**Abstract:** Molybdenum disulfide (MoS$_2$), with a two-dimensional (2D) structure, has attracted huge research interest due to its unique electrical, optical, and physicochemical properties. MoS$_2$ has been used as a co-catalyst for the synthesis of novel heterojunction composites with enhanced photocatalytic hydrogen production under solar light irradiation. In this review, we briefly highlight the atomic-scale structure of MoS$_2$ nanosheets. The top-down and bottom-up synthetic methods of MoS$_2$ nanosheets are described. Additionally, we discuss the formation of MoS$_2$ heterostructures with titanium dioxide (TiO$_2$), graphitic carbon nitride (g-C$_3$N$_4$), and other semiconductors and co-catalysts for enhanced photocatalytic hydrogen generation. This review addresses the challenges and future perspectives for enhancing solar hydrogen production performance in heterojunction materials using MoS$_2$ as a co-catalyst.

**Keywords:** photocatalysis; heterojunction; layers structure materials; hydrogen production

1. Introduction

Hydrogen is a clean, renewable energy source and alternative to fossil fuels [1] that can be stored at high mass-specific energy density, and its only product on combustion is water [2]. At present, about 96% of hydrogen is industrially produced from coal gasification and steam methane reformation processes [1,2]. However, these processes of hydrogen production also generate secondary pollutants or greenhouse gases, such as CO$_2$ and N$_2$O, that affect the environment [2]. Methane pyrolysis produces hydrogen and solid carbon as a byproduct [3]. This process generates CO$_2$-free hydrogen and has an advantage over conventional steam methane reformation and coal gasification processes. However, methane pyrolysis is a temporary solution and not a sustainable process due to the depletion of natural gas reserves [3].

To overcome energy challenges and environmental problems, hydrogen production from electrochemical water splitting using highly active catalysts is a promising strategy [4,5]. Less than 4% of hydrogen is produced through electrocatalysis at the industrial level [2]. The electrocatalysis of water for hydrogen production is a high-cost technique, which has hindered its large-scale industrialization. As an alternative, photocatalytic hydrogen evolution reaction (HER) from water splitting over a particular semiconductor material has been the most interesting way to address these issues. Generally, the photocatalytic efficiency depends upon three processes, including light absorption in the solar spectrum, charge separation, and surface active sites for catalytic activity [1,2,6].

A photocatalyst that can absorb sunlight across the whole solar spectrum is considered to be an ideal candidate for photocatalysis [6,7]. In 1972, Fujishima et al. reported photo-induced water splitting on TiO$_2$ electrodes [8]. Since then, much research has been focused on TiO$_2$ and other related semiconducting materials such as metal oxides, metal sulfides, conjugated polymers, nanosheets, graphitic carbon nitride, metal organic frameworks, and covalent organic frameworks, etc., as photocatalysts for hydrogen production [9–17].
However, the available photocatalysts for hydrogen production are still limited due to low visible light absorption and high electron–hole recombination rates. Molybdenum disulfide (MoS$_2$), with a 2D nanostructure, has attracted huge attention due to its outstanding optical and electronic properties and promising applications [18–22]. MoS$_2$ nanomaterials as co-catalysts are promising photocatalysts for HER [18,23]. It is reported that the exposed edges of layers of MoS$_2$ contain active sites for catalytic activity while its basal planes are mostly inactive [19,24]. In addition to the active photocatalytic sites, the band gap of MoS$_2$ nanosheets is an important parameter for photocatalytic HER. The band gap of MoS$_2$ increases from bulk (1.2 eV) to single layer (1.9 eV) due to quantum confinement [19,24]. As a result, the location of the conduction band (CB) of MoS$_2$ moves towards a more negative potential than the proton reduction potential (H$^+$/$\text{H}_2$), which consequently enhances the reduction in adsorbed H$^+$ and photocatalytic hydrogen evolution.

It is widely reported that loading a co-catalyst over semiconductors is a promising approach with superior photocatalytic performance due to the photoelectron separation and charge transfer [18,19]. MoS$_2$-decorated semiconductor materials constitute a promising approach that has shown superior hydrogen production due to their heterojunctions with controllable nanoscale architectures, design for enhanced performance in terms of light absorption, charge separation, and surface catalytic reactions [15,19,23,24].

In this review, we briefly introduce the basic aspects and synthetic methods of MoS$_2$ nanosheets. Different types of MoS$_2$-based heterojunction composites are also discussed. The role of MoS$_2$ nanomaterials as co-catalysts in heterojunction composites for enhanced HER performance is addressed. Additionally, some important issues are highlighted and useful opinions are discussed to further improve photocatalytic hydrogen production using MoS$_2$ as a co-catalyst.

2. Atomic-Scale Structure of MoS$_2$

A single layer of MoS$_2$ has a sandwich structure of S-Mo-S, where the Mo atoms are covalently bonded with the S atoms (Figure 1). MoS$_2$ has several polymorphs, including 1T$_1$, 1T$_2$, 1H, 2T, 2H, 2R$_1$, 2R$_2$, 3H$_{\alpha}$, 3H$_{\beta}$, 3R, and 4T [25–29]. Among them the 1T MoS$_2$, 2H MoS$_2$, and 3R-MoS$_2$ polymorphs of MoS$_2$ have been most investigated for different applications [25,27–29]. A single-layer 1T MoS$_2$ sheet is metallic and has good electrical properties [30,31], while single-layer 2H MoS$_2$ and 3R-MoS$_2$ sheets behave as a semiconductor with a direct band gap [28,32].

![Figure 1](image-url). (a) Side and (b) top views of MoS$_2$ single layer.
Generally, MoS$_2$ sheets are stacked together by weak van der Waals forces and form few-layer MoS$_2$ nanosheets. As the band gap of MoS$_2$ nanosheets increases from bulk (1.2 eV) to single layer (1.9 eV) [33], it absorbs the visible region of the solar spectrum. Thus, MoS$_2$ can play an important role as a co-catalyst during photocatalysis [29]. MoS$_2$-based semiconductor composites act as co-catalysts that can significantly enhance the efficiency of photocatalytic hydrogen production [7,34–37].

3. Photochemical Hydrogen Evolution Reaction

As mentioned above, Fujishima and Honda reported on photo-induced water splitting on TiO$_2$ electrodes. Hydrogen can also be directly produced from photochemical water splitting. Usually, a photoelectrolytic cell is designed to carry out the photochemical water splitting process. A typical photoelectrolytic cell for water splitting is shown in Figure 2a [38]. Using light sources, the photocatalytic water splitting takes place in several steps: the absorption of light by catalyst on electrode; the generation of charges followed by the excitation of electrons in the valence band; the separation of charge as well as the transport of charge carriers; and the oxidation of water and generation of hydrogen during water splitting, which occur at separate electrodes. The pure, overall water splitting process comprises two half-reactions to generate hydrogen and oxygen molecules, as shown in Figure 2b [39]. Water oxidation occurs at the anode to produce oxygen, whereas H$^+$ ions are reduced on the cathode into hydrogen gas. For more details of photocatalytic water splitting, see the review of Jeong et al. [39].

Figure 2. (a) Schematic device illustration of photoelectrochemical water splitting. Reprinted with permission from Ref. [38] (Copyright 2019 Elsevier). (b) Schematic representation of the photoelectrochemical water splitting process in a common PEC water splitting system consisting of a photoanode and a metal counterpart. Reprinted from Ref. [39].

4. Synthesis of MoS$_2$

Nanostructured MoS$_2$ can be fabricated via both top-down and bottom-up approaches. In the case of the top-down method, the commercially available bulk crystal of MoS$_2$ is physically downsized into MoS$_2$ nanomaterials (Figure 3) [29,40,41], while in the bottom-up approach, MoS$_2$ nanomaterials are synthesized via chemical reaction with small molecules using chemical vapor deposition (CVD) and hydrothermal or solvothermal methods, etc. [42–44]. Single layers, multilayers, nanoparticles, and quantum dots of MoS$_2$ have also been reported [45–48]. Continued efforts have been reported for the fabrication of MoS$_2$ nanomaterials via the top-down and bottom-up strategies [16–19,28–31,40–44].
Waals interactions between Au and MoS$_2$ were characterized using a bright-field optical microscope and an atomic force microscope (AFM). From the AFM measurements, the height of a single MoS$_2$ sheet was found to be 0.8 nm, while the thickness of two, three, and four layers of MoS$_2$ nanosheets was 1.5, 2.1, and 2.9 nm, respectively (Figure 4). The MoS$_2$ nanosheet monolayers showed an enhanced optical performance, especially single-layer MoS$_2$ nanosheets due to its strong affinity for sulfur. It can exfoliate the MoS$_2$ monolayer from the bulk because of the strong van der Waals interactions between Au and MoS$_2$ layers [55–57]. Huang et al. prepared large-area MoS$_2$ nanosheets using a Au-assisted exfoliation strategy [58]. In a typical synthesis, a Au thin layer was deposited on a Ti or Cr adhesion-covered substrate. To develop good contact between a MoS$_2$ bulk crystal on tape and a Au-covered substrate, it should be passed under high pressure. The monolayer sheets with a large area were collected from the surface of the Au after peeling off the tape.

4.1. Top-Down Approach

Exfoliation of MoS$_2$

Due to the layered structure and van der Waals interactions, MoS$_2$ nanosheets can be easily prepared through the exfoliation method. Mechanical, chemical, electrochemical, and liquid-phase exfoliation processes have been reported for the synthesis of MoS$_2$ nanosheets [39–52]. For example, in the mechanical exfoliation technique, the suitable MoS$_2$ flakes are peeled off from the bulk crystal of MoS$_2$ using adhesive tape and shifted onto a specific substrate [46,53]. When the scotch tape is detached, some parts of MoS$_2$ remain on the substrate. As result, single- or few-layer MoS$_2$ nanosheets with random shapes and sizes are obtained. The 2D materials prepared by the exfoliation method have good quality and allow to study the pristine properties of materials and device performance. However, during this process, the thickness and size of the MoS$_2$ are difficult to control, and the resulting materials are inappropriate for large-scale production and scaled-up applications [53,54]. Li et al., mechanically exfoliated single- and multilayer MoS$_2$ nanosheets from SiO$_2$/Si with the adhesive tape method [41]. The flakes of MoS$_2$ were mechanically stripped on Si/SiO$_2$ substrate. The obtained single-layer and multilayer MoS$_2$ materials were characterized using a bright-field optical microscope and an atomic force microscope (AFM). From the AFM measurements, the height of a single MoS$_2$ sheet was found to be 0.8 nm, while the thickness of two, three, and four layers of MoS$_2$ nanosheets was 1.5, 2.1, and 2.9 nm, respectively (Figure 4). The MoS$_2$ nanosheet monolayers showed an enhanced optical performance, especially single-layer MoS$_2$ nanosheets.
It was observed that the van der Waals interactions between MoS$_2$ to SiO$_2$ were much weaker. For this purpose, gold can be used as a substrate to exfoliate the MoS$_2$ nanosheets using a Au-assisted exfoliation strategy. Huang et al. prepared large-area MoS$_2$ nanosheets using a Au-assisted exfoliation strategy and even be directly deposited on the plastic substrate [62]. Recently, metal organic CVD has been reported for the synthesis of MoS$_2$ nanosheets, and MoS$_2$ can even be directly deposited on the plastic substrate [62]. Plasma-enhanced CVD requires a low temperature (150–300 °C) catalyst such as Au [61]. Plasma-enhanced CVD requires a low temperature (150–300 °C) for the growth of MoS$_2$ nanosheets, and MoS$_2$ can even be directly deposited on the plastic substrate [62]. Recently, metal organic CVD has been reported for the synthesis of MoS$_2$ nanosheets [63,64], where organometallic precursors were used as starting materials.

4.2. Bottom-Down Approach

4.2.1. Chemical Vapor Deposition

The CVD technique has a long history and is commonly used for the synthesis of high-quality semiconductor materials. In a typical CVD process of MoS$_2$ nanosheets, the Mo sources are solid precursors of Mo or MoO$_3$ powder, and the S sources are H$_2$S gas or solid S powder [58–61]. The solid MoO$_3$ and vaporized S react with each other in a low-pressure chamber, forming nuclei for the growth of MoS$_2$ [58]. Then, MoS$_2$ slowly grows and enlarges its size on the substrates under carrier gas flow. The temperatures at which MoS$_2$ grows during the CVD process are usually between 700 and 1000 °C, with a metal catalyst such as Au [61]. Plasma-enhanced CVD requires a low temperature (150–300 °C) for the growth of MoS$_2$ nanosheets, and MoS$_2$ can even be directly deposited on the plastic substrate [62]. Recently, metal organic CVD has been reported for the synthesis of MoS$_2$ nanosheets [63,64], where organometallic precursors were used as starting materials.

4.2.2. Physical Vapor Deposition

Advanced technology such as molecular beam epitaxy (MBE) can be used to prepare single-crystal semiconductor thin films. However, its applications are limited to the synthesis of 2D materials [65]. Ordinaty physical vapor deposition is rarely reported for 2D materials. A MoS$_2$–Ti composite was prepared by direct current magnetron sputtering, using Ti and MoS$_2$ materials [66]. In this process, the MoS$_2$ was amorphous.

4.2.3. Solution-Based Process

Solution-based processes are commonly used to synthesize MoS$_2$ nanosheets. Hydrothermal and solvothermal methods are the most interesting for the preparation of MoS$_2$ nanosheets [67,68]. In these methods, the Mo source is commonly a molybdate, such as Na$_2$MoO$_4$ or (NH$_4$)$_6$Mo$_7$O$_{24}$, and the S source is thiourea and thioacetamide and L-cysteine [69–73]. The molybdate reacts with the S or S compound in a stainless steel autoclave. The physicochemical reaction takes place at high temperatures (160–200 °C) and
pressure for at least a few hours. In the solvothermal method, organic solvents such as 1-methyl-2-pyrrolidinone, N,N-dimethylformamide, and polyethylene glycol-600 are used to proceed with the reaction, while in the hydrothermal method, water is used as a solvent. The MoS$_2$ powders obtained from these methods have different sizes and shapes. The sizes and shapes of the products can be adjusted by altering the experimental conditions. To improve the crystalline quality of MoS$_2$, the products are usually post-annealed at high temperature.

The MoS$_2$ nanomaterials prepared through different bottom-up approaches have various sizes, shapes, morphologies, and thicknesses and can be used for many applications.

5. Application of MoS$_2$ as a Co-Catalyst in Photocatalysis for Hydrogen Production

5.1. MoS$_2$/Titanium Dioxide Composites

The semiconducting material titanium dioxide (TiO$_2$) has been employed for hydrogen production due to its good UV light response, non-toxic nature, low cost, chemical stability, and good availability [1,12,24]. However, the photocatalytic energy conversion efficiency of TiO$_2$ for hydrogen production is low due to its wide band gap structure (E$_g$ \(\approx\) 3.2 eV), photogenerated charge recombination, and some reverse reactions [1,2,12,24]. Many strategies have been attempted to improve the catalytic activity of TiO$_2$ nanomaterials, including micro/nanostructure constructing, crystal facet, crystal phase, surface, and tailoring the band gap [9,74,75], but the photocatalytic activity of TiO$_2$ still cannot reach the expected efficiency.

MoS$_2$ is considered a potential co-catalyst for TiO$_2$ materials to boost the efficiency of photocatalytic hydrogen production. Zhu and his coworkers fabricated MoS$_2$/TiO$_2$ photocatalysts with various compositions through a facial mechanochemistry method [76]. The photocatalytic activity of the prepared composite was studied for hydrogen generation under UV irradiation. The 4% MoS$_2$ loaded on TiO$_2$ (4%-MoS$_2$/TiO$_2$) showed maximum hydrogen production at a rate of 150.7 \(\mu\)mol h$^{-1}$, which is about 48.6 times higher than that of pure TiO$_2$ at \(\sim\)3.1 \(\mu\)mol h$^{-1}$. The improved photocatalytic activity of MoS$_2$/TiO$_2$ composites is mainly due to electron transfer from TiO$_2$ to MoS$_2$ nanosheets and the active sites that produce hydrogen. Meanwhile, the recombination rate of electron–hole pairs is also reduced. Furthermore, the relatively good conductivity of MoS$_2$ nanosheets also assisted the photo-induced charge separation, leading to an enhanced photocatalytic performance. Ma et al. reported flower-like MoS$_2$/TiO$_2$ nanohybrid composite photocatalysts obtained from a metal organic framework-derived precursor via facial hydrothermal methods [77]. The flower-like morphology of the MoS$_2$/TiO$_2$ composites was confirmed from SEM images, as shown in Figure 5. In order to investigate the photocatalytic activity, the experiments were conducted under visible light conditions with fluorescein as a photosensitizer. An outstanding improvement in the photocatalytic activity was achieved for the optimized sample (14.6 wt% MoS$_2$ loaded on TiO$_2$) with a hydrogen evolution rate of 10046 \(\mu\)mol h$^{-1}$·g$^{-1}$. They concluded that this high performance of the MoS$_2$/TiO$_2$ composites is associated with the formation of active centers as well as the uniform distribution of MoS$_2$ and TiO$_2$ phases, inducing electrons’ motion to reduce protons. In the proposed photocatalytic activity mechanism, excited electrons from fluorescein transfer to the CB of TiO$_2$. These electrons further move to the surface of MoS$_2$ and combine with protons to produce hydrogen. Liu and his coworker prepared MoS$_2$ nanosheets rooted in TiO$_2$ nanofibers (TiO$_2$@MoS$_2$) using a hydrothermal strategy [19]. They reported single- to few-layer MoS$_2$ nanosheets and TiO$_2$ nanofibers’ porous structure. The MoS$_2$ nanosheets grew vertically on the porous structure of TiO$_2$, and deep rooting MoS$_2$ nanosheets into TiO$_2$ nanofibers put them in close contact for the electron transfer process and structural stability. The hydrogen production rates of the TiO$_2$@MoS$_2$ sample were 1.68 under UV-vis light and 0.49 mmol h$^{-1}$·g$^{-1}$ under visible light.
were studied for photocatalytic HER under visible light conditions. MoS2 with covalently crosslinked MoS2 were evaluated for photocatalytic H2 with an optimal ratio are believed to enhance solar absorption, increase the interfaces, and decrease the electron transfer distance of the photo-excited electrons between C3N4 and MoS2 co-catalysts. Among them, MoS2 and g-C3N4 were mainly responsible for the outstanding photocatalytic hydrogen production rates up to several times.

5.2. MoS2/Graphitic Carbon Nitride Composites

Graphitic carbon nitride (g-C3N4) is considered one of the promising candidates for photocatalysis due to its high chemical stability, environmentally friendly nature, and suitable energy bands that can efficiently absorb solar spectrum irradiation [78–81]. However, g-C3N4 suffers from a small specific surface area, high exciton binding energy, stacking back into a bulk, and low efficiency under visible light [82–84]. Recently, much interest has been devoted to g-C3N4-based composites for solar hydrogen production under visible light. To enhance the efficiency of its photocatalytic activity, various non-precious co-catalysts such as Co2P, Mo2C, and MoS2 have been incorporated with C3N4 [85–87]. Among them, MoS2 as a co-catalyst in MoS2/C3N4 composites shows promising efficiency for photogenerated hydrogen production [87,88].

The design of and nano-interface coupling between MoS2 and C3N4 can significantly enhance the photocatalytic HER performance. The appropriate MoS2/C3N4 composites with an optimal ratio are believed to enhance solar absorption, increase the interfaces, and decrease the electron transfer distance of the photo-excited electrons between C3N4 and MoS2 co-catalysts. Yuan’s group reported MoS2/g-C3N4 composites with various contents of MoS2 developed using the solvent thermal method. The composite catalysts were evaluated for photocatalytic H2 generation [87]. They found that MoS2/g-C3N4 composites containing 0.75% MoS2 nanosheets performed better and had a reaction rate of 1155 μmol·h−1·g−1 under visible light irradiation. The apparent quantum yield was about 6.8% under a monochromatic light of 420 nm. Furthermore, they explained that the large surface area of g-C3N4 nanosheets and the nano-interface coupling between MoS2 nanosheets and g-C3N4 were mainly responsible for the outstanding photocatalytic hydrogen production of the MoS2/g-C3N4 composite. Recently, Li et al., reported the in situ synthesis of a g-CN/MoS2 composite [89]. The composite exhibited enhanced photocatalytic hydrogen production compared to pristine g-CN under visible light irradiation. The rod-like MoS2 plays an important role as co-catalyst in the g-CN/MoS2 composite in the enhancement of the hydrogen production rate. Zhang et al. reported sulfur-doped C3N4 with covalently crosslinked MoS2 nanosheets (MoS2/SC3N4) for improved photocatalytic hydrogen production [88]. The ultrathin array-like nanosheet structure of the MoS2/SC3N4 composites was observed by SEM characterizations (see Figure 6). MoS2/SC3N3 composites were studied for photocatalytic HER under visible light conditions. MoS2/SC3N3 with 2.5%...
MoS2 nanosheets showed the optimal hydrogen production rate of 702.53 μmol·h⁻¹·g⁻¹. The array-like porous morphology had a rich exposed surface, covalent bonding structure, and enhanced visible light absorption by the cyano group of MoS2/SC3N3 composites. This facilitates the photogenerated electrons’ transfer from the CB of SC3N3 to MoS2 via a heterojunction interface that consequently enhances the photocatalytic hydrogen evolution. Zhang et al. reported a MoS2/Fe3O3/g-C3N4 ternary composite photocatalyst under hydrothermal conditions for hydrogen production [90]. The obtained ternary composite showed a hydrogen production rate about five times higher compared to g-C3N4. In addition, 1T MoS2/C3N4 composites also show enhanced photocatalytic hydrogen production [91–94]. Li et al. loaded metallic 1T-phase MoS2 quantum dots onto CdS nanorods (1T-MoS2-CdS) using a one-step hydrothermal method at different temperatures [91]. The 1T-MoS2-CdS composite prepared at 180 °C showed remarkable photocatalytic hydrogen production (131.7 mmol·h⁻¹·g⁻¹) under visible light (λ > 420 nm). This rate of hydrogen evolution was over 65 times greater than that of pure CdS (mmol·h⁻¹·g⁻¹) and two times that of Pt-loaded CdS.

**Figure 6.** SEM images of (a) SC3N2, (b) MoS2 and ultrathin array-like nanosheet, (c) MoS2/SC3N4-0.5%, (d) MoS2/SC3N4-1.5%, (e), MoS2/SC3N4-2.5%, and (f) MoS2/SC3N4-5.0%. Reprinted with permission from Ref. [88]. Copyright 2021 Elsevier.

Besides 1T-phase MoS2, amorphous MoSx nanomaterials are efficient electrocatalysts as well as co-catalysts for hydrogen production [95–97]. They provide more unsaturated active S atoms, which can rapidly capture protons from the solution to convert them into hydrogen molecules. Yu et al. reported amorphous MoSx/g-C3N4 (a-MoSx/g-C3N4) composites developed using an adsorption in situ transformation method [95]. The a-MoSx/g-C3N4 composites were compared with crystalline MoSx/g-C3N4 and g-C3N4 catalysts, and all of the a-MoSx/g-C3N4 catalysts displayed better photocatalytic performances than the crystalline MoSx/g-C3N4 and C3N4 catalysts. Among the a-MoSx/g-C3N4 composites, the a-MoSx/g-C3N4 catalyst with 3 wt% Mo showed the best photocatalytic performance and a hydrogen production rate of 273.1 μmol·h⁻¹·g⁻¹.

Similar to TiO2/MoS2 photocatalysts, MoS2/g-C3N4 heterojunction composites can improve hydrogen production.

5.3. MoS2 Coupling with Other Semiconductor Materials

As discussed earlier, MoS2 as a co-catalyst for other semiconductor compounds can efficiently enhance the photocatalytic activity of hydrogen generation. The interfacial coupling of MoS2 with semiconductor compounds has been designed in many strategies.
An appropriate ratio, increased interface area, and decreased migration distance of the photogenerated electrons between the MoS$_2$ and the semiconductor compounds can effectively improve photocatalytic hydrogen production. Zhang et al. reported MoS$_2$/CdS composites with willow branch-shaped morphology developed using a one-pot hydrothermal method [98]. The MoS$_2$/CdS composite with 5 wt% MoS$_2$ as a co-catalyst displayed an enhanced photocatalytic performance and produced 250.8 µmol h$^{-1}$ hydrogen evolution with an apparent quantum efficiency of 3.66% at 420 nm. Preparation of the willow branch-shaped nano-heterojunction morphology enhances the visible light absorption and also promotes the separation of photogenerated electron–hole pairs.

Ma et al. reported a layered CdS/MoS$_2$ heterostructure photocatalyst developed using ultrasonicated MoS$_2$ and CdS nanosheets, produced from hydro- and solvothermal methods, respectively [99]. When MoS$_2$ co-catalysts were loaded onto CdS nanosheets, the photocatalytic performance of the CdS/MoS$_2$ heterostructure was twice that of the pure CdS photocatalyst. The designing of a layered CdS/MoS$_2$ heterostructure could efficiently enhance the photogenerated charge separation and electron transfer, which improves the surface hydrogen evolution kinetics. Patriarchea and coworkers synthesized CdS nanoparticles using polymer-templated oxidative aggregation, and subsequently, MoS$_2$ nanosheets were deposited on it via the wet chemical method [100]. The obtained optimized MoS$_2$/CdS catalyst showed a good hydrogen production rate of about 0.4 mmol h$^{-1}$ under visible light compared to the CdS catalyst. The enhanced hydrogen generation was due to the presence of the MoS$_2$ co-catalyst.

Samaniego-Benitez and coworkers prepared ZnS/MoS$_2$ heterostructure materials using a one-pot solvothermal method [101]. The hydrogen production yield of the ZnS/MoS$_2$ sample with 10% Mo reached 2600 µmol h$^{-1}$ under UV light for 4 h. They concluded that the enhanced photocatalytic activity was due to the synergistic effect between ZnS and MoS$_2$ and sulfur vacancies created in the ZnS structure during the synthesis process. In the proposed mechanism, a photoexcited electron moves from the CB of ZnS to the CB of MoS$_2$, where it interacts with the proton and produces hydrogen.

Recently, Guan et al., used MoS$_2$ as a co-catalyst for methylammonium lead iodide to split hydrogen iodide for photocatalytic HER [102]. The methylammonium lead iodide microcrystals and MoS$_2$ nanoflowers (MAPbI$_3$/MoS$_2$) formed a heterostructure. The MoS$_2$ nanoflowers have plenty of active catalyst sites for hydrogen evolution. The hydrogen evolution rate of MAPbI$_3$/MoS$_2$ reached ~30,000 µmol h$^{-1}$·g$^{-1}$ and a solar-derived hydrogen iodide splitting efficiency of 7.35% was achieved under visible light irradiation. This hydrogen evolution rate is more than 1000 times higher compared to that of pristine MAPbI$_3$. The MoS$_2$ can induce charge separation and provide abundant active sites for photocatalytic hydrogen evolution.

For these examples, we can conclude that MoS$_2$ is an efficient co-catalyst for CdS, ZnS, and MAPbI$_3$ etc, catalysts to produce hydrogen.

5.4. MoS$_2$ and Other Co-Catalyst Heterojunction Composites

The heterojunction of a MoS$_2$ co-catalyst with other co-catalysts is an attractive strategy because it can improve the photogenerated electron transfer from a semiconductor to a MoS$_2$ co-catalyst during photocatalysis, which enhances the activity via the catalytic sites on MoS$_2$ co-catalysts [103–105]. The heterojuctions between MoS$_2$ and highly conductive co-catalysts decrease the resistance effect and increase the electron transfer process during photocatalysis [106].

For improved photocatalytic H$_2$ evolution, a widely studied example of anchoring a MoS$_2$ co-catalyst on graphene has been reported [107,108]. Xiang et al., synthesized a TiO$_2$/MoS$_2$/graphene hybrid photocatalyst for hydrogen production [18]. The hybrid photocatalyst showed significant enhancement of photocatalytic H$_2$ generation under UV illumination, with an apparent quantum efficiency of 9.7% at 365 nm. The improved activity is described in terms of synergetic effects between MoS$_2$ and the conductive graphene co-catalysts and TiO$_2$ leading to outstanding photocatalytic hydrogen evolution activity.
These authors have proposed a mechanism for the significant boost of photocatalytic H2 generation. They reported that this enhancement is due to the transfer of photogenerated electrons from the CB of TiO2 nanoparticles to the CB of MoS2 nanosheets through highly conductive graphene sheets (Figure 7), where H+ ions are adsorbed at an active site of MoS2. Apart from graphene, other highly conductive materials such as metal sulfides and phosphides can also be used as interfacial electron transfer sources to enhance photocatalytic hydrogen evolution. Lu and coworkers synthesized g-C3N4, Ni2P, and MoS2 heterojunctions by hydrothermal and ultrasonic methods [109]. The hydrogen production rate of the g-C3N4-1%Ni2P-1.5%MoS2 composite was about 532.41 μmol·h⁻¹·g⁻¹ under visible light, which is 5.15- and 2.47-fold higher than those of g-C3N4-1%Ni2P and g-C3N4-1.5%MoS2, respectively. The Ni2P co-catalyst could be acting as an interface electron bridge between g-C3N4 and MoS2 nanosheets. It provides interfacial electron transfer channels in g-C3N4/MoS2 heterostructure composites and prevents the rapid recombination process of photogenerated charge carriers.

Finally, we summarize some heterojunction composites with semiconducting and MoS2 materials in which the MoS2 nanomaterial acts as a co-catalyst for enhanced photocatalytic hydrogen production. Table 1 and Figure 8 show different strategies used for various types of catalysts combined with a MoS2 co-catalyst to form heterojunction composites for enhanced photocatalytic hydrogen production.

![Figure 7. Schematic illustration of the charge transfer and proposed mechanism of electron transfer in TiO2/MoS2/graphene composites. Reprinted with permission from Ref. [18]. Copyright 2012 American Chemical Society.](image-url)
Table 1. Summary of MoS₂ usage as a co-catalyst for various materials to form heterostructures for photocatalytic hydrogen generation.

| Catalyst | Synthesis Method | Light Source | Photocatalytic Activity | No. of Cycles | Total Times of Cycles (h) | Ref. |
|----------|------------------|--------------|-------------------------|---------------|----------------------------|------|
| MoS₂ nanoparticles/TiO₂ nanoparticles | Mechanochemistry | 300 W Xe lamp (λ = 250–380 nm) | 150.7 µmol·h⁻¹·g⁻¹ | 3 | 18 | [76] |
| TiO₂ nanofibers@MoS₂ nanosheets | Hydrothermal | 300 W xenon lamp (λ > 320 nm) | 1.68 mmol·h⁻¹·g⁻¹ | 6 | 30 | [19] |
| Flower-like MoS₂@TiO₂ nanohybrids | Metal organic framework-derived | 300 W Xe lamp (λ ≥ 420 nm) | 10046 µmol·h⁻¹·g⁻¹ | 3 | 10 | [77] |
| MoS₂ nanosheets/TiO₂ nanotubes | Hydrothermal process | 300 W Xe-lamp (λ ≥ 420 nm) | 143.32 µmol·h⁻¹·g⁻¹ | 4 | 14 | [110] |
| MoS₂ nanosheets/g-C₃N₄ nanosheets | Solvothermal method | Visible LED lamp | 1155 µmol·h⁻¹·g⁻¹ | 3 | 12 | [87] |
| S-doped C₃N₄ nanosheets/MoS₂ nanosheets | One-step solid-state strategy | | 702.53 µmol·h⁻¹·g⁻¹ | 6 | 30 | [80] |
| Amorphous MoSₓ nanoparticles/g-C₃N₄ nanosheets | Adsorption in situ transformation method | Low-power LEDs (3W, 420 nm) | 273.1 µmol·h⁻¹·g⁻¹ | 4 | 12 | [95] |
| g-C₃N₄/NCDS/MoS₂ | Thermal polymerization and solvothermal approach | 300 W Xe lamp (λ ≥ 420 nm) | 212.41 µmol·h⁻¹·g⁻¹ | 4 | 16 | [111] |
| ZnS/MoS₂ particles | One-pot solvothermal | Hg pen-lamp (254 nm), (4.4 mW/cm²) | 606 µmol·h⁻¹·g⁻¹ | - | - | [101] |
| MoS₂ clusters/CdS nanorod | Solvothermal method | 300 W Xe lamp (λ ≥ 420 nm) | 12.38 mmol·h⁻¹·g⁻¹ | 4 | | [112] |
| MoS₂/ZnIn₂S₄ microspheres | Impregnation method | 300 W Xe lamp (λ ≥ 420 nm) | 3.06 mmol·h⁻¹·g⁻¹ | 3 | 15 | [113] |
| MoS₂ nanosheets/ZnIn₂S₄ microspheres | In situ photo-assisted deposition | 300 W Xe lamp (λ ≥ 420 nm) | 8.047 mmol·h⁻¹·g⁻¹ | - | - | [114] |
| MoS₂ nanoflake-Mn₀.₂Cd₀.₈S nanorod/MnS nanoparticle | One-pot solvothermal | 300 W Xe lamp (λ ≥ 420 nm) | 995 µmol·h⁻¹ | 5 | 20 | [115] |
We are thankful to the National Natural Science Foundation of China (under research grant no. 22150410332) and the start-up foundation for the introduction of talent at Jiangsu University of Science and Technology, China.

Informed Consent Statement: Not Applicable.

Conflicts of Interest: The authors declare no conflict of interest.

Author Contributions: Conceptualization and validation, S.A.S., I.K. and A.Y.; writing—original draft preparation, S.A.S. and I.K.; writing—review and editing, S.A.S. and A.Y.; supervision, A.Y. All authors have read and agreed to the published version of the manuscript.

Institutional Review Board Statement: Not Applicable.

Data Availability Statement: No supporting data is reported.

Funding: This research received no external funding.

6. Conclusions and Outlook

In summary, we highlighted the significance of MoS₂ as a co-catalyst to improve hydrogen evolution. A comprehensive analysis of the literature led us to conclude that MoS₂ is a good co-catalyst for other semiconducting materials such as TiO₂, C₃N₄, CdS, ZnS, etc., which form heterostructure nanocomposites and consequently boost the photocatalytic hydrogen generation ability. However, there are still some critical issues that must be resolved, such as the downsizing of MoS₂ nanosheets for appropriate band gap alignment and the high density of catalytic active sites. These issues can be solved by reducing the size of MoS₂ to quantum dots or the molecular level, which will certainly enhance the catalytic active sites. The photoexcited electron transfers between photocatalysts and the MoS₂ co-catalyst play an important role during photocatalytic hydrogen generation. The electron transfer mechanism at the interface of a semiconductor photocatalyst and a MoS₂ co-catalyst is yet to be fully investigated and completely understood. It is important to conduct theoretical studies such as density functional theory (DFT) simulations and apply in situ testing methods to understand electron transfer paths. Although MoS₂ nanosheets as a co-catalyst are a promising candidate for photocatalytic hydrogen production, all the challenges require further efforts and study.

Author Contributions: Conceptualization and validation, S.A.S., I.K. and A.Y.; writing—original draft preparation, S.A.S. and I.K.; writing—review and editing, S.A.S. and A.Y.; supervision, A.Y. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not Applicable.

Data Availability Statement: No supporting data is reported.

Acknowledgments: We are thankful to the National Natural Science Foundation of China (under research grant no. 22150410332) and the start-up foundation for the introduction of talent at Jiangsu University of Science and Technology, China.

Conflicts of Interest: The authors declare no conflict of interest.
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