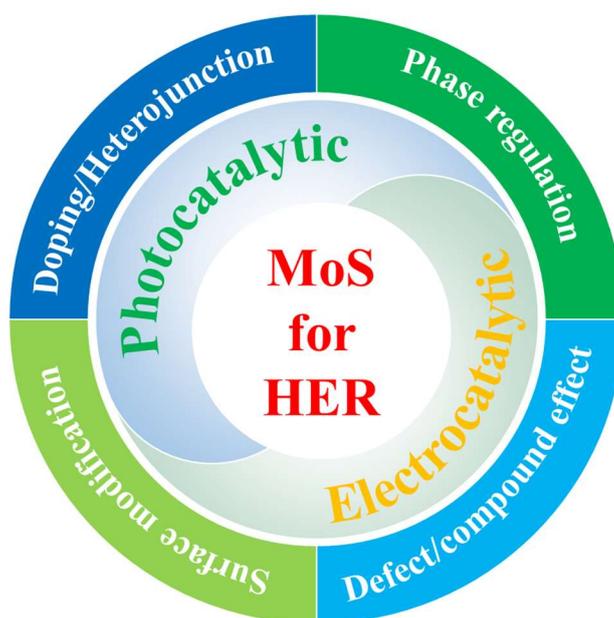
**Abstract:** Hydrogen (H<sub>2</sub>) plays a crucial role in the transformation of the energy structure due to its environmental friendliness, renewability and high energy density. The photocatalytic and electrocatalytic hydrogen evolution reaction (HER) presents a promising approach for H<sub>2</sub> production. Molybdenum disulfide (MoS<sub>2</sub>) has emerged as a promising catalyst in photocatalytic and electrocatalytic HER due to its high activity, easy preparation and cheapness. However, it suffers from poor stability and inactive basal planes. In this review, we encapsulated the research advancements of MoS<sub>2</sub> for photocatalytic and electrocatalytic HER in the past ~10 years. The latest strategies to enhance the catalytic activity of MoS<sub>2</sub>, such as doping, phase adjustment, surface modification and others, are also summarized. The relationship between structure and activity for enhanced H<sub>2</sub> generation by different means is briefly introduced. The challenges and directions of MoS<sub>2</sub> materials in photocatalysis and electrocatalysis for HER are also discussed, aiming to provide promising guidelines for future research.

**Keywords:** photocatalysis; electrocatalysis; hydrogen evolution reaction; molybdenum disulfide

## 1. Introduction

Hydrogen (H<sub>2</sub>) is considered as one of the options for the transformation of the future energy structure due to its advantages of being non-polluting and renewable and having a high energy density (142 MJ·kg<sup>-1</sup>), which holds the potential to replace fossil fuels and alleviate global warming and atmospheric pollution [1–5]. Moreover, H<sub>2</sub>, as a highly combustible diatomic gas, is also the least dense gas [6]. Under standard conditions, the mass of H<sub>2</sub> is only 6.897% of the air mass at the same volume [7]. In addition, H<sub>2</sub> is the most common element in the universe with high volatility, high calorific value of combustion and high energy, which can be used as an energy carrier and fuel. At present, H<sub>2</sub> can be produced through fossil fuel conversion, biomass conversion and photocatalytic and electrocatalytic water electrolysis [4,8–10]. Among them, hydrogen evolution reaction (HER) via photocatalytic and electrocatalytic water electrolysis has been considered as the most potential method for efficient catalysis. Catalysts play a crucial role in photocatalytic and electrocatalytic HER processes [11–13]. Catalysts based on the noble metal Pt show an excellent HER property but their extensive application is severely limited by scarcity and high cost. Therefore, developing low-cost, highly active catalysts with attractive stability is of great significance.

Two-dimensional (2D) layered MoS<sub>2</sub> has received enormous attention due to its unique crystal structures and electronic and optical properties. MoS<sub>2</sub> has three tunable phases: 1T, 2H and 3R [14]. These properties allow MoS<sub>2</sub> as an excellent catalyst in various catalytic reactions, such as electrocatalysis and photocatalysis (**Scheme 1**). Previous works in the literature have confirmed that MoS<sub>2</sub> has active edge sites and inert basal planes [14,15]. However, the intrinsic activity of MoS<sub>2</sub> is restricted by its limited active edge sites. Therefore, new strategies to improve the intrinsic activity of 2D MoS<sub>2</sub> have aroused great research interest. Herein, the article focused on the recent research progress of MoS<sub>2</sub> for photocatalytic and electrocatalytic HER. The characteristics and modification methods of MoS<sub>2</sub> materials are introduced.

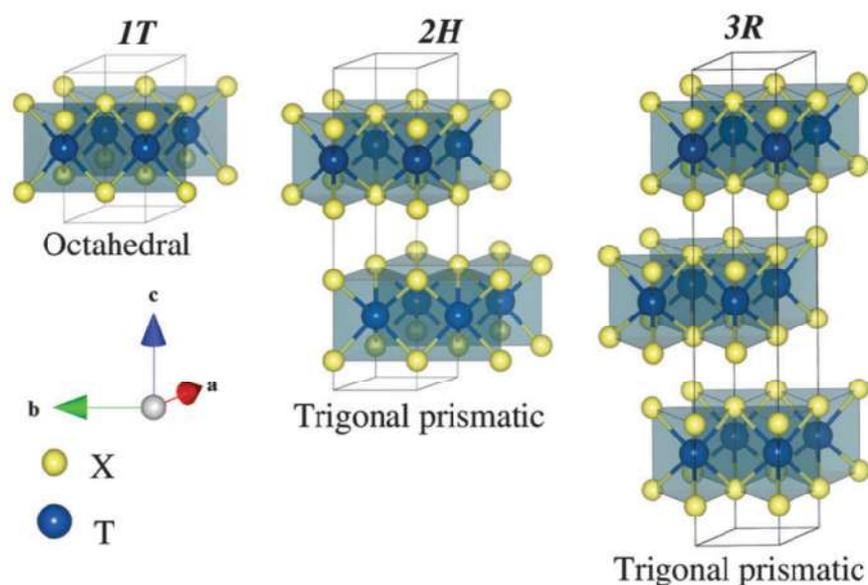


**Scheme 1.** Schematic highlight of MoS<sub>2</sub> for photocatalytic and electrocatalytic HER.

## 2. Structural feature

Generally, MoS<sub>2</sub> contains three different phase structures of 1T, 2H and 3R, where T, H and R represent tetragonal, hexagonal and rhombohedral, respectively, while the numbers 1, 2 and 3 indicate the number of layers in a unit cell, respectively, as shown in **Figure 1** [16]. Each MoS<sub>2</sub> monolayer is made up of three atomic layers with sandwiched molybdenum atoms between two layers of sulfur atoms. Generally, 1T-MoS<sub>2</sub> is metastable and possesses a single-layer atomic structure with octahedral metal coordination [17]. This structure leads to the metallic feature of 1T-MoS<sub>2</sub> in nature, meaning highly conductive. 2H-MoS<sub>2</sub> refers to a two-layer atomic structure with an adjacent monolayer spacing of 6–7 Å, where each layer is made up of a hexagonal arrangement of molybdenum atoms. 3R-MoS<sub>2</sub> is a rhombohedral structure with a band gap of 1.415 eV. However, 3R-MoS<sub>2</sub> is unstable at ambient temperature, which limits research on its reactivity. Interestingly, bulk MoS<sub>2</sub> is composed of multiple monolayers with weak van der Waals interactions, making them easy to separate. The adjacent monolayer distance can be tuned via chemical, electrochemical and solvothermal/hydrothermal methods. In addition, MoS<sub>2</sub> with different phases can

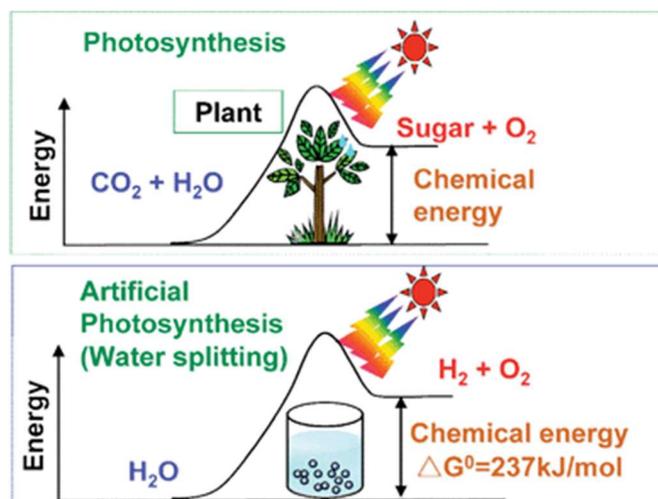
provide many unique features by constructing active unsaturated S/Mo atoms [14]. These enable MoS<sub>2</sub> to be utilized in various energy-related fields, including electrocatalysis, photocatalysis, rechargeable batteries, supercapacitors, fuel cells, etc. [18–21]. In this paper, the recent progress in photocatalytic and electrocatalytic HER is discussed.



**Figure 1.** Structures of MoS<sub>2</sub>: 1T, 2H and 3R [16].

### 3. Recent progress of photocatalytic HER

Photocatalysis is a chemical reaction in which a substance is converted by the combined action of light energy and a catalyst. Since the discovery of light-assisted decomposition of water via TiO<sub>2</sub> electrode by Fujishima and Honda in 1972 [22], many photocatalysts have been developed to promote photocatalytic HER. Currently, photocatalytic technology has been widely studied in the fields of hydrogen preparation, pollutant degradation, CO<sub>2</sub> reduction, antimicrobial and air purification [23–28]. Among them, photocatalytic hydrogen production is an environmentally friendly and promising technology to obtain hydrogen by decomposing water through light energy and catalysts, and it has received increasing attention. As shown in **Figure 2**, there are many similarities between photocatalysis and plant photosynthesis, as both undertake material transformation under sunlight and decompose water [29]. The energy required for photocatalytic HER comes from solar energy, which is clean, harmless and easy to obtain, and the required device has a simple structure and no secondary pollution and is easy to control and very friendly to the environment [14]. Photocatalytic HER, however, is a very complex process. It is affected by the catalyst itself, such as the catalyst's crystal defects, particle size, morphology, specific surface area, interface barrier, etc. In addition, it is influenced by external environmental factors during the photocatalytic process, such as the light source, reaction temperature, pH value, stirring speed and so on [30,31].



**Figure 2.** Diagram of natural photosynthesis and artificial photochemical reaction [29].

### 3.1. Fundamentals of photocatalytic HER

The hydrogen evolution reaction of semiconductor photocatalysts can be roughly simplified as the following processes [29]:

- 1) Absorption of incident light and photo-generated charge separation: When the photon energy of the incident light is greater than or equal to the band gap of a semiconductor catalyst, the semiconductor is photoexcited to produce electrons (photogenerated electron carriers) in the valence band, which transition to the conduction band of the semiconductor, thus leaving positively charged holes (photogenerated hole carriers) in the valence band.
- 2) Photogenerated electrons and holes migrate to active sites on the surface of the semiconductor: The process of electron and hole separation and migration is also related to the structure, crystallinity and grain size of the photocatalyst. The higher the crystallinity of the crystal, the fewer the defects. Defects can trap photogenerated electrons or holes to inhibit recombination for improved photocatalytic activity, and excess defects will become the recombination center instead, resulting in the reduction of photocatalytic activity. In addition, the reduction of grain size can shorten the distance of photogenerated carriers' migration to the surface of the photocatalyst, reducing the recombination rate of photogenerated carriers in the process of migration and improving photocatalytic efficiency.
- 3) Redox reaction on the photocatalyst's surface: Photogenerated holes with oxidizing ability oxidize H<sub>2</sub>O adsorbed on the semiconductor's surface to O<sub>2</sub> and H<sup>+</sup>. Photogenerated electrons with reducing ability react with H<sup>+</sup> to produce hydrogen. The chemical reaction is affected by surface active sites and the surface area. A large specific surface area can provide more active sites for photogenerated carriers to participate in the redox reaction.

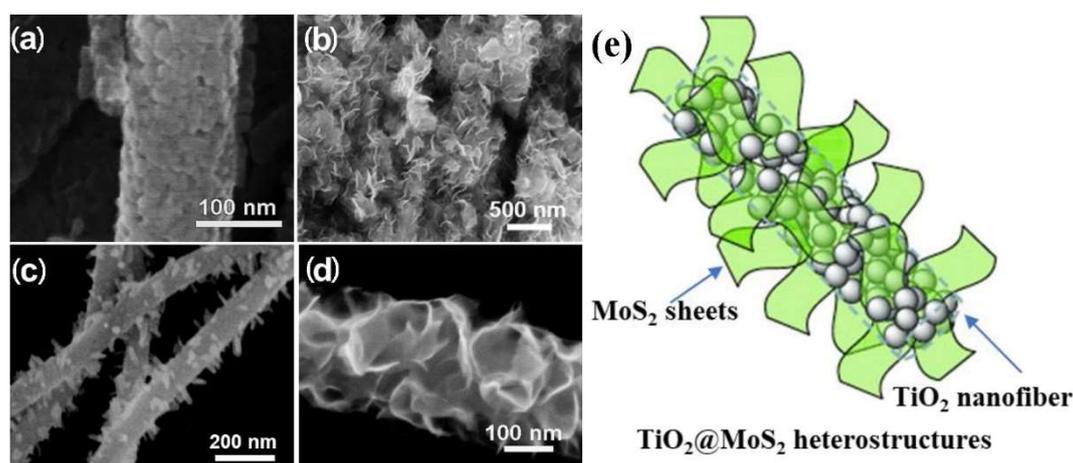
Semiconductor materials for photocatalytic hydrogen production also need to meet the requirements that the oxidation potential of the top of the valence band is higher than that of O<sub>2</sub>/H<sub>2</sub>O (1.23 eV), that the reduction potential of the bottom of the conduction band is lower than that of H<sup>+</sup>/H<sub>2</sub> (0 V vs. NHE), and that the band gap

width is greater than 1.23 eV. According to Equation (1), the wavelength of a light source directly used for photocatalytic hydrogen production should be less than about 1000 nm.

$$\text{Band gap (eV)} = \frac{1240}{\lambda} \text{ (nm)} \quad (1)$$

### 3.2. Recent progress of MoS<sub>2</sub> for photocatalytic HER

MoS<sub>2</sub> nanomaterials possess outstanding optical and electronic properties and have attracted huge attention. In photocatalysis, MoS<sub>2</sub> has been considered as a promising co-catalyst for HER [32,33]. Generally, the band gaps of MoS<sub>2</sub> materials are different, such as 1.2 eV for bulk MoS<sub>2</sub> and 1.9 eV for single-layer MoS<sub>2</sub> due to quantum confinement. Thus, the size and number of layers of MoS<sub>2</sub> could affect its band gap and consequently adjust its photocatalytic activity. In addition, MoS<sub>2</sub> has some disadvantages, including low stability, low conductivity and the fast recombination rate of photogenerated carriers during photocatalytic HER. To overcome these problems, researchers have tried a variety of approaches [34–36]. For instance, when MoS<sub>2</sub> as a co-catalyst is supported on CdS, the formation of p/n junctions and a large number of active sites of monolayer MoS<sub>2</sub> nanosheets can enhance photocatalytic efficiency [34,35]. Liu et al. [37] reported that active edge sites of MoS<sub>2</sub> can be more exposed via the construction of a vertical orientation of MoS<sub>2</sub>. **Figure 3(a,b)** show the structures of TiO<sub>2</sub> nanofibers and MoS<sub>2</sub> nanosheets. For the construction of a TiO<sub>2</sub>@MoS<sub>2</sub> heterostructure, MoS<sub>2</sub> nanosheets grow on TiO<sub>2</sub> nanofibers (**Figure 3(c,d)**). **Figure 3(e)** exhibits the schematic diagram of the TiO<sub>2</sub>@MoS<sub>2</sub> heterostructure model. The vertically grown MoS<sub>2</sub> on TiO<sub>2</sub> nanofibers can expose a large number of active edge sites [37]. In the following subsections, details of improved strategies for MoS<sub>2</sub> for photocatalytic HER are summarized.

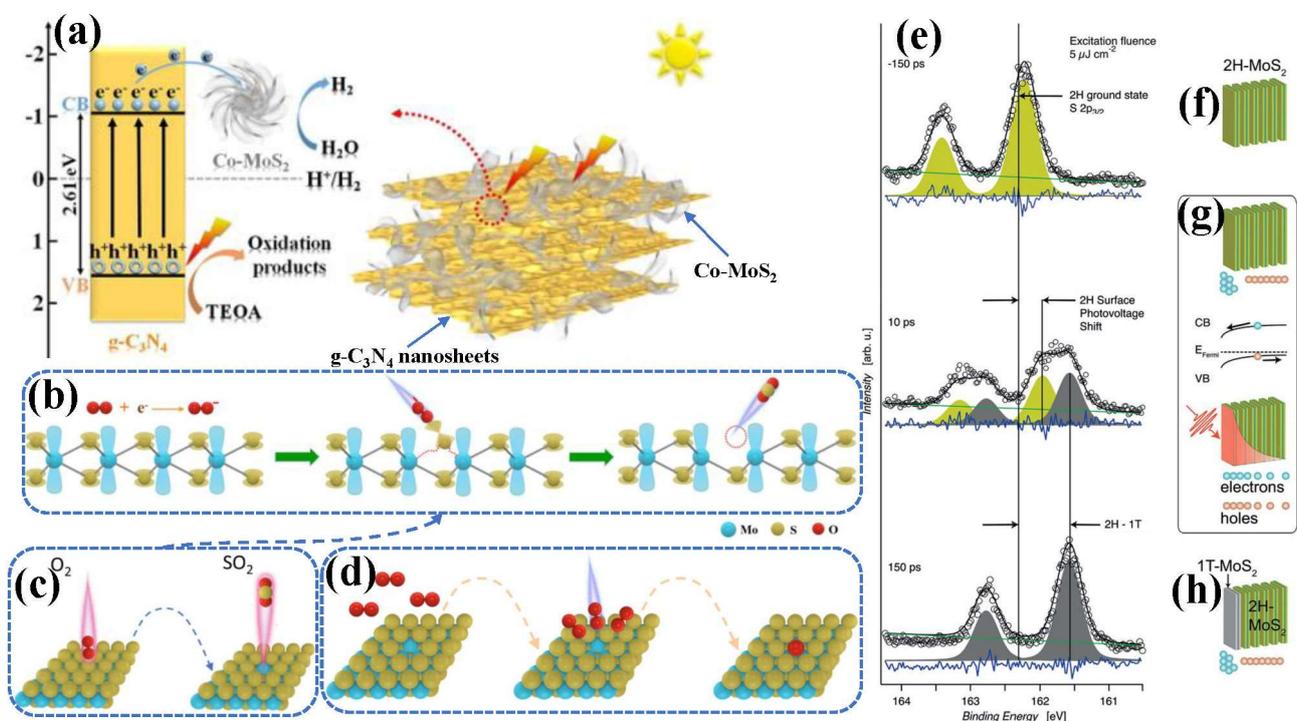


**Figure 3.** SEM images of (a) TiO<sub>2</sub> nanofibers, (b) pure MoS<sub>2</sub> nanosheets, (c) TiO<sub>2</sub>@MoS<sub>2</sub> heterostructure after 12 h and (d) TiO<sub>2</sub>@MoS<sub>2</sub> heterostructure after 24 h. (e) Schematic diagram of TiO<sub>2</sub>@MoS<sub>2</sub> heterostructure model [37].

#### 3.2.1. Doping

The progress of metal doping, non-metal doping and vacancy doping of MoS<sub>2</sub> was reviewed, and the effects of different types of doping on photocatalytic HER are summarized. It was found that doping can enlarge the light absorption range of a photocatalyst, increase its active sites, narrow its band gap, adjust its photogenerated

surface electron density, and reduce its charge transfer resistance [19,38–43]. Xue’s team [38] prepared a co-catalyst of Co-doped  $\text{MoS}_x$  grown on  $\text{TiO}_2$  nanoparticles using the photo-induction method and found that the formed highly active sites of “CoMoS” significantly improved HER activity. Co- $\text{MoS}_2/\text{g-C}_3\text{N}_4$  heterojunctions prepared by Wu et al. [19] improved the photocatalytic HER in a triethanolamine (TEOA) alkaline environment, where HER efficiency reached  $3193 \mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$ . Co doping was found to change the local electronic structure and exposed more active sites. As shown in **Figure 4(a)**, the photoexcited electrons produced by  $\text{g-C}_3\text{N}_4$  can move to the surface of Co- $\text{MoS}_2$ , and the co-catalyst Co- $\text{MoS}_2$  can efficiently capture the photoinduced electrons and simultaneously provide active sites to activate hydrogen by reducing  $\text{H}_2\text{O}$  to  $\text{H}_2$ . The density functional theory (DFT) calculation revealed that Co doping not only distorts  $\text{MoS}_2$  crystals but also reduces the H binding free energy of HER.



**Figure 4.** (a) Schematic illustration of photocatalytic mechanism of Co- $\text{MoS}_2/\text{g-C}_3\text{N}_4$  hybrids under simulated solar light irradiation [19]. (b) Schematic diagram of S vacancy formation triggered by external  $\text{O}_2$  and electrons. (c) Schematic diagram of oxidation reaction during formation of S vacancy. (d) Schematic diagram of formation of  $\text{MoS}_{2-x}\text{O}_x$  by oxygen occupying S vacancy in photocatalytic reaction [43]. (e) XPS spectra with laser excitation. (f) 2H- $\text{MoS}_2$  semiconductor. (g) Schematic diagram of creation of electron-hole pairs with exponential excitation profile from optical penetration depth. (h) Metallic 1T- $\text{MoS}_2$  phase on surface layer of 2H- $\text{MoS}_2$  [40].

In a study, the HER activity of Ni-doped flower-like  $\text{MoS}_2$  was found to reach  $404.3 \mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$  [39]. Compared with undoped  $\text{MoS}_2$ , the doped sample had better charge separation and a stronger photoresponse at 600–700 nm. After six cycles of photocatalytic HER experiment, the hydrogen production of the photocatalyst maintained 95% of the initial hydrogen production. Sorgenfrei et al. [40] found that the energy band of the p-type doping of 2H- $\text{MoS}_2$  bent downward. The transient aggregation of surface electrons caused the transformation of the reversible 2H phase (semiconductor) into the 1T phase (metal) of the surface layer, which was completed

in only a few tens of picoseconds. As shown in **Figure 4(e)**, laser excitation from X-ray photoelectron spectroscopy (XPS) caused surface photovoltage shifts in p-doped 2H-MoS<sub>2</sub> (marked with yellow-green), as well as chemical shifts in the S2p<sub>3/2</sub> and S2p<sub>1/2</sub> core level lines of 1T-MoS<sub>2</sub> (marked with gray). After 150 ps of laser stimulation, the peak produced by the 2H phase completely disappeared, indicating that the surface layer was now completely in the metallic 1T phase. The semiconductor 2H-MoS<sub>2</sub> is shown in **Figure 4(f)**, while the metallic 1T-MoS<sub>2</sub> phase on 2H-MoS<sub>2</sub>'s surface layer is shown in **Figure 4(h)**. **Figure 4(g)** shows the electron-hole pairs and the exponential excitation curves generated by the light penetration depth, as well as the surface region separation of p-doped 2H-MoS<sub>2</sub>, where electrons in the conduction band (denoted as CB) gather on the surface, while holes in the valence band (denoted as VB) migrate inward. The surface electron accumulation eventually produces and stabilizes the metallic 1T phase.

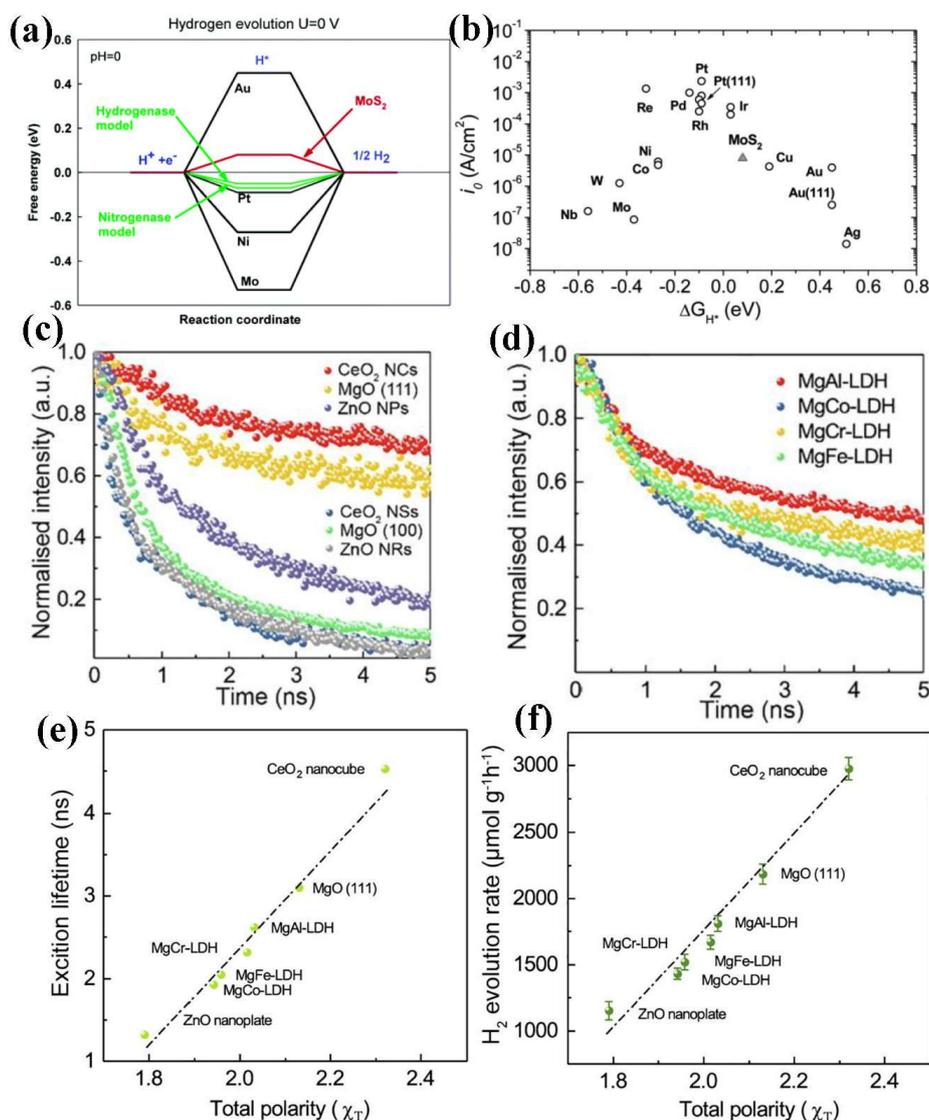
In addition, the entire basal plane of the 1T phase of MoS<sub>2</sub> has photocatalytic activity. Compared with the 2H phase, where only edge sites have photocatalytic activity, P-doped MoS<sub>2</sub> can improve HER efficiency under light irradiation. Using the hydrothermal method, Xin's team [41] prepared P-doped MoS<sub>2</sub>, which showed stronger light absorption in the visible range, faster carrier transfer speed and lower resistance. The photocatalytic hydrogen production rate of P-doped MoS<sub>2</sub>/CdS binary heterojunctions prepared by Xu et al. [42] in a mixed solution of Na<sub>2</sub>S and Na<sub>2</sub>SO<sub>3</sub> was 8.86 mmol·h<sup>-1</sup>·g<sup>-1</sup>. Studies have shown that P-doped heterojunctions have a more favorable band structure for photocatalytic HER.

Wang et al. [43] found that in the actual photocatalytic process, photogenerated electrons can induce slowly incoming pure oxygen to form active O<sub>2</sub><sup>-</sup>. When O<sub>2</sub><sup>-</sup> combines with S, the electron cloud is rearranged to break the Mo-S bond, forming SO<sub>2</sub> gas. Then, the SO<sub>2</sub> gas escapes from the surface of MoS<sub>2</sub>, thus producing the S vacancy (**Figure 4(b,c)**). The continuous incoming pure oxygen in the environment fills the S vacancy (**Figure 4(d)**). In this way, MoS<sub>2</sub> is dynamically converted into MoS<sub>2-x</sub>O<sub>x</sub>, and oxygen elements can be well dispersed in MoS<sub>2</sub>. The theoretical calculation showed that an appropriate amount of oxygen can make a sample undergo intrinsic deformation and optimize the surface's electronic state. In addition, the synergistic effect of strain engineering and O doping increases dynamic active sites on MoS<sub>2</sub> and decreases photogenerated charge transfer resistance.

### 3.2.2. Surface modification and morphology control

Generally, catalysis occurs at the surface of catalysts. Thus, the surface feature of catalysts plays an important role in efficient catalysis. The edge sites of MoS<sub>2</sub> have a low hydrogen adsorption free energy ( $\Delta G_H^*$ ) of 0.08 eV [44,45], which is comparable to those of many precious metal catalysts (**Figure 5(a,b)**), facilitating the desorption of hydrogen molecules on its surface. Li et al. [46] reported that strong local polarization occurred the surface of MoS<sub>2</sub> nanocrystals to promote charge separation by the introduction of polar-faceted metal oxides and layered double hydroxides (LDHs). The obtained catalyst (Ru:MoS<sub>2</sub>/CeO<sub>2</sub> nanocrystals) showed a high HER activity of 2977  $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$  and quantum efficiency reaching 66.8% at 473 nm of visible light irradiation. The exciton lifetimes of the Ru-MoS<sub>2</sub> catalyst were much prolonged by the assembly with CeO<sub>2</sub> nanocrystals and MgO (111) and ZnO

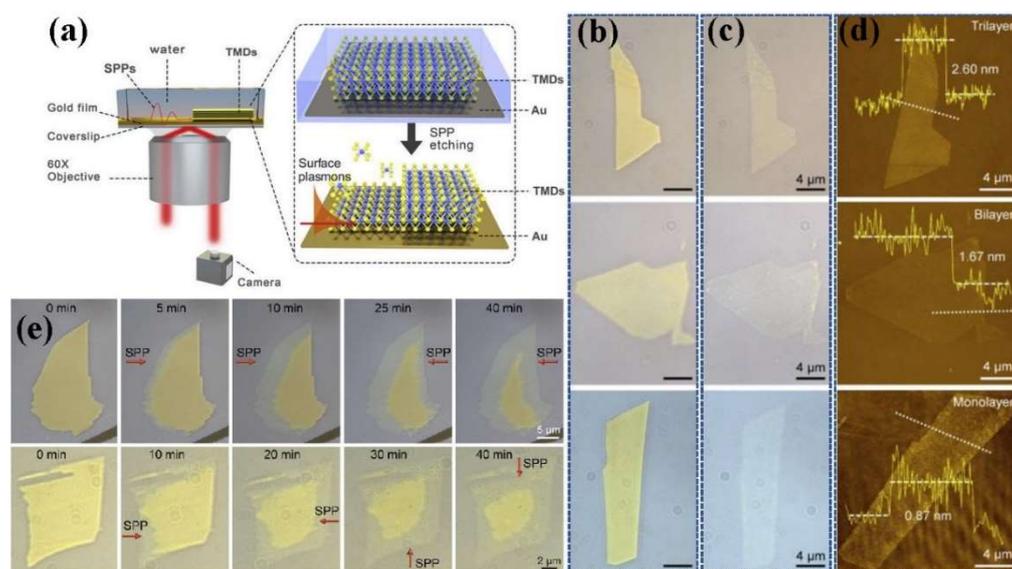
nanoparticles (**Figure 5(c)**). When the Ru-MoS<sub>2</sub> catalyst was mixed with LDHs, the exciton lifetime increased (**Figure 5(d)**). The polarity of metal oxides was linearly related to exciton lifetime and photocatalytic activity. The exciton lifetime and photocatalytic HER ability increased as the polarity of the metal elements increased (**Figure 5(e,f)**).



**Figure 5.** (a) Calculated free energy diagram for HER [45]. (b) Volcano plot of exchange current density as function of DFT-calculated Gibbs free energy of adsorbed atomic hydrogen for nanoparticulate MoS<sub>2</sub> and pure metals [44]. (c) Time-resolved photoluminescence spectra of Ru:MoS<sub>2</sub> mixed with polar-faceted oxide support. (d) Time-resolved photoluminescence spectra of Ru:MoS<sub>2</sub> mixed with non-polar-faceted oxide support. (e) Relationship between total polarity and exciton lifetimes. (f) Relationship between total polarity and photocatalytic HER activity [46].

In addition, a strategy to increase overall charge mobility has been proposed by using the exfoliation/etching method to expose more highly active edge sites [17]. Some studies have suggested that planar surface plasmon polaritons (SPPs) have a positive effect on the etching and thinning of MoS<sub>2</sub>. MoS<sub>2</sub> can be etched into the required layer number and transverse dimension by controlling light power and incident direction [47]. This can be attributed to the reactive oxygen species produced

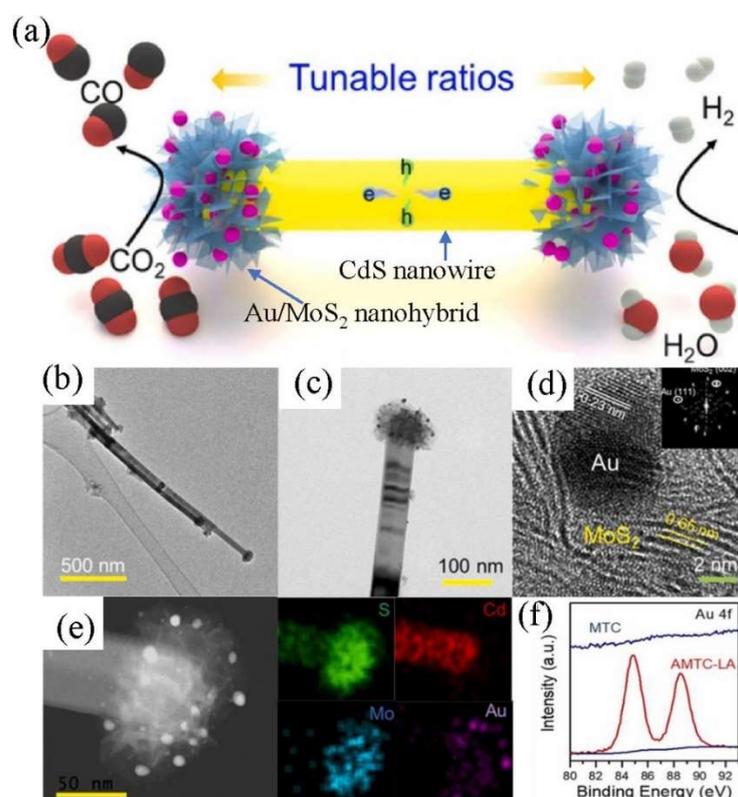
by plasma hot electrons weakening the interlayer interaction of MoS<sub>2</sub> and further promoting etching. **Figure 6(a)** shows the schematic illustration of inverted optical microscopy for triggering and monitoring the layer-controlled etching of MoS<sub>2</sub> nanoflakes. Excited SPPs are produced from the coupling of surface electromagnetic polaritons and oscillating free electrons propagated along the Au/water interface, generating an evanescent field with a penetration depth of approximately 200 nm. Atomic force microscopy (AFM) images of MoS<sub>2</sub> nanoflakes after etching (**Figure 6(b–d)**) indicate the decreased thicknesses of MoS<sub>2</sub>. As shown in **Figure 6(e)**, time-varying optical images show that the direction of etching of MoS<sub>2</sub> nanosheets can be controlled by manipulating the direction of the propagation of the SPPs. Further studies have shown that the generated holes by exciton-plasma coupling in the valence band of MoS<sub>2</sub> lead to interlayer repulsion, while the generated electrons by plasma decay lead to interlayer dissolution. Liu et al. [48] proposed a local etching strategy, which realized the adjustment of the thickness and transverse size of MoS<sub>2</sub> (WS<sub>2</sub>) and then adjusted the proportion of the photocatalyst's edges. Based on the method, the photocatalytic HER performance was 31 times and 47 times higher than those of unstripped MoS<sub>2</sub>/CdS and WS<sub>2</sub>/CdS, respectively. However, the preparation process of the local stripping method is relatively complicated and thus is not easy to be used for large-scale preparation.



**Figure 6.** (a) Surface-plasmon-polariton-driven etching (SPPE) strategy. (b) Optical images of pristine exfoliated MoS<sub>2</sub> nanoflakes. (c) Optical images of MoS<sub>2</sub> nanoflakes after etching. (d) AFM images and corresponding height profiles of MoS<sub>2</sub> nanoflakes after etching. (e) Optical images of different etching directions [47].

It is well known that a photocatalyst with unique morphology can efficiently expose active sites and improve the charge transfer efficiency of the photocatalyst. Li's team [49] weakened the interlayer van der Waals forces of 1T-MoS<sub>2</sub> by controlling the number of -NH and -NH<sub>2</sub> intercalations and modulated the crystallinity and layer thickness of MoS<sub>2</sub>. The HER efficiency of the obtained materials (P-1T-MoS<sub>2</sub>/CdS) in lactic acid was 235.0 mmol·h<sup>-1</sup>·g<sup>-1</sup> ( $\lambda > 420$  nm), which was 2.25 times that of naked CdS under the same experimental condition. Nanometer flower-like MoS<sub>2</sub> loaded with Au particles was loaded on both ends of nanorod-like CdS to obtain

dumbbell symmetrical-tip heterojunctions, as shown in **Figure 7(a)**. This special structure allowed electrons to migrate directionally to the tip and accumulate, maintaining the long life of photogenerated carriers. The TEM images of typical Au/MoS<sub>2</sub>-tipped CdS nanowires synthesized in an LA electrolyte (AMTC-LA) are shown in **Figure 7(b,d)**. The enlarged TEM image of the AMTC-LA in **Figure 7(c)** shows that Au nanoparticles with a diameter of ~10 nm were precisely deposited on the surface of MoS<sub>2</sub> tips, where the lattice spacing of Au was 0.23 nm (**Figure 7(d)**). Element mapping analyses demonstrated that the Au nanoparticles were concentrated on the tip of MoS<sub>2</sub>, while Cd was present in only the stem (**Figure 7(e)**). High-resolution XPS data indicated two peaks at 84.8 and 88.5 eV appearing in the Au spectrum of the AMTC-LA, corresponding to metallic Au (**Figure 7(f)**). In addition, the energy barrier at the MoS<sub>2</sub>/CdS interface was reduced by using an appropriate size of Au particles as a co-catalyst for photocatalytic HER electron transfer [50].

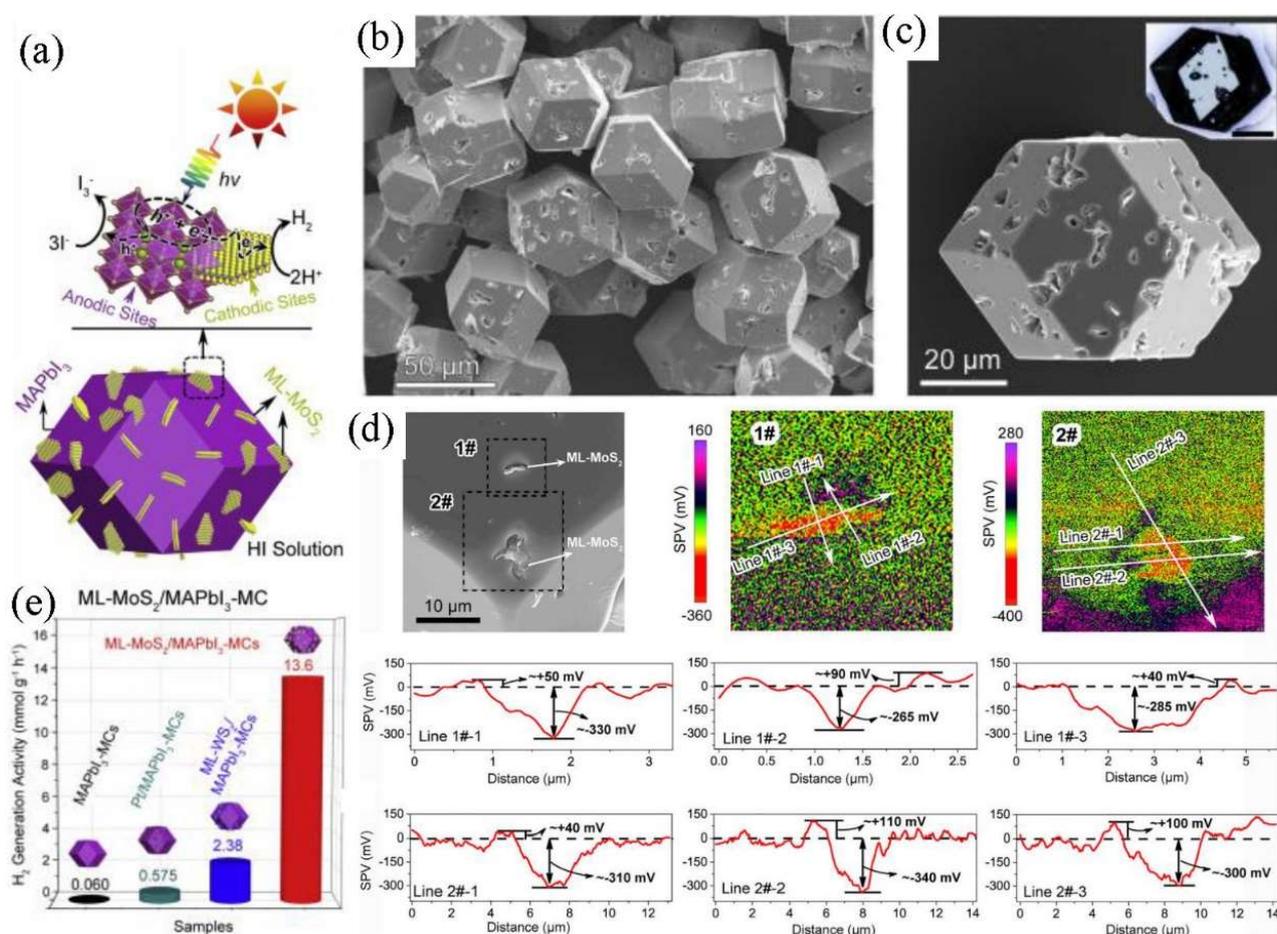


**Figure 7.** (a) Diagram of synthesis of dumbbell-shaped Au/MoS<sub>2</sub>/CdS heterojunctions. (b) TEM image of Au/MoS<sub>2</sub>-tipped CdS nanowires (AMTC-LA). (c) TEM image of AMTC-LA. (d) HR-TEM image of AMTC-LA (inset: fast Fourier transform pattern). (e) Element mapping of AMTC-LA. (f) XPS spectra of MTC and AMTC-LA [50].

### 3.2.3. Heterojunction construction

Previous studies have shown that the edge sites of monolayer MoS<sub>2</sub> are more stable than those of few-layer MoS<sub>2</sub>, which is due to the increase of exciton binding energy and the decrease of carrier lifetimes caused by the transition from an indirect to a direct semiconductor [51]. From the construction of heterojunctions using MoS<sub>2</sub>, the light absorption capacity in the visible range can be further increased and the band gap position of the composite can be adjusted to be more suitable for photocatalytic HER. For instance, Peng's team [52] showed HER enhancement of up to 40-fold

(compared with bare MoS<sub>2</sub>) when the localized surface plasmon resonance (LSPR) wavelength of Au nanocages matched the absorption edge of MoS<sub>2</sub>. With the aid of near-field enhancement, the energy of the surface plasma was transferred from Au nanocages to MoS<sub>2</sub> nanosheets, which promoted the electron-hole separation of MoS<sub>2</sub>. By inserting a single layer of MoS<sub>2</sub> (ML-MoS<sub>2</sub>) into a perovskite microcrystal nucleus by rapid recrystallization, Zhao's team [53] prepared ML-MoS<sub>2</sub>/MAPbI<sub>3</sub> type II heterojunctions, in which each MAPbI<sub>3</sub> microcrystal (MC) anchored with multiple small-sized ML-MoS<sub>2</sub> nanosheets (**Figure 8(a)**). The obtained ML-MoS<sub>2</sub>/MAPbI<sub>3</sub> MCs were uniformly sized rhombic dodecahedron-shaped MCs with an average size of 46 nm (**Figure 8(b,c)**). The surface photovoltage (SPV) diagram proved that the heterojunctions formed a strong internal electric field, which effectively inhibited charge recombination (**Figure 8(d)**). The ML-MoS<sub>2</sub>/MAPbI<sub>3</sub> MCs showed a high hydrogen generation activity of 13.6 mmol·g<sub>Cat</sub><sup>-1</sup>·h<sup>-1</sup> (**Figure 8(e)**). On the other hand, Guan's team [54] assembled MoS<sub>2</sub> nanoflowers and MAPbI<sub>3</sub> heterojunctions by colloidal precipitation. The results showed that the HER activity reached 29389 μmol·h<sup>-1</sup>·g<sup>-1</sup> and the photocatalytic efficiency was 7.35%, outperforming those of MAPbI<sub>3</sub> perovskite.

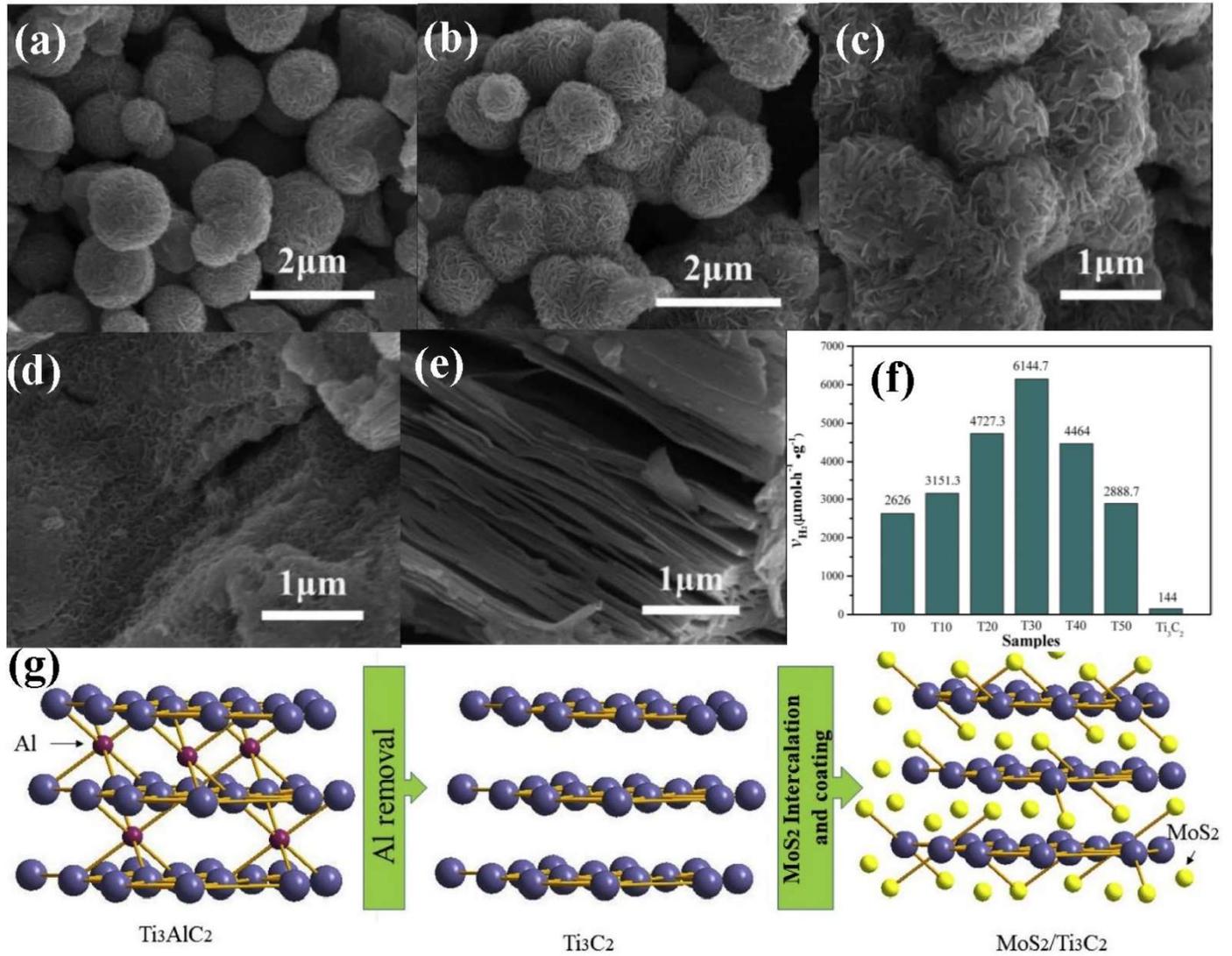


**Figure 8.** (a) Schematic illustration of structural configuration and redox processes of ML-MoS<sub>2</sub>/MAPbI<sub>3</sub> MCs. (b) SEM image of ML-MoS<sub>2</sub>/MAPbI<sub>3</sub> MCs. (c) SEM image of single ML-MoS<sub>2</sub>/MAPbI<sub>3</sub> MC (inset: optical microscopy image with scale bar of 20 μm). (d) SPV distribution of ML-MoS<sub>2</sub>/MAPbI<sub>3</sub> MCs. (e) Photocatalytic HER activity [53].

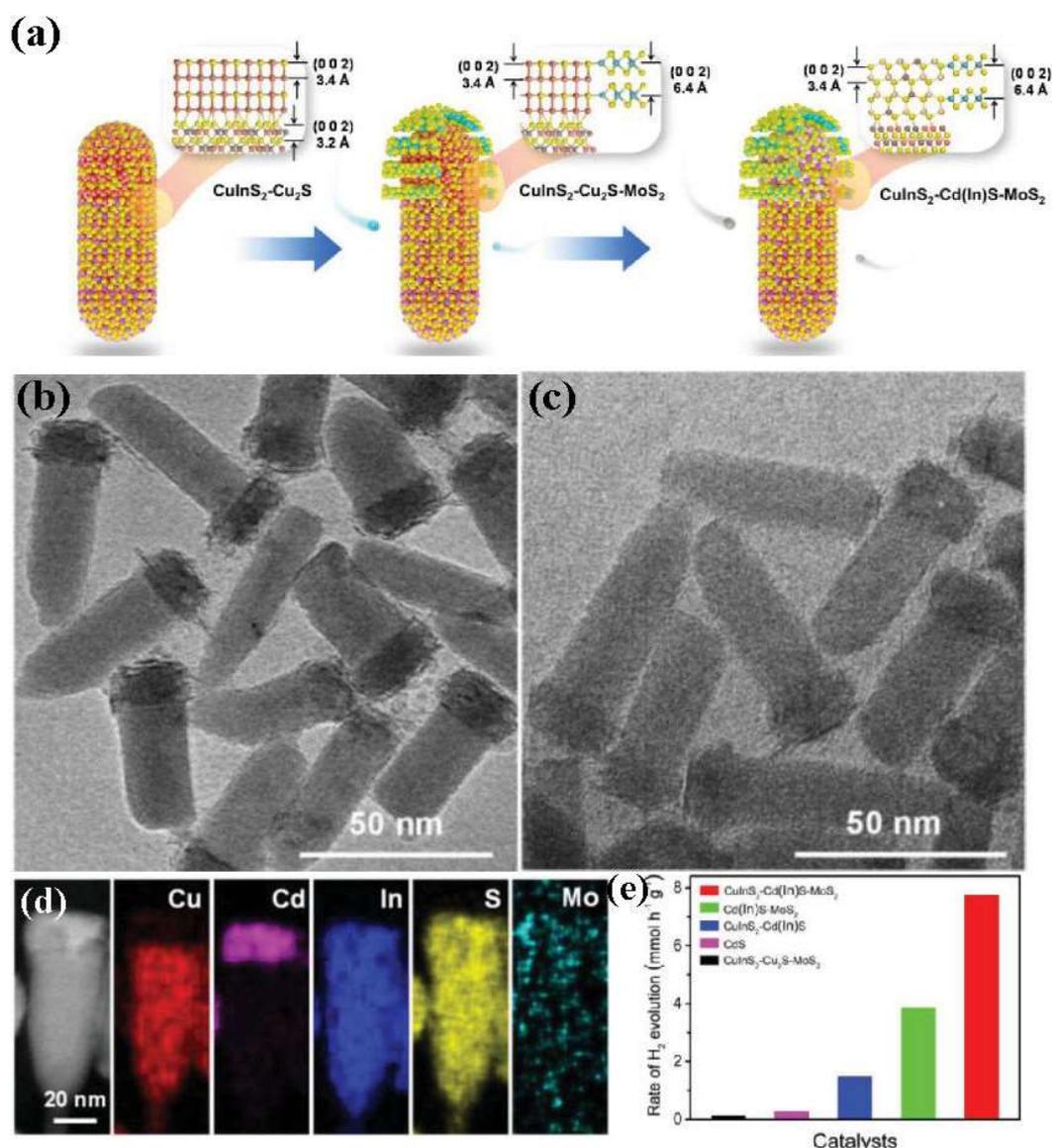
The photocatalytic HER efficiency of  $\text{Bi}_2\text{O}_3/\text{MoS}_2$  heterojunction was shown to be 10 times higher than those of pure  $\text{Bi}_2\text{O}_3$  and  $\text{MoS}_2$  [55]. This was due to the expanded light absorption range. In addition, the  $\text{Bi}_2\text{O}_3/\text{MoS}_2$  heterostructure formed p-n junctions, which had high-speed carrier transfer and can reduce the recombination of electrons and holes. Song et al. [56] prepared  $\text{MoS}_2/\text{ReS}_2@\text{CdS}$  heterojunctions with a hydrogen production rate of  $171900 \mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$ . The photo-response range of ternary heterojunctions significantly improved, thanks to the dual-Z-scheme electron transfer mechanism of the ternary heterojunctions.

Furthermore, by intercalating  $\text{Ti}_3\text{C}_2$  into  $\text{MoS}_2$  layers, the two thin-sheet photocatalysts can be closely connected (**Figure 9(g)**) [57]. The scanning electron microscopy (SEM) images of the samples are presented in **Figure 9(a–e)**. The size of the initial  $\text{MoS}_2$  spheres was approximately  $1 \mu\text{m}$  (**Figure 9(a)**).  $\text{Ti}_3\text{C}_2$  (**Figure 9(e)**) exhibited a clear multilayer structure, similar to that of exfoliated layered graphite. With the increase in  $\text{Ti}_3\text{C}_2$  loading,  $\text{MoS}_2$  completely covered the surface of the  $\text{Ti}_3\text{C}_2$  layer (**Figure 9(b–d)**). As shown in **Figure 9(f)**, the photocatalytic HER activities of pure  $\text{MoS}_2$  and  $\text{Ti}_3\text{C}_2$  were poor. However, the combination of  $\text{MoS}_2$  and  $\text{Ti}_3\text{C}_2$  greatly enhanced catalytic activity (the loading amounts of  $\text{Ti}_3\text{C}_2$  were 0 wt%, 10 wt%, 30 wt% and 50 wt% of the total mass, where the obtained samples were marked as T0, T10, T30 and T50, respectively). Especially, the T30 sample possessed a high photocatalytic HER rate of  $6144.7 \text{ mmol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ , which was 2.3 times higher than that of pure  $\text{MoS}_2$ . This enhancement can be attributed to the presence of  $\text{Ti}_3\text{C}_2$  promoting an efficient transfer of photogenerated electrons, indicating that the direction of charge transfer can be effectively controlled by a reasonable heterojunction design. In addition, CdS quantum dots were attached to  $\text{MoS}_2$  nanosheets using a link assembly assisted by L-cysteine or mercaptoalkanoic acids. Ultrafast transient absorption measurements showed that the transfer of electrons from the quantum dots to the semiconductor was accomplished in 0.5–2 ps. The surfactant's functionalized quantum dot hole trap was located at the lower energy and closest to the edge of the valence band. By comparing the length of the surfactant's bridging distance, it was found that the reduction of the bridging distance accelerated the transfer speed of electrons between the quantum dots and the nanosheets [58]. Generally,  $\text{CuInS}_2$  and  $\text{Cu(In)S}$  can effectively absorb light ranging from visible light to the near-infrared solar spectrum [59]. Vertical-epitaxial ultra-thin  $\text{MoS}_2$  grown on the tip of a  $\text{CuInS}_2/\text{CuS}$  rod-like photocatalyst provided a large number of edge S sites (**Figure 10(a)**). TEM images of  $\text{CuInS}_2\text{-CdS-MoS}_2$  HNs and  $\text{CuInS}_2\text{-Cd(In)S-MoS}_2$  HNs (**Figure 10(b,c)**) revealed a rod-like structure. Furthermore, element mapping images (**Figure 10(d)**) displayed that S and In were distributed throughout the entire structure with Cd<sup>-</sup>-rich and Mo<sup>-</sup>-rich tips and Cu<sup>-</sup>-rich stems, indicating that  $\text{In}^{3+}$  partially migrated to the tip along with  $\text{Cd}^{2+}$  ion incorporation. Cross-arranged  $\text{CuInS}_2/\text{Cu(In)S}/\text{MoS}_2$  Type II heterojunctions provided a good channel for electron transfer and also improved the stability of the photocatalytic materials. After 12 h of three cycles of photocatalysis, the HER activity, morphology, crystal structure, and chemical state of the sample remained good. In addition,  $\text{CuInS}_2/\text{Cd(In)S}/\text{MoS}_2$  heterojunctions were prepared via cationic exchange from the tip Cu to Cd, and the photocatalytic HER reached  $8000 \mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$  (**Figure 10(e)**). Recently, researchers prepared quaternary heterojunctions by using mesoporous graphitic carbon nitride,

black phosphorus and molybdenum disulfide and incorporating Ni and Co co-catalysts (m-CN/BP/MoS<sub>2</sub>-Y (Y: Ni, Co)), which formed Type I heterojunctions between BP and m-CN and formed Type II heterojunctions between m-CN and MoS<sub>2</sub>, in addition to forming Type II heterojunctions between MoS<sub>2</sub> and BP [60]. The photogenerated electrons were transferred to Ni or Co to form H<sub>2</sub>. The photocatalytic HER activity of the quaternary heterojunctions was 10 times higher than that of the BP/m-CN binary heterojunctions and 5 times higher than that of the m-CN/BP/MoS<sub>2</sub> ternary heterojunctions.



**Figure 9.** SEM images of MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub> heterostructure synthesized at different Ti<sub>3</sub>C<sub>2</sub> loading amounts: (a) T0, (b) T10, (c) T30, (d) T50 and (e) Ti<sub>3</sub>C<sub>2</sub> MXene. (f) Photocatalytic H<sub>2</sub> production of Ti<sub>3</sub>C<sub>2</sub> MXene and MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub> heterostructures at different Ti<sub>3</sub>C<sub>2</sub> loading amounts. (g) Schematic illustration of synthesis process of MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub> heterostructure [57].



**Figure 10.** (a) Schematic illustration for selective epitaxial-hybrid of tripartite HNs. (b) TEM image of CuInS<sub>2</sub>-Cu<sub>2</sub>S-MoS<sub>2</sub> HNs. (c) TEM image of CuInS<sub>2</sub>-Cd(In)S-MoS<sub>2</sub> HNs. (d) STEM-EDX elemental mapping images of single CuInS<sub>2</sub>-Cd(In)S-MoS<sub>2</sub>. (e) H<sub>2</sub> evolution rates of catalysts under visible light illumination ( $\lambda > 420$  nm) [59].

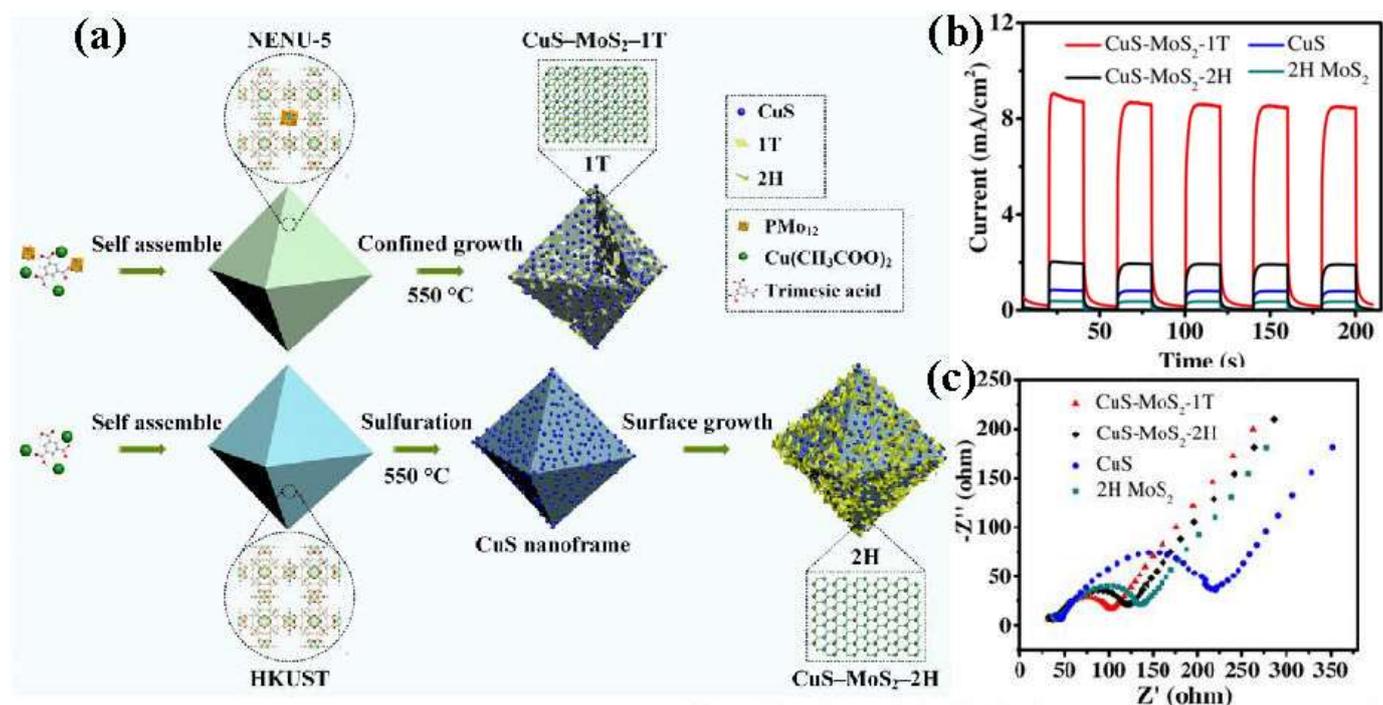
### 3.2.4. Phase transformation

1T-MoS<sub>2</sub> and 2H-MoS<sub>2</sub> have been widely researched as catalysts. Compared with the conventional 2H-MoS<sub>2</sub> semiconductor, it is believed that 1T-MoS<sub>2</sub> with its metallic phase has abundant active sites at both its edges and basal planes, which can be used as adsorption and reaction sites of reactant molecules to accelerate reaction kinetics [61]. Previous reports have shown that P doping can convert the 2H semiconductor phase into the 1T metal phase of MoS<sub>2</sub> [40,41]. Das et al. [62] used a 532 nm laser to induce MoS<sub>2</sub> from a 2H phase to a 1T phase. Li's team [15] prepared 1T/2H-MoS<sub>2</sub> heterojunctions with a hydrogen production rate of 22.4  $\mu\text{mol}\cdot\text{h}^{-1}$  by adjusting the molar ratio of Mo/S via the hydrothermal method. The various methods for modifying MoS<sub>2</sub> to enhance its photocatalytic HER are summarized in **Table 1**.

**Table 1.** HER properties of modified MoS<sub>2</sub> photocatalysts.

Category	Photocatalyst	Synthesis method	Incident light (nm)	Light source	Activity ( $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ )	Quantum yield (%)	Morphology	Ref.
Doping	Ni@MoS <sub>2</sub>	Hydrothermal	$\lambda = 420$	Xe lamp (300 W)	404	-	Microflowers	[39]
	P-MoS <sub>2</sub>	Hydrothermal	-	Xe lamp (300 W)	278.8	-	Interwoven nanosheets	[41]
	MoS <sub>2-x</sub> O <sub>x</sub>	Dynamic oxidation	$\lambda > 420$	Xe lamp (300 W)	1600	-	Nanosheets	[43]
Surface modification and morphology control	P-1T-MoS <sub>2</sub> /CdS	Hydrothermal	$\lambda > 420$	Xe lamp (300 W)	235,000	49% at 420 nm	Nanosheets/nanoflowers	[49]
	Au/MoS <sub>2</sub>	Deposition	$\lambda > 400$	Hg lamp (200 W)	11,900	-	Nanoparticles	[52]
	MoS <sub>2</sub> /MAPbI <sub>3</sub>	Colloidal precipitation	$\lambda > 420$	Xe lamp (280 W)	29,389	13.1% at 420 nm 22.1% at 500 nm	Rhombic dodecahedron-shaped microcrystals	[54]
Heterojunction construction	MoS <sub>2</sub> /Ti <sub>3</sub> C <sub>2</sub>	Hydrothermal	$\lambda > 420$	Xe lamp (300 W)	6144.7	-	Flower-like nanosheets	[57]
	CuInS <sub>2</sub> /Cd(In)S/MoS <sub>2</sub>	Hot injection	$\lambda > 420$	Xe lamp (300 W)	8000	3.8% at 420 nm	Nanorods	[59]
	CuS-MoS <sub>2</sub> -1T	Hydrothermal	$\lambda > 300$	Xe lamp (300 W)	9648.7	45.1% at 400 nm	Octahedrons	[63]
	O-1T/2H-MoS <sub>2</sub> /g-C <sub>3</sub> N <sub>4</sub>	Hydrothermal	$\lambda > 300$	Xe lamp (500 W)	1487	7% at 370 nm	Nanosheets	[64]

Currently, various 1T-MoS<sub>2</sub>-based heterojunctions have been developed for enhancing the catalytic performance of MoS<sub>2</sub>. Octahedral CuS/1T-MoS<sub>2</sub> heterojunctions were formed by the in-situ growth of mesopore-structured 1T-MoS<sub>2</sub> in octahedral Cu metal-organic frameworks. **Figure 11(a)** shows the schematic illustration of the synthesis process of CuS-MoS<sub>2</sub>-1T nanohybrid (via the confined template method) and CuS-MoS<sub>2</sub>-2H nanohybrid (without confinement). The photocurrent density-time (I-t) curves in **Figure 11(b)** exhibited that CuS-MoS<sub>2</sub>-1T generated the highest photocurrent because of the improved carrier transfer performance of 1T-MoS<sub>2</sub>. As shown in **Figure 8(c)**, CuS-MoS<sub>2</sub>-1T exhibited the smallest arc radius relative to those of CuS, 2H-MoS<sub>2</sub> and CuS-MoS<sub>2</sub>-2H, attributed to the high electronic conductivity of 1T-MoS<sub>2</sub> [63]. The coupling of O-doped 1T/2H-MoS<sub>2</sub> and g-C<sub>3</sub>N<sub>4</sub> increased the photocatalytic HER to 1487  $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$  because the metallic properties of the electronic structure of 1T-MoS<sub>2</sub> improved the electrical conductivity of the heterojunctions. The 1T-MoS<sub>2</sub> acted as an electron-trapping agent and promoted the separation of photogenerated charge carriers. In addition, the 1T-MoS<sub>2</sub> had a large number of HER active sites at both base and edge sites. In addition, the O doping of MoS<sub>2</sub> caused crystal distortion, thereby regulating the electronic structure [64].



**Figure 11.** (a) Schematic illustration of synthesis process of CuS-MoS<sub>2</sub>-1T and CuS-MoS<sub>2</sub>-2H nanohybrids. (b) EIS Nyquist plots. (c) Photocurrent responses [63].

MoS<sub>2</sub> materials have great potential and research value in the field of photocatalytic HER, far beyond the capabilities demonstrated today. Although, at present, MoS<sub>2</sub> materials during photocatalytic HER suffer from some problems and challenges, such as competing spectral absorption range and redox potential, low photocatalytic efficiency, insufficient stability and fast photogenerated electron-hole recombination. However, with improvements in exploration methods and strategies and a better understanding of photocatalytic HER, MoS<sub>2</sub> materials have a broad future in the field of photocatalytic HER. In the future, high-throughput DFT predictions and the addition of large models of artificial intelligence will give more modifications and new properties of MoS<sub>2</sub> materials [65]. This will save researchers a lot of time and effort for experimental studies.

Improvements in preparation methods and a deep understanding of the photocatalytic HER mechanism of MoS<sub>2</sub> are very important. The purity of MoS<sub>2</sub> prepared via the wet chemical method is not as high as those prepared via other methods. MoS<sub>2</sub> synthesis of heterojunction materials can improve the light absorption range and accelerate electron-hole transfer [39]. Compared with flat MoS<sub>2</sub>, wrinkled MoS<sub>2</sub> has faster electron relaxation [66]. It is generally believed that near-infrared light cannot directly excite MoS<sub>2</sub> catalysts to produce electrons and holes with sufficient energy to drive photocatalytic HER, but the infrared thermal effect can increase reaction temperature, mass transfer and the formation and breaking of chemical bonds in a catalytic reaction, thus contributing to a higher HER reaction rate [67]. In addition, the relationship between MoS<sub>2</sub>'s basal planes and edge sites, the change in its phase during photocatalysis and the transfer path of electrons are still unclear. Moreover, the formation mechanism and interface force of heterojunctions constructed by MoS<sub>2</sub> have not been reported. The large-scale and commercial application of photocatalytic MoS<sub>2</sub>

materials is also one of the future development directions. For example, the total solar-hydrogen conversion efficiency of photocatalyzed HER via a hydrogen farm strategy was found to exceed 1.85% [68].

## 4. Recent progress of electrocatalytic HER

### 4.1. Mechanism of electrocatalytic HER

Electrochemical HER involves a two-electron transfer pathway, which can be expressed by following two steps: (1) the formation of adsorbed H intermediates (H\*), called the Volmer step, and (2) H<sub>2</sub> generation from the combination of H\*, called the Heyrovsky or Tafel step. In general, there are significant differences in the Volmer reaction in different pH environments (**Table 2**). In alkaline and neutral electrolytes, the Volmer reaction process needs to undergo water dissociation with H-OH breakthrough to form H\* intermediates. The slow kinetics of water dissociation is a bottleneck for water electrolysis in an alkaline or neutral medium. In acidic electrolytes, the Volmer reaction can directly capture H<sup>+</sup> from electrolytes to form H\* intermediates. Subsequently, H<sub>2</sub> may be produced through the Heyrovsky reaction or Tafel reaction, which is determined by the low or high coverage of H\* intermediates, respectively. The true catalytic mechanism is mainly related to the surface element composition, surface roughness and electronic structure of the electrocatalyst. For the HER process, the Tafel slope is an efficient method to estimate the catalytic mechanism by the following equation (Equation (2)):

$$\eta = a + b \log |j| \quad (2)$$

where  $\eta$  is the overpotential,  $j$  is the current density and  $b$  is the Tafel slope. The theoretical Tafel slope values for Volmer, Heyrovsky and Tafel reactions are 117, 39 and 29 mV·dec<sup>-1</sup>, respectively. It is worth noting, however, that the Tafel slopes of samples are different at various potential ranges, which implies that the HER mechanism changes at different potentials. Thus, the region for Tafel slope analysis is crucial for determining the HER mechanism and comparison with other reported materials.

**Table 2.** HER reaction mechanisms in alkaline, neutral and acidic media.

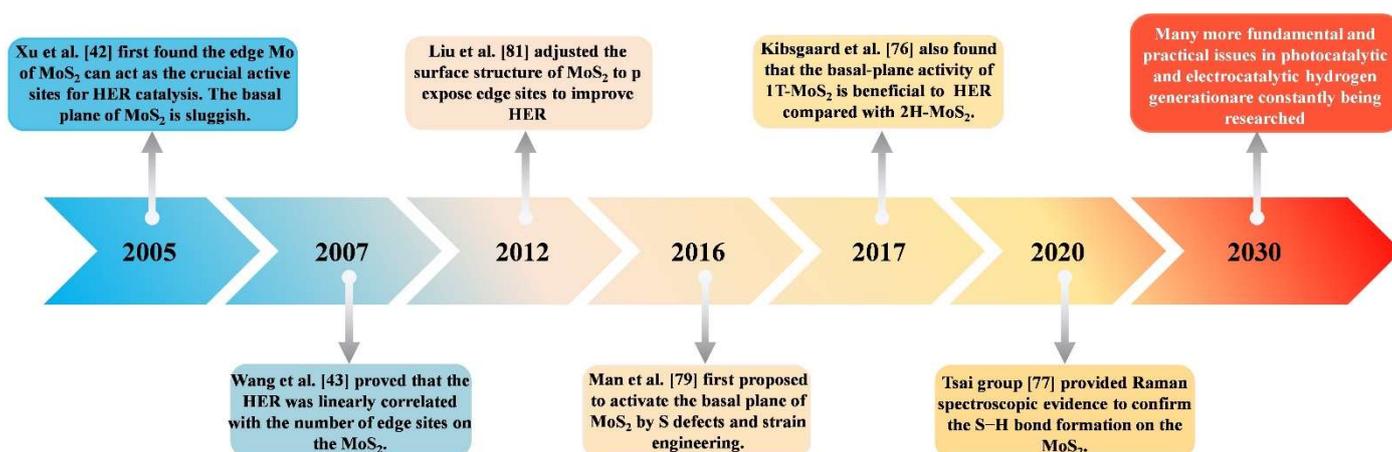
Alkiline and neutral meidia	Process	Acid media
$\text{H}_2\text{O} + * + \text{e}^- \rightarrow \text{H}^* + \text{OH}^-$	Volmer	$\text{H}^+ + * + \text{e}^- \rightarrow \text{H}^* + \text{H}_2\text{O}$
$\text{H}^* + \text{H}_2\text{O} + \text{e}^- \rightarrow * + \text{OH}^- + \text{H}_2$	Heyrovsky	$\text{H}^+ + \text{H}^* + \text{e}^- \rightarrow \text{H}_2 + * + \text{H}_2\text{O}$
$\text{H}^* + \text{H}^* \rightarrow * + \text{H}_2$	Tafel	$\text{H}^* + \text{H}^* \rightarrow * + \text{H}_2$

\* represents active sites

### 4.2. Recent progress of MoS<sub>2</sub> for electrocatalytic HER

As a typical sulfide, MoS<sub>2</sub> has been widely used in many energy-related fields, such as electrocatalysis, battery, photocatalysis and thermocatalysis, due to its unique physical and chemical properties [69,70]. Especially, MoS<sub>2</sub> has emerged as a promising alternative to Pt-based electrocatalysts for HER due to its excellent catalytic activity and earth-abundance (**Scheme 2**). This is attributed to the favorable electronic structure of MoS<sub>2</sub>, which allows for efficient adsorption and activation of H\*

intermediates. Furthermore, MoS<sub>2</sub> can be easily synthesized via various methods using tunable morphologies, such as nanoparticles, nanosheets and nanospheres. Hinnemann et al. [45] were the first to find that Mo edges (1010) of MoS<sub>2</sub> have similar properties with hydrogenases and can produce stable H\* intermediates. The theoretical calculations revealed that the unsaturated Mo edges of MoS<sub>2</sub> are crucial active sites for catalytic HER and has attractive free energy of H adsorption. The basal planes of MoS<sub>2</sub> are catalytically sluggish. The results confirmed MoS<sub>2</sub> as an HER electrocatalyst, and thus MoS<sub>2</sub> received great attention. Thereafter, Jaramillo and co-authors [44] identified the relationship between MoS<sub>2</sub>'s active sites for HER and electrocatalytic activity. They determined the surface sites of MoS<sub>2</sub> using scanning tunneling microscopy and then systematically tuned the active site distribution. The electrocatalytic results showed that the HER activity linearly correlated with the number of edge sites on MoS<sub>2</sub>. Zhang et al. [71] also studied the origin of active sites in monolayer MoS<sub>2</sub>. They found that its HER property positively related to Mo-terminated edge sites and the phase structure transition. The basal plane activity of 1T-MoS<sub>2</sub> was found to be beneficial to catalytic HER compared with that of 2H-MoS<sub>2</sub>. Chen et al. [72] provided Raman spectroscopic evidence that confirmed the S–H bond formation on MoS<sub>2</sub>'s surface via in-situ Raman measurements. This suggests that S sites on the surface of MoS<sub>2</sub> can act as catalytically active sites for HER.



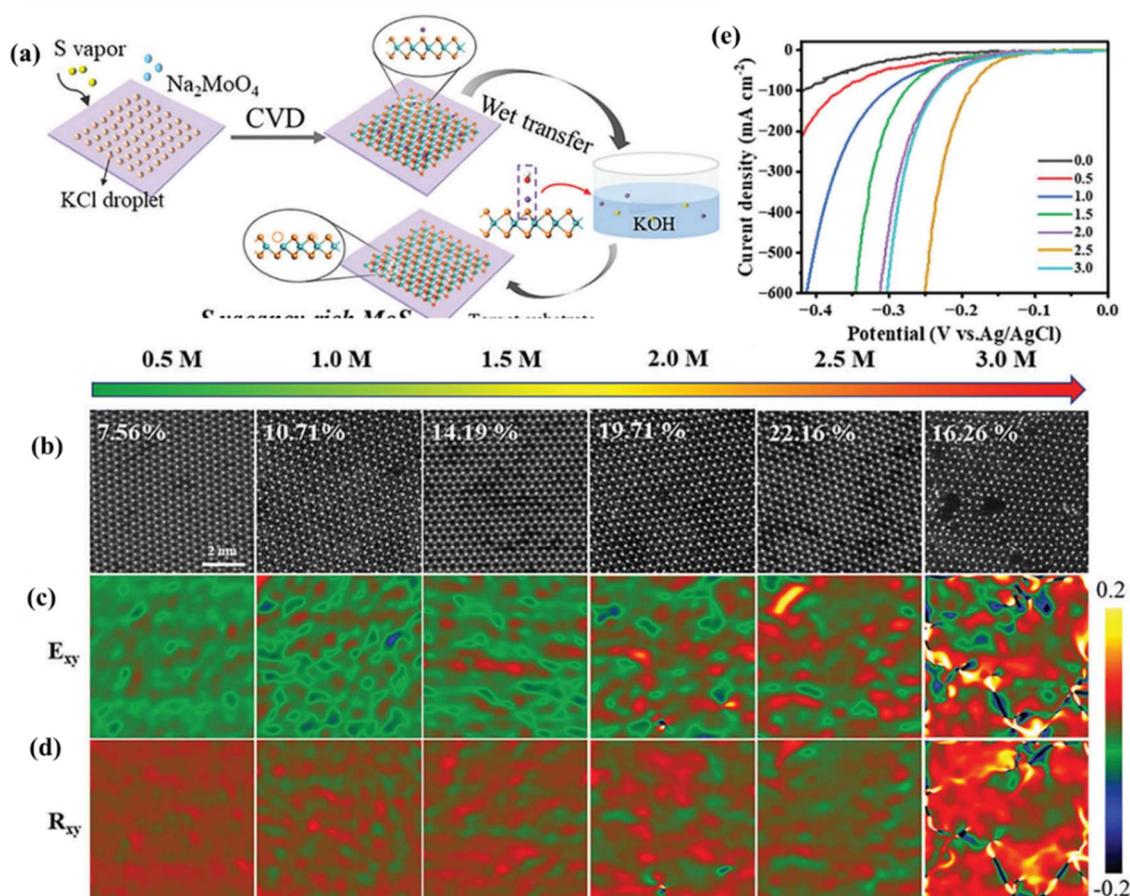
**Scheme 2.** Recent progress of MoS<sub>2</sub> for electrocatalytic HER.

Although MoS<sub>2</sub> has been confirmed as a potential candidate for an excellent electrocatalytic HER, its intrinsic activity still needs to be further enhanced compared with those of Pt-based electrocatalysts. Various methods, such as the exposure of edge sites, phase regulation, heterostructure construction, defect engineering, doping and compound effect, have been proposed to improve the catalytic HER activity of MoS<sub>2</sub>.

#### 4.2.1. Exposure of edge sites

Generally, MoS<sub>2</sub> contains active edge sites and inert basal planes. To enhance its catalytic HER activity, efficient strategies have been proposed to construct active edge sites on its inert basal planes [73–76]. Li et al. [74] were the first to propose activating the basal planes of 2H-MoS<sub>2</sub> by introducing S defects and strain engineering. The theoretical and experimental results revealed that the strained S vacancies were new active sites in the basal planes and that the free energy for H adsorption ( $\Delta G_{\text{H}}$ ) was

also tuned, contributing to the high intrinsic HER property. Hence, various S vacancies have been constructed using efficient methods to activate the basal planes of 2H-MoS<sub>2</sub>. Tsai et al. [77] adopted electrochemical desulfurization to generate scalable S vacancies on the basal planes of MoS<sub>2</sub>, which can be regulated by changing the applied desulfurization potential. The resulting stable active sites showed a good HER performance with a high per-site turnover frequency value. Liu and co-authors [78] employed point defects and vacancies to synergistically activate the inert basal planes of MoS<sub>2</sub> for improved HER performance. By combining on-chip electrochemical tests with theoretical calculations, they found that the type and amount of defect configurations played a crucial role in the catalytic HER. Man et al. [79] reported sulfur-vacancy-rich 2H-MoS<sub>2</sub> via a unique salt-assisted chemical vapor deposition method (**Figure 12(a)**). **Figure 12(b–d)** shows the distribution of sulfur vacancies and the corresponding strain maps. The vacancy density was controllably tuned with S vacancy ratios from 7.56% to 22.16%. In the strain maps, the strain value can be up to 14% with the increase in KCl concentration. The obtained MoS<sub>2</sub> exhibited a small overpotential of  $\approx 158.8$  mV at  $100 \text{ mA}\cdot\text{cm}^{-2}$  in an acid electrolyte, outperforming previously reported MoS<sub>2</sub>-based electrocatalysts.

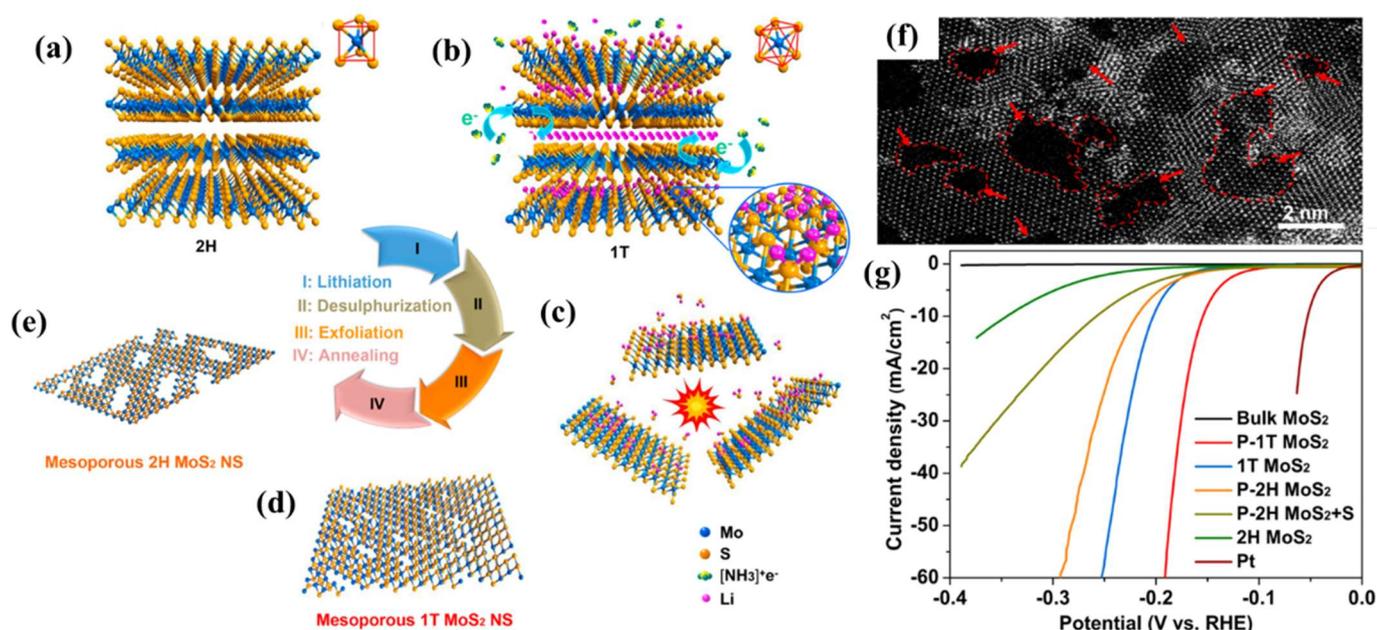


**Figure 12.** (a) Synthesis process of S-vacancy-rich MoS<sub>2</sub>. (b) Sulfur vacancy ratios marked on high-resolution STEM images. (c) Strain color scale of shear strain ( $E_{xy}$ ). (d) Strain color scale of rotation lattice (rotation- $xy$ , or  $R_{xy}$ ). (e) HER performances [79].

In addition, metal or heteroatom doping [18,80–82] has been found to be another efficient way to activate basal planes and increase active sites. For instance, Xiao et al. [80] found that N dopants in MoS<sub>2</sub> exhibited a small overpotential of 35 mV with a low Tafel slope of 41 mV·dec<sup>-1</sup>. The experimental and first-principle approach confirmed that N dopants activated S-edge sites and enhanced the conductivity of MoS<sub>2</sub>. Fu et al. [18] used metal Zn to produce S vacancies on MoS<sub>2</sub> via Zn doping, as well as to activate the basal planes. The obtained MoS<sub>2</sub> had a decreased  $\Delta G_{\text{H}}$  on S vacancy sites of MoS<sub>2</sub> near Zn atoms, which contributed to a low HER overpotential of 194 mV at 10 mA·cm<sup>-2</sup>. Anjum et al. [83] prepared an all-in-one MoS<sub>2</sub> electrocatalyst with NH<sub>3</sub> molecules intercalation (ammoniated MoS<sub>2</sub>, or A-MoS<sub>2</sub>). Subsequently, the A-MoS<sub>2</sub> was in-situ reduced to remove the intercalated NH<sub>3</sub> and H<sub>2</sub>S and to form all-in-one MoS<sub>2</sub> with multifunctional active sites (R-MoS<sub>2</sub>). The electrocatalytic HER performance of the R-MoS<sub>2</sub> was even superior to that of commercial Pt/C, indicating its high potential for HER systems.

#### 4.2.2. Phase regulation

As we know, MoS<sub>2</sub> has three different phase structures, which are 1T, 2H and 3R. 2H-MoS<sub>2</sub> has been widely researched as an electrocatalyst. Recently, a considerable amount of works in the literature revealed that 1T-MoS<sub>2</sub> exhibited an enhanced catalytic HER activity than 2H-MoS<sub>2</sub> due to its high conductivity and unique structural advantage. Lukowski et al. [84] reported the fabrication of 1T-MoS<sub>2</sub> nanosheets using chemical exfoliation, which showed superior catalytic HER activity, attributing to favorable reaction kinetics, good conductivity and increased density of active sites. Yin et al. [85] systematically explored the correlation among the phase structure, edge sites, S vacancies and catalytic HER activity. They synthesized porous 1T-MoS<sub>2</sub> (P-1T-MoS<sub>2</sub>) via lithiation, desulfurization and exfoliation (**Figure 13(a–d)**); steps I, II and III) and porous 2H-MoS<sub>2</sub> nanosheets (P-2H-MoS<sub>2</sub>, **Figure 13(e)**) via facile annealing from the synthesized P-1T-MoS<sub>2</sub> (Step IV). The porous feature of P-1T-MoS<sub>2</sub> was confirmed via TEM, as indicated by red arrows in **Figure 13(f)**. **Figure 13(g)** shows the linear sweep voltammetry (LSV) curves, in which P-1T-MoS<sub>2</sub> displayed a much higher HER performance with 153 mV at  $j = -10 \text{ mA}\cdot\text{cm}^{-2}$  than other types of MoS<sub>2</sub>. The results revealed that the HER performance of 1T-MoS<sub>2</sub> generally was superior to that of 2H-MoS<sub>2</sub>, indicating that the phase played a crucial role in catalytic HER. In addition, both edge sites and S vacancies also enhanced the catalytic HER property. This study offers a reference for developing highly active MoS<sub>2</sub> electrocatalysts.

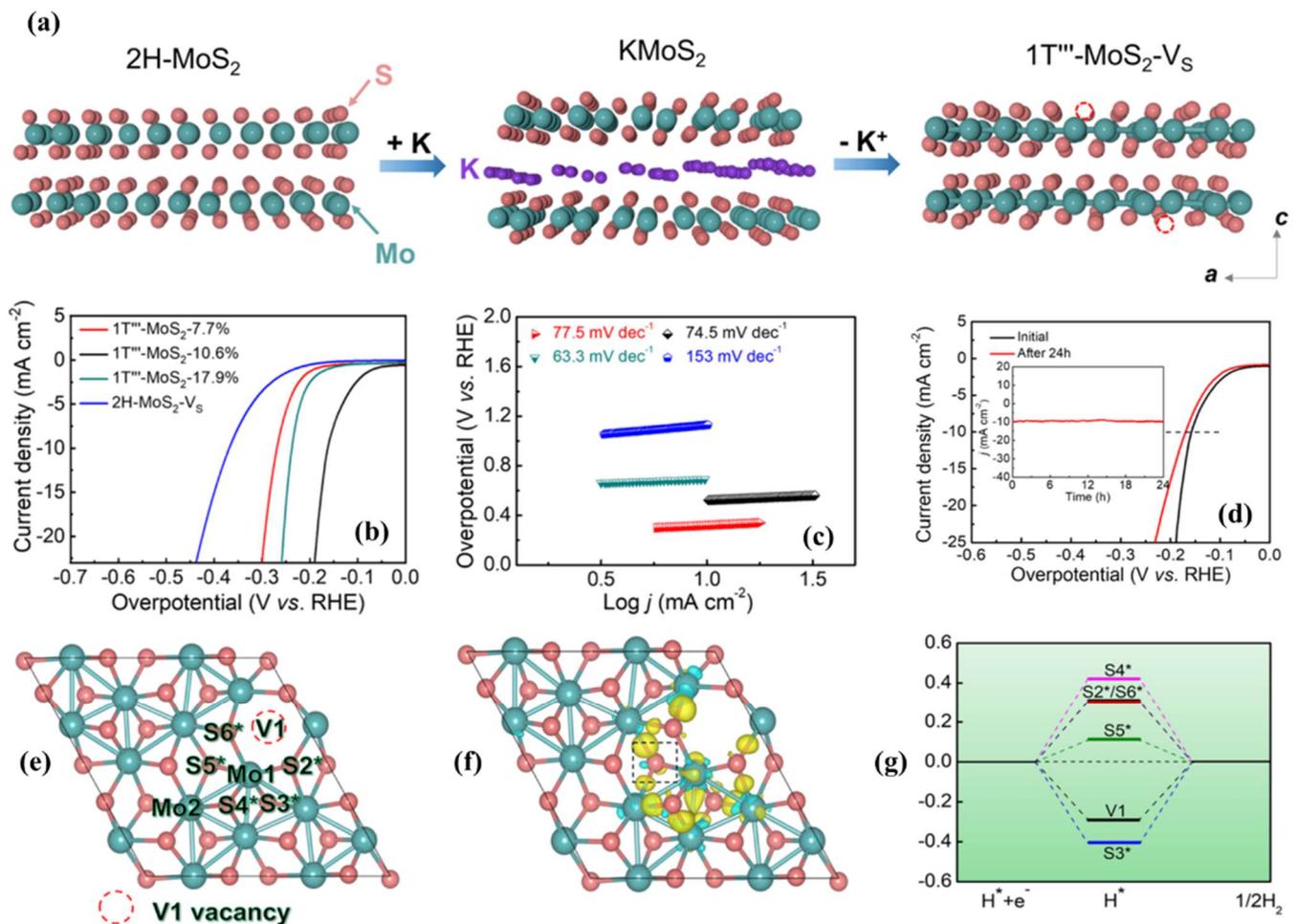


**Figure 13.** Schematic illustration of preparation of mesoporous 1T-MoS<sub>2</sub> nanosheets from bulk MoS<sub>2</sub> via (a) lithiation (b), desulfurization and (c) exfoliation. (d) P-1T-MoS<sub>2</sub> from Steps I, II and III. (e) P-2H-MoS<sub>2</sub> from Step IV. (f) TEM image of 1T-MoS<sub>2</sub>. (g) Catalytic activities of samples [85].

For facile and controllable preparation of 1T-MoS<sub>2</sub>, numerous studies have been devoted to developing efficient synthesis methods. Chang's group [86] accurately fabricated the different phases of MoS<sub>2</sub> by using Li-molten salt and tuning the calcination temperature via exfoliation. The obtained monolayer 1T-MoS<sub>2</sub> was found to directly rely on annealing temperature and had excellent catalytic HER activity. Zhu et al. [87] reported a scalable phase-engineering strategy to obtain monolayer 1T-MoS<sub>2</sub> using weak Ar-plasma bombardment. The existence of S vacancies (point defects) was found to stabilize the 1T-MoS<sub>2</sub> phase. Liu et al. [88] developed a simple hydrothermal route to prepare 1T-MoS<sub>2</sub> nanosheet arrays vertically grown on a carbon cloth (1T-MoS<sub>2</sub>/CC), which was stable for 45 days under ambient conditions. The obtained 1T-MoS<sub>2</sub>/CC provided rich active sites, enhanced accessibility and good conductivity, leading to an attractive HER activity with 151 mV to reach 10 mA·cm<sup>-2</sup>. Besides, Li et al. [89] synthesized defect-rich 1T-MoS<sub>2</sub> via the solvothermal method, where the proportion of the 1T-MoS<sub>2</sub> was tuned using the amount of acetic acid. The optimized 1T-MoS<sub>2</sub> delivered a low overpotential of 136 mV at 10 mA·cm<sup>-2</sup> and a small Tafel slope of 45 mV·dec<sup>-1</sup>. Yang's group [90] reported a large-scale strategy for high-concentration 1T-MoS<sub>2</sub> with an excellent HER performance via ionic-liquid-assisted hydrothermal reaction, which can be extended to prepare 1T-WS<sub>2</sub>, 1T-MoSe<sub>2</sub> and 1T-WSe<sub>2</sub>.

Although many synthesis methods have been proposed, the thermodynamic metastability of 1T-MoS<sub>2</sub> extensively limits its stability. Recently, atom intercalation in MoS<sub>2</sub> has been confirmed to stabilize MoS<sub>2</sub>'s phase structure. For instance, Ekspong et al. [91] developed sulfur-rich intercalated 1T-MoS<sub>2</sub> on graphitic nanoribbons with an S:Mo ratio of ~2.3:1, which sustained its stability for several months. Both experimental and theoretical results found that the active sites on the basal planes were activated with an outstanding  $\Delta G_H$  value of 0.06 eV, which in turn improved catalytic

activity. Gao's group [92] confirmed that the formation of 1T-MoS<sub>2</sub> can be induced using metal doping. Their results found that Co/Ni co-doping provided abundant electrons for Mo atoms, subsequently leading to phase transition. The obtained Co/Ni-MoS<sub>2</sub> possessed an excellent alkaline HER property. Jiang et al. [93] proposed a strategy of Se and O co-insertion to induce the transition of MoS<sub>2</sub> from the 2H phase to the 1T phase. Guo's group [94] reported a chemical etching method to construct 1T-MoS<sub>2</sub> with different S vacancies (1T-MoS<sub>2</sub>-V<sub>S</sub>) for efficient catalytic HER. **Figure 14(a)** shows the schematic of the synthesis of 1T-MoS<sub>2</sub>-V<sub>S</sub>. K<sup>+</sup> ions intercalated in the interlayer of 2H-MoS<sub>2</sub> to form KMoS<sub>2</sub>, and 1T-MoS<sub>2</sub> was obtained by the extraction of K<sup>+</sup> from KMoS<sub>2</sub>. Afterward, the 1T-MoS<sub>2</sub> was immersed in an acidic K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution to obtain S vacancies. The electrochemical measurements are shown in **Figure 14(b–d)**. The 1T-MoS<sub>2</sub>-V<sub>S</sub> exhibited a lower overpotential of 158 mV at 10 mA·cm<sup>-2</sup> and a smaller Tafel slope of 74.5 mV·dec<sup>-1</sup>. A little degradation in its current density after a continuous 24-h test suggested remarkable stability for HER. Particularly, the electronic states of the 1T-MoS<sub>2</sub>-V<sub>S</sub> (**Figure 14(e–g)**) demonstrated the charge redistribution with the activated Mo-Mo bonds, which led to an optimal  $\Delta G_{H^*}$  value for catalytic HER.

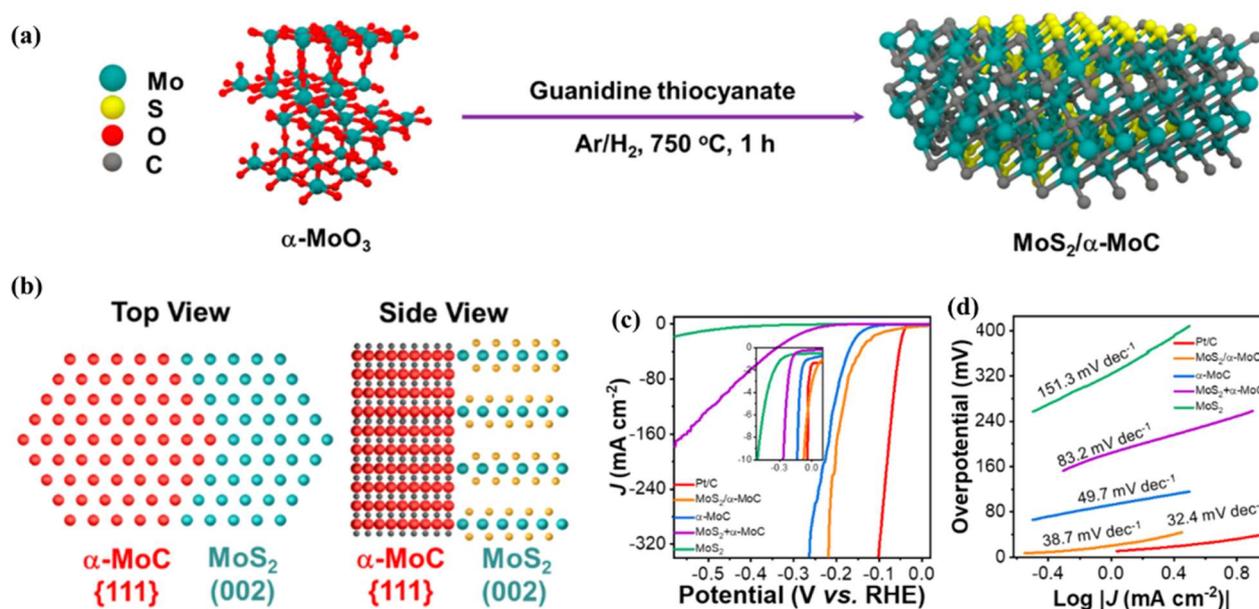


**Figure 14.** (a) Fabrication procedure of 1T-MoS<sub>2</sub>-V<sub>S</sub>. (b) LSV curves of 1T-MoS<sub>2</sub>-V<sub>S</sub>. (c) Tafel slope of 1T-MoS<sub>2</sub>-V<sub>S</sub>. (d) Stability result of 1T-MoS<sub>2</sub>-V<sub>S</sub>. (e) Optimized structure, (f) Calculated charge density difference. (g)  $\Delta G_{H^*}$  in different exposed S atoms of 1T-MoS<sub>2</sub>-V<sub>S</sub> [94].

### 4.2.3. Heterostructure construction

Recently, heterostructure construction has been shown to demonstrate outstanding performance for electrocatalysis, including electrocatalytic HER, OER, etc. Usually, heterostructured catalysts are composed of two/multiple functional components with tunable electronic interaction and distinct synergetic effects. Herein, MoS<sub>2</sub> heterostructured electrocatalysts for HER are summarized. A MoS<sub>2</sub>-Ni<sub>3</sub>S<sub>2</sub> heterostructure was reported by Yang's group [95] which was directly supported by Ni foam. MoS<sub>2</sub> nanosheets were hierarchically decorated on Ni<sub>3</sub>S<sub>2</sub> nanorods, in which the hierarchical MoS<sub>2</sub>-Ni<sub>3</sub>S<sub>2</sub> heterostructure showed highly active heterointerfaces and facilitated charge transport, thus presenting a low overpotential of 98 mV to reach 10 mA·cm<sup>-2</sup>. A Ni<sub>2</sub>P/MoS<sub>2</sub> heterostructure is constructed by Kim et al. [96] which were hybridized with conductive N-doped carbon supports. The generated electrocatalyst delivered Pt-like catalytic HER activity. N-doped carbon played a key role in the conductivity and stability of the Ni<sub>2</sub>P/MoS<sub>2</sub> heterostructure, enhancing the potential for hydrogen production. Kim et al. [97] developed a 0D-2D Co<sub>9</sub>S<sub>8</sub>-MoS<sub>2</sub> heterostructure, where ultras-small Co<sub>9</sub>S<sub>8</sub> nanoparticles were loaded on the surface of MoS<sub>2</sub> using Co-S-Mo covalent bonds. The Co<sub>9</sub>S<sub>8</sub>-MoS<sub>2</sub> heterostructure offered electron-rich Mo sites generated by the interface charge redistribution from Co to Mo sites. Furthermore, S defects, which were formed due to reductive annealing, activated adjacent Mo atoms to increase catalytic HER. The experimental and DFT results revealed that the 0D-2D Co<sub>9</sub>S<sub>8</sub>-MoS<sub>2</sub> heterostructure presented an excellent catalytic HER activity in electrolytes with a wide range of pH.

As mentioned above, 1T-MoS<sub>2</sub> has much higher electrical conductivity and a better catalytic HER performance than those of 2H-MoS<sub>2</sub>. Wang et al. [98] proposed constructing 1T-2H-MoS<sub>2</sub> heterostructures via a simple one-pot annealing treatment, which showed improved electrical conductivity, had more active sites and delivered promoted electrocatalytic HER properties. Cheng et al. [99] constructed a MoS<sub>2</sub>/α-MoC heterostructure using two straightforward and facile steps, as shown in **Figure 15(a)**, which formed an in-plane heterostructure of MoS<sub>2</sub>(002)/α-MoC(111) (**Figure 15(b)**). The MoS<sub>2</sub>/α-MoC led to lattice strain with an adjustable electronic configuration and thus presented Pt-like activity for HER with only a low 78 mV of overpotential at 10 mA·cm<sup>-2</sup> and a small Tafel slope of 38.7 mV·dec<sup>-1</sup> (**Figure 15(c,d)**). Besides, Sun et al. [100] developed Mo-MoS<sub>2</sub> Mott-Schottky heterojunctions (Mo-MoS<sub>2</sub> MSH) by combining the semiconductor MoS<sub>2</sub> with the metal Mo. The electronic structure of the Mo-MoS<sub>2</sub> MSH was effectively optimized with enhanced H adsorption. The Mo-MoS<sub>2</sub> MSH only needed overpotentials of 91, 138 and 128 mV to achieve 10 mA·cm<sup>-2</sup> in acid, alkaline and neutral solution, respectively.

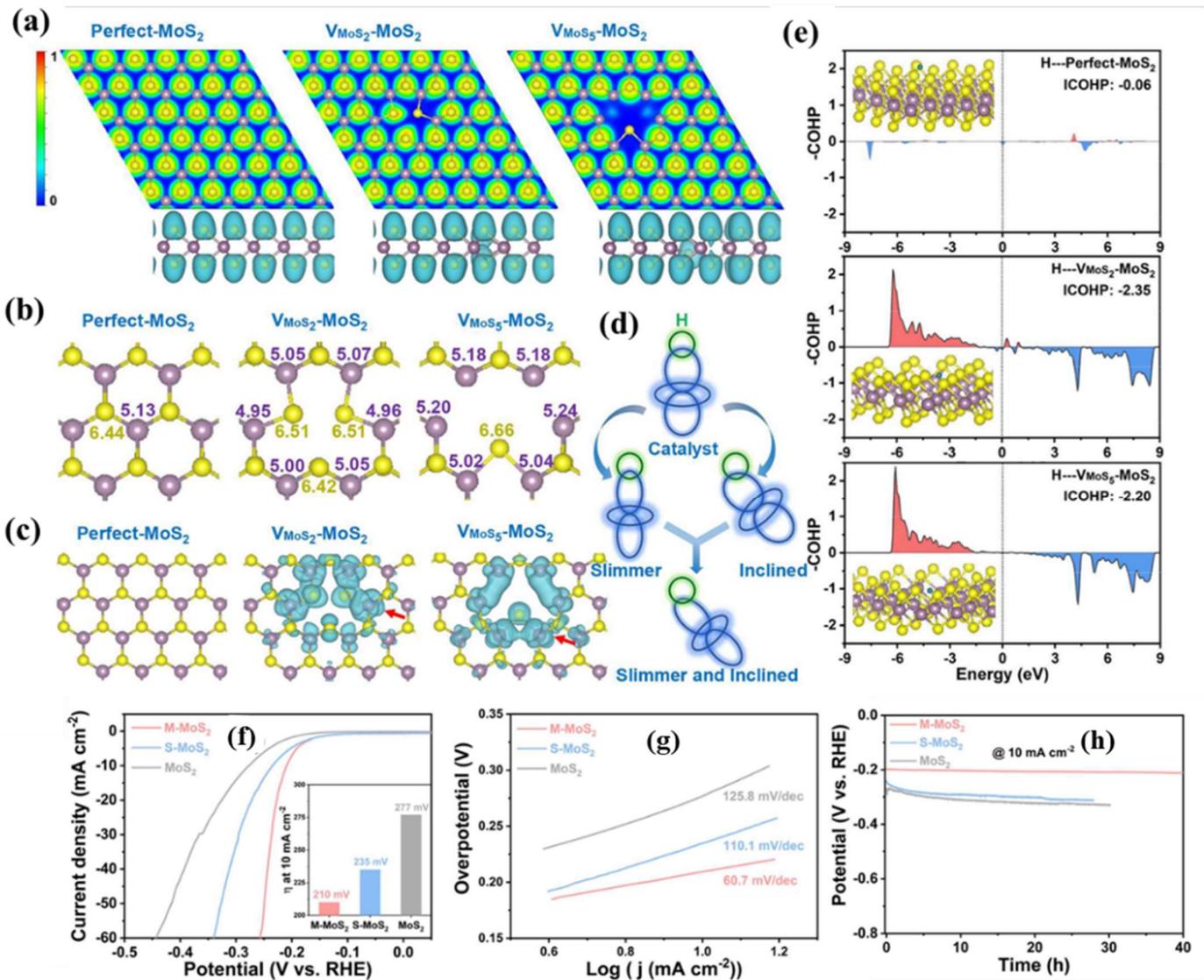


**Figure 15.** (a) Schematic illustration of synthesis of MoS<sub>2</sub>/α-MoC heterostructure. (b) Hypothesized top and side views of in-plane structure. (c) Polarization curves. (d) Tafel slopes [99].

#### 4.2.4. Defect/vacancy engineering

Defect/vacancy engineering is an efficient strategy to construct specific unsaturated active centers and tune electronic structures. Unsaturated active centers can serve as active sites for intermediate adsorption/desorption, thereby enhancing catalytic properties. S-vacancy and Mo-vacancy engineering have been widely confirmed as efficient methods to expose more active sites in MoS<sub>2</sub> and improve HER [101–104]. Generally, S vacancies are more easily formed during the synthesis process. Ye et al. [105] reported the defect engineering of monolayer MoS<sub>2</sub> using O plasma annealing, which resulted in improved HER performance. They illustrated the correlation between changes in MoS<sub>2</sub>'s microscale structure and HER properties for the first time, proving that defect engineering could produce more catalytic active edge sites and thus promote HER activity. Li et al. [101] also explored the relationship between HER activity and surface S vacancies of MoS<sub>2</sub>. With the increase in S vacancies, two different domains were reported, which were point defects at low S-vacancy concentrations and a large number of undercoordinated Mo atoms at high S-vacancy concentrations. The HER activity rapidly accelerated by the point defects, but the highest HER performance was obtained from the formation of undercoordinated Mo atoms through S stripping. This work provides a reference for the development of defected MoS<sub>2</sub> to boost HER. Wang's group [104] initially regulated the state (concentration and distribution) of S vacancies via high throughput calculations. The state of S vacancies was experimentally modulated using etching parameters (etching duration, etching temperature and etching solution concentration). The results found that MoS<sub>2</sub> with single S vacancies exhibited optimal HER performance than that of MoS<sub>2</sub> with agglomerate S vacancies. The outstanding property can be attributed to the more effective adjustment of the surface electronic structure and electrical transportation.

Zhan et al. [106] explored the relationship between the local atomic environment of vacancies and HER performance of MoS<sub>2</sub>. A series of models with different vacancies were first built to theoretically evaluate  $\Delta G_{H^*}$ . The calculation results confirmed that H\* can be adsorbed on Mo atoms and that  $\Delta G_{H^*}$  decreased due to the existence of vacancies. Among these models, M-MoS<sub>2</sub> (V<sub>MoS<sub>5</sub></sub>-MoS<sub>2</sub>) with more Mo-terminated vacancies had the lowest  $\Delta G_{H^*}$  of 0.04 eV. Generally,  $\Delta G_{H^*}$  was found to rely on the interfacial electronic structure. As shown in **Figure 16(a)**, exposed Mo atoms in M-MoS<sub>2</sub> can obtain more electrons to increase the electron density of Mo atoms, which can be verified via the Bader charge (**Figure 16(b)**). The average Bader charge of Mo atoms in M-MoS<sub>2</sub> was  $\sim 5.20$ , which was higher than those of MoS<sub>2</sub> (perfect MoS<sub>2</sub>) and S-MoS<sub>2</sub> (V<sub>MoS<sub>2</sub></sub>-MoS<sub>2</sub>). Electron-rich Mo atoms contributed to the Volmer reaction for HER. Additionally, the larger electron cloud (**Figure 16(c)**) on Mo sites in M-MoS<sub>2</sub> produced a stronger electronic coupling and more efficient orbital interaction (**Figure 16(d)**) for more favorable H desorption. Specifically, the calculation of integrated crystal orbital Hamilton populations (ICOHPs) resulted in more negative values, as shown in **Figure 16(e)**, which further revealed enhanced H desorption. The ICOHP values of MoS<sub>2</sub>, M-MoS<sub>2</sub> and S-MoS<sub>2</sub> were  $-0.06$ ,  $-2.20$  and  $-2.35$ , respectively. M-MoS<sub>2</sub> possessed a moderate ICOHP value, suggesting beneficial H adsorption. These results showed that the atomic environment surrounding vacancies was crucial for effectively regulating the Volmer step and H adsorption. MoS<sub>2</sub> with more Mo terminated vacancies was favorable for better HER performance. As seen from LSV curves in **Figure 16(f)**, MoS<sub>2</sub> with the fewest vacancies had the largest overpotential of 277 mV at 10 mA·cm<sup>-2</sup> ( $\eta_{10}$ ). The overpotential for S-MoS<sub>2</sub> decreased to 235 mV. M-MoS<sub>2</sub> was identified as the optimal sample for HER with the smallest  $\eta_{10}$  value of 210 mV. In particular, along with an overpotential of 250 mV, M-MoS<sub>2</sub> showed a current density of 51.4 mA·cm<sup>-2</sup>, which was about four-fold that of S-MoS<sub>2</sub> and eight-fold that of MoS<sub>2</sub>. The Tafel plots in **Figure 16(g)** show slopes of 60.7, 110.1 and 125.8 mV·dec<sup>-1</sup> for M-MoS<sub>2</sub>, S-MoS<sub>2</sub> and MoS<sub>2</sub>, respectively, where a lower Tafel slope represents better HER kinetics. As shown in **Figure 16(h)**, M-MoS<sub>2</sub> remained almost unchanged for 40 h to generate H<sub>2</sub>. This work provides a more profound understanding of defect engineering for the design of highly active catalysts.



**Figure 16.** (a) Top view of (001) planes and side view of electron localization function maps. (b) Bader charges of atoms around vacancy in MoS<sub>2</sub> (perfect MoS<sub>2</sub>), S-MoS<sub>2</sub> (VMoS<sub>2</sub>-MoS<sub>2</sub>) and M-MoS<sub>2</sub> (VMoS<sub>5</sub>-MoS<sub>2</sub>). (c) Unoccupied orbital distribution near Fermi level of MoS<sub>2</sub>, S-MoS<sub>2</sub> and M-MoS<sub>2</sub> (red arrow denotes H-adsorption site). (d) Schematic diagram of orbital interaction under different conditions. (e) ICOHP values of H adsorption on MoS<sub>2</sub>, S-MoS<sub>2</sub> and M-MoS<sub>2</sub> (bonding and antibonding states in ICOHP are depicted in red and blue, respectively). (f) Linear sweep voltammetry (LSV) curves in 0.5M H<sub>2</sub>SO<sub>4</sub> with scan rate of 5 mV·s<sup>-1</sup> (inset: overpotential values at 10 mA·cm<sup>-2</sup>). (g) Tafel slopes. (h) Long-term stability [106].

Mo-vacancy engineering has also been considered as a good method to improve metal sulfides for energy storage and conversion [107–109] and especially for electrocatalysis. Ge et al. [108] developed abundant Mo vacancies in a MoS<sub>2</sub>-based composite. Experimental and theoretical calculations revealed that Mo vacancies modulated the electronic structure of S sites to regulate the free energy of H adsorption, thus enhancing catalytic HER. Shi et al. [109] reported a Frenkel-defected monolayer MoS<sub>2</sub> catalyst, in which S and Mo vacancies co-existed in MoS<sub>2</sub> to generate charge distributions. The obtained Frenkel-defected MoS<sub>2</sub> exhibited an outstanding HER activity with a low overpotential of 164 mV.

#### 4.2.5. Element doping

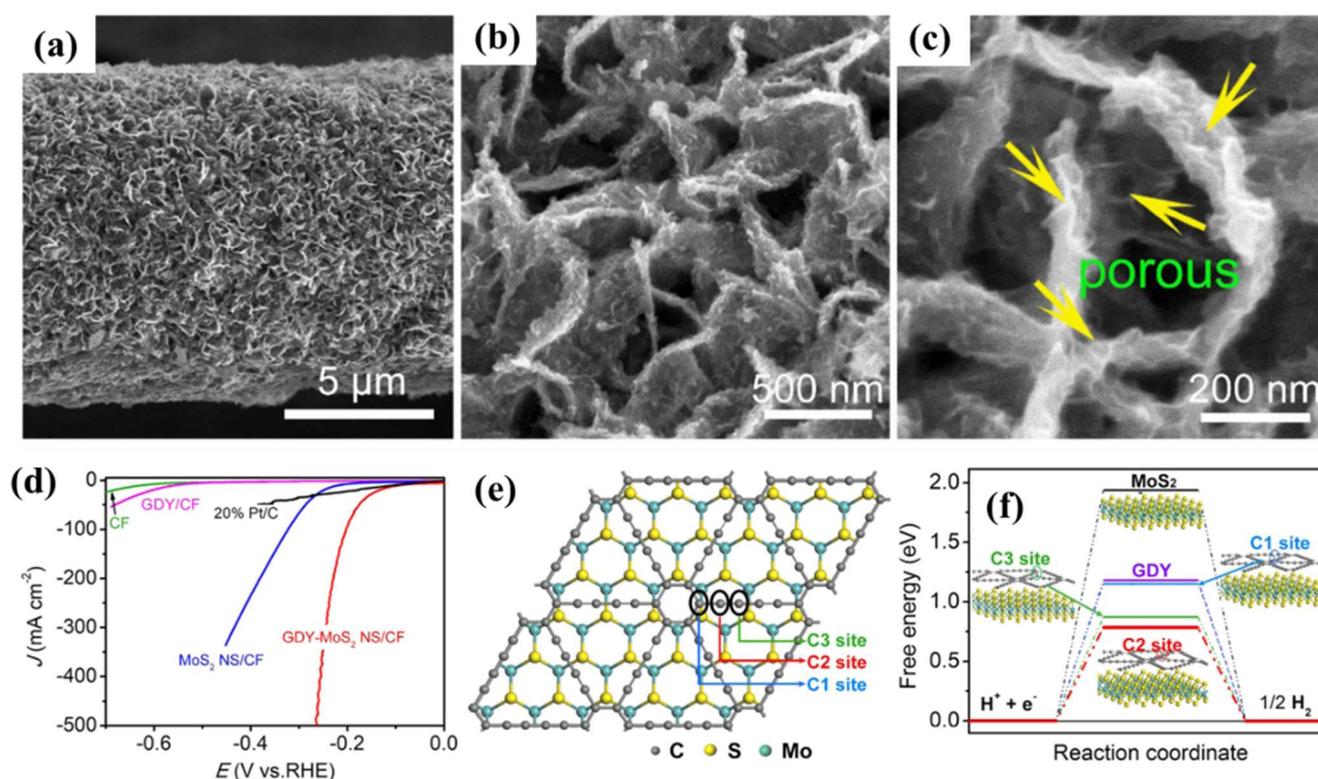
In electrocatalysis, element doping has been deemed to be an effective method to regulate active sites of catalysts for various reactions. Element doping comprises two types: metal doping and heteroatom doping (nonmetal doping). Metal doping (e.g., Zn, Co, Ni, etc.) [110–113] can effectively adjust the electronic structure of Mo sites in MoS<sub>2</sub> to promote high HER performance. For instance, Xu et al. [110] proposed transition metal Zn doping of MoS<sub>2</sub> to engineer its energy level for efficient HER. They found that Zn doping provided an energy level matching the HER's kinetic acceleration, resulting in a superior electrochemical HER activity. Xue et al. [112] developed ultra-small Ni-doped MoS<sub>2</sub> nanosheets on hollow carbon microtubes. The results confirmed that moderate Ni doping tuned the electronic structure of active sites in MoS<sub>2</sub>. As a result, the obtained catalyst exhibited excellent activity with enhanced HER kinetics, requiring a low overpotential of 88 mV at 10 mA·cm<sup>-2</sup> and demonstrating better stability in 0.5M H<sub>2</sub>SO<sub>4</sub>. Kong et al. [114] used rare earth Ce for a doping strategy to prepare Ce-doped MoS<sub>2</sub>. The Ce-doped MoS<sub>2</sub> was rich in defects and regulated the electronic structure, further promoting HER performance with a small overpotential of 113.78 mV.

Heteroatom doping (N, F, P, etc.) [115–119] for enhancing catalytic HER has also received great attention. Li et al. reported N-doped MoS<sub>2</sub>, fabricated via a simple one-step hydrothermal strategy, as an efficient HER catalyst [115]. The N doping produced rich S defects to expose Mo sites and adjust the electron density of S atoms to activate S atoms as active sites. The N-doped MoS<sub>2</sub> revealed a much lower overpotential of 168 mV at 10 mA·cm<sup>-2</sup> than that of pure MoS<sub>2</sub>. Zhang et al. [118] developed F-doped MoS<sub>2</sub> with controllable active sites by using a plasma etching strategy. F atoms possess larger electronegativity than S atoms, thus leading to more moderate-free-energy carriers for H\* intermediates and delivering five-fold activity enhancement for HER. Shi et al. [119] constructed P-doped 2H-MoS<sub>2</sub> nanoflowers with a crystalline-amorphous heterostructure via a simple calcination method. Rich S vacancies were generated from the P doping. Benefiting from P doping, the crystalline-amorphous heterostructure and S vacancies, the P-doped 2H-MoS<sub>2</sub> demonstrated pH-universal HER activity and excellent stability.

#### 4.2.6. Compound construction by coupling with conductive materials

Although MoS<sub>2</sub> has been regarded as a promising HER electrocatalyst, its low number of active edge sites and its semiconductor feature result in a relatively low activity toward HER. Compound construction by coupling MoS<sub>2</sub> with conductive graphene [120,121], carbon nanotube [122,123], graphdiyne [124,125], etc., has also been reported as a good method to improve HER performance. The unique synergistic effect can be generated to modulate MoS<sub>2</sub> for efficient HER. A rational design of MoS<sub>2</sub>-based compounds can adjust the conductivity and expose the active edge sites of MoS<sub>2</sub> [124,126,127]. Li et al. [120] synthesized MoS<sub>2</sub>@reduced graphene oxide (RGO) as a highly active HER electrocatalyst. The unique synergistic effect between MoS<sub>2</sub> with RGO enhanced the HER activity with a small overpotential of 64 mV at 10 mA·cm<sup>-2</sup>. Wu et al. [128] reported hierarchical MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>-MXene@C compounds with a good catalytic HER. The results revealed that the MoS<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>-MXene@C showed greatly improved electrical conductivity and structural stability.

The synergy of compounds also promotes the HER kinetics of MoS<sub>2</sub>, thus leading to an outstanding HER performance. Graphdiyne, with its unique atomic arrangement, good conductivity and abundant natural pore structure, has attracted great attention. Hui's group [125] reported a simple strategy to synthesize graphdiyne-encapsulated MoS<sub>2</sub> nanosheets on carbon fiber (GDY-MoS<sub>2</sub> NS/CF), as shown in **Figure 17(a–c)**. It can be clearly seen in **Figure 17(d)** that the GDY-MoS<sub>2</sub> NS/CF had the best catalytic activity among all catalysts, exhibiting a high current density ( $J$ ) at the low overpotential ( $\eta$ ). The experimental and theoretical calculations verified that graphdiyne on the surface of MoS<sub>2</sub> induced a phase transformation from 2H-MoS<sub>2</sub> to 1T-MoS<sub>2</sub> and decreased the free energy for H adsorption (**Figures 17(e,f)**). Song et al. [126] found that the construction of MoS<sub>2</sub>@carbon quantum dots (CQDs) enabled hydrogen spillover to accelerate HER activity. The CQDs on the surface of MoS<sub>2</sub> led to charge redistribution and electrons gradually transferring from C sites in the CQDs to S sites in MoS<sub>2</sub>, promoting hydrogen spillover.



**Figure 17.** (a–c) SEM images of GDY-MoS<sub>2</sub> NS/CF. (d) LSV curves in alkaline solution. (e) Top view of optimized structure of GDY-MoS<sub>2</sub>. (f) Free energy diagram of HER [125].

## 5. Conclusion and prospects

This review summarized the recent progress and improved strategies of MoS<sub>2</sub> for photocatalytic HER and electrocatalytic HER. For photocatalytic HER, many novel strategies have been proposed to enhance the photocatalytic activity of MoS<sub>2</sub>, such as surface engineering, heterostructure construction and defect engineering. These approaches have led to significant improvements in the efficiency of MoS<sub>2</sub>-based photocatalysts. In addition, considerable efforts have also focused on improving the light absorption range of MoS<sub>2</sub> photocatalysts through bandgap engineering and

doping with heteroatoms, which allow for more efficient utilization of solar energy for photocatalytic reactions. Some new synthesis methods and surface passivation techniques have also been found to decrease the photo-corrosion of MoS<sub>2</sub> under light conditions and promote long-term performance. Also, there has been significant progress in MoS<sub>2</sub> as an electrocatalyst in electrocatalytic hydrogen production. The edge sites of MoS<sub>2</sub> serve as active sites for catalytic HER, and MoS<sub>2</sub> exhibits high catalytic HER activity under both acidic and alkaline conditions. The electronic structure of MoS<sub>2</sub> can be manipulated via morphology tuning, element doping, nanostructure design, heterostructure construction and chemical composition construction to accelerate its electrocatalytic HER activity.

Overall, although recent research works on MoS<sub>2</sub> for photo/electrocatalysis have effectively enhanced its HER activity, which is even close to those of many advanced HER catalysts, there are still some issues during photo/electrocatalysis. New sustainable synthesis methods for MoS<sub>2</sub> should be developed to minimize the use of toxic precursors and energy-intensive processes, which can contribute to the large-scale preparation of MoS<sub>2</sub> catalysts. Efforts should be devoted to enhancing the catalytic activity of MoS<sub>2</sub> catalysts for HER. Specially, the electrocatalytic HER performance of MoS<sub>2</sub> catalysts still lags behind those of commercial Pt-based catalysts. It is urgent to further investigate the fundamental catalytic mechanisms of MoS<sub>2</sub> for HER through operando characterization techniques and theoretical modeling, which can provide insights into the structure-property relationships and guide the rational design of the catalysts. In addition, practical applications require catalysts with excellent long-term stability and strong corrosion resistance, i.e., not limited to only tens of hours in the laboratory. Despite the efficient utilization of 2D MoS<sub>2</sub> for electrocatalysis and photocatalysis, enormous challenges remain, and ongoing research is expected to make significant progress soon.

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**Conflict of interest:** The authors declare no conflict of interest.

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