

Recent Progress in Cadmium Sulfide Photocatalysts for Efficient Solar-Driven Hydrogen Production

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Abstract: With the increasingly serious environmental pollution and gradual depletion of fossil fuels, the development of efficient green energy conversion technology has become an urgent global issue. Photocatalytic water splitting for hydrogen production has attracted extensive attention due to its ability to directly convert solar energy into hydrogen energy. However, it still faces bottlenecks such as low light utilization efficiency and low quantum efficiency. Cadmium sulfide (CdS) has become a research hotspot because of its suitable band gap, excellent band structure and low-cost advantages. Nevertheless, problems such as severe photocorrosion and high carrier recombination rate of CdS have seriously restricted its practical application. This paper reviews the research progress in the characteristics, preparation methods and performance improvement strategies of CdS-based photocatalysts in recent years. It elaborates on the basic properties of CdS photocatalysts and several common preparation methods. On this basis, various modification strategies for CdS photocatalysts in hydrogen production are emphatically discussed, including morphology regulation strategy, solid solution engineering strategy, heterojunction construction strategy and element doping strategy, focusing on the efficient utilization of charges, the preparation of CdS-based material composite systems and the improvement of photocatalytic activity. Finally, the development prospects and challenges of CdS-based photocatalytic materials in photocatalytic hydrogen production are prospected.

Key words: Photocatalysis; Cadmium sulfide; Modification strategy; Hydrogen production; Nanostructure

Citation: Wang X Y, Wu G Y, Yan H Q, et al. Recent Progress in Cadmium Sulfide Photocatalysts for Efficient Solar-Driven Hydrogen Production. *Environmental Chemistry and Safety*, 2026, 2, 9600035. <https://doi.org/10.26599/ECS.2026.9600035>

1. Introduction

In contemporary society, the energy crisis and global warming caused by the massive consumption of fossil resources have become imminent problems, and the development and utilization of clean new energy are particularly important [1-4]. Renewable resources such as solar energy, wind energy and hydropower have become the key to solving environmental degradation and energy crisis due to their continuous regeneration ability and relatively low environmental impact [5, 6]. Among them, solar energy is efficiently converted into low-carbon energy through photovoltaic and photothermal technologies, showing particularly prominent application prospects [7, 8].

Among numerous renewable energy sources, hydrogen energy is particularly important due to its high efficiency and cleanliness [9-12], and has important strategic significance [13,

14]. The advantages of hydrogen energy are mainly reflected in three aspects: first, high energy density. The energy density of hydrogen reaches 33.33 kWh/kg, far exceeding that of gasoline (12.7 kWh/kg) [15], making it uniquely potential in the fields of aerospace and mobile transportation; second, zero carbon emission. The combustion of hydrogen only produces water, completely avoiding the emission of greenhouse gases and pollutants [16]; in addition, it has the characteristics of diversified raw material sources, which can be produced through various ways such as water electrolysis, natural gas reforming with carbon capture and biomass [17-19], reducing the risk of energy external dependence. Therefore, accelerating the research and development and application of renewable energy, especially hydrogen energy technology, is of crucial significance for promoting the sustainable development of energy [20, 21]. Current mainstream hydrogen production technologies face significant bottlenecks: natural gas reforming relies on fossil fuels and has high carbon emissions [22, 23]; coal gasification is highly polluting; biomass conversion is limited by raw materials and efficiency [24-26]; water electrolysis needs to rely on clean electricity and has high costs [27-29]. In contrast, photocatalytic water splitting for hydrogen production directly uses solar energy to drive water splitting without external power input [30], which has both environmental protection and economic potential, and has become a key path to

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Received: March 11, 2026; Revised: April 27, 2026; Accepted: May 6, 2026

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build a hydrogen energy economy.

Since Fujishima and Honda discovered TiO_2 photocatalytic water splitting for hydrogen production in 1972, photocatalytic technology has developed rapidly [31], but its industrialization still faces three major challenges [32, 33]: 1. Limited spectral response and low visible light utilization efficiency. Most existing catalysts rely on ultraviolet light, which only accounts for a small part of the solar spectrum; 2. High carrier recombination rate. Photo-generated electron-hole pairs are prone to recombination, resulting in insufficient separation efficiency [34]; 3. Insufficient stability. The stability of photocatalysts decreases during long-term light irradiation and reaction processes, and their structure and chemical composition may change, thereby affecting their photocatalytic activity and hydrogen production efficiency [35]. Therefore, developing new photocatalyst modification strategies to optimize the generation of photo-generated charges, improve their separation efficiency, expand the light absorption range, and develop efficient and stable photocatalysts have become the current research focus in the field of photocatalysis.

As an efficient energy conversion technology, photocatalytic technology plays a crucial role in solving the global energy crisis and promoting sustainable development. This technology realizes the efficient conversion and utilization of solar energy by using light energy to excite semiconductor materials to generate electron-hole pairs and drive a series of chemical reactions. The reaction mechanism of photo-generated carriers under light irradiation is shown in Figure 1. It includes fields such as photocatalytic water splitting for hydrogen production, CO_2 reduction and photoelectrochemical cells, thus providing innovative solutions for solving the problem of traditional energy dependence and environmental challenges [22, 36, 37].

Photocatalytic water splitting for hydrogen production refers to the process of decomposing water into hydrogen and oxygen using solar energy under the action of photocatalysts [38]. The key of this process is to efficiently use light energy to excite semiconductor materials to generate sufficient electron-hole pairs, and effectively separate and transport these charge carriers to drive the redox reaction of water. As shown in Figure 2, step (1) Light absorption and charge generation: the photocatalytic process first involves the absorption of light energy by the photocatalyst. When the energy of incident light is greater than the band gap of the semiconductor photocatalyst, the electrons located in the valence band will absorb energy and jump to the conduction band, forming free electrons and hole pairs. Step (2) Separation and migration of charge carriers: under ideal conditions, the generated electrons will quickly migrate from the conduction band to the surface of the photocatalyst to participate in the reduction reaction; at the same time, holes migrate from the valence band to the surface for oxidation reaction. The recombination of charge carriers will significantly reduce the photocatalytic efficiency. Therefore, reducing the recombination of electrons and holes is the key to improving the efficiency of photocatalytic water splitting for hydrogen production; step (3) Surface reaction kinetics: on the surface of the photocatalyst, electrons and holes participate in reduction and oxidation reactions respectively. Holes can oxidize water molecules to produce oxygen and protons, while electrons can reduce protons to generate hydrogen. Therefore, photocatalytic water splitting for hydrogen production technology can effectively use solar energy to excite semiconductor materials to generate and separate electron-hole pairs, thereby driving the redox reaction of water, which not only improves the energy conversion efficiency, but also provides an important path for the development of sustainable energy technology.

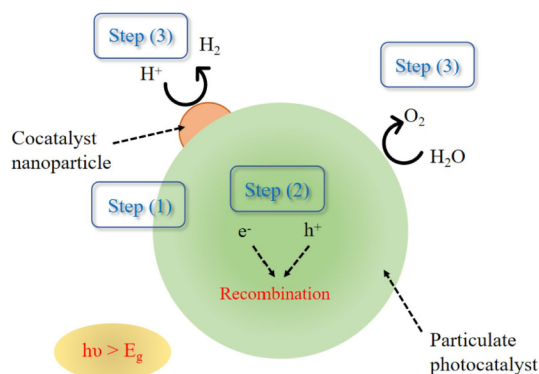


Fig. 2. Three main steps in photocatalytic full water splitting using catalysts.

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Photocatalytic CO_2 reduction is a technology that uses semiconductor photocatalysts driven by solar energy to activate CO_2 and realize its conversion into high calorific value chemicals and fuels [39]. Figure 3 illustrates the basic steps of photocatalytic CO_2 reduction: CO_2 is first adsorbed onto the surface of the photocatalyst, and then catalytically converted into chemicals such as methanol and methane by photoexcited electron-hole pairs [40]. The band structure of the catalyst determines the light absorption and charge carrier separation efficiency, while the surface active sites affect CO_2 adsorption and

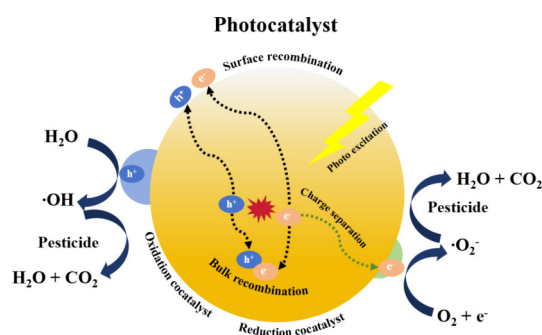


Fig. 1. Reaction mechanism of photogenerated carriers in photocatalysts under light.

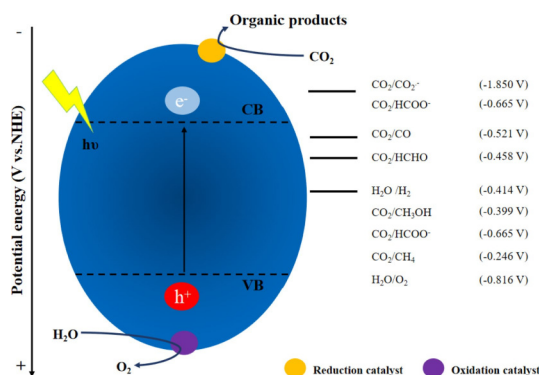


Fig. 3. The basic steps that occur in the photocatalytic reduction of CO_2 .

activation, together governing the reaction kinetics and product selectivity [41, 42]. Therefore, optimizing electronic properties, surface activity, and CO₂ interaction is crucial.

2. Performance Characteristics of Several Representative Semiconductor Photocatalysts

Faced with the challenges of environmental pollution and sustainable energy supply, photocatalytic technology has become an important field of scientific research and technological application due to its high efficiency and environmental friendliness. The core of this technology lies in the innovative development and application of semiconductor photocatalysts, which are widely used in environmental purification, energy conversion and other fields [43-46]. At present, there are many types of photocatalysts applied, and the following are several representative and common photocatalysts:

2.1. Organic Semiconductor Catalysts

Organic semiconductor catalysts refer to materials that use organic materials with semiconductor properties as catalytic active centers or catalytic active carriers, combining the structural design flexibility of organic materials with the photoelectric properties of semiconductor materials [47-50]. They mainly generate photo-generated electron-hole pairs by absorbing light energy, and use these high-energy carriers to drive chemical reactions (such as oxidation, reduction, organic synthesis, etc.) to realize photocatalytic functions. Organic semiconductor catalysts provide a broad space for the development of new high-efficiency, low-cost and environmentally friendly photocatalysts, and are suitable for green catalytic processes using solar energy, such as photocatalytic water splitting for hydrogen production, CO₂ reduction, pollutant degradation and organic synthesis [51-55].

For example, graphitic carbon nitride (g-C₃N₄), as a typical polymer, has attracted long-term attention from researchers due to its characteristics such as low specific gravity, good chemical stability, excellent biocompatibility and suitable band structure [56, 57], and has great application potential in the design of membrane materials, the synthesis of metal nitrides and the preparation of catalysts and catalyst carriers [58-60]. However, due to the fast electron-hole recombination rate and small surface area, the photocatalytic efficiency of g-C₃N₄ is still not ideal [61, 62]. In this regard, many researchers have modified g-C₃N₄ through methods such as morphology regulation and element doping [63, 64]. Lin et al. reported the synthesized composite material of g-C₃N₄/CdS, developed CdS nanosheets on the surface of g-C₃N₄ through in-situ sol-gel method, and found that g-C₃N₄/CdS can effectively inhibit the recombination of photo-generated electrons and holes, and transfer electrons faster than pure g-C₃N₄ [65].

2.2. Inorganic Semiconductor Catalysts

Inorganic semiconductor catalysts are inorganic solid materials that use their semiconductor properties to accelerate specific chemical reactions and maintain their own chemical properties unchanged before and after the reaction. The main characteristics of inorganic semiconductor catalysts are having a specific band gap, being able to absorb photons with energy greater than or equal to its band gap, and realizing the directional migration of carriers under an external electric field to generate highly active photo-generated electrons and photo-

generated holes. In addition, inorganic semiconductor catalysts have the characteristics of high chemical stability and easy solid-state separation, making them key materials in the field of photocatalysis [66].

Titanium dioxide (TiO₂) is a commonly used semiconductor photocatalyst, which is well-known for its excellent chemical stability, low toxicity, wide resource availability and effective photocatalytic performance. However, the photocatalytic application of TiO₂ is limited by its disadvantage of only absorbing ultraviolet light (accounting for about 5% of the solar spectrum), which limits its efficiency in photocatalytic applications [67, 68].

CdS is another type of II-VI semiconductor material, which has shown great application potential in the field of photocatalysis due to its excellent physical and chemical properties. CdS has a narrow band gap (about 2.4 eV), which can effectively absorb visible light, making it highly efficient in photocatalytic applications. In addition, CdS has a high valence band position, which is conducive to oxidation reactions, making it outstanding in fields such as photocatalytic water splitting for hydrogen production or photocatalytic degradation of organic pollutants. However, CdS faces problems such as photocorrosion and low photocatalytic efficiency in practical applications, which limit its photocatalytic performance and environmental safety [69].

Despite the above challenges, CdS still has broad research and application prospects due to its excellent visible light-driven performance, and has become one of the hotspots in the field of photocatalytic research. The research on CdS is promoting the development of environmental purification and green energy conversion technologies. To improve its application performance in fields such as photocatalytic water splitting, organic pollutant degradation and energy conversion, continuous improvement of CdS structure and performance is crucial to ensure the stability of its photocatalytic activity and promote the innovation of related technologies. By developing more stable and efficient CdS-based photocatalysts, their application efficiency can be significantly improved, thereby contributing to the realization of sustainable development goals. These efforts not only show the close combination of technological innovation and environmental protection, but also provide an important scientific basis for solving global environmental and energy problems.

3. Cadmium Sulfide Photocatalysts

3.1. Characteristics of Cadmium Sulfide Materials

In the 1970s, with the growth of demand for renewable energy and the enhancement of environmental protection awareness, scientists sought ways to efficiently utilize solar energy. In this process, semiconductor materials have become the focus of research due to their ability to trigger chemical reactions under light irradiation. As one of the II-VI semiconductor materials, CdS initially attracted attention because of its unique photoelectric properties [70]. Studies have found that CdS can effectively generate electron-hole pairs under visible light irradiation, showing strong light absorption capacity, thus demonstrating potential application value in the field of photocatalysis. Further experimental studies have confirmed the photocatalytic activity of CdS: under light irradiation condi-

tions, water molecules or other small molecules adsorbed on the surface of CdS can be decomposed through the redox reaction of photo-generated electrons or holes to drive photocatalytic reactions. This research has laid the foundation for the application of CdS in fields such as photocatalytic water splitting and organic matter degradation. With the further exploration of the CdS photocatalytic mechanism and the improvement of its photocatalytic efficiency and stability, the application prospects of CdS in the field of photocatalysis have been widely recognized, stimulating more in-depth scientific research. CdS have the following significant characteristics: first, in terms of photoelectric properties, CdS has a direct band gap and can effectively absorb a wide spectrum from visible light to ultraviolet region. This characteristic makes it occupy an important position in photoelectric conversion and photocatalytic applications. Second, CdS has high electron mobility, which is of great significance for manufacturing high-efficiency electronic devices and photodetectors. At the same time, the band gap of CdS is adjustable, and the band gap width of CdS can be adjusted through specific synthesis methods or modification technologies to meet diverse application needs. In addition, under specific conditions, CdS exhibits certain biocompatibility, providing possibilities for its application in the field of biological labeling and imaging [71]. Rapid recombination of photogenerated electron-hole pairs and fast photocorrosion are the main issues faced by CdS materials. Most current reports attribute the primary cause of photocorrosion to the accumulation of photogenerated holes on the surface, which oxidize lattice sulfur ions into elemental sulfur or sulfate, thereby destroying the catalyst structure. In addition, dissolved oxygen in water exacerbates the corrosion: on one hand, oxygen itself is oxidizing; on the other hand, oxygen can combine with photogenerated electrons to form superoxide radicals (O_2^-), further accelerating the decomposition of CdS. Therefore, there are two main pathways for the photocorrosion of CdS: one is the hole-dominated oxidation pathway, and the other is the oxygen-accelerated corrosion pathway.

3.2. Preparation Methods of Cadmium Sulfide Photocatalysts

There are various preparation methods for CdS photocatalysts, and different preparation technologies will affect the morphology, structure, light absorption performance and photocatalytic efficiency of photocatalysts to varying degrees. The common preparation methods of CdS are as follows:

3.2.1. Chemical Vapor Deposition Method

The chemical vapor deposition (CVD) method is a process of guiding gaseous precursors to react on the substrate to form thin films or nanostructures under high temperature conditions [72]. In the synthesis of CdS, precursor gases containing sulfur and cadmium react in the reaction chamber under controlled temperature and pressure conditions to form CdS. This technology can precisely control the thickness, composition and morphology of the film, and is suitable for preparing CdS films with high crystallinity and excellent photoelectric properties [73]. For example, Peng et al. used CVD technology to construct a heterojunction photoanode with a unique core-shell nanostructure, using one-dimensional (1D) oriented CdS nanorods (NR) in a plane-to-plane stacking manner. The obtained CdS/MoS₂ heterojunction structure exhibits better cor-

rosion resistance and higher photostability [74]. However, the high temperature requirement and equipment dependence of the CVD method may limit its wide use in low-cost and scalable application fields [75].

3.2.2. Room Temperature Solution Growth Method

The solution growth method is a method for preparing CdS nanomaterials through chemical reactions in solutions. This method usually uses aqueous solutions or organic solvents containing cadmium sources and sulfur sources as reaction media. By adjusting reaction conditions such as temperature, time, pH value and adding surfactants, various forms of CdS nanostructures can be directly grown in the solution, including nanoparticles, nanorods, nanowires and nanoflowers. For example, Andre Slonopas et al. explored the influence of temperature changes on the growth mechanism and performance of CdS under room temperature solution growth conditions [76]. The solution growth method has the advantages of simple operation, low cost and easy large-scale production, and is one of the commonly used methods for preparing CdS nanomaterials [77].

3.2.3. Microwave-Assisted Synthesis Method

As an efficient and rapid chemical synthesis technology, microwave-assisted synthesis method has been widely used in the preparation of various nanomaterials. This method uses the characteristics of microwave radiation to directly heat the reactants in the solution, significantly accelerating the rate of chemical reactions by promoting intermolecular collisions and energy conversion, thereby obtaining the desired nanomaterials in a short time. Compared with traditional thermal heating methods, microwave heating can achieve more uniform and rapid heating, avoiding uneven reaction problems caused by temperature gradients and thermal inertia, thus enabling the preparation of CdS nanomaterials with higher purity and more uniform size distribution [78]. For example, Deng et al. prepared layered binary CdS/BiOCl heterojunctions using a microwave-assisted method, reducing carrier recombination loss and prolonging the lifetime of electron-hole pairs, achieving efficient photocatalytic hydrogen production [79].

3.2.4. Hydrothermal/Solvothermal Method

The hydrothermal/solvothermal method is widely recognized as an effective low-temperature synthesis strategy. This method relies on water or other organic solvents as the reaction medium in a closed container, and utilizes specific temperature and pressure conditions to promote chemical reactions, thereby realizing the preparation of CdS nanomaterials. A significant advantage of this technology is its ability to produce high-purity and high-crystallinity CdS nanomaterials at relatively low temperatures, which is particularly important for application scenarios such as photocatalysis. By precisely regulating experimental parameters (e.g., reaction temperature, pressure, time, and precursor concentration), the solvothermal method can effectively adjust the morphology and size of the products. For example, Yang et al. synthesized cubic and hexagonal phase CdS respectively by changing the reaction time using the hydrothermal method [80]. The hydrothermal/solvothermal method can not only achieve precise control of various structures ranging from zero-dimensional to three-dimensional, but also further optimize the microstructure of products by introducing template methods or self-assembly

technologies to meet the needs of specific applications. Compared with traditional solution growth methods, the solvothermal method has obvious advantages [81]. First, it enables the synthesis of nanomaterials at lower temperatures, which helps maintain the purity and crystallinity of the materials. Second, this method provides an approach to conduct chemical reactions in a closed environment, facilitating precise control of reaction conditions and high-efficiency conversion. In addition, the solvothermal method can achieve precise regulation of the microstructure of products, thereby obtaining CdS nanomaterials with excellent optoelectronic properties. CdS nanomaterials prepared by this method, due to their high purity, high crystallinity and adjustable microstructure, exhibit good application prospects when applied in the field of photocatalysis. The development of this synthesis strategy provides new ideas and methods for the design and application of nanomaterials.

4. Performance Improvement Strategies of Cadmium Sulfide Photocatalysts

As an important photocatalytic material, CdS has attracted much attention in the field of photocatalysis, especially in water splitting for hydrogen production, due to its suitable band gap width (about 2.4 eV) and strong visible light response ability [82-84]. To further improve the performance of CdS in photocatalytic hydrogen production activity, the key is to optimize the following key limiting factors: 1. Improvement of charge separation and migration efficiency; 2. Expansion of light absorption capacity; 3. Increase of active sites; 4. Enhancement of photochemical stability and photocorrosion resistance [85-87]. Common improvement strategies are shown in Figure 4: morphology regulation strategy, solid solution engineering strategy, heterojunction construction strategy and element doping strategy.

4.1. Morphology Regulation Strategy

In the photocatalytic application of CdS, the crystal structure and microscopic morphology have an important impact on its performance. CdS has two main crystal phases: cubic zinc

blende structure and hexagonal wurtzite structure [88]. The hexagonal wurtzite structure is generally considered to perform better in photocatalysis due to its higher surface activity and more effective charge carrier separation ability. In addition, the microscopic morphology of CdS, such as nanowires [89], nanotubes [90] and nanosheets [91], can not only increase active sites, but also promote the rapid migration and efficient separation of photo-generated carriers, thereby greatly improving photocatalytic performance. Morphology regulation can be achieved through various synthesis technologies, including solution method, hydrothermal method, solvothermal method, chemical vapor deposition and other synthesis technologies. Through these technologies, the microstructure of CdS can be precisely regulated, and various forms of photocatalytic materials with excellent photocatalytic properties can be prepared. Table 1 summarizes CdS with different morphologies and their corresponding performance in photocatalytic hydrogen production.

4.1.1. Zero-Dimensional Structures

Zero-dimensional structures such as quantum dots and nanoparticles are confined in all three dimensions, resulting in significant quantum size effects. The band gap is adjustable (the band gap of bulk CdS is about 2.4 eV, and the band gap of nanoparticles increases with decreasing size, and the absorption/emission spectrum blue-shifts). Zero-dimensional struc-

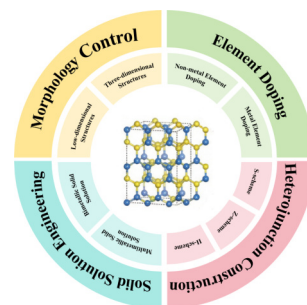


Fig. 4. Common Modification Strategies for Cadmium Sulfide-based Materials.

Table 1. Shows research progress in improving the photocatalytic hydrogen production performance of CdS via morphology regulation strategies.

Photocatalysts	Type	Field	Experimental condition	Light source	Yield (mmol/g/h)	Ref
CdS QDs/P-CNT	0D	HER	10 mg catalyst, Na ₂ SO ₃ (0.35 M), Na ₂ S (0.35 M)	300 W Xe-lamp (λ = 420 nm)	H ₂ : 1.58	[92]
CdS/MoO _{3-x}	0D	HER	25 mg catalyst, 80 mL lactic acid solution (10 vol.%)	350 W Xenon	H ₂ : 7.44	[93]
CdS/Ni-MOF	0D	HER	30 mg catalyst, 3.6 mL lactic acid	300 W Xenon (λ = 420 nm)	H ₂ : 19.6	[94]
CW-3	0D	HER	30 mg catalyst, 10 mL lactic acid,	300 W Xenon (λ > 420 nm)	H ₂ : 14.34	[95]
Ni(OH) ₂ /Zn _{0.5} Cd _{0.5} S	0D	HER	40 mg catalyst, Na ₂ SO ₃ (0.35 M), Na ₂ S (0.35 M)	300 W Xe-lamp (λ > 400 nm)	H ₂ : 6.87	[96]
MnO ₂ @CdS	1D	HER	50 mg catalyst, Na ₂ SO ₃ (0.35 mol/L), Na ₂ S (0.35 mol/L)	300 W Xe-lamp (λ = 420 nm)	H ₂ : 3.94	[97]
WC	1D	HER	10 mg catalyst, 10 mL lactic acid	300 W Xe-lamp (λ = 420 nm)	H ₂ : 70	[98]
CZZ	1D	HER	10 mg catalyst, Na ₂ SO ₃ (0.35 mol/L), Na ₂ S (0.35 mol/L)	225 W Xe-lamp (λ 320-780 nm)	H ₂ : 27.25	[99]

Table 1. (Continued)

Photocatalysts	Type	Field	Experimental condition	Light source	Yield (mmol/g/h)	Ref
CdS-MX	1D	HER	5 mg catalyst, 10 mL C ₂ H ₅ OH, 30 mM H ₂ SO ₄	300 W Xe-lamp (λ = 420 nm)	H ₂ : 15.4	[100]
WS ₂ /CdS	2D	HER	3 mg catalyst, 20 mL lactic acid (10 vol.%)	300 W Xenon (λ = 420 nm)	H ₂ : 58.1	[101]
CdS/2%Ni ₂ SP	2D	HER	5 mg catalyst, Na ₂ SO ₃ (0.25 M), Na ₂ S (0.25 M)	300 W Xe-lamp (λ = 420 nm)	H ₂ : 18.96	[102]
CM3	2D	HER	10 mg catalyst, Na ₂ SO ₃ (0.25 mol/L), Na ₂ S (0.35 mol/L)	300 W Xenon (λ = 420 nm)	H ₂ : 65.4	[103]
CdS-COF	2D	HER	10 mg catalyst, 0.1 M ascorbic acid	300 W Xenon (λ = 420 nm)	H ₂ : 15.1	[104]
MX-CdS/WO ₃	2D	HER	5 mg catalyst, 10 wt.% lactic acid	300 W Xe-lamp (λ > 420 nm)	H ₂ : 27.5	[105]
CM-20	1D	HER	10 mg catalyst, 10 wt.% ascorbic acid	300 W Xe-lamp (λ = 420 nm)	H ₂ : 2.41	[106]
CdS/n-rGO	3D	HER	10 mg catalyst, Na ₂ SO ₃ (0.35 M), Na ₂ S (0.25 M)	300 W Xe-lamp (λ 420-760 nm)	H ₂ : 2.17	[107]
3DOM g-C ₃ N ₄ /CdS	3D	HER	50 mg catalyst, Na ₂ SO ₃ (0.1 mol/L), Na ₂ S (0.1 mol/L), 3 wt.% Pt,	300 W Xe-lamp (λ ≥ 420 nm)	H ₂ : 0.72	[108]
CdS/3DGN	3D	HER	50 mg catalyst, Na ₂ SO ₃ (0.5 M), Na ₂ S (0.5 M), 1 wt.% Pt	300 W Xenon (λ > 400 nm)	H ₂ : 2.31	[109]

tures have the characteristics of high specific surface area and large proportion of surface atoms, and are prone to surface modification or functionalization [110-113]. Zero-dimensional CdS structures can be prepared by sol-gel method, hydrothermal/solvothermal method, thermal decomposition method and other methods. Qian et al. modified CdS quantum dots (CdS QDs, zero-dimensional structure) on phosphorus-doped hexagonal carbon nanotubes (P-CNT, one-dimensional structure) using an oil bath method to prepare a 0D/1D heterojunction photocatalyst [92]. From the TEM image, it can be seen that the CdS nanoparticles are uniformly loaded in P-CNT (Figure 5a). Through ultraviolet-visible diffuse reflectance spectroscopy (UV-Vis DRS) (Figure 5b), the visible light absorption capacity of the CdS QDs/P-CNT composite system is significantly better than that of pure P-CNT, CNT and bulk CdS, proving the enhancement effect of the zero-dimensional structure on light absorption. Zero-dimensional CdS QDs can be uniformly dispersed on carbon nanotubes, effectively solving the agglomeration defect of bulk CdS materials, avoiding the shielding of active sites caused by particle agglomeration, and reducing the light absorption shielding effect. Under the conditions of a 300 W xenon lamp (420 nm cut-off filter) and Na₂S/Na₂SO₃ sacrificial agent, the hydrogen production rate of the heterojunction reaches 1579 μmol h⁻¹ g⁻¹, while the hydrogen production rates of pure P-CNT and pure CdS are 50 μmol h⁻¹ g⁻¹ and 233 μmol h⁻¹ g⁻¹ respectively. The hydrogen production efficiency of the composite material is 31.6 times and 4.7 times that of pure P-CNT and pure CdS respectively. Similarly, Peng et al. loaded CdS nanoparticles (0D) on MoO_{3-x} nanosheets (2D) through a co-precipitation method to form a 0D/2D S-scheme heterojunction, effectively avoiding the agglomera-

tion of CdS nanoparticles [93]. The composite material exhibits efficient hydrogen production (Figure 5c), which is mainly due to the short charge migration distance of 0D CdS and the electron transport capacity of the 2D carrier.

The current challenges of zero-dimensional CdS are mainly insufficient separation efficiency of photogenerated charge carriers, as well as the risks of photocorrosion and agglomeration caused by high surface energy. Future strategies include constructing S-scheme or Z-scheme heterojunctions to enhance charge separation, improving photocorrosion resistance through surface modification, and developing controllable and scalable preparation techniques for precise regulation of morphology and dispersion.

4.1.2. One-dimensional Structure

Common morphologies of one-dimensional structures include nanowires, nanorods, nanotubes, etc. One-dimensional CdS nanorods and nanowires with high aspect ratios are characterized by nanoscale confinement in the diameter direction and extension in length. This unique morphology induces significant quantum confinement effects and surface/interface effects at the microscale. Compared with traditional zero-dimensional nanoparticles and two-dimensional nanosheets, one-dimensional nanorods provide longer charge transport paths, which greatly reduces the recombination rate of electrons and holes during migration [114-116]. These significant performance improvements enable CdS nanorods to exhibit outstanding efficiency advantages in the application of photocatalytic water splitting for hydrogen production. For example, Peng et al. designed a one-dimensional hierarchical nanorod array composed of CdS/Au/SnO₂ for efficient hydrogen production [117]. Li et al., on the other hand, combined one-dimensional

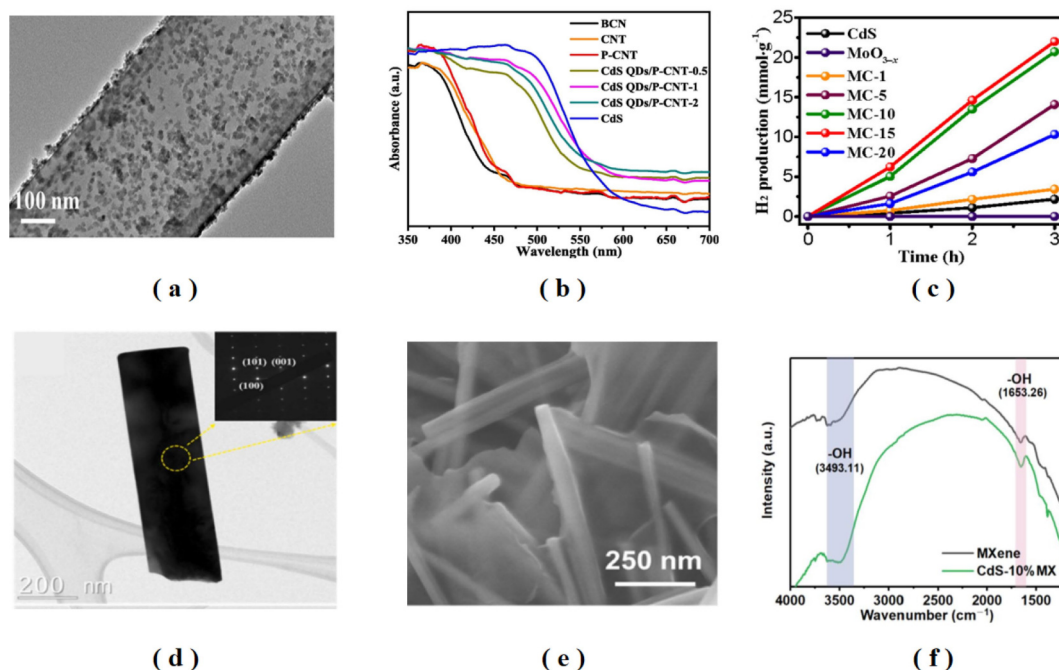


Fig. 5. (a) HRTEM image of CdS QDs/P-CNT-1, (b) UV-vis absorption spectra of CdS, BCN, CNT, P-CNT and CdS QDs/P-CNT composite. Reproduced with permission [92]. Copyright 2020, Academic Press Inc. (c) Photocatalytic H_2 evolution performances. Reproduced with permission [93]. Copyright 2021, ELSEVIER. (d) Low magnification TEM image and SAED pattern (insert) of the single-crystalline CdS nanorod. Reproduced with permission [117]. Copyright 2021, ELSEVIER. (e) SEM images of binary CdS-MX, (f) FT-IR results of MXene and CdS-10%MX. Reproduced with permission [100]. Copyright 2020, ELSEVIER.

(1D) CdS nanowires with two-dimensional (2D) MXene structures [100]. The low-magnification TEM image and SAED pattern of the CdS nanorod indicate that it has a single-crystal structure (Figure 5d), which is conducive to axial electron transport. Meanwhile, the 1D array structure provides a stable substrate for the loading of Au and SnO_2 , forming a uniform heterojunction interface. MXene forms a heterojunction through electrostatic self-assembly, and the 1D structure offers an axial electron transport channel, enhances interface contact, and effectively inhibits MXene agglomeration (Figure 5e). FT-IR spectroscopy data (Figure 5f) provide additional confirmation: the composite exhibits stronger $-\text{OH}$ signals at 3493.11 and 1653.26 cm^{-1} than pure MXene. This signifies that cadmium sulfide inhibits the agglomeration of MXene nanowires. The resulting higher surface area exposes a greater number of $-\text{O}$ end groups on MXene, which in turn enables faster H_2 release. Similarly, Li et al. constructed an organic-inorganic composite membrane photocatalytic system with high activity, high stability, and scalability by a three-step modification process using one-dimensional CdS nanorods as the core, involving SiO_2 coating, Pt loading, and PVDF composite film formation. This provides a new approach for the practical application of plate-type photocatalytic hydrogen production [118].

Although one-dimensional CdS have lower charge recombination rates than zero-dimensional ones, they still face issues such as photocorrosion and easy agglomeration, as well as challenges like difficulty in precise orientation control. Future development can focus on further optimizing 1D/2D (e.g., CdS/MXene) or 1D/0D heterojunctions to enhance charge separation efficiency; designing ordered one-dimensional arrays and multilayer composite membrane structures to promote the practical application of flat-plate photocatalytic hydrogen

production; and enhancing photocorrosion resistance through surface modification (e.g., SiO_2 coating, Pt loading).

4.1.3. Two-dimensional Structure

Two-dimensional structures, such as nanosheets and nanobelts, are regarded as ideal choices for improving photocatalytic efficiency due to their large specific surface area and enhanced light absorption efficiency [119, 120]. Using a solvothermal approach, T.Y. Huang and colleagues achieved the in-situ epitaxial growth of two-dimensional CdS nanosheets onto the surface of 2D MXene, successfully fabricating a 2D/2D $\text{Ti}_3\text{C}_2\text{X}_x$ MXene/CdS (CMX) heterojunction catalyst (Figure 6a) [103]. The two-dimensional nanosheet structure endows the material with a larger specific surface area (Figure 6b) and exposes more catalytic active sites. UV-Vis spectroscopy (Figure 6c) shows that its light absorption range is extended to the near-infrared region. Photocurrent tests and electrochemical impedance spectroscopy confirm that it possesses high carrier separation efficiency and excellent carrier transport performance. Photocatalytic hydrogen production experiments indicate that the hydrogen production rate of this catalyst reaches $28.7\text{ mmol g}^{-1}\text{ h}^{-1}$, which is 4.2 times that of pure CdS (Figure 6d).

Two-dimensional cadmium sulfide (e.g., nanosheets) offers advantages such as large specific surface area, abundant active sites, an extended light absorption range into the near-infrared region, and excellent charge carrier separation and transport performance. However, it still faces the inherent issue of photocorrosion of CdS. Moreover, two-dimensional nanosheets are prone to interlayer stacking or agglomeration during preparation and use, and challenges remain in the precise control of orientation, layer number, and interfacial contact. In the future, further optimization of 2D/2D heterojunc-

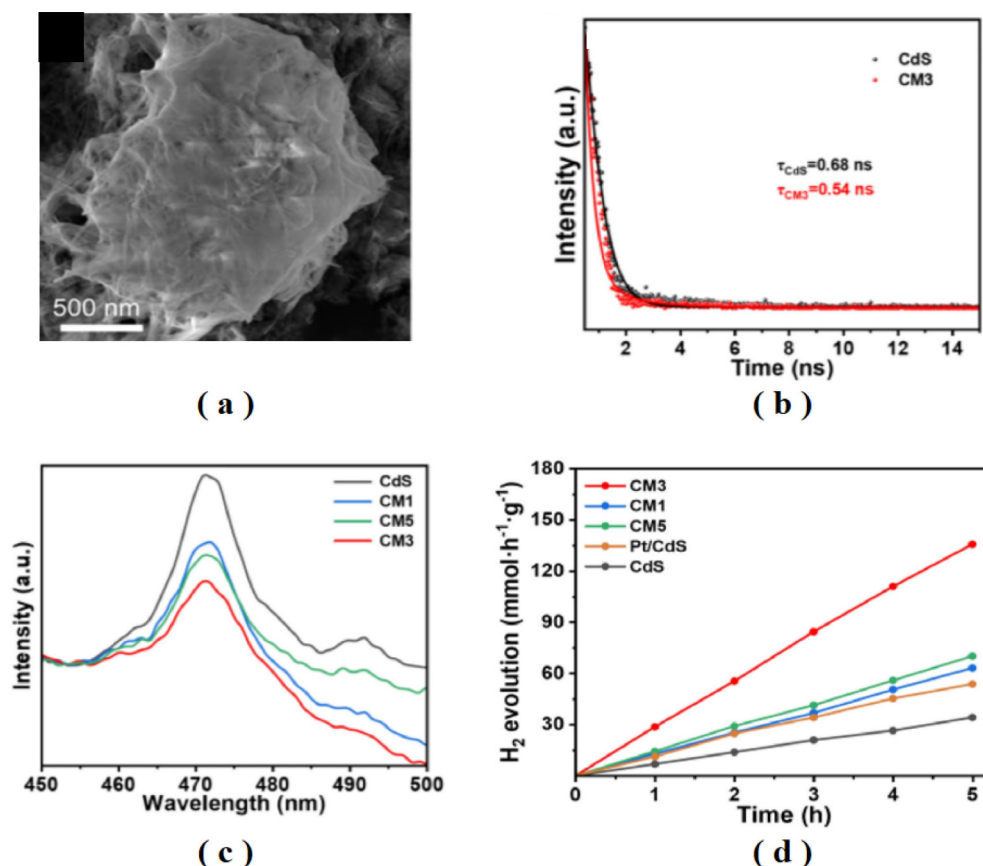


Fig. 6. (a) SEM image of CM3, (b) PL decay spectra of CdS and CMX, (c) UV-vis diffuse reflectance spectra of CdS and CMX, (d) Hydrogen evolution of different samples. Reproduced with permission [103]. Copyright 2024, ELSEVIER.

tion interfaces can enhance charge separation, and photocorrosion can be suppressed through surface modification or doping, thereby promoting practical applications in photocatalytic hydrogen production.

4.1.4. Three-dimensional Structure

In recent years, three-dimensional structural nanomaterials have attracted much attention in academic and industrial circles. Compared with traditional two-dimensional and one-dimensional materials, the unique spatial architecture of three-dimensional materials can provide more active sites, more efficient charge transport paths, and better structural stability [121]. In the field of nanomaterials, researchers are committed to developing novel three-dimensional structures to improve material performance. For example, preparation technologies such as template method and self-assembly method are used to construct nanomaterials with complex three-dimensional network topological structures, so as to meet the special performance requirements of materials in different fields.

The complex structure of three-dimensional cadmium sulfide endows it with an extremely high specific surface area, which can provide a large number of surface active sites and enhance photocatalytic activity. For example, Qi et al. prepared a three-dimensional structure using cellulose nanofibrils (CN) as the skeleton [122] and CdS quantum dots modified by titanate nanofibers (TN) (TN-CdS) as the photocatalyst (Figure 7a, b). The specific surface area of this heterojunction reaches 31.90 m²/g, which is significantly higher than that of CN (6.70 m²/g) and TN-CdS (0.56 m²/g). The three-dimensional pores increase the effective contact area by more than 5

times (Figure 7c). Tong Tian et al. fabricated a three-dimensional (3D) network structure photocatalyst of cadmium sulfide/ethylenediamine hybrid nanowires (CdS/EDA NW) with adjustable sulfur vacancy concentration using the hot melt method (Figure 7d) [123]. In this structure, the protonated EDA molecules modified on the surface of CdS assemble into a 3D structure with a large specific surface area and a hierarchical pore structure. This not only enhances visible light capture capability but also provides fast channels for mass transport. Meanwhile, the three-dimensional architecture shortens the carrier migration distance. Combined with the capture of photo-generated electrons by sulfur vacancies and the inhibition of charge recombination by ethylenediamine molecules, it effectively promotes charge separation and achieves efficient hydrogen production.

The construction of three-dimensional cadmium sulfide skeletons can significantly optimize carrier transport dynamics. For example, Wang et al. successfully constructed a three-dimensionally ordered macroporous (3DOM) g-C₃N₄/CdS heterojunction structure by combining the silica template method with a light-assisted deposition strategy (Figure 7e) [108]. Time-resolved photoluminescence (TRPL) spectroscopy shows that the average carrier lifetime of 3DOM g-C₃N₄/CdS (4.90 ns) is significantly shorter than that of bulk g-C₃N₄ (8.39 ns) (Figure 7f); meanwhile, the 3DOM composite exhibits the smallest arc radius in electrochemical impedance spectroscopy (EIS) (Figure 7g). The above results confirm that the reduced pore wall thickness effectively shortens the migration path of photo-generated electron-hole pairs and inhibits non-radiative recombination. Li et al. loaded single-atom Ti

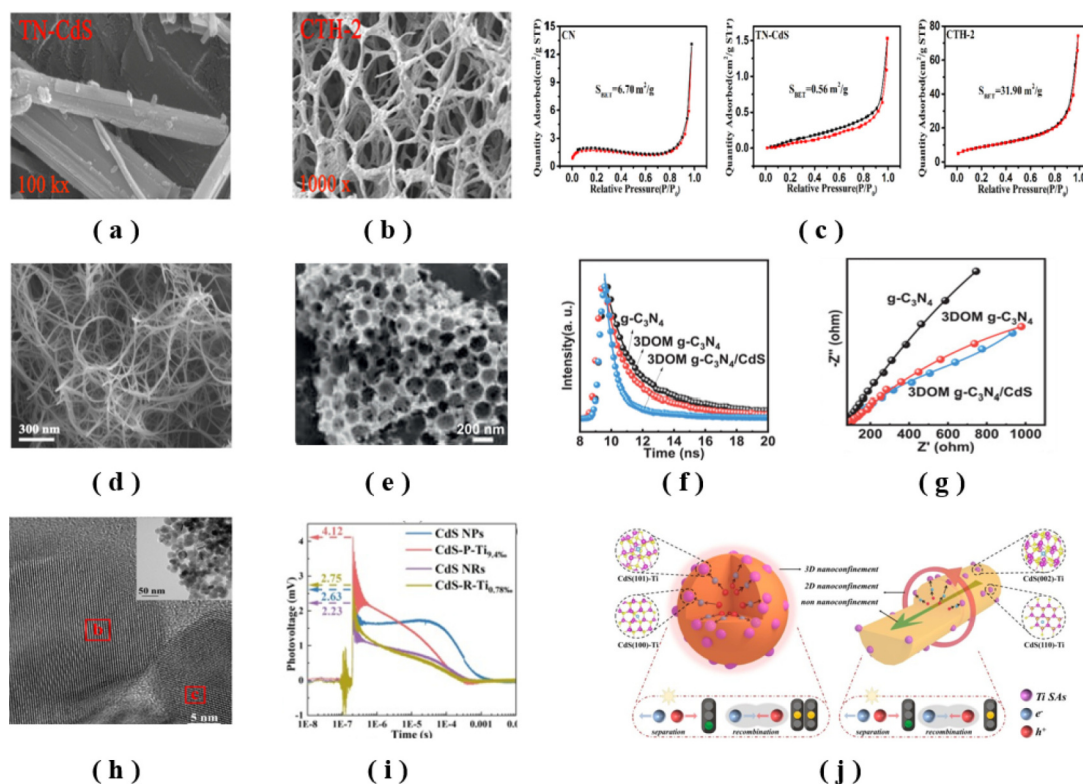


Fig. 7. (a) SEM image of TN-CdS, (b) SEM image of CTH-2, (c) N₂ adsorption-desorption isotherm for CN, TN-CdS and CTH-2. Reproduced with permission [122]. Copyright 2024, ELSEVIER SCI LTD. (d) SEM image of CdS/EDA NW, Reproduced with permission [123]. Copyright 2022, ELSEVIER. (e) TEM image of 3DOM g-C₃N₄, (f) decay time spectra of samples, (g) EIS curves of samples. Reproduced with permission n [108]. Copyright 2022, ELSEVIER. (h) HRTEM images of CdS-P-Ti_{9.49%}, (i) Photocurrent curves of samples with time at applied potential 0.3 V, (j) the comparison of H₂ evolution rates for samples. Reproduced with permission [124]. Copyright 2023, ELSEVIER SCIENCE SA.

onto three-dimensional CdS nanoparticles and one-dimensional CdS nanorods, respectively, and elucidated the intrinsic mechanism by which three-dimensional nanoconfinement enhances photoexciton migration dynamics [124]. Surface photovoltage (TPV) measurements (Figure 7h) show that the intensity of the three-dimensional CdS particles is much higher than that of the CdS nanorods, indicating that the migration efficiency of photoexcitons from the bulk to the surface is significantly improved in the three-dimensional CdS. Furthermore, the kinetic mechanism diagram (Figure 7i) reveals that the three-dimensional CdS has a higher proportion of exposed facets, exposing more S atom sites, which facilitates the formation of synergistic H-G dynamics and significantly reduces the energy barriers for H₂O adsorption/dissociation and H* adsorption/reduction.

Benefiting from the advantages brought by their unique spatial architecture, researchers have developed the structures of three-dimensional structural nanomaterials using preparation technologies such as template method and self-assembly method to improve their performance. This section focuses on three-dimensional cadmium sulfide nanomaterials in enhancing specific surface area, optimizing carrier transport dynamics, and their photocatalytic applications. The unique three-dimensional spatial architecture endows them with an extremely high specific surface area, which can provide a large number of surface active sites and improve catalytic, adsorption and other properties. For example, three-dimensional CdS heterojunctions and CdS/EDA NW three-dimensional network structures both enhance photocatalytic

activity and CO₂ adsorption capacity due to their large specific surface area. In addition, compared with one-dimensional and two-dimensional structural materials that are prone to agglomeration and structural damage, the spatial architecture of three-dimensional materials can enhance their own stability and prolong their service life. A reasonable three-dimensional structure (such as ordered pores and skeleton structures) can construct efficient charge transport paths, shorten the carrier migration distance, and inhibit charge recombination. However, three-dimensional materials still face many challenges, such as cumbersome processes, high costs, and insufficient interfacial bonding strength between different components, which are likely to affect performance. Based on the above analysis, the future development of three-dimensional materials can focus on green preparation paths to reduce preparation costs. In terms of performance improvement, surface modification methods such as doping and coating can be used to increase the interfacial bonding force between components in three-dimensional composite materials, optimize electron transport channels, reduce interfacial charge recombination, and enhance performance synergy.

4.2. Solid Solution Engineering Strategy

The construction of solid solutions by integrating CdS with other semiconductor materials to form a homogeneous mixed solid solution provides an effective pathway for enhancing the performance of photocatalysts [125, 126]. This strategy offers several advantages: First, precise regulation of band structure: The formation of solid solutions enables the adjustment of the band gap of CdS to enhance its visible light absorption capac-

ity, thereby improving solar energy utilization efficiency. Taking the CdS-ZnS solid solution as an example, adjusting the band structure can significantly broaden the light absorption range [91]. Therefore, precise regulation and design of the band structure of the material to manipulate the edge positions of the conduction band and valence band have become a key research direction in the field of photocatalysis. As shown in the Figure 8, the band gap energy diagrams of several common photocatalysts are listed; Second, optimization of charge carrier separation and migration: By forming solid solutions, new energy levels are introduced into CdS, enabling effective separation of electrons and holes and thereby suppressing their recombination within the semiconductor.

In addition, some solid solution structures can provide additional charge migration channels to accelerate charge transfer speed; Third, enhancement of surface active sites: The formation of solid solutions may cause changes in the surface structure, thereby increasing the active sites for photocatalytic reactions. This change is conducive to improving the adsorption of reactants on the surface of the photocatalyst and promoting the enhancement of photocatalytic efficiency; Fourth, enhancement of chemical and photostability: Certain solid solutions can improve the chemical and photostability of CdS through their unique structures, effectively resisting photocorrosion and extending the service life of the photocatalyst. Therefore, the construction of solid solutions not only plays a key role in regulating the light absorption performance and charge carrier dynamics of CdS but also exhibits significant effects in enhancing surface active sites and stability, thereby effectively improving its photocatalytic activity. However, the specific enhancement effect depends on the selected paired materials, preparation methods, and specific composition ratio of the solid solution, which requires optimization through precise experimental design. Table 2 summarizes bimetallic solid solutions and multi-metallic solid solutions and their corresponding performance in photocatalytic hydrogen production.

4.2.1. Bimetallic Solid Solution

A bimetallic sulfide solid solution is a novel inorganic compound formed by integrating two different metal sulfides via solid solution technology, in which different metal atoms are uniformly distributed in the lattice structure through atomic-level mixing. The core characteristic of a bimetallic sulfide solid solution is that the metal elements in its composition can

be mutually dissolved in the solid phase through perfect lattice matching without causing any lattice defects or dislocations, such as manganese-cadmium sulfide solid solutions and zinc-cadmium sulfide solid solutions.

Manganese-cadmium sulfide ($\text{Mn}_x\text{Cd}_{1-x}\text{S}$) is a class of photocatalytic materials constructed by doping manganese (Mn) into CdS or forming a solid solution with it, which is mainly designed to address the problems of high recombination rate of photo-generated carriers and severe photocorrosion in CdS. Regulating the band structure of CdS by introducing Mn elements can systematically optimize its optoelectronic properties. The incorporation of Mn can not only expand the visible light response range and enhance the ability to capture the solar spectrum, but also effectively promote the separation and migration of photo-generated electron-hole pairs and improve the photochemical stability of the material in the reaction environment [132, 143]. Relative to pure CdS, manganese-cadmium sulfide solid solutions achieve significantly improved activity and stability in photocatalytic processes such as hydrogen generation and organic pollutant decomposition, contributing valuable insights for the rational design of efficient and robust sulfide photocatalysts.

The combination of manganese-cadmium sulfide with cocatalysts constitutes an effective strategy for enhancing photocatalytic hydrogen production performance. Rational design of the composition and structure of cocatalysts can significantly optimize charge separation efficiency and surface reaction activity. The surface active sites of cocatalysts can facilitate the adsorption and activation of water, lowering the energy barrier of the hydrogen production reaction. For instance, Xiong et al. prepared a CoP/MCS-0.5 composite [127]. BET tests revealed that after loading CoP, the BET surface area of the 5 wt.% CoP/MCS-0.5 composite was superior to that of MCS-0.5 (Figure 9a), which increased the number of active sites and thereby enhanced the activity of the photocatalytic reaction (Figure 9b). Cocatalysts can also couple with MCS by constructing heterojunctions to strengthen the water adsorption and activation capacity on the catalyst surface. As an example, Guo et al. fabricated a $\text{Ni}_x\text{Se}/\text{Mn}_{0.4}\text{Cd}_{0.6}\text{S}$ composite via the hydrothermal method [129]. As shown in the Gibbs free energy diagram (Figure 9c), the hydrogen adsorption free energies of the Ni sites ($|\Delta G_{\text{H}^*}| = -0.23 \text{ eV}$) and Se sites ($|\Delta G_{\text{H}^*}| = -0.32 \text{ eV}$) in the heterojunction were significantly lower than

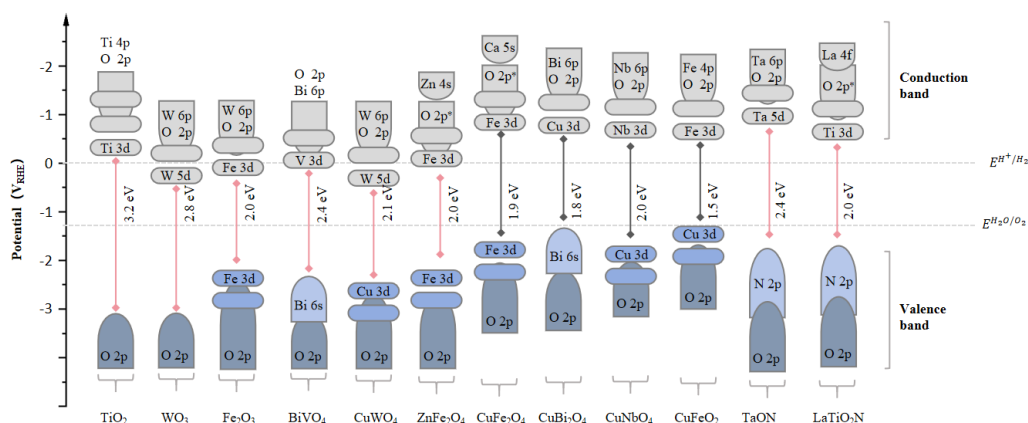


Fig. 8. Band positions of several common photocatalysts.

Table 2. Shows research progress on enhancing the photocatalytic hydrogen production performance of CdS through solid solution engineering strategies.

Photocatalysts	Type	Field	Experimental condition	Light source	Yield (mmol/g/h)	Ref
5 wt.% CoP/MCS-0.5	Bimetallic solid solution	HER	10 mg catalyst, 5 mL lactic acid	300 W Xe-lamp ($\lambda \geq 420$ nm)	H ₂ : 42.95	[127]
MCS/HCN-1.0	Bimetallic solid solution	HER	20 mg catalyst, Na ₂ S (0.25 M), Na ₂ SO ₃ (0.35 M)	300 W Xenon ($\lambda = 420$ nm)	H ₂ : 26.68	[128]
Ni _{0.85} Se/MCS	Bimetallic solid solution	HER	5 mg catalyst, Na ₂ S (0.57 M), Na ₂ SO ₃ (1.25 M)	10 W LED lamp ($\lambda = 420$ nm)	H ₂ : 42.5	[129]
10-MMC/MCS	Bimetallic solid solution	HER	10 mg catalyst, Na ₂ S (0.35 M), Na ₂ SO ₃ (0.25 M)	300 W Xe-lamp ($\lambda > 420$ nm)	H ₂ : 9.72	[130]
Ni@NC/MCS	Bimetallic solid solution	HER	10 mg catalyst, Na ₂ S (0.35 M), Na ₂ SO ₃ (0.25 M)	300 W Xe-lamp (320 < λ < 780 nm)	H ₂ : 0.39	[131]
Mn _{0.2} Cd _{0.8} S/CoP ₃	Bimetallic solid solution	HER	50 mg catalyst, Na ₂ SO ₃ (0.5 mol/L), Na ₂ S (0.5 mol/L)	300 W Xe-lamp ($\lambda = 420$ nm)	H ₂ : 29.53	[132]
ZCS QD	Bimetallic solid solution	HER	20 mg catalyst, 1 M glycerol, 20 μ L (10 mg/mL) NiCl ₂ ·6H ₂ O	300 W Xe-lamp ($\lambda = 420$ nm)	H ₂ : 1.22	[133]
15-ZCS/TiO ₂	Bimetallic solid solution	HER	10 mg catalyst, 10% triethanolamine	300 W Xe-lamp ($\lambda = 420$ nm)	H ₂ : 5.58	[134]
Zn _{0.5} Cd _{0.5} S-1% Ni ₃ C	Bimetallic solid solution	HER	50 mg catalyst, Na ₂ S (0.35 M), Na ₂ SO ₃ (0.25 M)	300 W Xe-lamp ($\lambda \geq 420$ nm)	H ₂ : 0.78	[135]
ZCS@h-M	Bimetallic solid solution	HER	30 mg catalyst, Na ₂ S (0.2 M), Na ₂ SO ₃ (0.2 M)	300 W Xe-lamp ($\lambda \geq 400$ nm)	H ₂ : 58.1	[136]
ZCS/TiO ₂	Bimetallic solid solution	HER	20 mg catalyst, Na ₂ SO ₃ (0.25 M), Na ₂ S (0.35 M)	300 W Xe-lamp ($\lambda = 420$ nm)	H ₂ : 16.68	[137]
0.4ZCS/BA	Bimetallic solid solution	HER	30 mg catalyst, Na ₂ SO ₃ (0.5 M), Na ₂ S (0.35 M)	300 W Xenon ($\lambda = 420$ nm)	H ₂ : 10.52	[138]
WO/ZCS	Bimetallic solid solution	HER	50 mg catalyst, Na ₂ SO ₃ (3.15 g), Na ₂ S·9H ₂ O (8.40 g)	300W Xe-lamp ($\lambda \geq 420$ nm)	H ₂ : 3.94	[139]
CoZC0.5	Multi-metallic Solid Solution	HER	5 mg catalyst, Na ₂ SO ₃ (0.25 M), Na ₂ S (0.35 M)	300 W Xe-lamp ($\lambda \geq 420$ nm)	H ₂ : 12.13	[140]
(ZnS) _x (CuInS ₂) _{1-x}	Multi-metallic Solid Solution	HER	50 mg catalyst, Na ₂ SO ₃ (0.5 M), Na ₂ S (0.5 M)	300 W Xe-lamp ($\lambda \geq 420$ nm)	H ₂ : 0.09	[141]
(Zn _{0.95} Cu _{0.05}) _{1-x} Cd _x S	Multi-metallic Solid Solution	HER	0.3 mg catalyst, Na ₂ SO ₃ (0.35 M), Na ₂ S (0.25 M)	300 W Xe-lamp ($\lambda \geq 420$ nm)	H ₂ : 1.17	[142]

those of the Mn (−0.96 eV), Cd (−0.51 eV) and S ($|\Delta G_H^*| = 2.37$ eV) sites in MCS, and were close to zero. This indicates that the introduction of the cocatalyst greatly enhanced the hydrogen adsorption capacity of MCS, thus effectively improving hydrogen production performance. In addition, cocatalysts can regulate the height of the Schottky barrier to optimize the efficiency of electron transfer. Li et al. synthesized MCS heteronanotubes (HNRS) loaded with TM@NC (TM = Co, Ni and Cu) nanoparticles through a three-step method [131]. MCS has a relatively low work function (~4.2 eV), while TM@NC features a higher work function (~5.0 – 5.3 eV). Upon contact, electrons flow from MCS to TM@NC until the Fermi levels are aligned, forming a Schottky barrier at the interface. This barrier prevents electrons from flowing back from TM@NC to MCS, effec-

tively reducing charge recombination and improving photocatalytic performance (Figure 9d).

Zinc-cadmium sulfide (Zn_xCd_{1-x}S, ZCS) is an important Group II-VI ternary solid solution semiconductor material. By adjusting the Zn/Cd ratio ($0.3 \leq x \leq 0.7$), its band gap can be continuously tuned in the range of 2.4 - 3.7 eV. ZCS combines the visible light absorption capacity of CdS with the strong redox capacity of ZnS [144]. In addition, the introduction of Zn²⁺ inhibits the formation of sulfur vacancies, which enhances the photostability of ZCS compared with CdS. Moreover, its surface can more easily construct high-efficiency heterojunctions with cocatalysts (e.g., CoP) or two-dimensional materials (e.g., MXene), making it attract extensive attention in the field of photocatalysis in recent years.

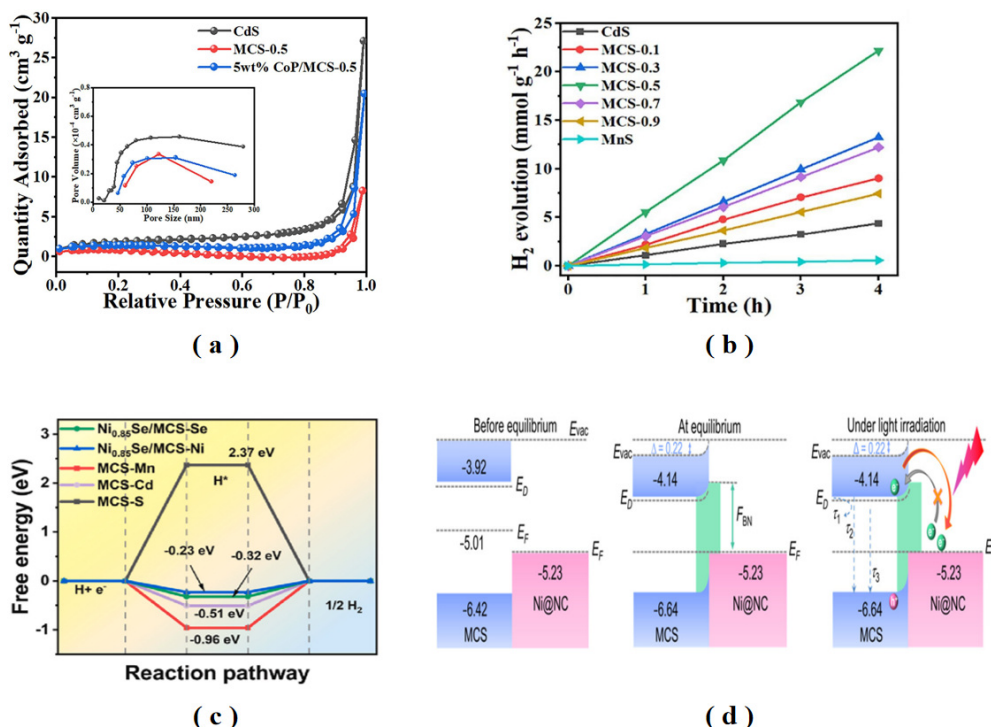


Fig. 9. (a) N₂ adsorption-desorption isotherms and the corresponding pore size distributions (insert) of different samples, (b) photocatalytic H₂ evolution rates of different samples. Reproduced with permission [127]. Copyright 2022, ELSEVIER. (c) Gibbs free energy of HER on Ni_{0.85}Se/MCS and MCS catalysts, Reproduced with permission [129]. Copyright 2025, ELSEVIER SCI LTD. (d) Illustration of band structures of the bare MCS NRs and Ni@NC NPs, and charge transfer pathway in the Ni@NC/MCS HNRs under irradiation. Reproduced with permission [131]. Copyright 2024, ELSEVIER.

At present, the severe recombination of photo-generated carriers is a key bottleneck restricting the further breakthrough of photocatalytic performance. To suppress the rapid recombination of photo-generated electron-hole pairs and further improve the photocatalytic performance of ZCS, the effective strategy of introducing cocatalysts is proposed. Shen et al. constructed a low-cost non-noble metal catalyst, Ni₃C nanoparticles (NPs), and prepared the Ni₃C/twinned nanocrystalline Zn_{0.5}Cd_{0.5}S composite via the grinding method [135]. The synergistic effect between the homojunction of ZCS and the nickel carbide cocatalyst effectively enhanced the photocatalytic performance of the composite: the hydrogen production efficiency of pure ZCS was 272 μmol h⁻¹, while that of the composite reached 783 μmol h⁻¹, which was 2.88 times that of pure ZCS. Photoelectrochemical tests and photoluminescence spectra indicated that Ni₃C could significantly reduce the transfer resistance at the solid-liquid interface and improve the charge transfer efficiency, which was beneficial to photocatalytic hydrogen production. According to the band structure diagram (Figure 10a), it can be found that loading Ni₃C as a cocatalyst could slightly raise the conduction band minimum energy of the composite, thereby enhancing the reduction capacity of photo-generated electrons. Wang et al. adopted dual cocatalysts, Ti₃C₂T_x and CoP, which served as oxidation and reduction sites respectively, realizing the separation of redox sites, maximizing the transfer efficiency of electrons and holes, and simultaneously suppressing carrier recombination, thus improving the hydrogen production efficiency of the material [145]. Its reaction mechanism is shown in the following figure (Figure 10b): When CoP and ZCS interface, electrons diffuse from

ZCS to CoP due to the higher work function of CoP, bending the energy band of ZCS upward until the Fermi levels balance and creating a Schottky barrier. In comparison, at the Ti₃C₂T_x/ZCS interface, The lower work function of Ti₃C₂T_x prompts electron diffusion toward ZCS, bending the energy band of ZCS downward and forming an ohmic contact upon Fermi level alignment. Driven by the Schottky barrier, photo-generated electrons excited on the ZCS surface migrate continuously to and accumulate on the CoP surface, where they participate in a reduction reaction with adsorbed hydrogen ions, ultimately generating and desorbing hydrogen. The ohmic contact has almost no potential barrier, and promotes the charge transfer from Ti₃C₂T_x to ZCS under the action of the internal electric field. Meanwhile, the holes in Ti₃C₂T_x undergo an oxidation reaction with the sacrificial agent. This novel method for improving charge mobility is conducive to a better enhancement of photocatalytic activity.

In addition, ZCS currently suffers from severe photocorrosion, where photo-generated holes oxidize S²⁻ to form sulfur, resulting in structural damage and activity degradation. Traditional modification strategies mainly inhibit photocorrosion through methods such as element doping and defect engineering. Recently, Zheng et al. proposed a controllable photocorrosion strategy, which guides and confines the traditionally destructive photocorrosion process to a superficial and beneficial range. Meanwhile, the corrosion products are utilized to construct a new highly active surface, ultimately achieving a rather enhanced instead of reduced photocatalytic activity along with long-term stability [146]. They synthesized ZnCdS via a sulfur-rich butyldithiocarbamic acid (BDCA) solution

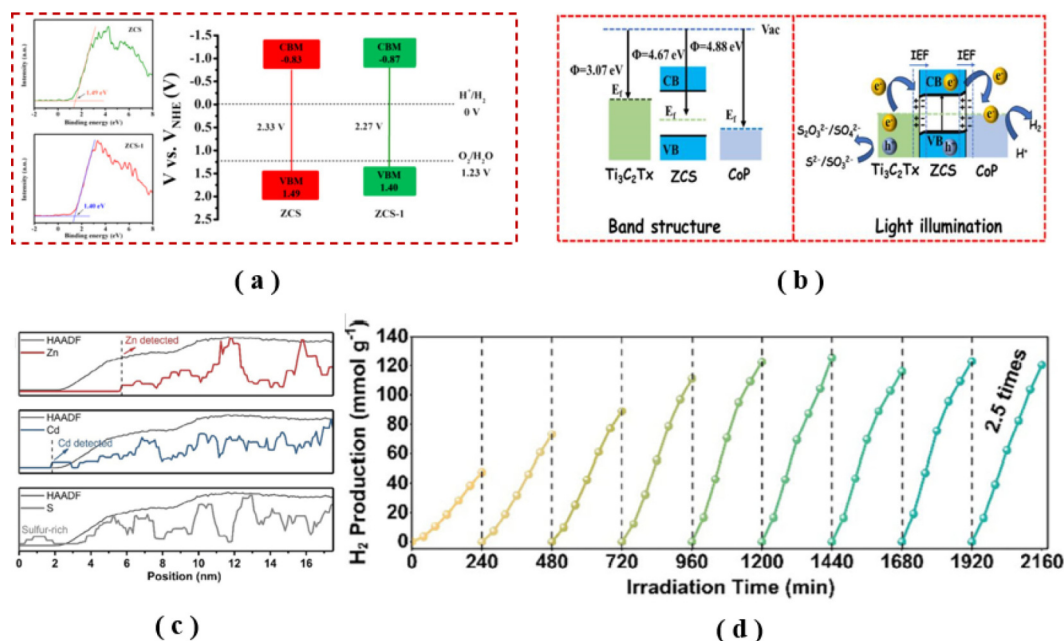


Fig. 10. (a) Valence-band XPS profile of twin nanocrystal ZCS solid solution (ZCS). Reproduced with permission [135]. Copyright 2021, ELSEVIER. (b) The band structure diagram and possible mechanism diagram of ZCS, Ti₃C₂Tx and CoP. Reproduced with permission [145]. Copyright 2025, Elsevier BV. (c) STEM-EDS line-scanning profile, (d) Photostability of ZnCdS. Reproduced with permission [146]. Copyright 2025, AMER CHEMICAL SOC.

method, and the obtained samples possessed a sulfur-rich surface and a Zn subsurface distribution (Figure 10c). In the initial stage of the reaction, photo-generated holes first consume the sacrificial sulfur species on the sulfur-rich surface accompanied by the photocorrosion of the surface cadmium sulfide lattice. With the progress of corrosion, when the process reaches the Zn subsurface region, the photocorrosion is greatly slowed down or even basically stopped due to the high bond strength of Zn-S bonds that are not easily oxidized and cleaved by holes. The elemental sulfur precipitated on the surface does not leach out but accumulates on the catalyst surface, forming a new active surface rich in sulfur clusters. Density functional theory (DFT) calculations show that these sulfur clusters are excellent HER active sites with hydrogen adsorption free energy close to the ideal value, thus realizing controllable photocorrosion ultimately (Figure 10d).

Integrating CdS with other semiconductors to construct solid solutions is an effective pathway for enhancing the performance of photocatalysts. By regulating the proportion of metal components to precisely tune the band structure, it can broaden the light absorption range to improve solar energy utilization efficiency, optimize the separation and migration efficiency of charge carriers, increase surface active sites, and enhance chemical and photostability through bimetallic synergistic effect, thereby reducing photocorrosion. However, bimetallic solid solutions also have obvious shortcomings: for instance, the recombination rate of photo-generated electron-hole pairs is still relatively high in some systems; complex components make it difficult to control uniformity during the preparation process; the design of high specific surface area structures is challenging; and long-term cycling stability needs to be improved. In future development, we can utilize precision synthesis technologies (such as ion exchange and template method) to optimize the uniformity and microstructure of

solid solutions, combine defect engineering and heterojunction construction to further suppress charge recombination, expand its application research in diverse scenarios such as photocatalytic hydrogen production and pollutant degradation, and further promote the development of bimetallic sulfide solid solutions.

4.2.2. Polymetallic Solid Solution

A polymetallic sulfide solid solution is a sulfide composed of more than two different metals, forming a homogeneous solid solution through the mutual substitution of atoms or ions. By adjusting the proportion of different metal sulfides, the band gap of the polymetallic solid solution can be flexibly tuned, which greatly improves the utilization efficiency of visible light. Meanwhile, the mixing of different metal ions can effectively facilitate the separation of photo-generated electron-hole pairs, reduce carrier recombination, and thereby enhance the efficiency of photocatalytic hydrogen production.

Tang et al. prepared a Zn_{1-x}Cd_xCo_xS quaternary solid solution, achieving tunable band gaps by adjusting the Cd content [140]. With increasing Cd content, the band gap of the solid solution gradually decreased, and the light absorption range correspondingly extended into the visible region. Similarly, Zhang et al. synthesized a (Zn_{0.95}Cu_{0.05})_{1-x}Cd_xS ternary solid solution using a room-temperature coprecipitation method [142]. By varying the Cd content, they effectively modulated the band gap and conduction band position of the material, and the solid solution exhibited optimal performance when X = 0.33 (Figure 11a). Further structural characterization results revealed that for the (Zn_{0.95}Cu_{0.05})_{1-x}Cd_xS series samples b-f, as the X value increased, their (111) diffraction peaks gradually shifted from the position of sample a towards that of sample g, displaying a continuous peak shift phenomenon (Figure 11b). This clearly confirms that the as-prepared materials are solid solutions formed between Zn_{0.95}Cu_{0.05}S and CdS,

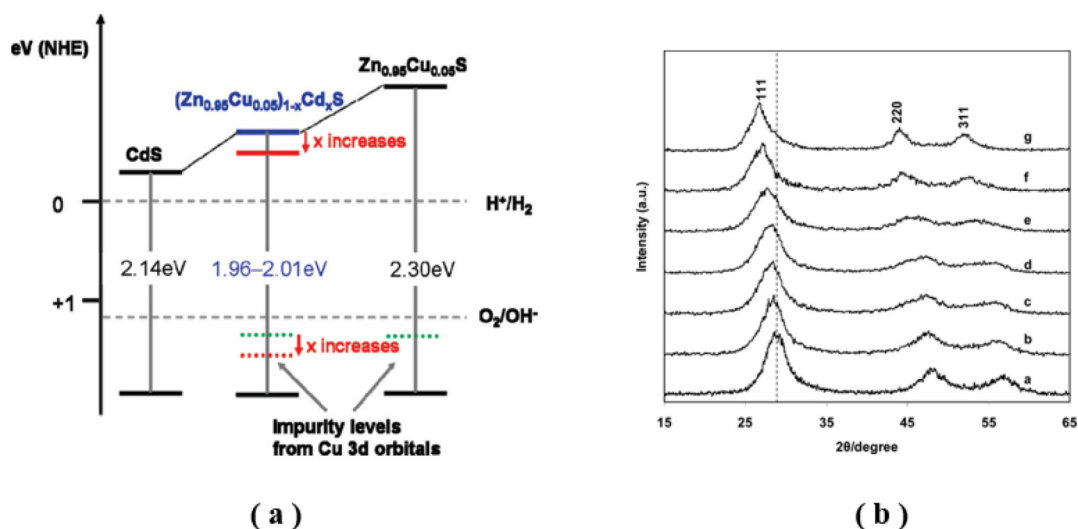


Fig. 11. (a) The band structures of CdS, $\text{Zn}_{0.95}\text{Cu}_{0.05}\text{S}$, and $(\text{Zn}_{0.95}\text{Cu}_{0.05})_{1-x}\text{Cd}_x\text{S}$ solid solutions. (b) XRD patterns for $(\text{Zn}_{0.95}\text{Cu}_{0.05})_{1-x}\text{Cd}_x\text{S}$ samples with different compositions. Reproduced with permission [142]. Copyright 2008, AMER CHEMICAL SOC.

rather than simple mixtures of the two.

In the field of photocatalytic hydrogen production, the advantages and disadvantages of polymetallic sulfide solid solutions are closely related to their unique structural and compositional characteristics. Through the interaction between multiple metal components, they achieve continuous tunability of the band gap and efficient separation of photo-generated carriers, significantly enhancing the efficiency of photocatalytic hydrogen production. Meanwhile, some systems exhibit excellent chemical stability, which can maintain long-term catalytic activity. However, their practical application is still limited by photocorrosion and harsh synthesis methods. In future research, defect regulation strategies can be developed to enhance anti-photocorrosion ability by constructing core-shell structures; at the same time, attention should be paid to developing green and low-cost large-scale preparation processes to promote the application of materials from laboratories to industrialization.

4.3. Heterojunction Construction Strategy

In the field of photocatalysis, to overcome the inherent issues

of rapid electron-hole pair recombination and severe photocorrosion in CdS, the construction of heterojunctions has emerged as a pivotal research direction. The design of heterojunctions is based on the band alignment between two or more different semiconductor materials, aiming to optimize the separation and migration efficiency of photo-generated carriers [147]. Through the precise regulation of the band structures of materials, the carrier separation efficiency can be significantly enhanced, thereby boosting photocatalytic activity. For example, constructing a heterojunction between CdS and $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (BTO) to form an efficient charge transfer channel, thereby suppressing the recombination of charge carriers [148]. Figure 12 illustrates the construction strategies of heterostructures, which are roughly divided into the following categories: Type II heterojunction, Z-scheme heterojunction, and S-scheme heterojunction. Table 3 summarizes the Type-II, Z-scheme, and S-scheme heterojunctions and corresponding performance in photocatalytic hydrogen production.

4.3.1. Type II Heterojunction

A Type II heterojunction is a structure with a staggered band

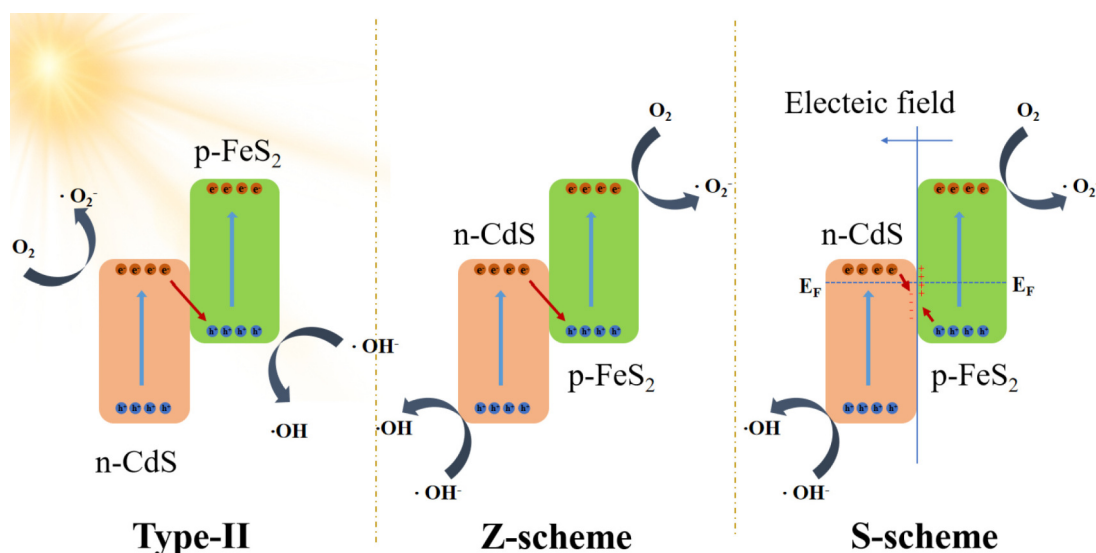


Fig. 12. CdS/FeS₂ diagrams of different types of heterojunctions.

Table 3. Shows the research progress on improving the photocatalytic hydrogen production performance of CdS through heterojunction construction strategies.

Photocatalysts	Type	Field	Experimental condition	Light source	Yield (mmol/g/h)	Ref
1-Pd/CV-5	S-scheme	HER	3 mg catalyst, 20 vol.% lactic acid	300 W Xe-lamp ($\lambda = 475$ nm)	H ₂ : 82.5	[149]
CdS-In ₂ O ₃	S-scheme	HER	5 mg catalyst, 1 mL triethanolamine	300 W Xe-lamp ($\lambda \geq 420$ nm)	H ₂ : 2.26	[150]
ZnIn ₂ S ₄ /CdS	S-scheme	HER	10 mg catalyst, Na ₂ SO ₃ (0.25 M), Na ₂ S (0.35 M)	300 W Xe-lamp ($\lambda > 400$ nm)	H ₂ : 5.68	[151]
NZM/CdS-30	S-scheme	HER	10 mg catalyst, Na ₂ SO ₃ (0.25 M), Na ₂ S (0.35 M)	5 W Led	H ₂ : 5.34	[152]
GaZnON/CdS	II-scheme	HER	10 mg catalyst, Na ₂ SO ₃ (0.35 M), Na ₂ S (0.25 M), 1 wt.% Pt	300 W Xe-lamp	H ₂ : 14.76	[153]
CPG-25	S-scheme	HER	10 mg catalyst, 30 mL L-lactic acid	5 W Incandescent lamp	H ₂ : 3.76	[154]
CdS-F/WO ₃	S-scheme	HER	5 mg catalyst, 10 vol.% lactic acid	5 W Incandescent lamp	H ₂ : 34.12	[34]
CoS ₂ /CdS-L	S-scheme	HER	10 mg catalyst, 30 mL 10% lactic acid	5 W Led	H ₂ : 19.22	[155]
CdS/NU-M	Z-scheme	HER	2 mg catalyst, 0.2M L-ascorbic acid aqueous solution, 16 wt.% Pt	300 W Xenon	H ₂ : 84.3	[149]
1.5% COF/CdS	S-scheme	HER	40 mg catalyst, Na ₂ SO ₃ (0.25 M), Na ₂ S (0.35 M)	300 W Xe-lamp ($\lambda = 420$ nm)	H ₂ : 8.67	[156]
MX-CdS/WO ₃	S-scheme	HER	5 mg catalyst, 10 wt.% lactic acid	300 W Xe-lamp ($\lambda > 420$ nm)	H ₂ : 27.5	[105]
H ₂ CdS/0.7Pt@NU-1000	S-scheme	HER	20 mg catalyst, 70 vol.% NaOH, 10 vol.% lactic acid	300 W Xe-lamp ($\lambda = 420$ nm)	H ₂ : 3.60	[157]
CdS/FePc	Z-scheme	HER	10 mg catalyst, 20 mL lactic acid,	300 W Xenon	H ₂ : 0.07	[158]
NPS-V _{PS} /CS	S-scheme	HER	10 mg catalyst, 30 mL TEOA	300 W Xe-lamp (AM 1.5)	H ₂ : 18.24	[159]
3DOM-HxWO ₃ /Pt/CdS	Z-scheme	HER	3 mg catalyst, 3 wt.% Nafion solution	300 W Xe-lamp ($\lambda > 420$ nm)	H ₂ : 39.2	[160]
Ti ₃ C ₂ /ZIS/CdS	S-scheme	HER	5 mg catalyst, 15% triethanolamine,	300 W Xe-lamp ($\lambda > 420$ nm)	H ₂ : 8.93	[161]
CdS/PI	Z-scheme	HER	50 mg catalyst, 10 vol.% lactic acid aqueous solution	300 W Xe-lamp ($\lambda = 420$ nm)	H ₂ : 0.61	[162]
MC-15	S-scheme	HER	25 mg catalyst, 10 vol.% lactic acid solution	359 W Xe-lamp ($\lambda > 420$ nm)	H ₂ : 7.44	[93]
g-C ₃ N ₄ /BiOI/CdS	Z-scheme	HER	100 mg catalyst, 3 wt.% Pt	300 W Xe-lamp ($\lambda > 420$ nm)	H ₂ : 0.86	[163]

alignment, which achieves efficient separation of photo-generated charges by combining semiconductor materials with different conduction band and valence band energy levels. CdS can readily construct high-efficiency Type II heterojunctions with various oxides and sulfides based on the band alignment criterion, owing to its moderate band gap, high electron mobility and relatively negative conduction band position. In addition, through its mechanism of driving the rapid separation and transfer of carriers via the built-in electric field, the Type II heterojunction can effectively avoid or reduce the trapping of electrons by defect states such as sulfur vacancies on the CdS surface, thereby suppressing charge recombination and enhancing the performance of the material [164–166].

In recent years, the structural design of photocatalytic het-

erofunctions has shown a progressive development trend. Han Huang et al. designed a composite material with CdS nanoparticles grown in an edge-oriented manner on nickel metal-organic framework nanosheets, and successfully constructed a Type II heterojunction (Figure 13a), which effectively improved the efficiency of photocatalytic hydrogen production (Figures 13b, c) [94]. Qiu et al. constructed a tandem heterojunction composed of Z-scheme and Type II heterojunctions on the basis of the existing Type II heterojunctions (Figure 13d). Among them, CdS and KPW (potassium phosphotungstate dodecahedron) form a Z-scheme heterojunction; KPW can serve as the oxidation terminal for constructing the Z-scheme heterojunction, providing highly oxidizing holes to degrade pollutants or oxidize H₂O to generate •OH. CdS and

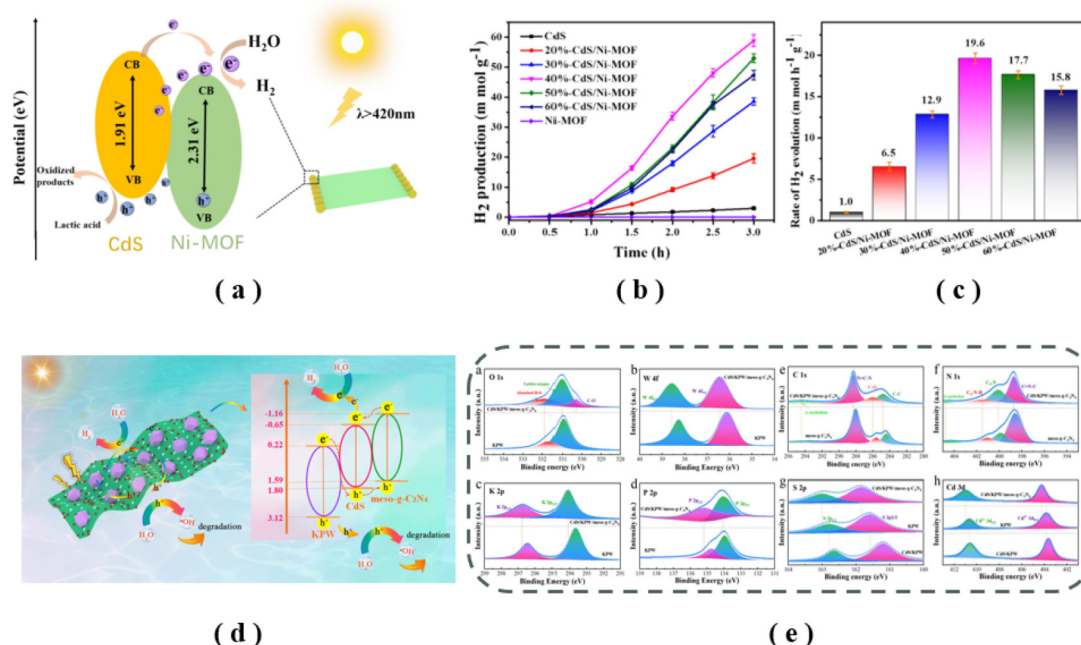


Fig. 13. (a) Diagram illustrating the possible mechanism of the CdS/Ni-MOF composite photocatalyzed H₂ generation, (b) Comparison of the H₂ production amount for different samples under visible light, (c) H₂ evolution average rate of each sample. Reproduced with permission [94]. Copyright 2024, Academic Press Inc. (d) Schematic diagram of the photocatalytic mechanism for CdS/KPW/meso-g-C₃N₄ tandem heterojunction under visible light irradiation, (e) The XPS spectra of different samples [167]. Copyright 2024, Academic Press Inc.

meso-g-C₃N₄ (oxygen-doped mesoporous graphitic carbon nitride) form a Type II heterojunction; meso-g-C₃N₄ acts as the carrier separation layer for constructing the Type II heterojunction, whose mesoporous structure provides active sites and oxygen doping optimizes the band structure. It can be seen from the XPS spectra that the binding energies of KPW and meso-g-C₃N₄ shift systematically after compounding with CdS, indicating strong interfacial coupling and charge redistribution, which provides direct spectroscopic evidence for the formation of the Z-scheme heterojunction and the efficient charge separation mechanism of the subsequent tandem heterojunction (Figure 13e). Through the synergy of band alignment and charge transfer between the Z-scheme and Type II heterojunctions, the synchronous enhancement of light response range, carrier separation efficiency and photocatalytic stability was achieved, which broke through the performance bottleneck of single heterojunctions and provided an effective solution for addressing the performance defects of single photocatalysts [167]. Huang et al. adopted a sandwich structural design to construct a CdS/Au/g-C₃N₄ ternary heterojunction: g-C₃N₄ was used as the substrate, Au nanoparticles (NPs) were sandwiched in the middle, and CdS was selectively deposited on the surface of Au/g-C₃N₄ [168]. This structure can form a Type II heterojunction, and simultaneously, the localized surface plasmon resonance (LSPR) effect and charge conduction effect of Au are utilized to enhance charge separation and transfer.

Despite its remarkable advantages in charge separation, the Type II heterojunction still has some inherent limitations, such as the attenuation of the redox capacity of photo-generated carriers and the increased transport resistance potentially caused by interface barriers. The future development trend will focus on the elaborate construction of multicomponent heterojunctions, the integration of external field enhancement effects including interface engineering optimization,

and the realization of more efficient, stable and broad-spectrum responsive photocatalytic systems through band structure regulation and structural design, thereby promoting its practical application in the energy and environmental fields.

4.3.2. Z-scheme Heterojunction

Z-scheme heterojunction is a special semiconductor composite structure composed of two different semiconductor materials with suitable band structures and energy level matching. Structurally, it typically exhibits intimate interfacial contact, which enables the efficient transfer of photo-generated carriers between the two semiconductors. Its band structure has unique characteristics: The transfer and separation of photo-generated carriers are driven by a particular arrangement of the conduction and valence band positions in the two semiconductors. An important advantage of the Z-scheme heterojunction is its ability to retain the redox capacity of photo-generated carriers [149, 169, 170]. Type II heterojunctions excel in both charge separation efficiency and ease of fabrication, making them well-suited to a variety of photocatalytic processes. In contrast, Z-scheme heterojunctions offer an irreplaceable advantage in maintaining high redox capability through their unique charge transfer pathways, which is particularly beneficial for challenging photocatalytic reactions [171].

Adjusting the ratio of CdS to other semiconductors is one of the strategies for enhancing the performance of CdS-based Z-scheme heterojunctions, as different ratios directly affect the band structure and charge transfer efficiency of the heterojunctions. For example, Mashuri et al. investigated the effect of the ZnO/CdS ratio on the material performance in ZnO/CdS heterojunctions [172], whose band structure diagram is shown in Figure 14a. Samples were named Z₁C₃, Z₁C₁ and Z₃C₁ corresponding to the different molar ratios of ZnO/CdS (1:3, 1:1, 3:1), respectively. Analysis of the Tauc plots (Figure 14c) shows that pure ZnO has a band gap of 3.30 eV with its light

response limited to the ultraviolet region; after constructing a heterojunction with CdS, the band gap of the composite material is reduced to 2.46 – 2.58 eV, which is successfully extended to the visible light region (Figure 14b). The band structure diagrams (Figure 14d) further demonstrate that with the increase in the molar ratio of CdS, the valence band maximum energy of the composite material increases to 2.40, 2.35 and 2.34 eV, respectively. Owing to the inherent 2.40 eV band gap and long carrier diffusion length of CdS itself, the composite with ZnO forms an interfacial band offset, which effectively lowers the work function of electrons and thus facilitates the progress of photocatalytic reactions.

In terms of structural design, besides the construction of classical Z-scheme heterojunctions, researchers have also explored various alternative fabrication approaches. For instance, Zhang et al. synthesized a novel hollow-structured CoS_x/CdS Z-scheme heterojunction photocatalyst via the ZIF-67 template method, which forms a double Z-scheme heterojunction (Figure 15a) and effectively enhances the charge separation efficiency [173]. Huang et al. successfully constructed the $\text{CdS}/\text{g-C}_3\text{N}_4/\alpha\text{-Fe}_2\text{O}_3$ photocatalyst, which innovatively integrates the advantages of the Type II heterojunction ($\text{CdS}/\text{g-C}_3\text{N}_4$) and the Z-scheme heterojunction ($\text{g-C}_3\text{N}_4/\alpha\text{-Fe}_2\text{O}_3$). The synergy of the two heterojunctions enables electrons to accumulate on CdS (a strong reduction site) and holes on $\alpha\text{-Fe}_2\text{O}_3$ (a strong oxidation site) (Figure 15b), thus simultaneously boosting the charge separation efficiency and reaction driving force [174]. Cui et al. designed a hollow core-shell structured photocatalyst $\text{KMoP@CdS@Bi}_2\text{S}_3$ (potassium phosphomolybdate@cadmium sulfide@bismuth sulfide) (Figure 15c) [175], This catalyst is a core-shell Z-scheme tandem heterojunction; the hol-

low structure enlarges the specific surface area, while the heterojunction promotes charge separation, which effectively enhances the material performance and advances the application of heterojunction photocatalysts in environmental remediation and energy conversion.

In summary, through the precise matching of band structures and unique carrier migration pathways, Z-scheme heterojunctions achieve efficient separation of photo-generated electron-hole pairs while maximally retaining their strong redox capacity, which constitutes their core advantage over traditional heterojunctions. Studies have shown that elaborately regulating the component ratios and designing multicomponent composite structures can effectively optimize the specific surface area, charge separation efficiency and reactive sites of materials, thereby significantly enhancing photocatalytic performance. However, the construction of Z-scheme heterojunctions still faces challenges such as complex preparation processes and insufficient interfacial stability of materials. Future research needs to devote to developing more precise synthesis methods, exploring novel semiconductor combinations and deepening the research on interfacial charge transfer mechanisms, so as to promote the large-scale application of Z-scheme heterojunctions in the field of photocatalytic energy conversion.

4.3.3. S-scheme Heterojunction

S-scheme heterojunctions, as an innovative design for photocatalytic systems, enable efficient charge separation and maximize the retention of carriers with strong oxidizing and reducing properties [176–179]. This mechanism not only inherits the advantage of classical Z-scheme heterojunctions in retaining strong redox capacity, but also significantly enhances the quan-

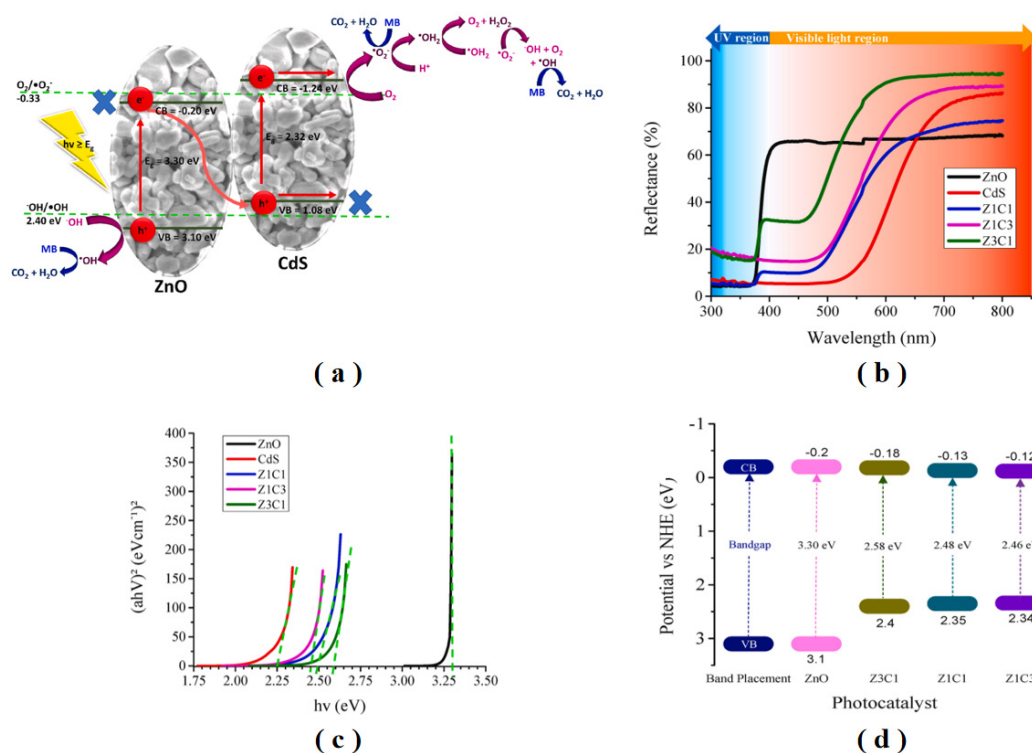


Fig. 14. (a) The proposed mechanism of Z-scheme ZnO/CdS, (b) The reflectance edge of different samples, (c) the Tauc plot of ZnO, Z_1C_1 , Z_1C_3 , and Z_3C_1 , (d) the proposed valence band and conduction band positions of different samples. Reproduced with permission [172]. Copyright 2023, PERGAMON-ELSEVIER SCIENCE LTD.

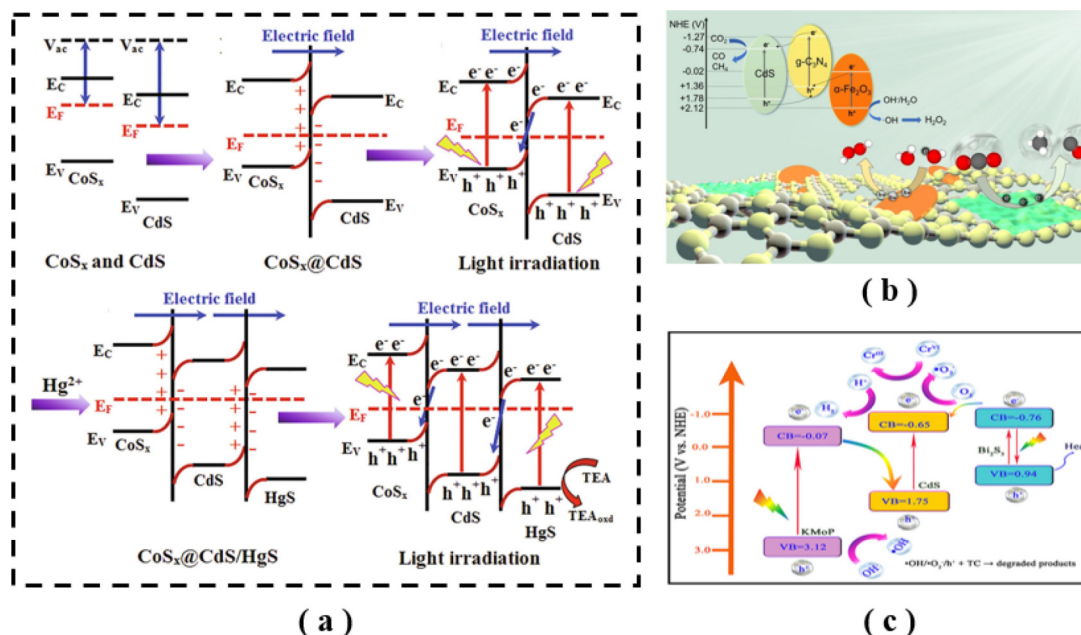


Fig. 15. (a) Charge transfer mechanism between direct Z-scheme double heterojunction and HgS/CdS@CoS_x photocatalyst. Reproduced with permission [173]. Copyright 2020, ELSEVIER SCIENCE SA. (b) Photocatalytic mechanism of CdS/g-C₃N₄/α-Fe₂O₃ heterojunction. Reproduced with permission [174]. Copyright 2022, Academic Press Inc. (c) Photocatalytic mechanism of KMo@CdS@Bi₂S₃ heterojunction. Reproduced with permission [175]. Copyright 2022, Academic Press Inc.

tum efficiency and reaction activity of photocatalysts via intimate interfacial contact and well-defined carrier migration pathways, and has been widely applied in high-efficiency photocatalytic water splitting, CO₂ reduction and pollutant degradation systems [180, 181].

Liu et al. combined CdS nanospheres with purple tungsten oxide (W₁₈O₄₉) nanowires via the hydrothermal method to construct a 3D heterojunction (Figure 16a), which facilitates carrier separation and suppresses photocorrosion. The

optimal sample (10 wt.% W₁₈O₄₉/CdS) achieved a hydrogen production rate of 9.7 mmol g⁻¹ h⁻¹, which is 7.5 times that of pure CdS [34]. Sun et al. constructed a core-shell S-scheme heterojunction, denoted as CSK, by coupling hollow dodecahedral K₃P W₁₈O₄₉ (KPW) with CdS nanoparticles [182]. Its band structure diagram is shown in Figure 16b. The core-shell structure endows the material with an intimately bonded interface, enhancing electron transfer; meanwhile, the different Fermi levels lead to the formation of a distinct built-in electric field

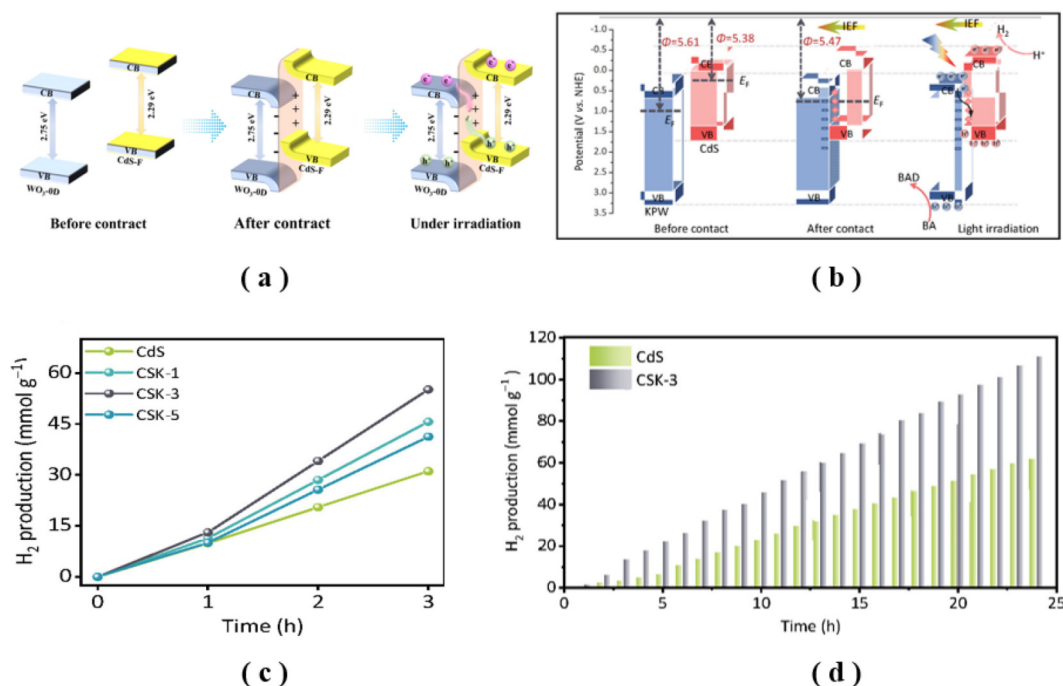


Fig. 16. (a) Charge transfer mechanism of S-scheme heterojunction composed of CdS-F and WO₃-0D. Reproduced with permission [34]. Copyright 2024, Progress in Journal of Materials Science & Technology. (b) Band structure over CSK-3, (c) Time-caused photocatalytic H₂ production activity, (d) Long-term light irradiation experiments. Reproduced with permission [182]. Copyright 2023, Progress in Chinese Journal of Catalysis.

between CdS and KPW, which induces the redistribution of interfacial charges and thus favors S-scheme carrier migration (Figure 16c). Compared with the basic S-scheme heterojunction, this core-shell S-scheme heterojunction exhibits a much higher hydrogen production rate of $18.7 \text{ mmol g}^{-1} \text{ h}^{-1}$ along with excellent stability (Figure 16d).

In addition, defect regulation can optimize carrier trapping and migration, reduce interfacial recombination, and simultaneously enhance the performance stability of heterojunctions. For instance, Liu et al. employed the high-temperature calcination method to dope CdS with phosphorus (CP) for band structure regulation, which reduced carrier recombination. They further compounded CP with graphdiyne (GDY) to form an S-scheme heterojunction, thereby further improving the separation efficiency of photo-generated carriers and the photocatalytic hydrogen production performance [154]. As can be seen from the band structure diagrams of the samples (Figures 17a, b), the introduction of P elements results in a wider band gap of CP compared with pure CdS, making it more difficult for photo-generated carriers to retreat and recombine to produce fluorescence. After the addition of GDY, the heterojunction formed by the two further separates the photo-generated carriers; however, the heterojunction formed is distinct due to the variation in the conduction band. Evidently, the S-scheme heterojunction formed between CP and GDY enables a more efficient separation of photo-generated carriers.

In summary, owing to its unique charge transfer pathways and band alignment characteristics, the S-scheme heterojunction exhibits remarkable advantages in improving carrier separation efficiency, enhancing photostability and suppressing photocorrosion. However, the fabrication process of such heterojunctions is complex, the interfacial regulation still needs to be optimized, and the in-depth understanding of the Fermi level difference theory for their interfaces and the whole system remains inadequate. Future research should devote to developing more precise synthesis methods to achieve atomic-level interfacial regulation, and combine theoretical calculations with in-situ characterization technologies to elucidate the carrier transport mechanism. In addition, the band structure also plays a crucial role in S-scheme heterojunctions; the introduction of vacancies and heteroatom doping both alter the band structure, thereby exerting an influence on the performance of S-scheme heterojunctions. Going forward, it is necessary to explore more S-scheme heterojunctions with visible light response and high stability to promote the practical

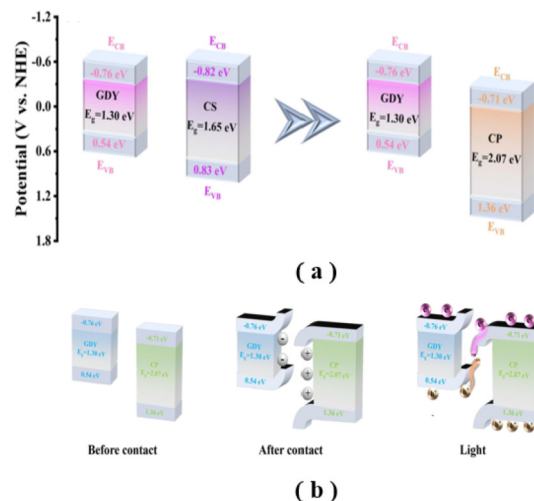


Fig. 17. (a) Energy band structure diagram of CS, GDY and CP, (b) Mechanism of photocatalytic hydrogen evolution in CPG-25. Reproduced with permission [154]. Copyright 2024, ELSEVIER SCIENCE SA.

application of photocatalytic hydrogen production technology.

4.4. Element Doping Strategy

Element doping of CdS primarily modulates its photoelectric properties by introducing foreign atoms [183, 184]. Metal element doping mainly involves the substitution of partial cadmium ions in the CdS lattice with other metal cations, and common metal doping elements include Fe [185], Ag [186], Cu [187, 188], Mg [189], Ni [190, 191] et al. Non-metal element doping, by contrast, refers to the substitution of partial sulfur ions in the CdS lattice with non-metal anions [192], with typical non-metal doping elements including N, F, and others. Metal doping introduces impurity energy levels within the bandgap to enhance visible light absorption, effectively suppresses photocorrosion, improves stability, and can even introduce ferromagnetism. In contrast, non-metal doping can form a built-in electric field, which facilitates the migration and separation efficiency of photogenerated charge carriers. Currently, metal doping is mostly carried out using a simple one-step hydrothermal method with a relatively mature process, whereas non-metal doping sometimes requires high-temperature treatment under an inert atmosphere, making the process more complex. Table 4 summarizes metal doping and non-metal doping and their corresponding performance in photocatalytic hydrogen production.

Table 4. Shows research progress on enhancing the photocatalytic hydrogen production performance of CdS through elemental doping strategies.

Photocatalysts	Type	Field	Experimental condition	Light source	Yield (mmol/g/h)	Ref
1%Pt, Au/CdS	Metal	HER	10 mg catalyst, 2 mL TEOA	300 W Xe-lamp ($\lambda = 380 \text{ nm}$)	H_2 : 6.71	[193]
CoP ₂ /CdS	Metal	HER	1 mg catalyst, 20 mL aqueous solution	300 W Xenon ($\lambda = 420 \text{ nm}$)	H_2 : 1071	[194]
CdS-3	Metal	HER	2 mg catalyst, Na ₂ S (0.35 M), Na ₂ SO ₃ (0.25 M)	300 W LED ($\lambda \geq 420 \text{ nm}$)	H_2 : 21.8	[195]
3.7%Ni ₂ P@CdS-Ni-3	Metal	HER	2 mg catalyst, 10% lactic acid	300 W Xe-lamp ($\lambda \geq 420 \text{ nm}$)	H_2 : 176.6	[196]
CdS/MO (0.38)-VC (5wt.%)	Metal	HER	40 mg catalyst, 100 mL lactic acid aqueous	300 W Xe-lamp ($\lambda > 420 \text{ nm}$)	H_2 : 2.27	[197]

Table 4. (Continued)

Photocatalysts	Type	Field	Experimental condition	Light source	Yield (mmol/g/h)	Ref
0.5 wt.% Pt-5 wt.% BP/CdS	Metal	HER	20 mg catalyst, 20 vol.% lactic acid	300 W Xe-lamp ($\lambda \geq 420$ nm)	H ₂ : 24.17	[198]
PtP ₂ @C/CdS (10 wt.%)	Metal	HER	50 mg catalyst, 80 mL lactic acid	3 W LED-Lamps ($\lambda = 420$ nm)	H ₂ : 9.76	[199]
9%Ni@NiS _x -CdS	Metal	HER	5 mg catalyst, 0.25 M Na ₂ SO ₃ , 0.35 M Na ₂ S	300 W Xe-lamp ($\lambda > 420$ nm)	H ₂ : 78.7	[200]
CdS/2%Ni ₂ SP	Metal	HER	5 mg catalyst, 80 mL Na ₂ S-Na ₂ SO ₃	350 W -lamp ($\lambda = 420$ nm)	H ₂ : 18.96	[102]
S-Ta ₂ O ₅ /CdS	non-Metal	HER	5 mg catalyst, 0.25 M Na ₂ SO ₃ , 0.3 M Na ₂ S	300 W Xe-lamp ($\lambda > 420$ nm)	H ₂ : 54.51	[201]
CuIn-CdS ₁₀	Metal	HER	10 mg catalyst, 0.25 M Na ₂ SO ₃ , 0.35 M Na ₂ S	300 W Xenon (λ 320-780 nm)	H ₂ : 105.44	[202]
1.0% MNC	Metal	HER	10 mg catalyst, 70 mL lactic acid aqueous	300 W Xenon ($\lambda > 420$ nm)	H ₂ : 5.64	[203]
OMoS-0.3	non-Metal	HER	10 mg catalyst, 10 vol.% aqueous lactate	300 W Xe-lamp ($\lambda > 420$ nm)	H ₂ : 58.47	[204]
16wt.%F-TiO ₂ /CdS	Metal	HER	50 mg catalyst, 0.35 M Na ₂ SO ₃ , 0.25 M Na ₂ S	300 W Xe-lamp ($\lambda \geq 420$ nm)	H ₂ : 1.70	[205]
P-Mo ₂ CT _x (2:1)/CdS	Metal	HER	10 mg catalyst, 10 vol.% latic acid	300 W Xe-lamp ($\lambda = 420$ nm)	H ₂ : 7.36	[206]
N _{0.2} -CdS	non-Metal	HER	10 mg catalyst, 15 vol.% TEOA	300 W Xe-lamp ($\lambda \geq 420$ nm)	H ₂ : 3.98	[207]
Ni@NiO-CdS-3	Metal	HER	10 mg catalyst, 10 vol.% TEOA	300 W Xenon ($\lambda \geq 420$ nm)	H ₂ : 5.51	[208]
CdS _{0.9} Se _{0.1} QDs	Metal	HER	2 mg catalyst, 0.35 M Na ₂ SO ₃ , 0.25 M Na ₂ S-9H ₂ O	225 W Xenon ($\lambda \geq 320$ nm)	H ₂ : 29.12	[209]
2wt.% NiCo-LDH/P-CdS	Metal	HER	50 mg catalyst, 10 mL latic acid	300 W Xe-lamp ($\lambda = 420$ nm)	H ₂ : 8.67	[210]

4.4.1. Metal-doped Cadmium Sulfide

Metal element doping is a pivotal strategy for optimizing the performance of CdS. This approach enables the regulation of the band gap, realizes the redshift of the light absorption range toward the visible or near-infrared region, and introduces defect energy levels as trapping centers for electrons or holes. It thus effectively suppresses charge recombination to enhance carrier separation efficiency [211], while also strengthening the anti-photocorrosion ability of the material under light irradiation and improving its structural and chemical stability [212]. Common metal doping elements include Co, Cu, Zn, Mn, Ni and others. Metal element doping has broadened the practical application value of CdS in the fields of solar energy conversion, pollutant degradation, photoelectric sensing and beyond [213-215].

Ni element doping is an effective strategy for regulating the electronic structure of CdS to enhance its photocatalytic activity. Introducing Ni atoms into the CdS lattice enables the formation of a spin-polarized electric field and simultaneously strengthens the intensity of the built-in electric field, thereby driving charge separation more efficiently [216]. Thus, constructing a composite system of CdS and Ni is also regarded as one of the important approaches for developing high-efficiency and low-cost composite photocatalysts. Wu et al. adopted a hydrothermal-calcination method to construct a CoP@Ni-CdS Schottky junction composed of Ni-doped CdS nanorods and metalloid CoP nanoparticles. Ni doping not only induced a spin-polarized electric field (Figures 18a, b), but also enhanced

the intensity of the built-in interfacial electric field and increased the height of the Schottky barrier, which synergistically promoted the separation of photo-generated charges [217]. Similarly, Zhang et al. synthesized Ni-doped CdS (Ni-CdS) nanorods via a one-step solvothermal method, where Ni atoms substituted the Cd atoms in the CdS lattice [218]. The introduction of Ni dopants induced lattice distortion in CdS and the formation of sulfur vacancies, leading to an enhanced local dipole moment and a strengthened spin-polarized electric field. This, in turn, promoted the separation and migration of charge carriers, suppressed charge recombination, and ultimately resulted in a marked improvement in photocatalytic hydrogen evolution efficiency (Figures 18c, d).

Cobalt (Co) element doping in CdS exerts a core effect of constructing efficient electronic capture and transport channels in the CdS lattice, thereby simultaneously addressing the two bottleneck issues of severe photo-generated charge recombination and photocorrosion in CdS. Co doping can effectively prolong the lifetime of photo-generated carriers and increase the photocatalytic hydrogen production rate by promoting interfacial charge separation; meanwhile, the robust nature of Co-S bonds enhances lattice stability, leading to a significant improvement in catalytic stability [219]. Xiong et al. synthesized Co-doped CdS nanorods via a solvothermal method, which enhanced the reducibility of CdS (Figure 19a), reduced charge transfer resistance and improved charge separation efficiency. In addition, Co doping induced spin polarization (Figures 19b, c), which effectively suppressed electron-hole recom-

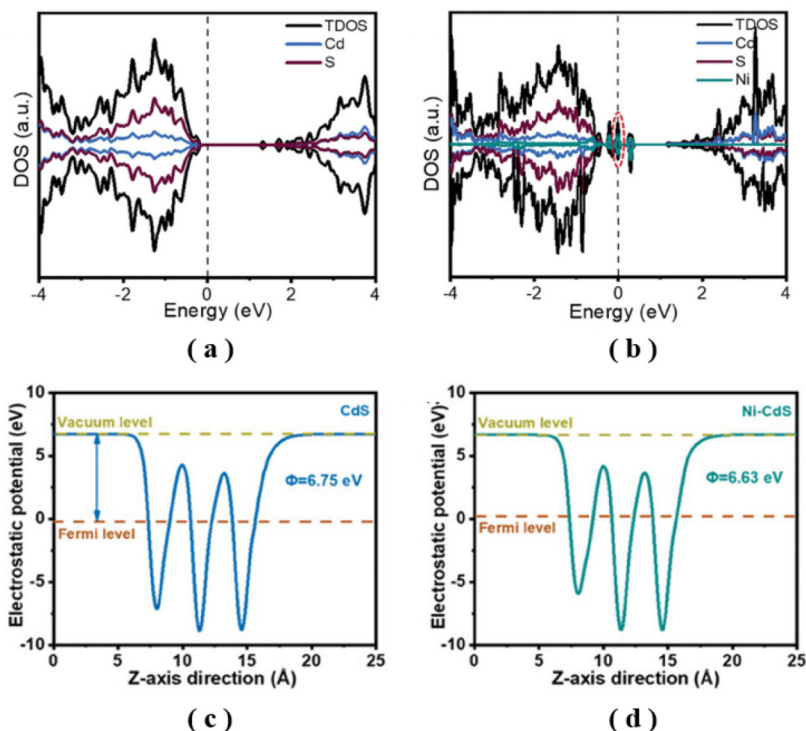


Fig. 18. (a) The TDOS of CdS, (b) The TDOS of Ni-CdS. Reproduced with permission [217]. Copyright 2024, WILEY. (c) Calculated electrostatic potentials of CdS, (d) Calculated electrostatic potentials of Ni-CdS. Reproduced with permission [218]. Copyright 2025, WILEY.

bination [220].

Multi-metal co-doped cadmium sulfide (CdS) constructs more complex defect structures and electronic states in the CdS lattice via multi-ion co-doping, which not only enables the more elaborate regulation of its band structure, but also establishes multiple electron trapping and transport channels, thus greatly promoting the separation and migration of photo-generated carriers. Ma et al. used Cu-In₂S₃ as the

inducer to synthesize multi-armed CdS nanorods via the in-situ growth method [202]. Doping with Cu and In reduced the band gap of CdS (Figure 19d) and expanded the light absorption range (Figure 19e). The hydrogen production rate of the optimal sample CuIn-CdS10 reached 105.44 mmol g⁻¹ h⁻¹, which was 55 times that of pure CdS.

Metal element doping is an effective means to enhance the photocatalytic performance of CdS, and its core advan-

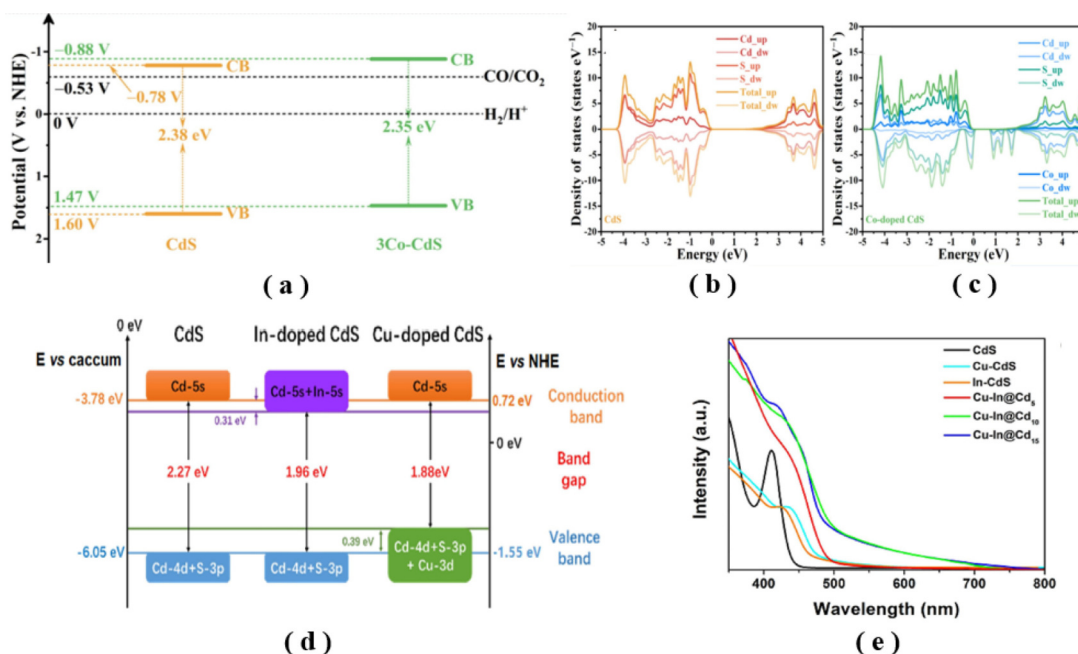


Fig. 19. (a) Energy band structure diagrams of the prepared CdS and 3Co-CdS samples, (b) Calculated total density of states of CdS, (c) Calculated total density of states of Co-doped CdS. Reproduced with permission [220]. Copyright 2025, ELSEVIER SCIENCE SA. (d) Schematic energy level diagram of pristine hexagonal CdS, In-doped hexagonal CdS and Cu-doped hexagonal CdS, (e) UV-vis absorption spectra of the as-synthesized samples. Reproduced with permission [202]. Copyright 2020, ELSEVIER SCIENCE SA.

tages lie in the effective regulation of band structures, the significant enhancement of charge separation efficiency, and the strengthened anti-photocorrosion ability, thus greatly improving the activity and stability of photocatalysts. However, this strategy still faces numerous challenges in practical applications. Doping uniformity is difficult to precisely control, which can easily lead to local compositional fluctuations in CdS, thereby affecting its stability. Meanwhile, some metal ions, once incorporated, may act as recombination centers for photo-generated charge carriers, exacerbating non-radiative recombination and thus reducing luminescence efficiency or photocurrent response. Furthermore, the doping mechanisms in complex doping systems remain unclear. Future research should focus on developing more accurate and controllable doping technologies, deeply elucidating carrier dynamics by combining in-situ characterization with theoretical calculations, and exploring multicomponent co-doping of low-toxicity and low-cost metal elements. This will promote the development of high-performance CdS-based photocatalysts and lay a solid foundation for their large-scale practical applications.

4.4.2. Non-metal-doped Cadmium Sulfide

Significant improvement in the photocatalytic efficiency of CdS nanorods can be achieved via non-metal element doping, which optimizes their electronic structure, boosts light absorption, and promotes the separation and transport of photo-generated charges [221, 222]. Herein, we summarize the effects of nitrogen (N), phosphorus (P) and chlorine (Cl) doping on the photocatalytic performance of CdS nanorods, as well as the performance of these doping strategies in practical photocatalytic applications.

N-doping partially substitutes sulfur atoms in the CdS lattice, and by virtue of its atomic radius similar to that of sulfur and higher electronegativity, it successfully introduces defect energy levels into the band gap of the material, which provides a stepwise transition pathway for electrons. This further

redshifts the optical absorption edge of CdS nanorods and expands the utilization range of the solar spectrum. Meanwhile, nitrogen atoms act as hole trapping centers, which can effectively separate and confine photo-generated holes, thereby suppressing the recombination of electron-hole pairs and improving the separation efficiency of photo-generated charges [223]. Experimental results show that N-doped CdS nanorods exhibit reduced photoluminescence intensity and prolonged carrier lifetime, which confirms the suppression of carrier recombination by N-doping (Figures 20a, b). In addition, as can be seen from the total density of states (TDOS) (Figure 20c), the electron density of N-CdS is lower than that of pure CdS, which verifies the existence of Cd-N coordination and provides theoretical evidence for promoting carrier migration. Therefore, N-doped CdS nanorods exhibit significantly enhanced photocatalytic hydrogen production performance via water splitting compared with undoped CdS [207].

Studies on P-doping have demonstrated that the incorporation of phosphorus atoms modulates the electronic structure and surface charge distribution of CdS, and introduces new energy levels, thus facilitating the efficient separation of photo-generated charges. Such structural modulation endows P-doped CdS nanorods with higher activity in photocatalytic hydrogen production via water splitting, which benefits from their excellent charge separation capability and improved light absorption performance [224]. P. Anil Kumar Reddy et al. developed a heterostructured composite photocatalyst consisting of P-doped Co_3S_4 quantum dots (QDs) anchored on CdS (denoted as P- Co_3S_4 @CdS) [225]. With its superior charge transfer capabilities and heightened reduction potential, the P- Co_3S_4 @CdS composite achieves a remarkable enhancement in hydrogen production efficiency. Based on the Mott-Schottky plots, the flat band potentials of CdS, Co_3S_4 and P-CoS were determined separately, which yields a conduction band potential of -1.10 V for P-CoS—more negative than that of pure

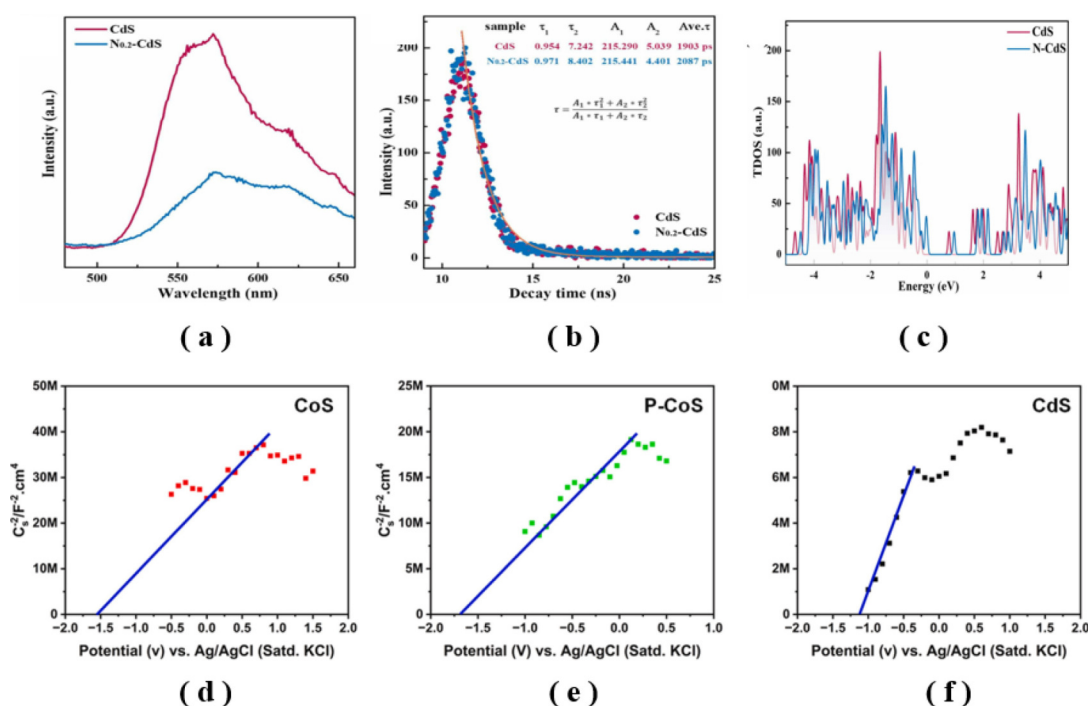


Fig. 20. (a) PL spectra, (b) TRPL spectra, (c) TDOS of CdS and N_{0.2}-CdS. Reproduced with permission [207]. Copyright 2022, ELSEVIER. (d) Mott-Schottky of CoS, (e) Mott-Schottky of P-CoS, (f) Mott-Schottky of CdS. Reproduced with permission [225]. Copyright 2025, ELSEVIER SCI LTD.

Co₃S₄ (0.98 V). This confirms that P-doping enhances the reducibility of photo-generated electrons (Figures 20d-f). According to the results of this research, the integration of phosphorus doping with cost-effective and readily available Co₃S₄ offers a promising approach to boost photocatalytic hydrogen generation and facilitate the oxidative degradation of dye pollutants in wastewater.

Carbon doping is a low-cost and green approach that can regulate the band structure of CdS, achieving bandgap narrowing and enabling more efficient utilization of sunlight, thereby improving light absorption efficiency. Meanwhile, carbon materials often possess high specific surface areas and unique pore structures, providing an ideal support for CdS nanoparticles. This not only effectively inhibits the agglomeration of CdS but also offers more active sites for photocatalytic reactions. Li et al. used glucose as a carbon source to prepare C-doped CdS via a one-step hydrothermal method [226]. The C doping forms a semiconductor-heteroatom electron transfer channel, accelerating the migration of photogenerated electrons. Furthermore, theoretical calculations indicate that C doping significantly reduces the activation energy for the conversion of H₂O to H[•] and the reaction barrier for the conversion of H[•] to H₂, providing a theoretical basis for the effective enhancement of photocatalytic hydrogen production by carbon doping.

Non-metal element doping offers a robust and flexible strategy for modulating the electronic structure and photocatalytic performance of CdS nanorods. It effectively narrows the band gap and broadens the photo-response range by introducing impurity energy levels, and significantly suppresses carrier recombination by acting as electron trapping centers. However, this strategy also faces challenges such as the difficulty in precisely controlling doping sites and concentrations, which can easily lead to difficulties in precisely controlling the crystal structure, the possible introduction of non-radiative recombination centers that significantly reduce luminescence efficiency and photocurrent response, as well as the leaching of doping elements during long-term cycling, resulting in decreased stability. Future research should devote to developing more precise doping technologies, deeply elucidating the action mechanisms of dopants by combining theoretical calculations with in-situ characterization techniques, and exploring the synergistic co-doping effects of multiple non-metal elements. This is aimed to maximize the photocatalytic efficiency while taking into account the environmental benignity of materials and the feasibility of large-scale preparation, so as to further advance the development of CdS-based photocatalysts.

5. Outlook

To date, research efforts on CdS-based materials have enriched our understanding of their material characteristics, fabrication processes, modification strategies, and application value in the field of semiconductor photocatalytic technology. In contrast to existing reviews (e.g., [227]), that offer a broad overview of cadmium sulfide, this paper concentrates on the design of CdS, systematically incorporating four strategies—morphology control, solid solution engineering, heterojunction construction, and elemental doping—with a special focus on critical challenges including photocorrosion suppression and scalable synthesis. This paper first introduces the fundamental principles and extensive applications of semiconduc-

tor photocatalytic technology, and also provides an overview of the preparation methods for CdS-based photocatalysts. Among these methods, the hydrothermal/solvothermal method has emerged as the most widely used fabrication process due to its advantages of precise morphological and structural control as well as low cost.

CdS-based photocatalysts exhibit suitable band gap width, excellent visible light absorption capacity, high electron mobility, and adjustable band structure, showing great application potential in the field of photocatalytic hydrogen production. This paper also summarizes the key factors affecting the photocatalytic performance of CdS-based materials and reviews the effective strategies for improving their photocatalytic hydrogen production performance, including morphology control, solid solution engineering, heterojunction construction, and element doping. The core goals of these strategies are to: broaden the range of solar light capture, suppress carrier recombination, increase the number of active sites, enhance corrosion resistance, and thereby effectively improve photocatalytic activity. Although remarkable achievements have been made so far, CdS-based materials still face enormous opportunities and challenges in terms of functions and performance. Firstly, in terms of stability, CdS-based materials still have problems. Low-dimensional materials tend to agglomerate, while high-dimensional materials have weak interface bonding strength between components; meanwhile, some solid solutions and doped materials suffer from photocorrosion or doping element leaching, all of which affect stability. Secondly, in terms of catalyst synthesis, the contradiction between large-scale production and uniformity is prominent: it is difficult to control the morphology and size of low-dimensional materials during large-scale synthesis; the complex components of solid solutions lead to poor uniformity; the preparation process of three-dimensional materials is cumbersome, costly, and difficult to precisely regulate; in doping technology, it is hard to accurately control the doping sites, concentration, and uniformity; and the ability of atomic-level interface regulation for heterojunctions and composite systems is insufficient. In addition, it is necessary to explore more environmentally friendly synthesis methods for preparing CdS-based photocatalysts to reduce the environmental impact during the synthesis process. At the same time, all materials involved in this paper are at the laboratory preparation level with low product yield. Scaling up the synthesis process of high-efficiency laboratory photocatalysts to achieve low-cost large-scale preparation is an important research direction in the field of photocatalysis in the future. From the perspective of practical application, although CdS-based materials have demonstrated excellent visible-light response and hydrogen production performance in the laboratory, there is still a considerable gap from true industrial application. Whether it is the issues related to stability, catalyst synthesis, and environmental pollution mentioned earlier, or the fact that the vast majority of highly active cadmium sulfide-based materials currently rely on sacrificial agents to consume holes, all these factors hinder the industrial preparation of CdS-based materials and urgently need to be addressed.

In response to the above bottlenecks, future breakthroughs can be pursued from the following aspects: (1) improving the design of catalyst nanostructures to enhance the

active catalyst surface area, thereby translating into better synergistic effects; (2) exploring more convenient, green, and high-yield synthesis routes that avoid the energy consumption and safety hazards associated with traditional high-temperature, high-pressure solvothermal methods; (3) the charge transfer mechanism of CdS-based materials has not yet been fully explored; using experimental and theoretical calculations to comprehensively understand the electron transfer mechanism will help improve process efficiency.

This review can provide comprehensive research perspectives and important references for novice researchers in the fields of photocatalysis and energy conversion. Although numerous remarkable achievements have been made so far, CdS-based materials still face tremendous opportunities and challenges in terms of performance and practical applications. Existing research is only the tip of the iceberg in this field, and there are still many directions that urgently need to be broken through in the relevant research conclusions, which await further in-depth exploration.

Acknowledgment

This study was financially supported by the State Key Laboratory of Heavy Oil Processing (WX20250145) and Drug Efficacy and Health Risk Assessment Key Laboratory of Zhenjiang (SS2024006).

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