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SPECIAL TOPIC: Advanced Photocatalytic Materials

# Nanostructured CdS for efficient photocatalytic H<sub>2</sub> evolution: A review

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ABSTRACT Cadmium sulfide (CdS)-based photocatalysts have attracted extensive attention owing to their strong visible light absorption, suitable band energy levels, and excellent electronic charge transportation properties. This review focuses on the recent progress related to the design, modification, and construction of CdS-based photocatalysts with excellent photocatalytic H<sub>2</sub> evolution performances. First, the basic concepts and mechanisms of photocatalytic H<sub>2</sub> evolution are briefly introduced. Thereafter, the fundamental properties, important advancements, and bottlenecks of CdS in photocatalytic H<sub>2</sub> generation are presented in detail to provide an overview of the potential of this material. Subsequently, various modification strategies adopted for CdS-based photocatalysts to yield solar H<sub>2</sub> are discussed, among which the effective approaches aim at generating more charge carriers, promoting efficient charge separation, boosting interfacial charge transfer, accelerating charge utilization, and suppressing charge-induced self-photocorrosion. The critical factors governing the performance of the photocatalyst and the feasibility of each modification strategy toward shaping future research directions are comprehensively discussed with examples. Finally, the prospects and challenges encountered in developing nanostructured CdS and CdS-based nanocomposites in photocatalytic H<sub>2</sub> evolution are presented.

**Keywords:** solar fuel, nanostructured cadmium sulfide-based photocatalysts, modification strategies, hydrogen production, photocharge utilization

## INTRODUCTION

Rapid urbanization and industrialization have led to a shortage of global energy resources, while significant amounts of harmful and toxic chemical pollutants are being discharged into the environment [1-5]. This necessitates research on environment-friendly technologies to solve the aforementioned environmental and energy crises. Tremendous efforts have been devoted toward developing technologies for producing clean and sustainable energy [6-9]. Among the available renewable energy options, solar energy conversion into chemical fuels has been extensively studied in recent decades [10-14]. Solar energy can become the greenest and most abundant energy source on earth if efficient harvesting and conversion are enabled [15-20]. Among the proposed technologies, visible-light-activated semiconductor photocatalytic technology has been considered one of the most promising strategies for simultaneously overcoming the challenges of environmental pollution and global energy shortage [21-26]. Visible-light semiconductor photocatalytic technologies can convert solar energy into valuable chemical fuels, such as clean H<sub>2</sub> and renewable hydrocarbon fuel, from water splitting, as well as from the photoreduction of CO<sub>2</sub> [27-36]. Concurrently, photocatalytic technology can be used for environmental purification via photocatalytic degradation of various harmful chemical pollutants [37-51]. The increasing public awareness of the impacts of global warming and energy shortages has led to efforts that promote research





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on new sustainable energy sources [52–55]. Hydrogen  $(H_2)$ —a clean energy carrier—has attracted widespread attention as an alternative to fossil fuel to reduce the current environmental pollution and energy crisis [45,56–61]. Carbon-free  $H_2$  can either be used in a typical internal combustion engine to power vehicles or to generate electricity through fuel cells. Presently,  $H_2$  is mainly acquired through the steam reforming of methane using natural gas, which relies on the use of nonrenewable fossil products [62–64].

Since Fujishima and Honda [65] first discovered the photoelectrochemical splitting of H<sub>2</sub>O using a Pt/TiO<sub>2</sub> electrode in 1972, solar H<sub>2</sub> generation via artificial photosynthesis has rapidly emerged as a promising method to convert and store solar energy in the form of carbon-free H<sub>2</sub>. Over the past few decades, photocatalytic water splitting for H<sub>2</sub> evolution has been studied in several systems, including organic-inorganic hybrid, molecular material-based homogeneous, and semiconductor-based heterogeneous systems [19,66-70]. The field of solar H<sub>2</sub> is rapidly expanding and involves multidisciplinary approaches, including the following branches: (1) understanding the fundamental photocatalytic mechanisms and constructing efficient photocatalytic systems [71-76]; (2) developing heterogeneous photocatalytic and homogeneous molecular-photosensitizer systems [19,77-79]; and (3) designing novel semiconductor photocatalysts with unique structures and properties [80-82]. The synergy among all these disciplines plays a key role in improving the efficiencies of photocatalytic systems.

The overall photocatalytic H<sub>2</sub>O splitting reaction (2H<sub>2</sub>O  $\rightarrow$  2H<sub>2</sub> + O<sub>2</sub>) requires a positive Gibbs energy change of 237.13 kJ mol<sup>-1</sup>, corresponding to a minimum energy of 1.23 eV [83]. The basic processes of overall photocatalytic

water splitting include three steps (Fig. 1a): (1) light absorption, (2) charge excitation from the valence band (VB) to the conduction band (CB) of the semiconductors to form electron-hole ( $e^-h^+$ ) pairs, and (3) migration of photoexcited charge carriers ( $e^-h^+$  pairs) to surface active sites to react with H<sub>2</sub>O to generate O<sub>2</sub> and H<sub>2</sub> [10,84– 86]. During step 3,  $e^-h^+$  recombination readily occurs, resulting in poor photocatalytic activity for overall water splitting. Notably, the CB, VB, and bandgap energies play crucial roles in influencing the photocatalytic performance of semiconductor photocatalysts [11,87]. The standard reduction potentials for the half-reactions of O<sub>2</sub> and H<sub>2</sub> evolution are described in Equations (1) and (2), respectively.

 $2H_2O \rightarrow 4H^+ + 4e^- + O_2 \text{ (pH 0, } E^0 = +1.23 \text{ V vs. NHE}$ (normal hydrogen electrode)), (1)

$$4H^{+} + 4e^{-} \rightarrow 2H_2 \text{ (pH 0, } E^0 = 0 \text{ V } \nu \text{s. NHE}\text{).}$$
 (2)

Over the past few years, numerous semiconductor photocatalysts have been developed for photocatalytic H<sub>2</sub> evolution water splitting, such as metal-free compounds (g-C<sub>3</sub>N<sub>4</sub> [11,88–94], SiC [78,95,96], and 6,13-pentacenequinone [97]), inorganic solid solutions ( $Zn_xCd_{1-x}S$  [98– 103], ZnIn<sub>2</sub>S<sub>4</sub> [104–108], Bi<sub>1-x</sub>In<sub>x</sub>TaO<sub>4</sub> [109], HNb<sub>x</sub>- $Ta_{1-x}WO_6$  [59], and  $Mn_xCd_{1-x}S$  [110,111]), oxynitrides (BaTaO<sub>2</sub>N [112], LaTaON<sub>2</sub>, and TaON [113]), sulfides (ZnS [114–117], NiCo<sub>2</sub>S<sub>4</sub> [118], Cu<sub>2</sub>ZnSnS<sub>4</sub> [119], MoS<sub>2</sub> [120–123], CuInS<sub>2</sub> [124–127], and CdS [128–130]), selenides (WSe<sub>2</sub> [131], CoSe<sub>2</sub> [132], CdSe [133-135]), and metal oxides (SrTiO<sub>3</sub> [136-138], Ga<sub>2</sub>O<sub>3</sub> [139], Fe<sub>2</sub>O<sub>3</sub> [140–142], Cu<sub>2</sub>O [143,144], ZrO<sub>2</sub> [145], TiO<sub>2</sub>[146–149], ZnO [150–152],  $Ta_2O_5$  [153,154], and  $CoO_x$  [155]). Among them, CdS is considered one of the most promising photocatalysts for H<sub>2</sub> production due to its ex-



Figure 1 (a) Schematic of the main processes for photocatalytic  $H_2O$  splitting on a semiconductor photocatalyst that typically include: (1) light absorption, (2) charge excitations, (3) charge transfer, (4)  $H_2$  evolution, and (5)  $O_2$  evolution. (b) Advantages of CdS semiconductor photocatalysts.

cellent photoresponse in visible light, which is empowered by its suitable bandgap, high stability, as well as low material and synthesis costs [156–158]. A few review papers have reported the progress in the use of inorganic cocatalysts, construction of heterojunctions, and charge transfer behaviors in heterogeneous photocatalytic H<sub>2</sub> production systems [159,160]. In recent years, some review papers have also discussed different classes of semiconductor photocatalysts, including g-C<sub>3</sub>N<sub>4</sub> [12] and TiO<sub>2</sub> [161,162], for photocatalytic H<sub>2</sub> production. However, there are only limited comprehensive reviews on the development of photocatalytic H<sub>2</sub> generation systems using CdS-based photocatalysts.

CdS—a classical and vital II–VI photo-semiconductor with a bandgap of 2.4 eV—has been extensively investigated as a promising photocatalyst owing to its several fundamental advantages, including excellent charge transport properties, ideal direct bandgap, high electronic mobility, and suitable band edge positions [17,163,164] (Fig. 1b). The CdS surface can be conveniently functionalized with a variety of ligands, which not only render the CdS-based photocatalysts hydrophobicity or hydrophilicity, but also offer selectivity for interaction with other relevant functional materials [165]. Furthermore, CdS evinces efficient photocatalytic performances under visible light (wavelength <520 nm). It also has excellent charge carrier transportation capacities, which can efficiently facilitate the migration of photoexcited  $h^+$  and  $e^-$  in a timely manner, thereby prolonging the lifetime of the photoexcited carriers and resulting in higher photocatalytic activity [166].

It is evident from Fig. 2a that research on  $H_2$  has rapidly expanded in recent years due to its attractiveness and sustainability. Notably, CdS has recently emerged as a hot research topic owing to its application in nanoscale optoelectronic devices and the potential merits of its known fundamental physical properties (Fig. 2b). The development of CdS photocatalysts has been a significant component of energy and environmental research over the past few years. In 1981, Kalyanasundaram et al. [167] reported the production of photocatalytic H<sub>2</sub> and oxygen  $(O_2)$  in stoichiometric proportions from overall water splitting in an aqueous suspension of CdS loaded with Pt and RuO<sub>2</sub> under visible light. In 2007, one-dimensional (1D) CdS nanowires (NWs) synthesized via a solvothermal method in ethylenediamine were found to exhibit a higher rate of photocatalytic H<sub>2</sub> production in the mixed aqueous solution of Na2S and Na2SO3 as sacrificial re-



Figure 2 (a) Number of publications since 1996 on photocatalytic  $H_2$ -production cocatalysts involving the use of "photo\* or light\*" and "hydrogen\* or  $H_2$  or H-2". (b) Number of publications since 1996 on photocatalytic CdS-based  $H_2$ -production cocatalysts involving the use of "CdS\* or Cadmium sulfide\*" and "hydrogen\* or  $H_2$  or H-2. (Reorganized from ISI Web of Science Core Collection, date of information search: May 16, 2020). (c) The roadmap of the development of CdS-based photocatalysts for  $H_2$  generation.

agents [168]. Meanwhile, CdS nanosheets with engineered thicknesses have been fabricated by different methods [169-172]. Subsequently, various noble-metal or non-noble-metal cocatalysts, such as Pt-PdS [173], MoS<sub>2</sub> [166], NiS [174], Ni(OH)<sub>2</sub> [175] and Ni<sub>3</sub>C [176], have been applied in photocatalytic H<sub>2</sub> evolution over CdSbased photocatalysts. Additionally, various CdS-based composite photocatalysts, such as ZnO/CdS [177], CdS/ WO<sub>3</sub> [178], CdS/a-Fe<sub>2</sub>O<sub>3</sub> Z-scheme heterojunction [179], CdS-cluster/graphene [180] and two-dimensional (2D) layered hybrid CdS nanosheets/MoS<sub>2</sub> heterojunctions [66], have also been reported for enhanced photocatalytic H<sub>2</sub> evolution. Despite the significant development, there are only a handful of reviews on CdS-based semiconductor photocatalysts [17,181]. Therefore, a comprehensive review on the strategies to promote CdS-based semiconductors' photocatalytic performances is essential for further development of solar H<sub>2</sub>.

An excellent CdS-based photocatalyst must be inexpensive, efficient, visible-light-driven, stable with fast kinetics, and highly efficient in photocatalytic H<sub>2</sub> evolution (Fig. 3). To achieve these goals, a great deal of effort has been devoted toward enhancing stability, reducing cost, improving charge separation and light absorption, as well as accelerating H<sub>2</sub> evolution kinetics. Herein, we mainly concentrate on the manipulation of the charge carriers of nanostructured CdS for efficient photocatalytic H<sub>2</sub> evolution (Fig. 4). This includes strategies for generating more charge carriers, promoting efficient charge separation, boosting interfacial charge transfer, accelerating charge utilization, and suppressing charge-induced self-photocorrosion. All these modification strategies are thoroughly discussed in this review. Exploring the important progress in this project may facilitate a new opportunity toward designing CdS-based nanostructured semiconductor photocatalysts for efficient photocatalytic H<sub>2</sub> evolution.

#### GENERATING MORE AVAILABLE CHARGE CARRIERS IN NANOSTRUCTURED CdS

#### Sensitization with dyes and plasmonic metals

As mentioned above, the application of nanostructured CdS for photocatalytic H<sub>2</sub> generation has been attracting considerable attention [182,183]. It is generally accepted that the ideal water-splitting bandgap for semiconductor photocatalysts is ~2.0 eV, wherein an adequate portion of visible light can be harvested to generate sufficient  $e^-$  and  $h^+$  with thermodynamic driving forces for photocatalytic



Figure 3 Factors governing the photocatalytic  $H_2$  evolution efficiency of CdS-based photocatalysts and the corresponding engineering and modification strategies.

redox reactions. However, the bandgap of CdS is 2.4 eV, which ensures the sole utilization of solar light with a wavelength shorter than 520 nm. Various methods have been developed to increase the visible-light absorption of CdS-based photocatalysts to generate more available charge carriers. Sensitized semiconductor photocatalysts have been widely used in photoelectrochemistry. Dye sensitization is also a promising strategy to promote photocatalytic H<sub>2</sub> production over CdS-based semiconductor materials, whereby the dye molecules normally do not exhibit photocatalytic H<sub>2</sub> production activities [184,185]. The effectiveness of this step is determined by choosing a suitable dye, light source, and e donor. Dye photosensitization can extend the visible-light absorption range of CdS-based photocatalysts, thereby improving the photon-harvesting efficiency. With increased light absorption, an extra population of excited e from the dye molecules that may speed up charge transfer is presented, resulting in highly efficient photoelectric conversion [186,187]. Through this method, the photoexcited e from the dye molecules with a suitable lowest unoccupied molecular orbital level can pass into the CB of CdS-based semiconductors, thereby contributing additional charges for reactions. Compared with hybridized inorganic materials serving as cocatalysts, metal-free organic dyes display a stronger visible-light absorption capacity, which makes them suitable for enhancing photocatalytic H<sub>2</sub> production activities [185]. Based on the sensitization strategy, semiconductor photocatalysts with narrow



Figure 4 Engineering the charge carriers of nanostructured CdS for efficient photocatalytic H<sub>2</sub> evolution through different modification strategies.

bandgaps, such as graphene quantum dots and conjugated polymers [188,189], have been extensively studied and are considered as good photosensitizer candidates for enhancing the visible-light-driven photocatalysis of CdSbased semiconductors.

Furthermore, coupling CdS photo-semiconductors with other plasmonic metals has been extensively applied in visible-light-driven water splitting activities. The plasmonic energy transfer from the metal to the semiconductor can enhance photocatalytic performances via light scattering, near-field enhancement, hot-electron injection, and resonant energy transfer. For example, Ma et al. [190] reported multi-interfacial plasmon coupling with CdS for efficient photocatalytic H<sub>2</sub> evolution (Fig. 5a). The (Au/AgAu)@CdS core-shell photocatalysts exhibited excellent photocatalytic performances owing to the strong plasmonic light absorption and near-field enhancement induced by the multi-interfacial plasmon coupling, which could significantly enhance the lightharvesting efficiency from the ultraviolet to the nearinfrared region (Fig. 5b and c). Meanwhile, as the number of Au/AgAu gaps increased, light harvesting gradually improved. The four-gap Au/AgAu hybrids displayed the highest extinction intensity and the broadest absorption band, accompanied by the red-shifting of the localized surface plasmon resonance peaks to 576 nm (Fig. 5d–g). Consequently, the (Au/AgAu)@CdS core–shell photocatalysts exhibited an excellent H<sub>2</sub> evolution performance of 4.71 mmol g<sup>-1</sup> h<sup>-1</sup>, which was 47.2 times higher than that of pure CdS photocatalyst [190]. It is envisaged that the combination of various sensitization strategies can be feasibly designed and applied to enhance the photocatalytic H<sub>2</sub> evolution of CdS-based semiconductors [191]. In the future, all these sensitization strategies are expected to be coupled with CdS-based cocatalysts and thoroughly studied with respect to the mechanisms.

#### Construction of multicomponent solid solutions

In addition to the extended visible-light absorption, adjusting the CB and VB redox potentials to achieve higher driving forces of the photoexcited charge carriers is another effective strategy. Notably, the fabrication of multicomponent solid-solution CdS-based photocatalysts provides a platform to fully maximize the advantages of the different components to generate more available charge carriers with considerable energetic redox potentials for photocatalytic reactions. Moreover, the bandgap energy  $(E_{\sigma})$  of multicomponent solid-solution photocatalysts can



Figure 5 (a) Transmission electron microscopy (TEM) image of (Au/AgAu)@CdS core-shell hybrids. (b) Extinction spectra of Au@CdS and multigap (Au/AgAu)@CdS core-shell hybrids. (c) Photocatalytic H<sub>2</sub> evolution rates of different samples. (d-g) Calculated local electric field distributions of one-, two-, three-, and four-gap Au/AgAu hybrids. Reprinted with permission from Ref. [190]. Copyright 2020, Royal Society of Chemistry.

be continuously tuned by controlling their constituent stoichiometry, which will be rather helpful to achieve an optimized balance between visible-light absorption and redox potential. In recent years, doping transitional metal ions (e.g.,  $Ni^{2+}$  [192],  $Cu^{2+}$  [193],  $Mn^{2+}$  [194, 195] and Zn<sup>2+</sup> [196-200]) with CdS to construct CdS-based solidsolution photocatalysts has proven to be effective for improving photocatalytic water splitting for H<sub>2</sub> evolution. Compared with the original CdS, solid solutions, such as  $Zn_xCd_{1-x}S$  and  $Mn_xCd_{1-x}S$ , possess some specific advantages, such as tunable band edge positions and bandgap width, more active sites, and better electrical conductivity [201,202]. Additionally, in long-term photocatalytic reactions, the construction of solid-solution photocatalysts can inhibit photocorrosion during visiblelight irradiation [195,203,204].

Among the solid solutions, Zn-doped CdS ternary alloys ( $Zn_xCd_{1-x}S$ ) have received ample attention in the past few years owing to the crystal structure similarity shared by both ZnS and CdS. A well-matched coordination mode between ZnS and CdS can be established [205,206]. However, most reports on  $Zn_xCd_{1-x}S$  solid solutions reveal the morphological features of micro-/nano-spheres or irregular particles. In a recent example, Han *et al.* [207] fabricated 1D cubic Cd<sub>0.8</sub>Zn<sub>0.2</sub>S solid-solution NWs *via* a facile solvothermal method. Thioglycolic acid (TGA) served as both the template agent and S source. The TGA revealed a "levelling effect" to nullify the disparity in the physicochemical properties of metal ions via its carboxyl and hydrosulfonyl groups, leading to the formation of a cubic Cd<sub>0.8</sub>Zn<sub>0.2</sub>S solid solution with a cylindrical morphology. Owing to the doping of Zn into the lattice of the CdS semiconductor, the absorption edges of the Cd<sub>0.8</sub>Zn<sub>0.2</sub>S semiconductor are extended to longer wavelengths than those of the CdS semiconductor [208]. In other words, with increasing Zn content in the  $Zn_xCd_{1-x}S$ semiconductor, its VB and CB levels shift to more positive and negative positions, respectively. Notably, a higher photo-semiconductor CB level induces a stronger reducing ability, which is pivotal for efficient H<sub>2</sub> generation. Hence, the Cd<sub>0.8</sub>Zn<sub>0.2</sub>S solid-solution photo-semiconductor displayed enhanced H<sub>2</sub> generation activity compared with pure CdS (52.3 mmol  $h^{-1}$ , with Na<sub>2</sub>S-Na<sub>2</sub>SO<sub>3</sub> as a sacrificial agent).

Li *et al.* [111] prepared a  $Mn_xCd_{1-x}S$  nanorod (NR) solid solution in a pure N<sub>2</sub> atmosphere through standard hot-injection synthesis. By adjusting the ratios of Cd and Mn, the  $E_g$  values of the  $Mn_xCd_{1-x}S$  (x = 0-1) solid-solution photocatalysts could be controlled over a wide range ( $E_g = 2.21-3.43$  eV). The improved photocatalytic H<sub>2</sub> generation performance of the  $Mn_xCd_{1-x}S$  NR solid solution was attributed to the stronger oxidation and

reduction ability, charge separation efficiency, as well as light absorption. In particular, the Mn<sub>0.5</sub>Cd<sub>0.5</sub>S NRs exhibited the highest photocatalytic H<sub>2</sub> generation rate of 26 mmol  $g^{-1} h^{-1}$  under visible-light irradiation, with an apparent quantum efficiency (AQE) of 30.3% at 400 nm. The photocatalytic performance of the solid-solution Mn<sub>x</sub>Cd<sub>1-x</sub>S NRs was evidently superior to that of the Mn<sub>x</sub>Cd<sub>1-x</sub>S solid solution and pristine CdS fabricated via the hydrothermal method [111]. The X-ray diffraction results proved that the sample formed a homogeneous  $Mn_rCd_{1-r}S$  rather than a simple mixture of h-CdS and y-MnS. The corresponding geometry supercell models for  $Mn_xCd_{1-x}S$  are illustrated in Fig. 6a, while the CB and VB edges of the Mn<sub>x</sub>Cd<sub>1-x</sub>S NR photocatalysts are presented in Fig. 6b. It was apparent that the CB became more negative with increasing Mn content, thereby resulting in a significantly extended bandgap. The improved H<sub>2</sub> generation activity of the Mn<sub>0.5</sub>Cd<sub>0.5</sub>S NR solid-solution photocatalysts could be ascribed to a suitable bandgap and an adjusted CB position. In addition, the separation and transfer capacity of photoexcited  $e^{-}$  and  $h^{+}$  play a key role in photocatalytic H<sub>2</sub> generation. Fig. 6c displays the transient photocurrent response of the Mn<sub>0.5</sub>Cd<sub>0.5</sub>S NRs under visible-light irradiation. Under the same conditions, the photocurrent of the Mn<sub>0.5</sub>Cd<sub>0.5</sub>S NR solid solution was evidently higher than that of bare CdS and MnS. Unfortunately, the photocatalytic H<sub>2</sub> generation performance of these multicomponent solid solutions remains insufficient for satisfying the basic requirements for practical applications. Therefore, it is highly desirable to exploit other novel strategies to further enhance the photocatalytic  $H_2$  generation performance of CdS-based solid-solution photocatalysts.

Although both the CB position and bandgap of CdSbased solid-solution semiconductor photocatalysts can be adjusted to a certain extent by tuning the value of x(stoichiometric ratio) to enhance the photocatalytic H<sub>2</sub> generation activity, the rapid recombination of photoexcited charges remains a crucial challenge that limits the further improvement of photocatalytic performances. The construction of CdS-based solid-solution photocatalysts results in a tunable bandgap, wherein these adjustable band potentials may lead to new photoredox reactions (beyond water splitting) and help in the chemical adsorption of specific reactants. Notably, the environmental concern of this type of composite semiconductor photocatalyst can also be assuaged by reducing the Cd content. In addition to constructing bimetallic solid solutions, the photocatalytic H<sub>2</sub> generation performance of CdS-based solid solutions can be further enhanced by intentionally introducing other transition metal ions.

#### PROMOTING EFFICIENT BULK CHARGE TRANSFER IN NANOSTRUCTURED CdS

In the past few years, efforts have been made to control the morphology, shape, and size of CdS with various



Figure 6 (a) Corresponding geometry supercell models for  $Mn_xCd_{1-x}S$ . (b) CB and VB of the  $Mn_xCd_{1-x}S$  NRs solid solutions. (c) *I-t* curves of  $Mn_{0.5}Cd_{0.5}S$ , MnS, and CdS. Reprinted with permission from Ref. [111]. Copyright 2018, Elsevier.

nanostructures (NSs). Many studies have reported the photocatalytic performance of CdS semiconductor photocatalysts with unique NSs, such as the 0D, 1D, 2D, and 3D structures. Different NSs impose varying effects on the photocatalytic H<sub>2</sub> generation performance of CdS photocatalysts (Fig. 7). Notably, the photocatalytic  $H_2$ generation performance of photocatalysts with different morphologies, structures, and sizes can be affected by different synthetic methods. Nevertheless, with regard to CdS and CdS-based nanocomposite photocatalysts, researchers have focused on environmentally friendly and low-cost synthetic methods. These approaches include sonochemical, solvothermal, chemical bath deposition, impregnation, template, and template-free methods. Some fabrication methods for CdS photo-semiconductors and CdS-based nanocomposites are listed in Table 1.

#### Construction of 0D nanostructures

There are many synthetic approaches, such as solvothermal, combustion, sonochemical, biogenic synthesis, complex thermolysis, microwave-assisted polyol synthesis, and chemical precipitation methods, for constructing 0D CdS NSs [73,258–264]. Researchers suggest that although 0D CdS nanomaterials possess large surface area, they are susceptible to severe agglomeration, which reduces the photocatalytic efficiency.

Wang *et al.* [265] fabricated 0D CdS nanoparticles (NPs) modified with covalent triazine-based frameworks (CTF-1) in a controlled manner by means of a facile one-pot solvothermal synthesis. As the triazine unit of CTF-1 has an apparent Lewis property on its nitrogen sites, size-

 Table 1
 Synthesis methods for CdS nanostructures



Figure 7 Descriptions of the morphologies of CdS photocatalysts.

controlled and highly dispersed CdS NPs can be prepared and stabilized on CTF-1 layers. The morphology of the as-fabricated 0D CdS NP nanocomposites was investigated *via* scanning electron microscopy (Fig. 8a). The formation processes of the porous CTF-1 frameworks and the subsequent decoration with 0D CdS NPs to form CdS/CTF-1 nanocomposite are presented in Fig. 8b. Compared with bare CdS, the electrochemical impedance spectrum of CdS/5%CTF-1 displays a smaller semicircle, implying that CdS/CTF-1 possesses a reduced charge transfer resistance for photoinduced e<sup>-</sup> (Fig. 8c). This result was further supported by the photoluminescence (PL) spectra, which were used to study the recombination rate of the photoexcited charge carriers (Fig. 8d). The PL peak intensity of CdS/5%CTF-1 was evidently lower than

Photocatalyst	Synthesis method	Morphology	Precursor materials	$\begin{array}{c} \text{HER} \\ (\text{mmol } \text{g}^{-1} \text{ h}^{-1}) \end{array}$	AQE (420 nm)	Ref.
CdS–TiO <sub>2</sub>	Hydrothermal	Nanodots	Cd(CH <sub>3</sub> COO) <sub>2</sub> ·2H <sub>2</sub> O, dimethyl 1.5 sulfoxide		11.9%	[209]
CdS	Hydrothermal synthesis	Nanoparticles	Graphdiyne, Cd(Ac) <sub>2</sub> ·2H <sub>2</sub> O	4.1	-	[210]
CdS	Hydrothermal	Nanoparticles	Cd(CH <sub>3</sub> COO) <sub>2</sub> ·2H <sub>2</sub> O, DMSO	58.9	-	[211]
CdS	Solid-state	Nanoparticles	$Cd(Ac)_2 \cdot 2H_2O$ , thioacetamide 1.15		16.5%	[212]
CdS	Microwave	Nanoparticles	$C_4H_{10}CdO_4$ ·2 $H_2O$ , $H_2NCSNH_2$	11.4	-	[213]
CdS	Hydrothermal	Nanoparticles	Cd(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O, NH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub>	0.56	-	[214]
CdS	Hydrothermal	Nanoparticles	Cd(CH <sub>3</sub> COO) <sub>2</sub> , Na <sub>2</sub> S	14.2	8.7%	[215]
CdS	Hydrothermal	Nanoparticles	Na <sub>2</sub> S, Cd(CH <sub>3</sub> COO) <sub>2</sub>	5.9	8.6%	[57]
CdS	Solvothermal	Nanoparticles	CdCl <sub>2</sub> ·2.5H <sub>2</sub> O, thiourea	$CdCl_2 \cdot 2.5H_2O$ , thiourea 1.89		[216]
CdS	Hydrothermal	Nanoparticles	Cd(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O, dimethyl sulfoxide	0.61	-	[217]
CdS	Hydrothermal	Nanoparticles	Cd(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O, thiourea	1.26	-	[218]
CdS/CdWO <sub>4</sub>	Hydrothermal	Nanoparticles	CH <sub>3</sub> CSNH <sub>2</sub> , Cd(CH <sub>3</sub> COO) <sub>2</sub> ·2H <sub>2</sub> O	9.17	-	[219]

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(Continued)

Photocatalyst	Synthesis method	Morphology	Precursor materials	$(\text{mmol } g^{-1} h^{-1})$	AQE (420 nm)	Ref.
CdS	Directly reacting	Nanoparticles	Na <sub>2</sub> S, Cd(CH <sub>3</sub> COO) <sub>2</sub>	5.89	19%	[220]
CdS	Hydrothermal	Nanoparticles	$NaS_2 \cdot 9H_2O$ , $Cd(NO_3)_2 \cdot 4H_2O$	0.33	34.3%	[221]
CdS	Hydrothermal	Nanoparticles	$Cd(Ac)_2 \cdot 2H_2O, CH_4N_2S$	2.85	10%	[222]
CdS/Cu <sub>2</sub> O/g-C <sub>3</sub> N <sub>4</sub>	Hydrothermal	Nanoparticles	Na <sub>2</sub> S, CdCl <sub>2</sub>	1.84	-	[223]
CdS-BCNNTs	Hydrothermal	Nanoparticles	Cd(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O, Na <sub>2</sub> S	0.526	4.01	[224]
CdS/ZnS	Solvothermal	Nanorod	CdCl <sub>2</sub> ·2.5H <sub>2</sub> O, thiourea	24.1	9.3%	[225]
CdS/TiO <sub>2</sub>	Solvothermal	Nanorod	Cd(NO <sub>3</sub> ) <sub>2</sub> , thiourea	1.118	-	[226]
CdS@MoO <sub>x</sub>	Solvothermal photode- position	Nanorod	Cd(NO <sub>3</sub> ) <sub>2</sub> , thiourea	5.42	-	[227]
CdS/g-C <sub>3</sub> N <sub>4</sub>	Solvothermal method	Core/shell nanowires	Cd(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O, thiourea	4.15	4.3%	[228]
CdS	Solvothermal	Nanowires	CdCl <sub>2</sub> ·2.5H <sub>2</sub> O, (C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> NCSSNa	0.15	44.9%	[229]
CdS	Self-templated synthesis	Nanoporous structures	CdCl <sub>2</sub> ·2.5H <sub>2</sub> O, NaOH, Na <sub>2</sub> S·9H <sub>2</sub> O	27.33	60.34%	[169]
CdS	One-pot synthesis	Nanorods	Cd(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O, CS(NH <sub>2</sub> ) <sub>2</sub> , H <sub>2</sub> PtCl <sub>6</sub>	10.29	-	[230]
CdS	Hydrothermal	Nanorods	(CH <sub>3</sub> CO <sub>2</sub> ) <sub>2</sub> Cd·xH <sub>2</sub> O, CH <sub>4</sub> N <sub>2</sub> S	15.56	-	[231]
CdS	Hydrothermal	Nanorods	Cd(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O, thioacetamide	24.15	-	[232]
CdS	Hydrothermal	Nanorods	Cd(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O, NH <sub>2</sub> CSNH <sub>2</sub>	15.55	6.9%	[233]
CdS	Hydrothermal	Nanorods	Cd(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O, thiourea	1.131	-	[234]
CdS	Hydrothermal	Nanorods	CdCl <sub>2</sub> ·2.5H <sub>2</sub> O, CH <sub>4</sub> N <sub>2</sub> S	106	29%	[235]
CdS	Hydrothermal	Nanorods	CdCl <sub>2</sub> ·2.5H <sub>2</sub> O, NH <sub>2</sub> CSNH <sub>2</sub>	4.64	11.8%	[236]
CdS	Hydrothermal	Nanorods	CdO, Na <sub>2</sub> S	11.58	16.3%	[237]
CdS	Solvothermal	Nanorods	CdCl <sub>2</sub> ·2.5H <sub>2</sub> O, thiourea	3.5	-	[155]
CdS/Ti <sub>3</sub> C <sub>2</sub>	Hydrothermal	Nanorods	Cd(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O	2.407	35.6%	[238]
Pt-CdS/g-C <sub>3</sub> N <sub>4</sub> -MnO <sub>x</sub>	Hydrothermal	Nanorods	Cd(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O	924,4	1.745%	[239]
CdS	Hydrothermal	Nanorods	Cd(NO <sub>3</sub> ) <sub>2</sub> , NH <sub>2</sub> CSNH <sub>2</sub>	1.84	21.2%	[240]
CdS	Hydrothermal	Nanorods	$Cd(NO_3)_2$ , thiourea	167.1	1.5%	[241]
CdS/ZnS	Solvothermal, chemical bath deposition	Nanorod	CdCl <sub>2</sub> , CH <sub>4</sub> N <sub>2</sub> S	239	16.8%	[18]
CdS	Solvothermal,	Nanorod	$Cd(Ac)_2 \cdot 2H_2O, CH_4N_2S$	20.2	-	[242]
CdS	Directly reacting	Nanorod	Cd(NO <sub>3</sub> ) <sub>2</sub> , thiourea	37.1	43%	[243]
CdS	Solvothermal	Nanorod	$Cd(NO_3)_2$ , thiourea	0.206	-	[244]
CdS/g-C <sub>3</sub> N <sub>4</sub>	vapor deposition	Nanotubes	CdCl <sub>2</sub> ·2.5H <sub>2</sub> O	0.392	-	[245]
CdS	Hydrothermal	Nanosheets	Cd(Ac) <sub>2</sub> ·2H <sub>2</sub> O, sulfocarbamide, ethylenediamine	27.8	14.7%	[246]
CdS/GO	Hydrothermal	Nanosheets	CdCl <sub>2</sub> ·2.5H <sub>2</sub> O, DETA	10.5	29.5%	[247]
CdS	Hydrothermal	Nanosheet	CdSO <sub>4</sub> , DL-dithiothreitol	1.293	-	[248]
CdS	Hydrothermal	Nanosheets	CdCl <sub>2</sub> ·2.5H <sub>2</sub> O, S powder	138.7	-	[249]
CdS-FeP	Hydrothermal	Nanosheets	CdCl <sub>2</sub> ·2.5H <sub>2</sub> O, S powder	18.63	11.2	[250]
CdS	Hydrothermal	Nanosheets	CdCl <sub>2</sub> ·2.5H <sub>2</sub> O, DETA	7.37	-	[251]
MoS <sub>2</sub> /CdS	Two-step hydrothermal	Core/shell-like	Ammonium molybdate, thiourea	38.75	14.7%	[252]
CdS	Precipitation	Cubic-Phase	Cd(NO <sub>3</sub> ) <sub>2</sub> , Na <sub>2</sub> S, Na <sub>2</sub> SO <sub>3</sub>	18	-	[253]
CdS	One-pot wet-chemical	Nanocrystals	CdO	1.98	-	[254]
CdS	Hydrothermal	Nanospheres	Cd(CH <sub>3</sub> COO) <sub>2</sub> ·2H <sub>2</sub> O, thiourea	4.65	7.31%	[255]
CdS	Hydrothermal	Nanospheres	Cd(CH <sub>3</sub> COO) <sub>2</sub> , thiourea	44.65	-	[256]
CdS	Hydrothermal	Nanospheres	$Cd(Ac)_2 \cdot 2H_2O$ , thiourea	1.44	-	[257]



**Figure 8** (a) SEM image of CdS, (b) schematic of the formation of 0D CdS NPs/CTF-1, (c) Nyquist plots, (d) PL spectra, and (e) amount of  $H_2$  evolved over CTF-1 (1), CdS (2), CdS NPs/0.5%CTF (3), CdS NPs/1%CTF (4), CdS NPs/3%CTF (5), CdS NPs/5%CTF (6), CdS NPs/10%CTF (7), without catalyst or visible-light irradiation (8), and physically mixed CdS and CTF-1 (9). Reprinted with permission from Ref. [265]. Copyright 2018, Royal Society of Chemistry.

that of the bare 0D CdS NPs, suggesting that the charge recombination rate decreased in the nanocomposites. The photocatalytic  $H_2$  generation performance of the as-fabricated CdS/CTF-1 was investigated using Pt as a cocatalyst in a lactic acid medium under visible-light irradiation. Fig. 8e shows that the  $H_2$  generation rate of CdS/5%CTF-1 was better than those of bare CdS NPs and CTF-1. An insignificant amount of  $H_2$  was released when bare CTF-1 was used as the catalyst. Hydrogen could not be detected without photocatalysts or visible-light irradiation, which suggested that  $H_2$  generation was induced by irradiating CdS/5%CTF-1.

#### **Construction of 1D nanostructures**

Generally, 1D CdS NRs with improved charge transport properties compared with the 0D CdS quantum dots displayed quantum constraint effects and directional charge carrier transport. This reduced the recombination losses at the grain boundaries and enhanced the light harvesting capability [266–268]. The visible-light absorption occurred along the longer dimensions (microns or more) of the 1D NSs, while carrier separation through diffusion took place over a short radial distance [269]. The enhanced light absorption, combined with the merits of long distance as well as fast charge transfer, makes the 1D NS a promising candidate for solar energy conversion. There is increasing attention on the fabrication of 1D photocatalytic NSs, such as NWs, NRs, and their core-shell structures [270–273].

In 1D CdS NRs, the transfer velocity of the carrier is different in the axial and radial directions. Generally, the carrier moves much faster in the radial direction than in the axial one [274]. Thus, it is particularly vital to construct the morphology of CdS nano-semiconductors for 1D NR semiconductors with ideal diameters and high aspect ratios. Several methods, including ion-exchange [163], ligand-assisted growth [275,276], and metal particle-seeded growth [277], have been developed to fabricate 1D rod-shaped semiconductor materials. For example, Wu et al. [278] prepared 1D CdS NRs using the seeded growth method and studied the effects of 1D CdS and CdS-Pt NRs with different diameters on the dissociation kinetics and exciton localization. They studied the excitation dynamics and electronic structure of the photocatalytic 1D CdS-Pt NRs. In the presence of Pt, e were efficiently transferred from CdS to Pt, and photoexcited  $e^{-}$ -h<sup>+</sup> pair recombination was suppressed. The tips of 1D CdS NRs can offer selective deposition sides for Pt, wherein the selectively tip-deposited Pt can promote the charge separation of 1D CdS NRs and CdS-based NSs. These results demonstrate that 1D CdS NRs with larger diameters possess more specific properties than tradi-

REVIEWS

tional CdS NR structures. Many factors, including reaction time and temperature, as well as reactant and surfactant amounts, influence the synthesis of 1D CdS NSs.

#### Construction of 2D nanostructures

The photochemical, optical, and photoelectrical properties of the photo-semiconductors can be indirectly influenced by their morphology, size, and structure [279– 281]. Since the discovery of 2D photocatalytic nanomaterials, 2D CdS NSs have attracted much attention because of their unique phase characteristics, and excellent photocatalytic properties, larger surface area and lower recombination rate of  $e^-h^+$  pairs [171,246,282,283]. To synthesize 2D CdS photo-semiconductors, it is important to seek a low-cost and environment-friendly process that can control the formation of reasonable sizes and predictable shapes.

Apparently, the decreased thickness of 2D semiconductor nanosheets can effectively reduce the migration distance of photogenerated e<sup>-</sup> from the bulk phase to the semiconductor photocatalyst surface, thereby preventing the recombination of photogenerated  $e^{-}h^{+}$  pairs inside the semiconductor. For instance, in 2013, Xu et al. [170] synthesized ultrathin CdS nanosheets with thickness of ~4 nm via ultrasonic-induced aqueous exfoliation of lamellar CdS-diethylenetriamine hybrid nanosheets using L-cysteine as a stabilizing agent. The as-obtained CdS ultrathin nanosheets achieved H<sub>2</sub> production rates of 41.1 mmol  $g^{-1} h^{-1}$  with an AQE of 1.38% at 420 nm. In 2018, Bie et al. [171] synthesized the thinnest CdS nanosheets (1.5-nm-thick) through a simple and low-cost oil-bath method using sodium citrate as the structuredirecting agent. They exhibited a photocatalytic H<sub>2</sub> production rate of 2.155 mmol  $g^{-1} h^{-1}$ , which was approximately 3.7 times higher than that of CdS NPs  $(0.582 \text{ mmol g}^{-1} \text{ h}^{-1})$ . More recently, Xie *et al.* [172] constructed five-layer ultrathin Cd<sub>4</sub>S<sub>5</sub> nanosheets with unsaturated surface S anions via chemical vapor deposition. The thickness of the CdS nanosheet was approximately 1 nm. The average H<sub>2</sub> evolution rate of the ultrathin nanosheets was 29.44 mmol  $g^{-1} h^{-1}$ . Evidently, this unique structure induces a higher CB position than that of their thicker counterparts, which can fundamentally improve electrical conductivity, reduce recombination rate, and eventually enhance the driving force for the H<sub>2</sub> evolution reaction (HER). Consequently, ultrathin CdS nanosheets achieve a high AQE of 4.15% under 420nm light irradiation.

Meanwhile, exposing the reactive facets on the surface of 2D CdS nanosheets is another strategy to boost the photocatalytic H<sub>2</sub> evolution. For instance, Li *et al.* [284] synthesized flake-like hexagonal phase CdS micro-/nanoleaves with exposed (0001) facets to promote the photocatalytic activity toward H<sub>2</sub> generation (Fig. 9a). The growth process of the dendrites is shown in Fig. 9b. Compared with CdS NPs, the photocatalytic H<sub>2</sub> generation activity of CdS micro-/nano-leaves with NR-branched NSs was significantly enhanced (468.4 mmol h<sup>-1</sup>) (Fig. 9c). The average H<sub>2</sub> evolution rate of photocatalytic reactions reached 740.9 mmol h<sup>-1</sup>, which was more than 6 times that of spheroidal particles under visible-light irradiation. The catalysts also evinced good stability (Fig. 9d). The enhanced activity of the CdS micro-/nanoleaves was partly due to the unique 2D micro-/NS and the exposure of high surface energy facets (0001) [284].

Additionally, constructing a 2D/2D NS coupled with layered composite photocatalysts could further boost charge separation between the CdS nanosheets and the other 2D cocatalysts owing to strongly coupled contact interfaces [179,285,286]. For example, Ma et al. [66] successfully synthesized 2D/2D layered hybrid CdS/MoS2 nanocomposites via a one-step hydrothermal method. The coupling of 2D MoS<sub>2</sub> NSs as cocatalysts boosted the photocatalytic H<sub>2</sub> evolution performance of CdS NSs (Fig. 10). It was confirmed that the 2D CdS/1%MoS<sub>2</sub> nanocomposites exhibited the highest photocatalytic H<sub>2</sub> generation activity (1.75 mmol  $g^{-1} h^{-1}$ ) in an aqueous solution containing sulfite and sulfide under visible light. The loading of ultrathin 2D MoS<sub>2</sub> NSs and the tight 2D/ 2D coupling interfaces led to excellent H<sub>2</sub> generation performances owing to the effectively boosted separation and migration of charge carriers as well as improved surface H<sub>2</sub> evolution kinetics. In our previous study, we demonstrated that the 2D/2D CdS/Cu<sub>7</sub>S<sub>4</sub> nanocomposite could serve as advanced photocatalysts for photocatalytic water splitting toward  $H_2$  generation [246]. The highest achieved H<sub>2</sub> generation rate of the 2D/2D CdS/2%Cu<sub>7</sub>S<sub>4</sub> nanocomposites was 27.8 mmol  $g^{-1} h^{-1}$ , which was approximately 11 times higher than that of pure CdS NSs (2.6 mmol  $g^{-1} h^{-1}$ ). The construction of the 2D/2D CdS/ Cu<sub>7</sub>S<sub>4</sub> heterojunction not only promoted photoexcited e<sup>-</sup>h<sup>+</sup> pair separation, boosted photoexcited e<sup>-</sup> transfer, and prolonged the lifetime of the photoexcited e, but also increased the visible-light absorption and H<sub>2</sub> generation kinetics.

Compared with the interfaces of 0D/1D, 0D/2D, 1D/ 1D, and 1D/2D, the 2D/2D coupled nanocomposites display a larger contact surface, which is conducive to more efficient interfacial charge migration [285]. Therefore, the construction of unique interfaces with tight 2D/



**Figure 9** (a) Crystal structure of the hexagonal CdS. (b) Schematic of the growth process of CdS. (c) Average photocatalytic H<sub>2</sub> generation rate of CdS. (d) Time courses of photocatalytic H<sub>2</sub> generation on CdS, (1) without HF, and with (2) 0.125 mol  $L^{-1}$  HF, (3) 0.200 mol  $L^{-1}$  HF, and (4) 0.500 mol  $L^{-1}$  HF. Reprinted with permission from Ref. [284]. Copyright 2012, Royal Society of Chemistry.

2D coupling and large surface areas is critical for achieving efficient charge separation and photocatalytic  $H_2$  generation activity.

#### Construction of 3D nanostructures

CdS photocatalysts with 3D NSs, such as hierarchical dendritic CdS, porous CdS flowers, and hollow spheres, have been widely studied [284,287-291]. Because of their unique structural characteristics, such as low material density and high surface/volume ratio, constructing 3D CdS NSs has been considered as a useful strategy to boost the photocatalytic activity. For example, to overcome the shortcomings of traditional non-porous CdS/TiO<sub>2</sub> spherical nanocomposites (rapid recombination of e<sup>-</sup>-h<sup>+</sup> pairs and inferior light absorption), Wu et al. [292] designed non-noble metal cocatalysts covered in hollow core-shell NSs for photocatalytic H<sub>2</sub> evolution. The unique hollow structure enhanced the absorption in the visible spectral range, while the non-noble metal cocatalysts provided active sites for H<sub>2</sub> evolution. The coupling of these three components reduced photogenerated e<sup>-</sup>-h<sup>+</sup> recombination. The synergistic effects of photocatalysts and  $e^{-}$ -h<sup>+</sup>

separation were preliminarily studied. Chen et al. [293] synthesized hollow core-shell CdS/TiO<sub>2</sub>/Ni<sub>2</sub>P photocatalysts for H<sub>2</sub> production with SiO<sub>2</sub> spheres as sacrificial templates (Fig. 11a and b). The formation of CdS/TiO<sub>2</sub> nanocomposites extended the absorption range of TiO<sub>2</sub> into the visible-light region, while the outer TiO2 layer protected the CdS core from photocorrosion. The hollow structure improved the transmission capacity of light and reduced the reflectance of visible light. The H<sub>2</sub> generation rate of CdS@TiO<sub>2</sub> (4.65 mmol  $g^{-1} h^{-1}$ ) showed significant improvement compared with that of CdS/TiO2/Ni2P nanocomposites (13.91 mmol  $g^{-1} h^{-1}$ ). The H<sub>2</sub> generation the CdS/TiO<sub>2</sub>/Pt nanocomposite for rate was 16.81 mmol  $g^{-1} h^{-1}$ , which was slightly higher than that of CdS/TiO<sub>2</sub>/Ni<sub>2</sub>P (Fig. 11c and d). The activity of CdS/Ni<sub>2</sub>P and CdS/TiO<sub>2</sub>/Ni<sub>2</sub>P remained rather unchanged after 5 cycles. However, CdS/Pt and CdS/TiO<sub>2</sub>/Pt exhibited a diminishing photocatalytic activity after each recovery cycle due to photocorrosion and poor stability of the Pt deposit (Fig. 11e) [293]. In the future, it is expected that more 3D CdS-based NS photocatalysts can be constructed through the self-assembly of promising 2D ultrathin CdS



**Figure 10** (a) TEM image of CdS/1%MoS<sub>2</sub>, (b) time-dependent of  $H_2$  generation (1: CdS NSs, 2: CdS-0.5% MoS<sub>2</sub>, 3: CdS-1% MoS<sub>2</sub>, 4: CdS-2% MoS<sub>2</sub>, 5: CdS-3% MoS<sub>2</sub>, 6: CdS-5% MoS<sub>2</sub>), (c) the average rate of photocatalytic  $H_2$  generation over the photocatalysts, and (d) comparison of  $H_2$  generation activities of CdS/1%MoS<sub>2</sub>, CdS/1%Pt, and physically mixed sample of CdS/1% MoS<sub>2</sub>. Reprinted with permission from Ref. [66]. Copyright 2017, Elsevier.

nanosheets, which could maximize all the advantages of 2D nanosheets by circumventing their unfavorable stacking.

## BOOSTING INTERFACIAL CHARGE SEPARATION IN NANOSTRUCTURED CdS

Boosting the interfacial charge transfer of CdS-based photocatalysts can also be achieved by constructing semiconductor heterojunctions, which induce an internal electrical field for interfacial charge transfer [10]. Usually, semiconductor heterojunctions are categorized into the Schottky junction, as well as carbon-based, direct Z-scheme, Type I, Type II, and Type III heterojunctions. The Schottky and Type II junctions are beneficial for constructing efficient CdS-based photocatalysts. For instance, heterojunctions between CdS and other semiconductors (such as  $Fe_2O_3$  [179], TiO\_2 [63,226,294,295], g-C\_3N\_4 [296,297], NiWO\_4 [298,299], BiOBr [300], WO\_3 [165,178,222,301], MoO\_2 [302], ZnO [150,303–306], LaFeO\_3 [307], SiC [308], Bi\_2WO\_6 [309], and Co\_3O\_4 [310]) have been widely used in photocatalytic H<sub>2</sub> evolution.

However, there are still debatable aspects associated with the separation mechanism of photogenerated  $e^-h^+$  pairs in these heterojunctions [311]. In addition, the reduction and oxidation potentials will be compromised

after forming the Type II heterojunction, restricting their activity enhancement. Therefore, various favorable heterojunctions, such as p-n, Z-scheme, Schottky-based, carbon-based, and multicomponent heterojunctions, have also been studied to improve the photocatalytic performance of CdS-based photocatalysts.

#### p-n heterojunction

The p-n heterojunction has been widely applied toward enhancing the photocatalytic performance of CdS-based photocatalysts. The formation mechanism of the p-n heterojunction is shown in Fig. 12 [311]. Under visiblelight illumination, the e<sup>-</sup> from the n-type semiconductor are transferred to the p-type semiconductor owing to the larger work function of the latter. This results in the formation of a built-in electric field, which is beneficial for the transfer of photogenerated e<sup>-</sup> between p-type and n-type semiconductors.

Ai *et al.* [224] designed novel CdS/boron carbon nitride nanotubes (BCNNTs) using a new band-matching transformation strategy. In this system, they realized the heterojunction transformation from Type I to Type II by tuning the carbon content of BCNNTs (Fig. 13a). The rational design of the band-matching process played an important role in constructing efficient photocatalysts *via* 

## **REVIEWS**



Figure 11 (a) Schematics of CdS@TiO<sub>2</sub>/Ni<sub>2</sub>P preparation, (b) TEM images of SiO<sub>2</sub>, SiO<sub>2</sub>/CdS, SiO<sub>2</sub>/CdS/TiO<sub>2</sub>, CdS/TiO<sub>2</sub>, and CdS/TiO<sub>2</sub>/Ni<sub>2</sub>P, (c) photocatalytic  $H_2$  evolution, (d) rate of  $H_2$  evolution and (e) stability of  $H_2$  evolution. Reprinted with permission from Ref. [292]. Copyright 2019, Elsevier.



**Figure 12** Formation mechanism of the p-n heterojunction: (a) before contact, (b) in contact, (c) photogenerated charge transfer, and (d) unsuccessful direct Z-scheme transfer of photogenerated charge carriers. Reprinted with permission from Ref. [311]. Copyright 2018, Elsevier.

the formation of a strong internal electric field to guarantee rapid charge separation and transfer. As the C content increased, the bandgap of BCNNTs decreased from 2.79 to 2.05 eV. At low C content, the CdS/BCNNTs belong to the Type I heterojunction, and all of the photogenerated  $e^-$  and  $h^+$  were transferred to the CB and VB of CdS, respectively. With a high C content, the CB potential of BCNNTs was more positive than that of CdS,

and VB was negative relative to CdS. This composite also belongs to the Type I heterojunction, wherein the CdS photogenerated e<sup>-</sup> and h<sup>+</sup> were all transferred to BCNNTs. However, with moderate C-doping, both the CB and VB of BCNNTs were more positive than those of pure CdS, thereby fulfilling the requirement for the formation of Type II heterojunctions (Fig. 13c). The internal electric field between the CdS and BCNNTs could boost the separation of photogenerated  $e^-$ - $h^+$  pairs. Hence, the photocatalytic performance of the Type II heterojunctions exceeded that of the Type I heterojunction between CdS and BCNNTs (Fig. 13b) [224]. Zhang et al. [310] constructed a ZIF-67(Co)-derived Co<sub>3</sub>O<sub>4</sub> framework modified with a CdS p-n heterojunction photocatalyst (Fig. 14a-c). The formation of p-n heterojunctions could effectively reduce the bandgap of the composite, enhance the light absorption intensity, shorten the fluorescence lifetime (2.61 ns), accelerate the electron injection rate  $(K_{\rm ET} = 1.17 \times 10^8 \, {\rm s}^{-1})$ , and improve electron injection efficiency ( $\eta_{ini}$  = 30.6%) (Fig. 14d–f). The hollow structure of the  $Co_3O_4$  framework served not only as a h<sup>+</sup> collector



Figure 13 (a) Schematic for band-matching transformation of the CdS/BCNNTs photocatalytic system, (b) average  $H_2$  evolution rate of CdS/BCNNTs, (c) schematic of the band-matching transformation process between BCNNTs (X= 1, 2, 3, 4, 5) and CdS. Reprinted with permission from Ref. [224]. Copyright 2020, Elsevier.

but also as a supporting material for CdS, thus increasing the specific surface area of the catalyst [310]. The results further confirmed the key roles of the p-n heterojunction toward achieving efficient charge separation and transfer across the heterojunction interface as well as the prolonged lifetime of the charge carriers.

#### Schottky junctions

Enhancing the photocatalytic activity of CdS-based semiconductors could also be realized by constructing Schottky junction-based internal electrical fields [4,87]. The Schottky junction can boost the spatial separation of  $e^-$  and  $h^+$ , thus delaying their recombination and lengthening their lifetime. Usually, for metal photosemiconductor systems, because of the higher work function ( $\Phi_m$ ) of the metal than that of the semiconductor ( $\Phi_s$ ), the photoexcited  $e^-$  in the photo-semiconductor migrate to the metal and realign their Fermi levels; this leads to the formation of a Schottky barrier with an upward band bending and depletion layer (Fig. 15). As an effective method to trap photogenerated  $e^-$ , Schottkybased heterojunctions can promote  $e^-h^+$  separation in photocatalysis [312].

When photo-semiconductors are coupled with metal, the e<sup>-</sup> in the CB of the photo-semiconductor approach the metal until the two Fermi energy levels are in equilibrium. A space-charge layer is formed on the surface of the metal, resulting in efficient separation of photoexcited  $e^{-}h^{+}$  pairs and migration of the charge carriers. For example, the work functions of metallic Cd clusters and CdS are 4.08 and 5.18 eV, respectively (Fig. 16a and b) [313]. After contact, the e in Cd migrate to the CdS until the Fermi levels are realigned, triggered by the higher Fermi level in metallic Cd than CdS. When CdS is excited by visible-light irradiation, the built-in field drives the migration of the photoexcited e on the CdS to the Cd sites. Thus, the construction of a Schottky junction can enhance visible-light-driven water splitting for H<sub>2</sub> generation. Similarly, Shang et al. [314] decorated CdS NPs on Cd nanosheets to form Schottky junctions by the polyol reduction method and oxidation-sulfurization process (Fig. 16c and d). The Cd nanosheets that served as a support were evidently better than those of carbon nanotubes and graphene in that study because the work function of Cd is much higher than that of the nanocarbon materials (Fig. 16e). More importantly, the black



Figure 14 (a) Schematic of the fabrication of  $[Co_3O_4/CdS/Ni]$ . Schematics for energy bands of p-CdS and n-Co<sub>3</sub>O<sub>4</sub> (b) before contact and (c) after the formation of the p-n heterojunction. (d) PL spectra, (e) time-resolved PL spectra, and (f) photocurrent of the as-prepared photocatalysts. Reprinted with permission from Ref. [310]. Copyright 2018, Elsevier.



**Figure 15** Schematic for the formation of the Schottky barrier  $(\Phi_m > \Phi_s)$ : (a) before contact and (b) thermal equilibrium after contact  $(E_g, \Phi, E_F)$ , and  $\chi$  represent the bandgap energy, work function, Fermi level, and electron affinity, respectively).

color of the nanocarbon shields a fraction of the visible light from reaching CdS [314]. Xiao *et al.* [238] demonstrated that a 1D CdS NR/2D MXene nanosheet with Schottky junctions reached an excellent photocatalytic H<sub>2</sub> evolution rate of 2407 µmol g<sup>-1</sup> h<sup>-1</sup>, which was attributed to the high charge carrier mobility of highly conducting metallic Ti<sub>3</sub>C<sub>2</sub> and strong interfacial coupling between CdS and Ti<sub>3</sub>C<sub>2</sub> [238].

Additionally, it is well known that nanocarbon mate-

rials (e.g., graphene [291,315–319], carbon quantum dots [211,236,257,320,321], carbon black [322], carbon fiber [323–325] and carbon nanotubes [78,326–328]) have been considered as outstanding promoters for photo-catalytic performances. The attraction is attributed to their superior adsorption capacity, unique electronic conductivity, nontoxicity, low cost, high stability, and large surface area. The formation of carbon-based Schottky junctions and the narrowing bandgap by carbon doping are both beneficial to photocatalytic reactions.

#### **Direct Z-scheme heterojunction**

Biomimetic artificial photosynthesis by constructing direct Z-scheme photocatalysts represents a feasible strategy the photocatalytic for improving performance [46,204,306,329-332]. Specifically, the direct Z-scheme photocatalytic system has a charge carrier transfer pathway similar to the letter "Z" (Fig. 17) [333]. During the photocatalytic reaction, the photoexcited e (with lower reduction capacity) in semiconductor A recombine with the photoexcited  $h^+$  (with lower oxidation capacity) in semiconductor B. Therefore, the photoexcited e (with high reduction capacity) in semiconductor B and photoexcited h<sup>+</sup> (with high oxidation capacity) in semiconductor A can be utilized. The direct Z-scheme



**Figure 16** (a) Schematic of the laser irradiation-induced formation of a CdS/Cd Schottky junction, (b) synthesis process [313], (c) schematic of photocatalytic  $H_2$  generation performance, (d) TEM image and (e) charge transfer mechanisms in CdS/Cd photocatalysts. Reprinted with permission from Ref. [314]. Copyright 2016, Wiley-VCH.



Figure 17 Mechanisms of charge carrier separation in the Z-scheme system.

photocatalyst possesses an enlarged and stronger redox capacity. Furthermore, the charge carrier transport for direct Z-scheme nanocomposites is more physically feasible because the transport of photoexcited  $e^-$  from the CB of photo-semiconductor A to the photoexcited  $h^+$ -rich VB of photo-semiconductor B is favorable due to the electrostatic attraction between  $h^+$  and  $e^-$ .

In 2009, Cheng's group [177] reported the direct Zscheme of CdS/ZnO heterostructure photocatalysts. They found that the formation of Z-scheme heterostructures between ZnO and CdS could effectively prolong the lifetime of photogenerated  $e^-$ , reaching a 14-fold improvement in H<sub>2</sub> evolution performance compared with that of pure CdS. Since then, numerous direct Z-scheme CdS-based photocatalysts have been applied in photo-

catalytic H<sub>2</sub> generation applications [334], including CdS/  $WO_{3-x}$  [222], FeC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O/CdS [335], CdS/WO<sub>3</sub> [165,301], CdS/MoO<sub>3-x</sub> [336], CdS/g-C<sub>3</sub>N<sub>4</sub> [337,338], CoWO<sub>4</sub>/CdS [44], CdS/Fe<sub>2</sub>O<sub>3</sub> [179], CdS/BiVO<sub>4</sub> [339], TiO<sub>2</sub>/CdS [329,340,341], CdS/CdWO<sub>4</sub> [219,342], ZnO/ CdS [306] and CdS/PI [217]. In our previous study, we reported the fabrication of 2D/2D CdS/g-C<sub>3</sub>N<sub>4</sub> direct Zscheme heterojunction nanocomposites through the insitu growth of 2D CdS NSs on 2D g-C<sub>3</sub>N<sub>4</sub> NSs [338]. As shown in Fig. 18a and b, the direct Z-scheme CdS/g-C<sub>3</sub>N<sub>4</sub> nanocomposites displayed improved photocatalytic H<sub>2</sub> generation activity compared with pure g-C<sub>3</sub>N<sub>4</sub> and CdS. The highest H<sub>2</sub> generation rate is realizable with the CdS/ g-C<sub>3</sub>N<sub>4</sub> direct Z-scheme heterostructures at 0.7 15.3 mmol  $g^{-1}$  h<sup>-1</sup>, which is 3000 and 4 times higher than those of bare  $g-C_3N_4$  and CdS, respectively. After 21 h of continuous visible-light irradiation, the 2D/2D CdS/0.7 g-C<sub>3</sub>N<sub>4</sub> maintained excellent photocatalytic H<sub>2</sub> generation activities without noticeable decay (Fig. 18c). The apparent efficiency of the direct Z-scheme CdS/0.7 g-C<sub>3</sub>N<sub>4</sub> was 6.86% at 420 nm (Fig. 18d). Based on the calculations and experimental results, a schematic for photocatalytic H<sub>2</sub> generation with CdS/g-C<sub>3</sub>N<sub>4</sub> nanocomposite photocatalysts was suggested (Fig. 18e). This work highlights the synergistic effect between the direct Z-scheme and the 2D/2D NS in promoting photocatalytic H<sub>2</sub> generation reactions.

Shen *et al.* [179] reported 2D/2D Z-scheme nanocomposites fabricated *via* the *in-situ* growth of CdS NSs on  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> NSs (Fig. 19a). In addition, the modification

## REVIEWS



**Figure 18** (a) Time-dependent photocatalytic  $H_2$  evolution, (b) average  $H_2$  evolution rates for different samples (1: g-C<sub>3</sub>N<sub>4</sub>, 2: CdS, 3: CdS/0.5g-C<sub>3</sub>N<sub>4</sub>, 4: CdS/0.6g-C<sub>3</sub>N<sub>4</sub>, 5: CdS/0.7g-C<sub>3</sub>N<sub>4</sub>, 6: CdS/0.8g-C<sub>3</sub>N<sub>4</sub>), (c) repeated time courses of photocatalytic  $H_2$  evolution, (d) apparent quantum efficiency for CdS/0.7 g-C<sub>3</sub>N<sub>4</sub>, and (e) proposed schematic for 2D/2D CdS/g-C<sub>3</sub>N<sub>4</sub> S-scheme heterostructures. Reprinted with permission from Ref. [338]. Copyright 2020, Wiley-VCH.

of CdS/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> Z-scheme nanocomposites could be performed with metallic  $\beta$ -NiS, which continued to construct an ohmic junction as H<sub>2</sub>-generation active sites (Fig. 19b). The CdS/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/NiS ultrathin 2D/2D heterojunction exhibited an outstanding H<sub>2</sub> generation rate (45 mmol g<sup>-1</sup> h<sup>-1</sup>) with high AQEs at 420 nm (46.9%). The outstanding photocatalytic performance was ascribed to: (1) ohmic-based heterojunction that offered a large number of H<sub>2</sub>-evolution sites; (2) large and intimate interfaces, which facilitated charge transfer; and (3) boosted charge migration in the direct Z-scheme heterojunction (Fig. 19c-e).

Besides 2D/2D Z-scheme nanocomposites, those with core-shell structures also offer advantages in photocatalytic water splitting. Compared to 2D/2D structures, core-shell structures can better protect CdS from photocorrosion. Ma *et al.* [304] synthesized CdS@ZnO coreshell structured photocatalysts *via* atomic layer deposition (ALD) (Fig. 20a). The growth of ZnO along certain facets was effectively controlled by the number of ALD cycles (Fig. 20b and c). The formation of core-shell structures in the Z-scheme composite could suppress the recombination of photogenerated  $e^-h^+$  pairs and induce strong and intimate heterojunction interfacial contact between CdS and ZnO. Upon loading Pt and PdS as cocatalysts on the CdS@ZnO surface, the photocatalytic  $H_2$  evolution rate reached 98.82 mmol  $g^{-1} h^{-1}$  with an AQE of 69.59% at 420 nm (Fig. 20d-f) [304].

These results highlight the promising performance of the 2D/2D layered Z-scheme heterojunctions with larger contact area for fast separation of photoexcited charge carriers across their interfaces with respect to the 0D/2D and 1D/2D coupling systems. Notably, coupling semiconductors at their active facets are apparently more promising for efficient photogenerated  $e^-$  transfer. It is expected that CdS-based composites with 2D/2D layered Z-scheme heterojunctions coupled with their active facets can be rationally fabricated for photocatalytic H<sub>2</sub> evolution [179,338].

#### ACCELERATING SURFACE CHARGE UTILIZATION OF NANOSTRUCTURED CdS

Structural defects in CdS may result in fast recombination of photo-excited  $e^-h^+$  pairs [257,343]. As photocatalytic H<sub>2</sub> generation from water is a thermodynamically unfavorable reaction, the sluggish kinetics on the CdS surface need to be addressed. It is common to use suitable



**Figure 19** (a) TEM image of  $CdS/\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, (b) photocatalytic mechanism of  $CdS/\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/NiS, (c) simulated charge density difference distribution at the  $CdS/\alpha$ -Fe<sub>2</sub>O<sub>3</sub> heterojunction interface, (d) and (e) the band bending in the space charge region at the interface before and after coupling  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and CdS. Reprinted with permission from Ref. [179]. Copyright 2020, Elsevier.



**Figure 20** (a) Synthesis process, (b) TEM image, and (c) HRTEM image of CdS@ZnO core-shell photocatalysts. (d)  $H_2$  evolution over CdS, ZnO, and CdS@ZnO; (e) average  $H_2$  evolution rate; (f) cyclic runs for photocatalytic  $H_2$  evolution over the CdS@ZnO-PdS. Reprinted with permission from Ref. [304]. Copyright 2017, Elsevier.

cocatalysts to promote the kinetics of photocatalytic H<sub>2</sub> generation. To date, various cocatalysts, such as Au [344,345], Pt [321,346,347], Ag<sub>2</sub>S [348], MXenes [238,349-352], CoMoS<sub>x</sub> [353], MoO<sub>x</sub>S<sub>y</sub> [354], MoS<sub>2</sub> [222,355–358], Ni<sub>3</sub>C[176], Ni<sub>2</sub>P [359,360], NiS<sub>x</sub> [63,322,361], NiCoP [362], CoP<sub>x</sub> [199,363],  $CuS_r$ [212,246], and WS<sub>2</sub> [364,365], have been coupled with CdS-based semiconductors for photocatalytic H<sub>2</sub> evolution. Typically, noble metals (Pt, Ag, and Au) are known as excellent cocatalysts for this application. For example, Liu et al. [232] demonstrated a facile and rapid ultrasonic-chemistry-based approach to load Pt onto CdS NRs, and the resulting Pt/CdS showed efficient H<sub>2</sub> evolution performances. The maximum H<sub>2</sub> evolution rate could reach 24.15 mmol  $g^{-1} h^{-1}$  over 0.5 wt.% Pt/CdS. Bao et al. [169] reported a facile aqueous solution process for the large-scale synthesis of nanoporous CdS NSs and CdS hollow NRs by the air-insensitive inorganic reactants of Na<sub>2</sub>S·9H<sub>2</sub>O and CdCl<sub>2</sub>·2.5H<sub>2</sub>O at room temperature. The obtained CdS/Pt exhibited the highest AQEs (60.34%) at 420 nm for photocatalytic H<sub>2</sub> generation.

However, the scarcity and high cost of noble metals restrict their large-scale applications in photocatalytic H<sub>2</sub> generation. Therefore, earth-abundant-metal-based and noble-metal-free cocatalysts have received increasing attention [4,18,366,367]. For example, Li et al. [229] found that a 0.2 molar ratio of NiS improved the average charge carrier lifetime of CdS by 97 times, potentially leading to more efficient charge separation and transfer. They synthesized CdS NWs and NiS with tight connections using a two-pot solvothermal synthesis. Tight interfaces between CdS and NiS with a smaller intrinsic bandgap led to significantly enhanced photocatalytic H<sub>2</sub> evolution activities. As the content increased, NiS aggregated on the surface of CdS and unfavorably caused fast recombination of photogenerated  $e^{-}h^{+}$  pairs. An evident decay was observed in the broad transient bleach signal after loading NiS, which indicated that the NiS improved the separation of CdS photogenerated  $e^-$  and  $h^+$  pairs. CdS with a NiS molar ratio of 20 reached an optimal photocatalytic  $H_2$  evolution rate of 1512.4 µmol g<sup>-1</sup> h<sup>-1</sup> in lignin and lactic acid aqueous solution, which was 5041 times higher than that of pristine CdS [229]. The resulting CdS/NiS also exhibited excellent stability for 900 min of experiments in the lignin and lactic acid solution [229].

Cocatalysts supported on semiconductors can facilitate the prompt separation and migration of photoexcited charge carriers. For example, we reported a novel strategy to form 2D/2D nanocomposites by coupling Ni<sub>2</sub>SP NSs with CdS NSs [286]. Fig. 21a depicts the ultrathin 2D NS of CdS/Ni<sub>2</sub>SP. The as-fabricated 2D/2D CdS/Ni<sub>2</sub>SP photocatalysts displayed an outstanding H<sub>2</sub> generation performance under visible light ( $\lambda \ge 420$  nm). The CdS/2%Ni<sub>2</sub>SP yielded the highest H<sub>2</sub> generation rate of 18.96 mmol  $g^{-1}$  h<sup>-1</sup>, which was approximately threefold higher than that of bare 2D CdS without the cocatalysts (Fig. 21b). As shown in Fig. 21c, the highest AQE was 4.8% at 420 nm. The *I-t* curve of CdS/2%Ni<sub>2</sub>SP composites is obviously higher than that of nanostructured CdS, indicating that the 2D Ni<sub>2</sub>SP cocatalysts promoted interfacial charge migration and accelerated charge utilization of nanostructured CdS (Fig. 21d). The interfacial coupling effects between the 2D Ni<sub>2</sub>SP cocatalyst and 2D CdS enhanced photocatalytic H<sub>2</sub> generation by increasing the number of active sites, thereby facilitating rapid charge separation and transfer, while enhancing H<sub>2</sub> generation kinetics (Fig. 21e).

Recently, single metal atoms (serving as active sites) have shown excellent performances in photocatalytic and electrocatalytic reactions. The atomically dispersed single metal atoms on the semiconductor surface exhibit unique catalytic performances. For example, Zhang et al. [368] designed atomically dispersed Ni single atoms anchored on the surface of CdS NRs. Under visible light, the photocatalytic H<sub>2</sub> rate reached 630.1 mmol  $g^{-1} h^{-1}$ . The single Ni atoms were stabilized by the Ni-O bonds. Density functional theory calculations revealed that the Ni atoms could optimize H<sub>2</sub> binding and electronic properties, thus improving the separation of photogenerated e<sup>-</sup>-h<sup>+</sup> pairs. Meanwhile, Ni-CdS composites showed a stabilized photocatalytic performance during 16 h of irradiation. Some examples of CdS photocatalysts modified with cocatalysts are presented in Table 2.

In future, dual cocatalysts that combine different types of cocatalysts [369,370], including metal, metal oxide/ sulfide/carbide/phosphide, and nanocarbons, might attract increasing attention in photocatalytic H<sub>2</sub> evolution over CdS-based photocatalysts. Additionally, apart from loading H<sub>2</sub> evolution cocatalysts, it should be noted that the oxidation cocatalysts are also expected to be loaded on CdS-based photocatalysts to boost charge separation and suppress photocorrosion, thereby fundamentally enhancing photocatalytic H<sub>2</sub> evolution [371].

#### SUPPRESSING CHARGE-INDUCED PHOTOCORROSION IN NANOSTRUCTURED CdS

Presently, research on the reaction mechanism and the fundamental carrier dynamics in CdS-based nanocomposite half-reaction systems has seen meaningful



**Figure 21** (a) HRTEM image of CdS/Ni<sub>2</sub>SP, (b) average rate of H<sub>2</sub> evolution (1: CdS, 2: CdS/1%Ni<sub>2</sub>SP, 3: CdS/2%Ni<sub>2</sub>SP, 4: CdS/3%Ni<sub>2</sub>SP, 5: CdS/4% Ni<sub>2</sub>SP, 6: Ni<sub>2</sub>SP, 7: CdS/2% Ni<sub>5</sub>SP nanoparticles), (c) AQEs of CdS/2%Ni<sub>2</sub>SP, (d) photocurrent responses, and (e) proposed mechanistic scheme: (a) CdS; (b) CdS/1%Ni<sub>2</sub>SP; (C) CdS/2%Ni<sub>2</sub>SP; (d) CdS/3%Ni<sub>2</sub>SP; (e) CdS/4%Ni<sub>2</sub>SP; (f) Ni<sub>2</sub>SP; (g) CdS/2%Ni<sub>5</sub>; (h) CdS/2%Ni<sub>2</sub>SP nanoparticles. Reprinted with permission from Ref. [286]. Copyright 2020, Elsevier.

progress. However, due to the photocorrosion phenomenon of CdS-based nanocomposites, the stability and durability of most reported CdS-based photocatalysts need further improvement. The accumulation of photoexcited  $h^+$  in its VB can induce the self-oxidation of  $S^{2^-}$  in CdS, which results in the dissolution of Cd<sup>2+</sup>. Apparently, the effective removal of photoexcited  $h^+$  from the VB of CdS impedes the self-oxidation of  $S^{2^-}$ , enhancing the durability and photostability of CdS. It is well known that the use of sacrificial reagents (such as Na<sub>2</sub>S–Na<sub>2</sub>SO<sub>3</sub>, ethanol, and lactic acid) as  $e^-$  donors for CdS photocatalysts in photocatalytic H<sub>2</sub> generation systems is an effective strategy to suppress photocorrosion of CdS.

Furthermore, Z-scheme heterojunctions could reduce the accumulation of  $h^+$  in the VB of CdS. Li *et al.* [381] found that the formation of CdS–MnS Z-scheme photocatalysts through a cation exchange process could maintain good stability over 42 h of measurement (Fig. 22a and b). The chopped photocurrent density–voltage measurements show that the pure CdS was photocorroded rapidly within 800 min of illumination (Fig. 22c). After the formation of the Z-scheme heterojunction between CdS and MnS, the photocorrosion phenomenon was suppressed. Moreover, the formation of Z-scheme heterojunctions also increased the light-absorption range from 520 to 800 nm (Fig. 22d). Consequently, the obtained CdS-MnS showed an optimal  $H_2$  evolution rate of 1595 µmol  $g^{-1}$  h<sup>-1</sup> with an AQE of 22.6% at 420 nm [381].

Constructing a p-n heterojunction is another strategy to transfer  $h^+$  from the VB of CdS. After the formation of the p-n heterojunction, the  $h^+$  in the VB of CdS could be transferred to the relatively positive VB of a p-type semiconductor, which effectively reduces h<sup>+</sup> accumulation in the VB of CdS. Ai et al. [382] designed CdS@ Ti<sub>3</sub>C<sub>2</sub>@CoO with a hierarchical tandem p-n heterojunction for photocatalytic HER. The insertion of  $Ti_3C_2$  on the surface of CdS served as a platform for the growth of CoO NPs, which were introduced as a bridge to consolidate CdS and CoO into a special tandem p-n heterojunction. Meanwhile, Ti<sub>3</sub>C<sub>2</sub> also served as a bridge with a powerful unidirectional internal electric field wherein another internal electric field was generated between Ti<sub>3</sub>C<sub>2</sub> and CoO, causing photogenerated carriers to transfer to Ti<sub>3</sub>C<sub>2</sub> and restricting  $h^+$  migration (Fig. 23a). Thus, CdS@

Nanocomposites	Content of cocatalysts	Light source	Sacrificial reagent	HER (mmol $g^{-1} h^{-1}$ )	AQE (420 nm)	Ref.
Pt-PdS/CdS	0.3 wt.%	300 W Xe lamp	Na <sub>2</sub> S-Na <sub>2</sub> SO <sub>3</sub>	29.23	93	[173]
MoS <sub>2</sub> /CdS	0.2 wt.%	300 W Xe lamp	Lactic acid	5.4	-	[166]
WS <sub>2</sub> /CdS	1 wt.%	300 W Xe lamp	Lactic acid	4.2	-	[364]
NiS/CDs/CdS	10 wt.%	350 W Xe lamp	Na <sub>2</sub> S-Na <sub>2</sub> SO <sub>3</sub>	1.44	-	[257]
CdS/Co-MoS <sub>x</sub>	2 mol%	300 W Xe lamp	Lactic acid	0.54	23.5	[263]
NiS/CdS	1.2 mol%	300 W Xe lamp	Lactic acid	2.18	51.3	[174]
CdS/WS <sub>2</sub> /graphene	4.2 wt.%	300 W Xe lamp	Na <sub>2</sub> S-Na <sub>2</sub> SO <sub>3</sub>	1.84	21.2	[240]
PdNi/CdS	2 wt.%	300 W Xe lamp	$(NH_4)_2SO_3$	32.4	63.97	[372]
PtNi <sub>x</sub> /CdS	2.0 wt.%	300 W Xe lamp	$(NH_4)_2SO_3$	11.4	51.24	[373]
CdS/g-C <sub>3</sub> N <sub>4</sub> /CuS	10 wt.%	350 W Xe lamp	Na <sub>2</sub> S-Na <sub>2</sub> SO <sub>3</sub>	1.15	16.5	[212]
CuS/CdS	25 wt.%	300 W Xe lamp	Lactic acid	5.62	19.7	[374]
Pt/CdS	0.5 wt.%	300 W Xe lamp	Lactic acid	24.15	-	[232]
MoS <sub>2</sub> /CdS	3 wt.%	300 W Xe lamp	Na <sub>2</sub> S-Na <sub>2</sub> SO <sub>3</sub>	11.4	-	[213]
Ni@NiO/CdS/g-C <sub>3</sub> N <sub>4</sub>	1 wt.%	300 W Xe lamp	Triethanolamine	1.26	-	[218]
Ni <sub>2</sub> P/CdS	3.51 wt.%	300 W Xe lamp	Na <sub>2</sub> S-Na <sub>2</sub> SO <sub>3</sub>	44.65	-	[256]
Co(OH) <sub>2</sub> /CdS	6.5 mol%	350 W Xe lamp	Lactic acid	14.43	-	[375]
NiSe <sub>2</sub> /CdS	5 wt.%	300 W Xe lamp	Na <sub>2</sub> S-Na <sub>2</sub> SO <sub>3</sub>	167.1	1.5	[241]
VC/CdS	15 wt.%	300 W Xe lamp	TEOA	14.2	8.7	[215]
Cobalt-salen/CdS	$0.015 \text{ mmol L}^{-1}$	300 W Xe lamp	Na <sub>2</sub> S-Na <sub>2</sub> SO <sub>3</sub>	106	29	[235]
NiO <sub>x</sub> /CdS	1 mol%	300 W Xe lamp	Methanol and Ni(CH <sub>3</sub> COO) <sub>2</sub>	5.9	8.6	[57]
NiS/CdS	20 mol%	300 W Xe lamp	Lignin and lactic acid	0.15	44.9	[229]
CDs/CdS-S	1 wt.%	300 W Xe lamp	Lactic acid	4.64	11.8	[236]
MoS <sub>2</sub> /CdS	5 wt.%	300 W Xe lamp	Na <sub>2</sub> S-Na <sub>2</sub> SO <sub>3</sub>	4.65	7.31	[255]
CdS/MnS	5 wt.%	300 W Xe lamp	Lactic acid	15.55	6.9	[233]
Cu2MoS4/CdS	5 wt.%	150 W Xe lamp	Lactic acid	15.56	-	[231]
Ni <sub>2</sub> P/MCdS-DETA	0.4 wt.%	300 W Xe lamp	Na <sub>2</sub> S-Na <sub>2</sub> SO <sub>3</sub>	6.84	26.4	[359]
Ni <sub>x</sub> B/CdS	0.8 wt.%	300 W Xe lamp	Lactic acid	4.8	21	[376]
RhP/CdS	20 wt.%	5 W LED	Lactic acid	0.33	34.3	[221]
P-MoS <sub>2</sub> /CdS	20 wt.%	300 W Xe lamp	$Na_2S-Na_2SO_3$	5.89	19	[220]
Mn <sub>13</sub> -cluster/CdS	7 wt.%	White-light LED	Lactic acid	3.6	-	[377]
Ni <sub>2-x</sub> Co <sub>x</sub> P/CdS	40 wt.%	300 W Xe lamp	Ethanol-water	218	76.3	[378]
CdS/Ti <sub>3</sub> C <sub>2</sub>	10%	300 W Xe lamp	Lactic acid	2.407	35.6	[238]
CdS/MoN <sub>2</sub>	-	300 W Xe lamp	Lactic acid	9.2	-	[379]
MXene@CdS	-	300 W Xe lamp	Na <sub>2</sub> S-Na <sub>2</sub> SO <sub>3</sub>	12.34	-	[349]
CdS/SnO <sub>2</sub>	5%	150 W Xe lamp	Lactic acid	20.2	-	[242]
CdS/Mo <sub>2</sub> C	3%	300 W Xe lamp	Na <sub>2</sub> S-Na <sub>2</sub> SO <sub>3</sub>	1.843	-	[380]
CdS-FeP	5%	300 W Xe lamp	Lactic acid	18.63	11.2	[250]

 Table 2
 Cocatalyst loading on CdS for photocatalytic H<sub>2</sub> production

 $Ti_3C_2@CoO (CTC-5-5)$  maintained good stability over 10 cycles, which was significantly better than that of CdS@Ti\_3C\_2 (CT-5) and CdS @CoO (CC-5) (Fig. 23b and c). These results indicate that its combination with a p-type semiconductor to form a p-n heterojunction can suppress the extent of photocorrosion [382].

cumulation of  $h^+$  in the VB of CdS, coating a chemically inert shell could also prevent the undesirable photocorrosion. Ning *et al.* [383] constructed a thin shell layer of Al<sub>2</sub>O<sub>3</sub> on CdS NPs, which could remove the dissolved O<sub>2</sub> to inhibit photocorrosion (Fig. 24a). During the photocatalytic reaction, the photogenerated  $h^+$  are trapped by the A1<sup>3+</sup> cationic vacancy network in amorphous

Besides constructing a heterojunction to avoid the ac-



Figure 22 (a) Schematic of the synthesis process, (b) cyclic experiment of  $H_2$  generation using CdS–MnS, (c) amperometric photocurrent density measurements (0.5 mol L<sup>-1</sup> Na<sub>2</sub>SO<sub>4</sub>, 100 mW cm<sup>-2</sup>, visible light), (d) Z-scheme electronic band structures between CdS and MnS heterojunction photocatalysts. Reprinted with permission from Ref. [381]. Copyright 2020, Wiley-VCH.



Figure 23 (a) Schematic of CdS@Ti<sub>3</sub>C<sub>2</sub>@CoO hierarchical tandem p-n heterojunction; recycling tests of photocatalytic  $H_2$  evolution of (b) CT-5 and CC-5, (c) CTC-5-5. Reprinted with permission from Ref. [382]. Copyright 2020, Elsevier.

 $Al_2O_3$ . Compared with pure CdS, only trace amounts of  $Cd^{2+}$  were dissolved in the reaction solutions. Thus, CdS/ $Al_2O_3$ -Pt exhibited excellent stability during the photocatalytic HER (Fig. 24b and c). Moreover, CdS/ $Al_2O_3$ -Pt could induce overall water splitting by avoiding photo-

corrosion (Fig. 24d) [383].

#### **CONCLUSIONS**

In recent years, CdS-based nanostructured photocatalysts have been widely investigated. Significant progress has



**Figure 24** (a) TEM image of  $CdS@Al_2O_3$ , (b) cyclic runs of the photocatalytic  $H_2$  evolution activity under visible light over various catalyst samples: (1) CdS NPs, (2) Pt/CdS, (3) Pt/CdS@Al\_2O\_3 with artificial gill and (4) Pt/CdS@Al\_2O\_3 without artificial gill, (c) the changes in cadmium ion concentration in the CdS NPs and Pt/CdS@Al\_2O\_3 composite solution with extended irradiation time, and (d) mechanism of overall water splitting over Pt/CdS@Al\_2O\_3 composite under visible illumination. Reprinted with permission from Ref. [383]. Copyright 2018, Elsevier.

been made in the field of solar-fuel conversion and environmental purification using CdS [15,213,364,384]. This review first systematically discusses the recent progress of CdS-based nanostructured photocatalysts with a detailed summary of the design strategies adopted to enhance  $H_2$  generation efficiency. Although great advances have been made in recent years, many challenges remain, entailing the need for an in-depth understanding of the underlying mechanism for the observed  $H_2$  evolution enhancement. Their intrinsic relations with modification routes should be unambiguously established [361,370,385,386].

Various strategies have been devised to increase photocatalytic  $H_2$  generation using photocatalytic CdS-based nanomaterials: constructing multicomponent solid solutions, loading cocatalysts, constructing Z-scheme heterojunctions, designing 2D NSs, and reducing photocorrosion. These aspects are thoroughly highlighted and discussed. Notably, 2D nanomaterials possess many advantages, such as good chemical and physical stability, high interlayer adhesion, large surface area, high electron mobility, and rich surface-active sites, which facilitate photocatalytic  $H_2$  evolution. In addition, bandgap tuning and heterojunction construction can be conveniently engineered by combining the strengths of different 2D nanomaterials in the form of 2D/2D layered nanocomposites [72,387]. Therefore, it is possible to obtain CdS photocatalysts with extended visible-light absorption and enhanced redox capacities, as well as better charge separation efficiencies. The durability and stability of photocatalysts remain an urgent problem that needs to be solved in the future.

A knowledge gap remains in the fundamental revelation of the actual active sites in CdS photocatalysts. Specifically, a far-reaching investigation into the detailed mechanisms of how CdS photocatalysts function through the advancement in situ/operando characterizations is highly sought. The e transfer mechanisms between the heterojunctions of CdS and other components are still debatable. Upon clarifying the transfer mechanism, targeted e transfer to the selected active sites can significantly improve the photocatalytic HER performance of CdS photocatalysts. In addition, shortening the migration distance is effective in increasing the consumption rate of the photogenerated  $e^{-}h^{+}$  pairs. The construction of single-layer CdS nanosheets could minimize the charge migration distance from the bulk to the CdS surface. Therefore, developing methodologies to

synthesize ultrathin CdS is expected to continue to receive widespread attention.

A theoretical mechanistic study using computational methods is another important aspect to assist in the rational design of CdS photocatalysts with ideal electronic structures, species adsorption, and other properties. In addition, it could provide insights into the cocatalyst/ semiconductor loading sites and interfacial interactions to guide the preparation of functional CdS. In summary, the exploration of new strategies to strengthen the overall performance of CdS-based nanocomposites, including their stability, can offer new opportunities toward the efficient utilization of solar energy for chemical fuel conversion.

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- 1 Xia Y, Yu J. Reaction: Rational design of highly active photocatalysts for  $\rm CO_2$  conversion. Chem, 2020, 6: 1039–1040
- 2 Fan X, Zhang L, Li M, *et al.* α-Ferrous oxalate dihydrate: a simple coordination polymer featuring photocatalytic and photoinitiated Fenton oxidations. Sci China Mater, 2016, 59: 574–580
- 3 Fan Y, Hu G, Yu S, *et al.* Recent advances in TiO<sub>2</sub> nanoarrays/ graphene for water treatment and energy conversion/storage. Sci China Mater, 2019, 62: 325–340
- 4 Li X, Yu J, Jaroniec M, *et al.* Cocatalysts for selective photoreduction of CO<sub>2</sub> into solar fuels. Chem Rev, 2019, 119: 3962–4179
- 5 Li X, Xie J, Jiang C, *et al.* Review on design and evaluation of environmental photocatalysts. Front Environ Sci Eng, 2018, 12: 14
- 6 Tang Y, Zhou P, Chao Y, et al. Face-to-face engineering of ultrathin Pd nanosheets on amorphous carbon nitride for efficient photocatalytic hydrogen production. Sci China Mater, 2019, 62: 351–358
- 7 Zhang Y, Zhang Q, Xia T, et al. The influence of reaction temperature on the formation and photocatalytic hydrogen generation of (001) faceted TiO<sub>2</sub> nanosheets. ChemNanoMat, 2015, 1: 270–275
- 8 Ma Y, Wang X, Jia Y, et al. Titanium dioxide-based nanomaterials for photocatalytic fuel generations. Chem Rev, 2014, 114: 9987–10043
- 9 Chen X, Li C, Grätzel M, et al. Nanomaterials for renewable energy production and storage. Chem Soc Rev, 2012, 41: 7909–7937
- 10 Li X, Yu J, Low J, *et al.* Engineering heterogeneous semiconductors for solar water splitting. J Mater Chem A, 2015, 3: 2485–2534
- 11 Wen J, Xie J, Chen X, et al. A review on g-C<sub>3</sub>N<sub>4</sub>-based photocatalysts. Appl Surf Sci, 2017, 391: 72–123
- 12 Fu J, Yu J, Jiang C, *et al.*  $g-C_3N_4$ -based heterostructured photocatalysts. Adv Energy Mater, 2018, 8: 1701503
- 13 Liu L, Chen X. Titanium dioxide nanomaterials: Self-structural modifications. Chem Rev, 2014, 114: 9890–9918
- 14 Zhang Y, Zhao H, Zhao X, *et al.* Narrow-bandgap  $Nb_2O_5$  nanowires with enclosed pores as high-performance photocatalyst. Sci China Mater, 2019, 62: 203–210
- 15 Zhao D, Sun B, Li X, *et al.* Promoting visible light-driven hydrogen evolution over CdS nanorods using earth-abundant CoP

as a cocatalyst. RSC Adv, 2016, 6: 33120-33125

- 16 Cui X, Wang Y, Jiang G, *et al.* A photonic crystal-based CdS-Au-WO<sub>3</sub> heterostructure for efficient visible-light photocatalytic hydrogen and oxygen evolution. RSC Adv, 2014, 4: 15689–15694
- 17 Cheng L, Xiang Q, Liao Y, et al. CdS-based photocatalysts. Energy Environ Sci, 2018, 11: 1362–1391
- 18 Jiang D, Sun Z, Jia H, et al. A cocatalyst-free CdS nanorod/ZnS nanoparticle composite for high-performance visible-light-driven hydrogen production from water. J Mater Chem A, 2016, 4: 675– 683
- 19 Chen X, Chen W, Lin P, *et al. In situ* photodeposition of nickel oxides on CdS for highly efficient hydrogen production *via* visiblelight-driven photocatalysis. Catal Commun, 2013, 36: 104–108
- 20 Zhang GQ, Ou W, Xu YS. Fluorescein supramolecular nanosheets: A novel organic photocatalyst for visible-light-driven H<sub>2</sub> evolution from water. Sci China Mater, 2018, 61: 1001–1006
- 21 Yu Q, Lin R, Jiang L, *et al.* Fabrication and photocatalysis of ZnO nanotubes on transparent conductive graphene-based flexible substrates. Sci China Mater, 2018, 61: 1007–1011
- 22 Yang C, Chen JF, Zeng X, *et al.* Enhanced photochemical performance of hexagonal WO<sub>3</sub> by metal-assisted S–O coupling for solar-driven water splitting. Sci China Mater, 2018, 61: 91–100
- 23 Zhou M, Hou Z, Chen X. Graphitic-C<sub>3</sub>N<sub>4</sub> nanosheets: synergistic effects of hydrogenation and n/n junctions for enhanced photocatalytic activities. Dalton Trans, 2017, 46: 10641–10649
- 24 Zhang X, Zhang P, Wang L, et al. Template-oriented synthesis of monodispersed SnS<sub>2</sub>@SnO<sub>2</sub> hetero-nanoflowers for Cr(VI) photoreduction. Appl Catal B-Environ, 2016, 192: 17–25
- 25 Zhang P, Wang T, Chang X, *et al.* Effective charge carrier utilization in photocatalytic conversions. Acc Chem Res, 2016, 49: 911–921
- 26 Zhang P, Li X, Shao C, *et al.* Hydrothermal synthesis of carbonrich graphitic carbon nitride nanosheets for photoredox catalysis. J Mater Chem A, 2015, 3: 3281–3284
- 27 Liu B, Ye L, Wang R, *et al.* Phosphorus-doped graphitic carbon nitride nanotubes with amino-rich surface for efficient CO<sub>2</sub> capture, enhanced photocatalytic activity, and product selectivity. ACS Appl Mater Interfaces, 2018, 10: 4001–4009
- 28 Ye S, Wang R, Wu MZ, et al. A review on g-C<sub>3</sub>N<sub>4</sub> for photocatalytic water splitting and CO<sub>2</sub> reduction. Appl Surf Sci, 2015, 358: 15–27
- 29 Han C, Wu L, Ge L, *et al.* AuPd bimetallic nanoparticles decorated graphitic carbon nitride for highly efficient reduction of water to H<sub>2</sub> under visible light irradiation. Carbon, 2015, 92: 31–40
- 30 Saha M, Ghosh S, De SK. Nanoscale Kirkendall effect driven Au decorated CdS/CdO colloidal nanocomposites for efficient hydrogen evolution, photocatalytic dye degradation and Cr(VI) reduction. Catal Today, 2020, 340: 253–267
- 31 Wang R, Yan J, Zu M, *et al.* Facile synthesis of interlocking g-C<sub>3</sub>N<sub>4</sub>/CdS photoanode for stable photoelectrochemical hydrogen production. Electrochim Acta, 2018, 279: 74–83
- 32 Wang Q, Li J, Bai Y, *et al.* Photochemical preparation of Cd/CdS photocatalysts and their efficient photocatalytic hydrogen production under visible light irradiation. Green Chem, 2014, 16: 2728–2735
- 33 Zhu S, Liang S, Bi J, *et al.* Photocatalytic reduction of CO<sub>2</sub> with H<sub>2</sub>O to CH<sub>4</sub> over ultrathin SnNb<sub>2</sub>O<sub>6</sub> 2D nanosheets under visible light irradiation. Green Chem, 2016, 18: 1355–1363
- 34 Li X, Wen J, Low J, et al. Design and fabrication of semiconductor photocatalyst for photocatalytic reduction of CO<sub>2</sub> to solar fuel. Sci

China Mater, 2014, 57: 70-100

- 35 Muhammad NA, Wang Y, Muhammad FE, et al. Photoreduction of carbon dioxide using strontium zirconate nanoparticles. Sci China Mater, 2015, 58: 634–639
- 36 Wang H, Naghadeh SB, Li C, et al. Enhanced photoelectrochemical and photocatalytic activities of CdS nanowires by surface modification with MoS<sub>2</sub> nanosheets. Sci China Mater, 2018, 61: 839–850
- 37 Sun J, Xu J, Grafmueller A, *et al.* Self-assembled carbon nitride for photocatalytic hydrogen evolution and degradation of pnitrophenol. Appl Catal B-Environ, 2017, 205: 1–10
- 38 Yang T, Peng J, Zheng Y, et al. Enhanced photocatalytic ozonation degradation of organic pollutants by ZnO modified TiO<sub>2</sub> nanocomposites. Appl Catal B-Environ, 2018, 221: 223–234
- 39 Zou L, Wang H, Wang X. High efficient photodegradation and photocatalytic hydrogen production of CdS/BiVO<sub>4</sub> heterostructure through Z-scheme process. ACS Sustain Chem Eng, 2017, 5: 303–309
- 40 Liu W, Liu Z, Wang G, *et al.* Carbon coated Au/TiO<sub>2</sub> mesoporous microspheres: a novel selective photocatalyst. Sci China Mater, 2017, 60: 438–448
- 41 Shenoy S, Jang E, Park TJ, et al. Cadmium sulfide nanostructures: Influence of morphology on the photocatalytic degradation of erioglaucine and hydrogen generation. Appl Surf Sci, 2019, 483: 696–705
- 42 Xiao F, Zhou W, Sun B, *et al.* Engineering oxygen vacancy on rutile TiO<sub>2</sub> for efficient electron-hole separation and high solardriven photocatalytic hydrogen evolution. Sci China Mater, 2018, 61: 822–830
- 43 Wang X, Peng W, Li X. Photocatalytic hydrogen generation with simultaneous organic degradation by composite CdS–ZnS nanoparticles under visible light. Int J Hydrogen Energy, 2014, 39: 13454–13461
- 44 Cui H, Li B, Zhang Y, *et al.* Constructing Z-scheme based  $CoWO_4/CdS$  photocatalysts with enhanced dye degradation and H<sub>2</sub> generation performance. Int J Hydrogen Energy, 2018, 43: 18242–18252
- 45 Wen J, Xie J, Zhang H, *et al.* Constructing multifunctional metallic Ni interface layers in the  $g-C_3N_4$  nanosheets/amorphous NiS heterojunctions for efficient photocatalytic H<sub>2</sub> generation. ACS Appl Mater Interfaces, 2017, 9: 14031–14042
- 46 Zhou P, Yu J, Jaroniec M. All-solid-state Z-Scheme photocatalytic systems. Adv Mater, 2014, 26: 4920–4935
- 47 Shen R, Xie J, Lu X, *et al.* Bifunctional Cu<sub>3</sub>P decorated  $g-C_3N_4$  nanosheets as a highly active and robust visible-light photocatalyst for H<sub>2</sub> production. ACS Sustain Chem Eng, 2018, 6: 4026-4036
- 48 Sun Z, Zhu M, Fujitsuka M, *et al.* Phase effect of  $Ni_xP_y$  hybridized with  $g-C_3N_4$  for photocatalytic hydrogen generation. ACS Appl Mater Interfaces, 2017, 9: 30583–30590
- 49 Xiong T, Cen W, Zhang Y, *et al.* Bridging the g-C<sub>3</sub>N<sub>4</sub> interlayers for enhanced photocatalysis. ACS Catal, 2016, 6: 2462–2472
- 50 Gu Q, Gao Z, Yu S, *et al.* Constructing  $Ru/TiO_2$  heteronanostructures toward enhanced photocatalytic water splitting *via* a  $RuO_2/TiO_2$  heterojunction and  $Ru/TiO_2$  Schottky junction. Adv Mater Interfaces, 2016, 3: 1500631
- 51 Cui X, Shi J. Sn-based catalysts for Baeyer-Villiger oxidations by using hydrogen peroxide as oxidant. Sci China Mater, 2016, 59: 675–700
- 52 Shen R, Xie J, Zhang H, et al. Enhanced solar fuel H<sub>2</sub> generation

over  $g-C_3N_4$  nanosheet photocatalysts by the synergetic effect of noble metal-free  $Co_2P$  cocatalyst and the environmental phosphorylation strategy. ACS Sustain Chem Eng, 2018, 6: 816–826

- 53 Xiang Q, Cheng B, Yu J. Hierarchical porous CdS nanosheetassembled flowers with enhanced visible-light photocatalytic H<sub>2</sub>production performance. Appl Catal B-Environ, 2013, 138: 299– 303
- 54 Zheng D, Zhang G, Hou Y, *et al.* Layering MoS<sub>2</sub> on soft hollow g-C<sub>3</sub>N<sub>4</sub> nanostructures for photocatalytic hydrogen evolution. Appl Catal A-General, 2016, 521: 2–8
- 55 Gu Q, Liao Y, Yin L, *et al.* Template-free synthesis of porous graphitic carbon nitride microspheres for enhanced photocatalytic hydrogen generation with high stability. Appl Catal B-Environ, 2015, 165: 503–510
- 56 Tian L, Yan X, Chen X. Electrochemical activity of iron phosphide nanoparticles in hydrogen evolution reaction. ACS Catal, 2016, 6: 5441–5448
- 57 Chen X, Chen W, Gao H, *et al.* In *situ* photodeposition of  $NiO_x$ on CdS for hydrogen production under visible light: Enhanced activity by controlling solution environment. Appl Catal B-Environ, 2014, 152: 68–72
- 58 He Z, Fu J, Cheng B, et al. Cu<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub> clusters: Novel noblemetal-free cocatalysts for efficient photocatalytic hydrogen production from water splitting. Appl Catal B-Environ, 2017, 205: 104–111
- 59 Liu Y, Xiong J, Yang Y, *et al.* HNb<sub>x</sub>Ta<sub>1-x</sub>WO<sub>6</sub> monolayer nanosheets solid solutions: Tunable energy band structures and highly enhanced photocatalytic performances for hydrogen evolution. Appl Catal B-Environ, 2017, 203: 798–806
- 60 He K, Xie J, Li M, *et al. In situ* one-pot fabrication of g-C<sub>3</sub>N<sub>4</sub> nanosheets/NiS cocatalyst heterojunction with intimate interfaces for efficient visible light photocatalytic H<sub>2</sub> generation. Appl Surf Sci, 2018, 430: 208–217
- 61 Zhao Z, Xing Y, Li H, *et al.* Constructing CdS/Cd/doped TiO<sub>2</sub> Z-scheme type visible light photocatalyst for H<sub>2</sub> production. Sci China Mater, 2018, 61: 851–860
- 62 Akple MS, Low J, Wageh S, et al. Enhanced visible light photocatalytic H<sub>2</sub>-production of g-C<sub>3</sub>N<sub>4</sub>/WS<sub>2</sub> composite heterostructures. Appl Surf Sci, 2015, 358: 196–203
- 63 Li N, Huang H, Bibi R, *et al.* Noble-metal-free MOF derived hollow CdS/TiO<sub>2</sub> decorated with NiS cocatalyst for efficient photocatalytic hydrogen evolution. Appl Surf Sci, 2019, 476: 378– 386
- 64 He J, Chen L, Yi ZQ, *et al.* Fabrication of two-dimensional porous CdS nanoplates decorated with  $C_3N_4$  nanosheets for highly efficient photocatalytic hydrogen production from water splitting. Catal Commun, 2017, 99: 79–82
- 65 Fujishima A, Honda K. Electrochemical photolysis of water at a semiconductor electrode. Nature, 1972, 238: 37–38
- 66 Ma S, Xie J, Wen J, et al. Constructing 2D layered hybrid CdS nanosheets/MoS<sub>2</sub> heterojunctions for enhanced visible-light photocatalytic H<sub>2</sub> generation. Appl Surf Sci, 2017, 391: 580–591
- 67 Yu J, Yu Y, Zhou P, *et al.* Morphology-dependent photocatalytic H<sub>2</sub>-production activity of CdS. Appl Catal B-Environ, 2014, 156: 184–191
- 68 Chen X, Shen S, Guo L, *et al.* Semiconductor-based photocatalytic hydrogen generation. Chem Rev, 2010, 110: 6503–6570
- 69 Hu J, Wang L, Zhang P, et al. Construction of solid-state Zscheme carbon-modified TiO<sub>2</sub>/WO<sub>3</sub> nanofibers with enhanced photocatalytic hydrogen production. J Power Sources, 2016, 328:

28-36

- Gao H, Zhang P, Hu J, *et al.* One-dimensional Z-scheme TiO<sub>2</sub>/WO<sub>3</sub>/Pt heterostructures for enhanced hydrogen generation. Appl Surf Sci, 2017, 391: 211–217
- 71 Liu Y, Zhang Y, Wang L, et al. Fast and large-scale anodizing synthesis of pine-cone TiO<sub>2</sub> for solar-driven photocatalysis. Catalysts, 2017, 7: 229
- 72 Lin B, Li H, An H, *et al.* Preparation of 2D/2D g-C<sub>3</sub>N<sub>4</sub> nanosheet@ZnIn<sub>2</sub>S<sub>4</sub> nanoleaf heterojunctions with well-designed high-speed charge transfer nanochannels towards high-efficiency photocatalytic hydrogen evolution. Appl Catal B-Environ, 2018, 220: 542–552
- 73 Zhou JJ, Wang R, Liu XL, et al. In situ growth of CdS nanoparticles on UiO-66 metal-organic framework octahedrons for enhanced photocatalytic hydrogen production under visible light irradiation. Appl Surf Sci, 2015, 346: 278–283
- 74 Li Q, Meng H, Yu J, *et al.* Enhanced photocatalytic hydrogenproduction performance of graphene- $Zn_xCd_{1-x}S$  composites by using an organic S source. Chem Eur J, 2014, 20: 1176–1185
- 75 Gao H, Zhang P, Zhao J, *et al.* Plasmon enhancement on photocatalytic hydrogen production over the Z-scheme photosynthetic heterojunction system. Appl Catal B-Environ, 2017, 210: 297–305
- 76 Zhao J, Zhang P, Wang Z, *et al.* Direct evidence of multichannelimproved charge-carrier mechanism for enhanced photocatalytic H<sub>2</sub> evolution. Sci Rep, 2017, 7: 16116
- 77 He K, Xie J, Yang Z, *et al.* Earth-abundant WC nanoparticles as an active noble-metal-free co-catalyst for the highly boosted photocatalytic H<sub>2</sub> production over g-C<sub>3</sub>N<sub>4</sub> nanosheets under visible light. Catal Sci Technol, 2017, 7: 1193–1202
- 78 Zhou X, Li X, Gao Q, et al. Metal-free carbon nanotube–SiC nanowire heterostructures with enhanced photocatalytic H<sub>2</sub> evolution under visible light irradiation. Catal Sci Technol, 2015, 5: 2798–2806
- 79 Yu J, Wang S, Cheng B, *et al.* Noble metal-free Ni(OH)<sub>2</sub>–g-C<sub>3</sub>N<sub>4</sub> composite photocatalyst with enhanced visible-light photocatalytic H<sub>2</sub>-production activity. Catal Sci Technol, 2013, 3: 1782–1789
- 80 Hong Y, Zhang J, Huang F, et al. Enhanced visible light photocatalytic hydrogen production activity of CuS/ZnS nanoflower spheres. J Mater Chem A, 2015, 3: 13913–13919
- 81 Jin J, Yu J, Liu G, et al. Single crystal CdS nanowires with high visible-light photocatalytic H<sub>2</sub>-production performance. J Mater Chem A, 2013, 1: 10927–10934
- 82 Shen S, Guo L, Chen X, *et al.* Effect of Ag<sub>2</sub>S on solar-driven photocatalytic hydrogen evolution of nanostructured CdS. Int J Hydrogen Energy, 2010, 35: 7110–7115
- 83 Kudo A, Miseki Y. Heterogeneous photocatalyst materials for water splitting. Chem Soc Rev, 2009, 38: 253–278
- 84 Li X, Yu J, Jaroniec M. Hierarchical photocatalysts. Chem Soc Rev, 2016, 45: 2603–2636
- 85 Li X, Yu J, Wageh S, et al. Graphene in photocatalysis: A review. Small, 2016, 12: 6640–6696
- 86 Tanveer M, Wu Y, Qadeer MA, *et al.* Atypical BiOCl/Bi<sub>2</sub>S<sub>3</sub> hetero-structures exhibiting remarkable photo-catalyst response. Sci China Mater, 2018, 61: 101–111
- 87 Shen R, Jiang C, Xiang Q, *et al.* Surface and interface engineering of hierarchical photocatalysts. Appl Surf Sci, 2019, 471: 43–87
- 88 Li Y, Jin Z, Zhang L, *et al.* Controllable design of Zn-Ni-P on g- $C_3N_4$  for efficient photocatalytic hydrogen production. Chin J

Catal, 2019, 40: 390-402

- 89 Li Z, Ma Y, Hu X, et al. Enhanced photocatalytic H<sub>2</sub> production over dual-cocatalyst-modified g-C<sub>3</sub>N<sub>4</sub> heterojunctions. Chin J Catal, 2019, 40: 434–445
- 90 Qi K, Lv W, Khan I, *et al.* Photocatalytic  $H_2$  generation *via* CoP quantum-dot-modified  $g-C_3N_4$  synthesized by electroless plating. Chin J Catal, 2020, 41: 114–121
- 91 Sun K, Shen J, Liu Q, *et al.* Synergistic effect of Co(II)-hole and Pt-electron cocatalysts for enhanced photocatalytic hydrogen evolution performance of P-doped g-C<sub>3</sub>N<sub>4</sub>. Chin J Catal, 2020, 41: 72–81
- 92 Xiao N, Li S, Liu S, et al. Novel PtPd alloy nanoparticle-decorated g-C<sub>3</sub>N<sub>4</sub> nanosheets with enhanced photocatalytic activity for H<sub>2</sub> evolution under visible light irradiation. Chin J Catal, 2019, 40: 352–361
- 93 Wen J, Xie J, Shen R, et al. Markedly enhanced visible-light photocatalytic H<sub>2</sub> generation over g-C<sub>3</sub>N<sub>4</sub> nanosheets decorated by robust nickel phosphide (Ni<sub>12</sub>P<sub>5</sub>) cocatalysts. Dalton Trans, 2017, 46: 1794–1802
- 94 Ma B, Zhao J, Ge Z, *et al.* 5 nm NiCoP nanoparticles coupled with g-C<sub>3</sub>N<sub>4</sub> as high-performance photocatalyst for hydrogen evolution. Sci China Mater, 2020, 63: 258–266
- 95 Zhou X, Gao Q, Yang S, et al. Carbon nanotube@silicon carbide coaxial heterojunction nanotubes as metal-free photocatalysts for enhanced hydrogen evolution. Chin J Catal, 2020, 41: 62–71
- 96 Zhou X, Gao Q, Li X, et al. Ultra-thin SiC layer covered graphene nanosheets as advanced photocatalysts for hydrogen evolution. J Mater Chem A, 2015, 3: 10999–11005
- 97 Yuan YJ, Yu ZT, Li YH, *et al.* A MoS<sub>2</sub>/6,13-pentacenequinone composite catalyst for visible-light-induced hydrogen evolution in water. Appl Catal B-Environ, 2016, 181: 16–23
- 98 Wang WN, Huang CX, Zhang CY, *et al.* Controlled synthesis of upconverting nanoparticles/Zn<sub>x</sub>Cd<sub>1-x</sub>S yolk-shell nanoparticles for efficient photocatalysis driven by NIR light. Appl Catal B-Environ, 2018, 224: 854–862
- 99 Chen M, Wu P, Zhu Y, *et al.* Enhanced photocatalytic H<sub>2</sub> production activity of CdZnS with stacking faults structure assisted by ethylenediamine and NiS. Int J Hydrogen Energy, 2018, 43: 10938–10949
- 100 Shi J, Islam IU, Chen W, *et al.* Two-dimensional ultrathin  $Zn_xCd_{1-x}S$  nanosheet with exposed polar facet by using layered double hydroxide template for photocatalytic hydrogen generation. Int J Hydrogen Energy, 2018, 43: 19481–19491
- 101 Gao R, Cheng B, Fan J, et al. Zn<sub>x</sub>Cd<sub>1-x</sub>S quantum dot with enhanced photocatalytic H<sub>2</sub>-production performance. Chin J Catal, 2021, 42: 15–24
- 102 Shen R, Ding Y, Li S, et al. Constructing low-cost Ni<sub>3</sub>C/twincrystal Zn<sub>0.5</sub>Cd<sub>0.5</sub>S heterojunction/homojunction nanohybrids for efficient photocatalytic H<sub>2</sub> evolution. Chin J Catal, 2021, 42: 25–36
- 103 Xue W, Chang W, Hu X, *et al.* 2D mesoporous ultrathin  $Cd_{0.5}Zn_{0.5}S$  nanosheet: Fabrication mechanism and application potential for photocatalytic H<sub>2</sub> evolution. Chin J Catal, 2021, 42: 152–163
- 104 Wang S, Guan BY, Wang X, et al. Formation of hierarchical Co<sub>9</sub>S<sub>8</sub>@ZnIn<sub>2</sub>S<sub>4</sub>heterostructured cages as an efficient photocatalyst for hydrogen evolution. J Am Chem Soc, 2018, 140: 15145–15148
- 105 Hou J, Yang C, Cheng H, et al. Ternary 3D architectures of CdS QDs/graphene/ZnIn<sub>2</sub>S<sub>4</sub> heterostructures for efficient photocatalytic H<sub>2</sub> production. Phys Chem Chem Phys, 2013, 15: 15660–

15668

- 106 Zhang Z, Liu K, Feng Z, *et al.* Hierarchical sheet-on-sheet ZnIn<sub>2</sub>S<sub>4</sub>/g-C<sub>3</sub>N<sub>4</sub> heterostructure with highly efficient photocatalytic H<sub>2</sub> production based on photoinduced interfacial charge transfer. Sci Rep, 2016, 6: 19221
- 107 Wang B, Ding Y, Deng Z, et al. Rational design of ternary NiS/ CQDs/ZnIn<sub>2</sub>S<sub>4</sub> nanocomposites as efficient noble-metal-free photocatalyst for hydrogen evolution under visible light. Chin J Catal, 2019, 40: 335–342
- 108 Zhang S, Duan S, Chen G, et al. MoS<sub>2</sub>/Zn<sub>3</sub>In<sub>2</sub>S<sub>6</sub> composite photocatalysts for enhancement of visible light-driven hydrogen production from formic acid. Chin J Catal, 2021, 42: 193–204
- 109 Yu J, Lei SL, Chen TC, *et al.* A new CdS/Bi1–InTaO<sub>4</sub> heterostructured photocatalyst containing solid solutions for  $H_2$  evolution from water splitting. Int J Hydrogen Energy, 2014, 39: 13105–13113
- 110 Estahbanati MRK, Feilizadeh M, Iliuta MC. Photocatalytic valorization of glycerol to hydrogen: Optimization of operating parameters by artificial neural network. Appl Catal B-Environ, 2017, 209: 483–492
- 111 Li L, Liu GN, Qi SP, *et al.* Highly efficient colloidal  $Mn_xCd_{1-x}S$ nanorod solid solution for photocatalytic hydrogen generation. J Mater Chem A, 2018, 6: 23683–23689
- 112 Higashi M, Abe R, Takata T, *et al.* Photocatalytic overall water splitting under visible light using  $ATaO_2N$  (A = Ca, Sr, Ba) and  $WO_3$  in a  $IO_3^{-}/I^{-}$  shuttle redox mediated system. Chem Mater, 2009, 21: 1543–1549
- 113 Higashi M, Abe R, Ishikawa A, *et al.* Z-scheme overall water splitting on modified-TaON photocatalysts under visible light ( $\lambda$ <500 nm). Chem Lett, 2008, 37: 138–139
- 114 Chen G, Li F, Fan Y, *et al.* A novel noble metal-free ZnS–WS<sub>2</sub>/ CdS composite photocatalyst for  $H_2$  evolution under visible light irradiation. Catal Commun, 2013, 40: 51–54
- 115 Jiang Z, Zhang X, Yang G, *et al.* Hydrogel as a miniature hydrogen production reactor to enhance photocatalytic hydrogen evolution activities of CdS and ZnS quantum dots derived from modified gel crystal growth method. Chem Eng J, 2019, 373: 814– 820
- 116 Li K, Chen R, Li SL, et al. Self-assembly of a mesoporous ZnS/ mediating interface/CdS heterostructure with enhanced visiblelight hydrogen-production activity and excellent stability. Chem Sci, 2015, 6: 5263–5268
- 117 Xie YP, Yu ZB, Liu G, *et al.* CdS-mesoporous ZnS core-shell particles for efficient and stable photocatalytic hydrogen evolution under visible light. Energy Environ Sci, 2014, 7: 1895–1901
- 118 Li C, Du S, Wang H, et al. Enhanced visible-light-driven photocatalytic hydrogen generation using NiCo<sub>2</sub>S<sub>4</sub>/CdS nanocomposites. Chem Eng J, 2019, 378: 122089
- 119 Yuan M, Wang JL, Zhou WH, et al. Cu<sub>2</sub>ZnSnS<sub>4</sub>-CdS heterostructured nanocrystals for enhanced photocatalytic hydrogen production. Catal Sci Technol, 2017, 7: 3980–3984
- 120 Iervolino G, Vaiano V, Sannino D, et al. Enhanced photocatalytic hydrogen production from glucose aqueous matrices on Rudoped LaFeO<sub>3</sub>. Appl Catal B-Environ, 2017, 207: 182–194
- 121 Liu Y, Niu H, Gu W, *et al. In-situ* construction of hierarchical CdS/MoS<sub>2</sub> microboxes for enhanced visible-light photocatalytic H<sub>2</sub> production. Chem Eng J, 2018, 339: 117–124
- 122 Xu J, Cao X. Characterization and mechanism of MoS<sub>2</sub>/CdS composite photocatalyst used for hydrogen production from water splitting under visible light. Chem Eng J, 2015, 260: 642–

648

- 123 Zhao J, Zhang P, Fan J, et al. Constructing 2D layered MoS<sub>2</sub> nanosheets-modified Z-scheme TiO<sub>2</sub>/WO<sub>3</sub> nanofibers ternary nanojunction with enhanced photocatalytic activity. Appl Surf Sci, 2018, 430: 466–474
- 124 Xu F, Zhang J, Zhu B, *et al.* CuInS<sub>2</sub> sensitized TiO<sub>2</sub> hybrid nanofibers for improved photocatalytic CO<sub>2</sub> reduction. Appl Catal B-Environ, 2018, 230: 194–202
- 125 Hu P, Ngaw CK, Tay YY, *et al.* A "uniform" heterogeneous photocatalyst: integrated p–n type CuInS<sub>2</sub>/NaInS<sub>2</sub> nanosheets by partial ion exchange reaction for efficient H<sub>2</sub> evolution. Chem Commun, 2015, 51: 9381–9384
- 126 Liu B, Xue Y, Zhang J, *et al.* Study on photo-induced charge transfer in the heterointerfaces of CuInS<sub>2</sub>/CdS co-sensitized mesoporous  $TiO_2$  photoelectrode. Electrochim Acta, 2016, 192: 370–376
- 127 Luo J, Lin Z, Zhao Y, *et al.* The embedded  $CuInS_2$  into hollowconcave carbon nitride for photocatalytic  $H_2O$  splitting into  $H_2$ with S-scheme principle. Chin J Catal, 2020, 41: 122–130
- 128 Wang W, Jin C, Qi L. Hierarchical CdS nanorod@SnO<sub>2</sub> nanobowl arrays for efficient and stable photoelectrochemical hydrogen generation. Small, 2018, 14: 1801352
- 129 Cheng L, Zhang D, Liao Y, *et al.* One-step solid-phase synthesis of 2D ultrathin CdS nanosheets for enhanced visible-light photocatalytic hydrogen evolution. Sol RRL, 2019, 3: 1900062
- 130 Li X, Deng Y, Jiang Z, et al. Photocatalytic hydrogen production over CdS nanomaterials: An interdisciplinary experiment for introducing undergraduate students to photocatalysis and analytical chemistry. J Chem Educ, 2019, 96: 1224–1229
- 131 Meng R, Jiang J, Liang Q, et al. Design of graphene-like gallium nitride and WS<sub>2</sub>/WSe<sub>2</sub> nanocomposites for photocatalyst applications. Sci China Mater, 2016, 59: 1027–1036
- 132 Mangiri R, Reddy DA, Subramanyam K, *et al.* Decorating  $MoS_2$ and  $CoSe_2$  nanostructures on 1D-CdS nanorods for boosting photocatalytic hydrogen evolution rate. J Mol Liquids, 2019, 289: 111164
- 133 Han HS, Han GS, Kim JS, et al. Indium-tin-oxide nanowire array based CdSe/CdS/TiO<sub>2</sub> one-dimensional heterojunction photoelectrode for enhanced solar hydrogen production. ACS Sustain Chem Eng, 2016, 4: 1161–1168
- 134 Vaneski A, Schneider J, Susha AS, et al. Aqueous synthesis of CdS and CdSe/CdS tetrapods for photocatalytic hydrogen generation. APL Mater, 2014, 2: 012104
- 135 Chang YS, Choi M, Baek M, *et al.* CdS/CdSe co-sensitized brookite  $\text{H:TiO}_2$  nanostructures: Charge carrier dynamics and photoelectrochemical hydrogen generation. Appl Catal B-Environ, 2018, 225: 379–385
- 136 Chang Y, Yu K, Zhang C, et al. Ternary CdS/Au/3DOM-SrTiO<sub>3</sub> composites with synergistic enhancement for hydrogen production from visible-light photocatalytic water splitting. Appl Catal B-Environ, 2017, 215: 74–84
- 137 Chang Y, Xuan Y, Zhang C, et al. Z-Scheme Pt@CdS/3DOM-SrTiO<sub>3</sub> composite with enhanced photocatalytic hydrogen evolution from water splitting. Catal Today, 2019, 327: 315–322
- 138 Yin XL, Li LL, Li DC, *et al.* Room temperature synthesis of CdS/ SrTiO<sub>3</sub> nanodots-on-nanocubes for efficient photocatalytic  $H_2$ evolution from water. J Colloid Interface Sci, 2019, 536: 694–700
- 139 Yanagida T, Sakata Y, Imamura H. Photocatalytic decomposition of  $H_2O$  into  $H_2$  and  $O_2$  over  $Ga_2O_3$  loaded with NiO. Chem Lett, 2004, 33: 726–727

- 140 She X, Wu J, Xu H, *et al.* High efficiency photocatalytic water splitting using 2D  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> Z-scheme catalysts. Adv Energy Mater, 2017, 7: 1700025
- 141 Preethi V, Kanmani S. Photocatalytic hydrogen production using Fe<sub>2</sub>O<sub>3</sub>-based core shell nano particles with ZnS and CdS. Int J Hydrogen Energy, 2014, 39: 1613–1622
- 142 Mahadik MA, Subramanian A, Chung HS, *et al.*  $CdS/Zr:Fe_2O_3$ nanorod arrays with  $Al_2O_3$  passivation layer for photoelectrochemical solar hydrogen generation. ChemSusChem, 2017, 10: 2030–2039
- 143 Wang L, Wang W, Chen Y, et al. Heterogeneous p-n junction CdS/Cu<sub>2</sub>O nanorod arrays: Synthesis and superior visible-lightdriven photoelectrochemical performance for hydrogen evolution. ACS Appl Mater Interfaces, 2018, 10: 11652–11662
- 144 Cheng WY, Yu TH, Chao KJ, et al. Cu<sub>2</sub>O-decorated CdS nanostructures for high efficiency visible light driven hydrogen production. Int J Hydrogen Energy, 2013, 38: 9665–9672
- 145 Sasikala R, Shirole AR, Bharadwaj SR. Enhanced photocatalytic hydrogen generation over ZrO<sub>2</sub>-TiO<sub>2</sub>-CdS hybrid structure. J Colloid Interface Sci, 2013, 409: 135–140
- 146 Shen J, Wang R, Liu Q, *et al.* Accelerating photocatalytic hydrogen evolution and pollutant degradation by coupling organic co-catalysts with TiO<sub>2</sub>. Chin J Catal, 2019, 40: 380–389
- 147 Zhu Y, Zhang Z, Lu N, et al. Prolonging charge-separation states by doping lanthanide-ions into {001}/{101} facets-coexposed TiO<sub>2</sub> nanosheets for enhancing photocatalytic H<sub>2</sub> evolution. Chin J Catal, 2019, 40: 413–423
- 148 Wang P, Xu S, Chen F, et al. Ni nanoparticles as electron-transfer mediators and NiS as interfacial active sites for coordinative enhancement of H<sub>2</sub>-evolution performance of TiO<sub>2</sub>. Chin J Catal, 2019, 40: 343–351
- 149 Zhang W, Zhang H, Xu J, et al. 3D flower-like heterostructured TiO<sub>2</sub>@Ni(OH)<sub>2</sub> microspheres for solar photocatalytic hydrogen production. Chin J Catal, 2019, 40: 320–325
- 150 Ma D, Shi JW, Zou Y, et al. Highly efficient photocatalyst based on a CdS quantum dots/ZnO nanosheets 0D/2D heterojunction for hydrogen evolution from water splitting. ACS Appl Mater Interfaces, 2017, 9: 25377–25386
- 151 Kuang PY, Su YZ, Xiao K, et al. Double-shelled CdS- and CdSecosensitized ZnO porous nanotube arrays for superior photoelectrocatalytic applications. ACS Appl Mater Interfaces, 2015, 7: 16387–16394
- 152 Zhao H, Dong Y, Jiang P, et al. Light-assisted preparation of a ZnO/CdS nanocomposite for enhanced photocatalytic H<sub>2</sub> evolution: An insight into importance of *in situ* generated ZnS. ACS Sustain Chem Eng, 2015, 3: 969–977
- 153 Xu L, Shi W, Guan J. Preparation of crystallized mesoporous CdS/ Ta<sub>2</sub>O<sub>5</sub> composite assisted by silica reinforcement for visible light photocatalytic hydrogen evolution. Catal Commun, 2012, 25: 54–58
- 154 Xu L, Guan J, Shi W. Enhanced interfacial charge transfer and visible photocatalytic activity for hydrogen evolution from a Ta<sub>2</sub>O<sub>5</sub>-based mesoporous composite by the incorporation of quantum-sized CdS. ChemCatChem, 2012, 4: 1353–1359
- 155 Liu Y, Ding S, Shi Y, *et al.* Construction of CdS/CoO<sub>x</sub> core-shell nanorods for efficient photocatalytic  $H_2$  evolution. Appl Catal B-Environ, 2018, 234: 109–116
- 156 Wu Q, Xiong S, Shen P, et al. Exceptional activity of sub-nm Pt clusters on CdS for photocatalytic hydrogen production: a combined experimental and first-principles study. Catal Sci Technol, 2015, 5: 2059–2064

- 157 Yu H, Huang Y, Gao D, *et al.* Improved H<sub>2</sub>-generation performance of Pt/CdS photocatalyst by a dual-function TiO<sub>2</sub> mediator for effective electron transfer and hole blocking. Ceramics Int, 2019, 45: 9807–9813
- 158 Yu G, Geng L, Wu S, et al. Highly-efficient cocatalyst-free H<sub>2</sub>evolution over silica-supported CdS nanoparticle photocatalysts under visible light. Chem Commun, 2015, 51: 10676–10679
- 159 Zhang J, Zhu Z, Feng X. Construction of two-dimensional MoS<sub>2</sub>/ CdS p-n nanohybrids for highly efficient photocatalytic hydrogen evolution. Chem Eur J, 2014, 20: 10632–10635
- 160 Ma B, Xu H, Lin K, et al. Mo<sub>2</sub>C as non-noble metal co-catalyst in Mo<sub>2</sub>C/CdS composite for enhanced photocatalytic H<sub>2</sub> evolution under visible light irradiation. ChemSusChem, 2016, 9: 820–824
- 161 Wen J, Li X, Liu W, *et al.* Photocatalysis fundamentals and surface modification of TiO<sub>2</sub> nanomaterials. Chin J Catal, 2015, 36: 2049– 2070
- 162 Unni SM, George L, Bhange SN, *et al.* Valorization of coffee bean waste: a coffee bean waste derived multifunctional catalyst for photocatalytic hydrogen production and electrocatalytic oxygen reduction reactions. RSC Adv, 2016, 6: 82103–82111
- 163 Yang C, Li M, Zhang WH, et al. Controlled growth, properties, and application of CdS branched nanorod arrays on transparent conducting oxide substrate. Sol Energy Mater Sol Cells, 2013, 115: 100–107
- 164 Li Q, Li X, Wageh S, et al. CdS/graphene nanocomposite photocatalysts. Adv Energy Mater, 2015, 5: 1500010
- Zhang Y, Hao X, Ma X, et al. Special Z-scheme CdS@WO<sub>3</sub> hetero-junction modified with CoP for efficient hydrogen evolution. Int J Hydrogen Energy, 2019, 44: 13232–13241
- 166 Zong X, Yan H, Wu G, *et al.* Enhancement of photocatalytic  $H_2$  evolution on CdS by loading MoS<sub>2</sub> as cocatalyst under visible light irradiation. J Am Chem Soc, 2008, 130: 7176–7177
- 167 Kalyanasundaram K, Borgarello E, Gráutzel M. Visible light induced water cleavage in CdS dispersions loaded with Pt and RuO<sub>2</sub>, hole scavenging by RuO<sub>2</sub>. HCA, 1981, 64: 362–366
- 168 Jang JS, Joshi UA, Lee JS. Solvothermal synthesis of CdS nanowires for photocatalytic hydrogen and electricity production. J Phys Chem C, 2007, 111: 13280–13287
- 169 Bao N, Shen L, Takata T, et al. Self-templated synthesis of nanoporous CdS nanostructures for highly efficient photocatalytic hydrogen production under visible light. Chem Mater, 2008, 20: 110–117
- 170 Xu Y, Zhao W, Xu R, et al. Synthesis of ultrathin CdS nanosheets as efficient visible-light-driven water splitting photocatalysts for hydrogen evolution. Chem Commun, 2013, 49: 9803–9805
- 171 Bie C, Fu J, Cheng B, et al. Ultrathin CdS nanosheets with tunable thickness and efficient photocatalytic hydrogen generation. Appl Surf Sci, 2018, 462: 606–614
- 172 Xie YM, Liu XH, Zhang R, et al. Ultrathin cadmium sulfide nanosheets for visible-light photocatalytic hydrogen production. J Mater Chem A, 2020, 8: 3586–3589
- 173 Yan H, Yang J, Ma G, et al. Visible-light-driven hydrogen production with extremely high quantum efficiency on Pt-PdS/CdS photocatalyst. J Catal, 2009, 266: 165–168
- 174 Zhang W, Wang Y, Wang Z, et al. Highly efficient and noble metal-free NiS/CdS photocatalysts for H<sub>2</sub> evolution from lactic acid sacrificial solution under visible light. Chem Commun, 2010, 46: 7631–7633
- 175 Ran J, Yu J, Jaroniec M. Ni(OH)<sub>2</sub> modified CdS nanorods for highly efficient visible-light-driven photocatalytic H<sub>2</sub> generation.

Green Chem, 2011, 13: 2708-2713

- 176 Ma S, Deng Y, Xie J, *et al.* Noble-metal-free Ni<sub>3</sub>C cocatalysts decorated CdS nanosheets for high-efficiency visible-light-driven photocatalytic  $H_2$  evolution. Appl Catal B-Environ, 2018, 227: 218–228
- 177 Wang X, Liu G, Chen ZG, *et al.* Enhanced photocatalytic hydrogen evolution by prolonging the lifetime of carriers in ZnO/ CdS heterostructures. Chem Commun, 2009, 23: 3452
- Zhang LJ, Li S, Liu BK, *et al.* Highly efficient CdS/WO<sub>3</sub> photocatalysts: Z-scheme photocatalytic mechanism for their enhanced photocatalytic H<sub>2</sub> evolution under visible light. ACS Catal, 2014, 4: 3724–3729
- 179 Shen R, Zhang L, Chen X, *et al.* Integrating 2D/2D CdS/α-Fe<sub>2</sub>O<sub>3</sub> ultrathin bilayer Z-scheme heterojunction with metallic β-NiS nanosheet-based ohmic-junction for efficient photocatalytic H<sub>2</sub> evolution. Appl Catal B-Environ, 2020, 266: 118619
- 180 Li Q, Guo B, Yu J, et al. Highly efficient visible-light-driven photocatalytic hydrogen production of CdS-cluster-decorated graphene nanosheets. J Am Chem Soc, 2011, 133: 10878–10884
- 181 Yuan YJ, Chen D, Yu ZT, et al. Cadmium sulfide-based nanomaterials for photocatalytic hydrogen production. J Mater Chem A, 2018, 6: 11606–11630
- 182 Lian Z, Xu P, Wang W, *et al.*  $C_{60}$ -decorated CdS/TiO<sub>2</sub> mesoporous architectures with enhanced photostability and photocatalytic activity for H<sub>2</sub> evolution. ACS Appl Mater Interfaces, 2015, 7: 4533–4540
- 183 Zhang LJ, Zheng R, Li S, *et al.* Enhanced photocatalytic H<sub>2</sub> generation on cadmium sulfide nanorods with cobalt hydroxide as cocatalyst and insights into their photogenerated charge transfer properties. ACS Appl Mater Interfaces, 2014, 6: 13406–13412
- 184 Qian XB, Peng W, Huang JH. Fluorescein-sensitized Au/g- $C_3N_4$ nanocomposite for enhanced photocatalytic hydrogen evolution under visible light. Mater Res Bull, 2018, 102: 362–368
- 185 Song T, Zhang P, Zeng J, *et al.* Boosting the photocatalytic  $H_2$ evolution activity of Fe<sub>2</sub>O<sub>3</sub> polymorphs ( $\alpha$ -,  $\gamma$ - and  $\beta$ -Fe<sub>2</sub>O<sub>3</sub>) by fullerene [C<sub>60</sub>]-modification and dye-sensitization under visible light irradiation. RSC Adv, 2017, 7: 29184–29192
- 186 Shen R, Xie J, Ding Y, et al. Carbon nanotube-supported Cu<sub>3</sub>P as high-efficiency and low-cost cocatalysts for exceptional semiconductor-free photocatalytic H<sub>2</sub> evolution. ACS Sustain Chem Eng, 2019, 7: 3243–3250
- 187 Wang L, Gao Z, Li Y, *et al.* Photosensitization of CdS by acid red-94 modified alginate: Dual ameliorative effect upon photocatalytic hydrogen evolution. Appl Surf Sci, 2019, 492: 598–606
- 188 Zhang X, Xiao J, Hou M, *et al.* Robust visible/near-infrared light driven hydrogen generation over Z-scheme conjugated polymer/ CdS hybrid. Appl Catal B-Environ, 2018, 224: 871–876
- 189 Lei Y, Yang C, Hou J, *et al.* Strongly coupled CdS/graphene quantum dots nanohybrids for highly efficient photocatalytic hydrogen evolution: Unraveling the essential roles of graphene quantum dots. Appl Catal B-Environ, 2017, 216: 59–69
- 190 Ma L, Chen YL, Yang DJ, et al. Multi-interfacial plasmon coupling in multigap (Au/AgAu)@CdS core-shell hybrids for efficient photocatalytic hydrogen generation. Nanoscale, 2020, 12: 4383-4392
- 191 Chiu YH, Naghadeh SB, Lindley SA, *et al.* Yolk-shell nanostructures as an emerging photocatalyst paradigm for solar hydrogen generation. Nano Energy, 2019, 62: 289–298
- 192 Li S, Zhang L, Jiang T, *et al.* Construction of shallow surface states through light Ni doping for high-efficiency photocatalytic hy-

drogen production of CdS nanocrystals. Chem Eur J, 2014, 20: 311-316

- 193 Wang P, Pu Z, Li Y, *et al.* Iron-doped nickel phosphide nanosheet arrays: An efficient bifunctional electrocatalyst for water splitting. ACS Appl Mater Interfaces, 2017, 9: 26001–26007
- 194 Murphy JR, Delikanli S, Scrace T, et al. Time-resolved photoluminescence study of CdSe/CdMnS/CdS core/multi-shell nanoplatelets. Appl Phys Lett, 2016, 108: 242406
- 195 Li H, Wang Z, He Y, *et al.* Rational synthesis of Mn<sub>x</sub>Cd<sub>1-x</sub>S for enhanced photocatalytic H<sub>2</sub> evolution: Effects of S precursors and the feed ratio of Mn/Cd on its structure and performance. J Colloid Interface Sci, 2019, 535: 469–480
- 196 Xue C, Li H, An H, et al. NiS<sub>x</sub> quantum dots accelerate electron transfer in Cd<sub>0.8</sub>Zn<sub>0.2</sub>S photocatalytic system via an rGO nanosheet "bridge" toward visible-light-driven hydrogen evolution. ACS Catal, 2018, 8: 1532–1545
- 197 Wu Y, Yue Z, Liu A, *et al.* p-Type Cu-doped Zn<sub>0.3</sub>Cd<sub>0.7</sub>S/graphene photocathode for efficient water splitting in a photoelectrochemical tandem cell. ACS Sustain Chem Eng, 2016, 4: 2569–2577
- 198 Zhang J, Qi L, Ran J, et al. Ternary NiS/Zn<sub>x</sub>Cd<sub>1-x</sub>S/reduced graphene oxide nanocomposites for enhanced solar photocatalytic H<sub>2</sub>-production activity. Adv Energy Mater, 2014, 4: 1301925
- 199 Dai D, Xu H, Ge L, et al. In-situ synthesis of CoP co-catalyst decorated Zn<sub>0.5</sub>Cd<sub>0.5</sub>S photocatalysts with enhanced photocatalytic hydrogen production activity under visible light irradiation. Appl Catal B-Environ, 2017, 217: 429–436
- 200 Ye L, Han C, Ma Z, et al. Ni<sub>2</sub>P loading on Cd<sub>0.5</sub>Zn<sub>0.5</sub>S solid solution for exceptional photocatalytic nitrogen fixation under visible light. Chem Eng J, 2017, 307: 311–318
- 201 Zhang J, Xu Q, Qiao SZ, *et al.* Enhanced visible-light hydrogenproduction activity of copper-modified  $Zn_xCd_{1-x}S$ . Chem-SusChem, 2013, 6: 2009–2015
- 202 Moradlou O, Tedadi N, Banazadeh A, *et al.* Effect of RGO/ Zn<sub>x</sub>Cd<sub>1-x</sub>S crystalline phase on solar photoactivation processes. RSC Adv, 2016, 6: 46282–46290
- 203 Li Y, Ruan Q, Lin H, et al. Unique Cd<sub>1-x</sub>Zn<sub>x</sub>S@WO<sub>3-x</sub> and Cd<sub>1-x</sub>-Zn<sub>x</sub>S@WO<sub>3-x</sub>/CoO<sub>x</sub>/NiO<sub>x</sub> Z-scheme photocatalysts for efficient visible-light-induced H<sub>2</sub> evolution. Sci China Mater, 2020, 63: 75–90
- 204 Mei F, Li Z, Dai K, et al. Step-scheme porous g-C<sub>3</sub>N<sub>4</sub>/Zn<sub>0.2</sub>Cd<sub>0.8</sub>S-DETA composites for efficient and stable photocatalytic H<sub>2</sub> production. Chin J Catal, 2020, 41: 41–49
- Wang P, Geng Z, Gao J, *et al.* Zn<sub>x</sub>Cd<sub>1-x</sub>S/bacterial cellulose bionanocomposite foams with hierarchical architecture and enhanced visible-light photocatalytic hydrogen production activity. J Mater Chem A, 2015, 3: 1709–1716
- 206 Lingampalli SR, Gautam UK, Rao CNR. Highly efficient photocatalytic hydrogen generation by solution-processed ZnO/Pt/CdS, ZnO/Pt/Cd<sub>1-x</sub>Zn<sub>x</sub>S and ZnO/Pt/CdS<sub>1-x</sub>Se<sub>x</sub> hybrid nanostructures. Energy Environ Sci, 2013, 6: 3589–3594
- 207 Han Z, Chen G, Li C, *et al.* Preparation of 1D cubic Cd<sub>0.8</sub>Zn<sub>0.2</sub>S solid-solution nanowires using levelling effect of TGA and improved photocatalytic H<sub>2</sub>-production activity. J Mater Chem A, 2015, 3: 1696–1702
- 208 Zhang X, Jing D, Liu M, *et al.* Efficient photocatalytic H<sub>2</sub> production under visible light irradiation over Ni doped  $Cd_{1-x}Zn_xS$ microsphere photocatalysts. Catal Commun, 2008, 9: 1720–1724
- 209 Jiang Z, Qian K, Zhu C, et al. Carbon nitride coupled with CdS-TiO<sub>2</sub> nanodots as 2D/0D ternary composite with enhanced photocatalytic H<sub>2</sub> evolution: A novel efficient three-level electron

transfer process. Appl Catal B-Environ, 2017, 210: 194-204

- 210 Lv JX, Zhang ZM, Wang J, et al. In situ synthesis of CdS/ graphdiyne heterojunction for enhanced photocatalytic activity of hydrogen production. ACS Appl Mater Interfaces, 2019, 11: 2655–2661
- 211 Shi W, Guo F, Li M, *et al.* N-doped carbon dots/CdS hybrid photocatalyst that responds to visible/near-infrared light irradiation for enhanced photocatalytic hydrogen production. Separation Purification Tech, 2019, 212: 142–149
- 212 Cheng F, Yin H, Xiang Q. Low-temperature solid-state preparation of ternary CdS/g-C<sub>3</sub>N<sub>4</sub>/CuS nanocomposites for enhanced visible-light photocatalytic H<sub>2</sub>-production activity. Appl Surf Sci, 2017, 391: 432–439
- 213 Jiang L, Wang L, Xu G, et al. A microwave-assisted thermolysis route to single-step preparation of MoS<sub>2</sub>/CdS composite photocatalysts for active hydrogen generation. Sustain Energy Fuels, 2018, 2: 430–435
- 214 Kang H, Kim JH. Utilization of a ZnS(en)<sub>0.5</sub> photocatalyst hybridized with a CdS component for solar energy conversion to hydrogen. Adv Powder Tech, 2017, 28: 2438–2444
- 215 Tian L, Min S, Wang F. Integrating noble-metal-free metallic vanadium carbide cocatalyst with CdS for efficient visible-lightdriven photocatalytic H<sub>2</sub> evolution. Appl Catal B-Environ, 2019, 259: 118029
- 216 Zhao J, Li W, Liu H, et al. Yolk-shell CdS@void@TiO<sub>2</sub> composite particles with photocorrosion resistance for enhanced dye removal and hydrogen evolution. Adv Powder Tech, 2019, 30: 1965–1975
- 217 Hu Y, Hao X, Cui Z, et al. Enhanced photocarrier separation in conjugated polymer engineered CdS for direct Z-scheme photocatalytic hydrogen evolution. Appl Catal B-Environ, 2020, 260: 118131
- 218 Yue X, Yi S, Wang R, *et al.* Cadmium sulfide and nickel synergetic co-catalysts supported on graphitic carbon nitride for visiblelight-driven photocatalytic hydrogen evolution. Sci Rep, 2016, 6: 22268
- 219 Jia X, Tahir M, Pan L, et al. Direct Z-scheme composite of CdS and oxygen-defected CdWO<sub>4</sub>: An efficient visible-light-driven photocatalyst for hydrogen evolution. Appl Catal B-Environ, 2016, 198: 154–161
- 220 Xu J, Yan X, Qi Y, et al. Novel phosphidated MoS<sub>2</sub> nanosheets modified CdS semiconductor for an efficient photocatalytic H<sub>2</sub> evolution. Chem Eng J, 2019, 375: 122053
- 221 Song L, Li T, Zhang S, *et al.* Synthesis of rhodium phosphide cocatalyst and remarkably enhanced photocatalytic hydrogen evolution over CdS under visible light radiation. Chem Eng J, 2017, 314: 498-507
- 222 Li F, Hou Y, Yu Z, *et al.* Oxygen deficiency introduced to Z-scheme CdS/WO<sub>3-x</sub> nanomaterials with MoS<sub>2</sub> as the cocatalyst towards enhancing visible-light-driven hydrogen evolution. Nanoscale, 2019, 11: 10884–10895
- 223 Nekouei F, Nekouei S, Pouzesh M, et al. Porous-CdS/Cu<sub>2</sub>O/graphitic-C<sub>3</sub>N<sub>4</sub> dual p-n junctions as highly efficient photo/catalysts for degrading ciprofloxacin and generating hydrogen using solar energy. Chem Eng J, 2020, 385: 123710
- 224 Ai Z, Zhang K, Shi D, *et al.* Band-matching transformation between CdS and BCNNTs with tunable p-n homojunction for enhanced photocatalytic pure water splitting. Nano Energy, 2020, 69: 104408
- 225 Lin Y, Zhang Q, Li Y, *et al.* The evolution from a typical type-I CdS/ZnS to type-II and Z-scheme hybrid structure for efficient

and stable hydrogen production under visible light. ACS Sustain Chem Eng, 2020, 8: 4537–4546

- 226 Qin Y, Li H, Lu J, *et al.* Nitrogen-doped hydrogenated  $\text{TiO}_2$ modified with CdS nanorods with enhanced optical absorption, charge separation and photocatalytic hydrogen evolution. Chem Eng J, 2020, 384: 123275
- 227 Jiang C, Zhang L, Gao F, et al. Promoting photocatalytic hydrogen production by a core-shell CdS@MoO<sub>x</sub> photocatalyst connected by an S-Mo "bridge". Catal Sci Technol, 2020, 10: 1368–1375
- 228 Zhang J, Wang Y, Jin J, et al. Efficient visible-light photocatalytic hydrogen evolution and enhanced photostability of core/shell CdS/g-C<sub>3</sub>N<sub>4</sub> nanowires. ACS Appl Mater Interfaces, 2013, 5: 10317–10324
- 229 Li C, Wang H, Naghadeh SB, et al. Visible light driven hydrogen evolution by photocatalytic reforming of lignin and lactic acid using one-dimensional NiS/CdS nanostructures. Appl Catal B-Environ, 2018, 227: 229–239
- 230 Zhang L, Fu X, Meng S, et al. Ultra-low content of Pt modified CdS nanorods: one-pot synthesis and high photocatalytic activity for H<sub>2</sub> production under visible light. J Mater Chem A, 2015, 3: 23732–23742
- 231 Hong S, Kumar DP, Reddy DA, et al. Excellent photocatalytic hydrogen production over CdS nanorods via using noble metalfree copper molybdenum sulfide (Cu<sub>2</sub>MoS<sub>4</sub>) nanosheets as cocatalysts. Appl Surf Sci, 2017, 396: 421–429
- 232 Liu S, Guo Z, Qian X, *et al.* Sonochemical deposition of ultrafine metallic Pt nanoparticles on CdS for efficient photocatalytic hydrogen evolution. Sustain Energy Fuels, 2019, 3: 1048–1054
- 233 Fang X, Cui L, Pu T, et al. Core-shell CdS@MnS nanorods as highly efficient photocatalysts for visible light driven hydrogen evolution. Appl Surf Sci, 2018, 457: 863–869
- 234 Zhang J, Qiao SZ, Qi L, *et al.* Fabrication of NiS modified CdS nanorod p–n junction photocatalysts with enhanced visible-light photocatalytic H<sub>2</sub>-production activity. Phys Chem Chem Phys, 2013, 15: 12088–12094
- 235 Chen H, Sun Z, Ye S, *et al.* Molecular cobalt–salen complexes as novel cocatalysts for highly efficient photocatalytic hydrogen production over a CdS nanorod photosensitizer under visible light. J Mater Chem A, 2015, 3: 15729–15737
- 236 Zhu C, Liu C, Fu Y, et al. Construction of CDs/CdS photocatalysts for stable and efficient hydrogen production in water and seawater. Appl Catal B-Environ, 2019, 242: 178–185
- 237 Li Q, Shi T, Li X, et al. Remarkable positive effect of Cd(OH)<sub>2</sub> on CdS semiconductor for visible-light photocatalytic H<sub>2</sub> production. Appl Catal B-Environ, 2018, 229: 8–14
- 238 Xiao R, Zhao C, Zou Z, et al. In situ fabrication of 1D CdS nanorod/2D Ti<sub>3</sub>C<sub>2</sub> MXene nanosheet Schottky heterojunction toward enhanced photocatalytic hydrogen evolution. Appl Catal B-Environ, 2020, 268: 118382
- 239 Zhou X, Fang Y, Cai X, et al. In situ photodeposited construction of Pt-CdS/g-C<sub>3</sub>N<sub>4</sub>-MnO<sub>x</sub> composite photocatalyst for efficient visible-light-driven overall water splitting. ACS Appl Mater Interfaces, 2020, 12: 20579–20588
- 240 Xiang Q, Cheng F, Lang D. Hierarchical layered WS<sub>2</sub>/graphenemodified CdS nanorods for efficient photocatalytic hydrogen evolution. ChemSusChem, 2016, 9: 996–1002
- 241 Chen Z, Gong H, Liu Q, et al. NiSe<sub>2</sub> nanoparticles grown in situ on CdS nanorods for enhanced photocatalytic hydrogen evolution. ACS Sustain Chem Eng, 2019, 7: 16720–16728
- 242 Rangappa AP, Kumar DP, Gopannagari M, et al. Highly efficient

hydrogen generation in water using 1D CdS nanorods integrated with 2D  $SnS_2$  nanosheets under solar light irradiation. Appl Surf Sci, 2020, 508: 144803

- 243 Li K, Han M, Chen R, *et al.* Hexagonal@cubic CdS core@shell nanorod photocatalyst for highly active production of  $H_2$  with unprecedented stability. Adv Mater, 2016, 28: 8906–8911
- 244 Chava RK, Son N, Kim YS, *et al.* Controlled growth and bandstructure properties of one dimensional cadmium sulfide nanorods for visible photocatalytic hydrogen evolution reaction. Nanomaterials, 2020, 10: 619
- 245 Li Z, Zhang L, Liu Y, *et al.* Surface-polarity-induced spatial charge separation boosts photocatalytic overall water splitting on GaN nanorod arrays. Angew Chem Int Ed, 2020, 59: 935–942
- 246 Ren D, Shen R, Jiang Z, et al. Highly efficient visible-light photocatalytic H<sub>2</sub> evolution over 2D–2D CdS/Cu<sub>2</sub>S<sub>4</sub> layered heterojunctions. Chin J Catal, 2020, 41: 31–40
- 247 Dai K, Hu T, Zhang J, et al. Carbon nanotube exfoliated porous reduced graphene oxide/CdS-diethylenetriamine heterojunction for efficient photocatalytic H<sub>2</sub> production. Appl Surf Sci, 2020, 512: 144783
- 248 Abbood HA, Alabadi A, Al-Hawash AB, et al. Square CdS micro/ nanosheets as efficient photo/piezo-bi-catalyst for hydrogen production. Catal Lett, 2020, 150: 3059–3070
- 249 Pan Z, Li J, Zhou K. Wrinkle-free atomically thin CdS nanosheets for photocatalytic hydrogen evolution. Nanotechnology, 2018, 29: 215402
- 250 Sun K, Shen J, Yang Y, *et al.* Highly efficient photocatalytic hydrogen evolution from 0D/2D heterojunction of FeP nanoparticles/CdS nanosheets. Appl Surf Sci, 2020, 505: 144042
- 251 Lv J, Zhang J, Liu J, et al. Bi SPR-promoted Z-scheme Bi<sub>2</sub>MoO<sub>6</sub>/ CdS-diethylenetriamine composite with effectively enhanced visible light photocatalytic hydrogen evolution activity and stability. ACS Sustain Chem Eng, 2018, 6: 696–706
- 252 Wu A, Tian C, Jiao Y, *et al.* Sequential two-step hydrothermal growth of MoS<sub>2</sub>/CdS core-shell heterojunctions for efficient visible light-driven photocatalytic H<sub>2</sub> evolution. Appl Catal B-Environ, 2017, 203: 955–963
- 253 Yu H, Zhong W, Huang X, *et al.* Suspensible cubic-phase CdS nanocrystal photocatalyst: facile synthesis and highly efficient H<sub>2</sub>-evolution performance in a sulfur-rich system. ACS Sustain Chem Eng, 2018, 6: 5513–5523
- 254 Chen J, Wu XJ, Yin L, *et al.* One-pot synthesis of CdS nanocrystals hybridized with single-layer transition-metal dichalcogenide nanosheets for efficient photocatalytic hydrogen evolution. Angew Chem Int Ed, 2015, 54: 1210–1214
- 255 Chai B, Xu M, Yan J, *et al.* Remarkably enhanced photocatalytic hydrogen evolution over MoS<sub>2</sub> nanosheets loaded on uniform CdS nanospheres. Appl Surf Sci, 2018, 430: 523–530
- 256 Yin XL, Li LL, Han SR, et al. Green and in-situ synthesis of noblemetal-free Ni<sub>2</sub>P/CdS nanoheterostructure for enhanced photocatalytic H<sub>2</sub> generation activity. J Taiwan Institute Chem Engineers, 2019, 103: 110–117
- 257 Wei RB, Huang ZL, Gu GH, et al. Dual-cocatalysts decorated rimous CdS spheres advancing highly-efficient visible-light photocatalytic hydrogen production. Appl Catal B-Environ, 2018, 231: 101–107
- 258 Zubair M, Svenum IH, Rønning M, *et al.* Facile synthesis approach for core-shell  $TiO_2$ -CdS nanoparticles for enhanced photocatalytic H<sub>2</sub> generation from water. Catal Today, 2019, 328: 15–20
- 259 Yao X, Liu T, Liu X, et al. Loading of CdS nanoparticles on the

(101) surface of elongated  $TiO_2$  nanocrystals for efficient visiblelight photocatalytic hydrogen evolution from water splitting. Chem Eng J, 2014, 255: 28–39

- 260 Zhou FQ, Fan JC, Xu QJ, et al. BiVO<sub>4</sub> nanowires decorated with CdS nanoparticles as Z-scheme photocatalyst with enhanced H<sub>2</sub> generation. Appl Catal B-Environ, 2017, 201: 77–83
- 261 Du J, Wang H, Yang M, *et al.* Pyramid-like CdS nanoparticles grown on porous  $TiO_2$  monolith: An advanced photocatalyst for H<sub>2</sub> production. Electrochim Acta, 2017, 250: 99–107
- 262 Zhao L, Jia J, Yang Z, et al. One-step synthesis of CdS nanoparticles/MoS<sub>2</sub> nanosheets heterostructure on porous molybdenum sheet for enhanced photocatalytic H<sub>2</sub> evolution. Appl Catal B-Environ, 2017, 210: 290–296
- 263 Lei Y, Hou J, Wang F, *et al.* Boosting the catalytic performance of  $MoS_x$  cocatalysts over CdS nanoparticles for photocatalytic  $H_2$  evolution by Co doping *via* a facile photochemical route. Appl Surf Sci, 2017, 420: 456–464
- 264 Girginer B, Galli G, Chiellini E, et al. Preparation of stable CdS nanoparticles in aqueous medium and their hydrogen generation efficiencies in photolysis of water. Int J Hydrogen Energy, 2009, 34: 1176-1184
- 265 Wang D, Li X, Zheng LL, et al. Size-controlled synthesis of CdS nanoparticles confined on covalent triazine-based frameworks for durable photocatalytic hydrogen evolution under visible light. Nanoscale, 2018, 10: 19509–19516
- 266 Weng B, Liu S, Zhang N, et al. A simple yet efficient visible-lightdriven CdS nanowires-carbon nanotube 1D–1D nanocomposite photocatalyst. J Catal, 2014, 309: 146–155
- 267 Wu K, Zhu H, Lian T. Ultrafast exciton dynamics and lightdriven H<sub>2</sub> evolution in colloidal semiconductor nanorods and Pttipped nanorods. Acc Chem Res, 2015, 48: 851–859
- 268 Appell D. Wired for success. Nature, 2002, 419: 553-555
- 269 Bierman MJ, Jin S. Potential applications of hierarchical branching nanowires in solar energy conversion. Energy Environ Sci, 2009, 2: 1050–1059
- 270 Shieh F, Saunders AE, Korgel BA. General shape control of colloidal CdS, CdSe, CdTe quantum rods and quantum rod heterostructures. J Phys Chem B, 2005, 109: 8538–8542
- 271 Fatahi P, Roy A, Bahrami M, et al. Visible-light-driven efficient hydrogen production from CdS nanorods anchored with cocatalysts based on transition metal alloy nanosheets of NiPd, NiZn, and NiPdZn. ACS Appl Energy Mater, 2018, 1: 5318–5327
- 272 Han B, Liu S, Zhang N, et al. One-dimensional CdS@MoS<sub>2</sub> coreshell nanowires for boosted photocatalytic hydrogen evolution under visible light. Appl Catal B-Environ, 2017, 202: 298–304
- 273 Li Q, Qiao XQ, Jia Y, *et al.* Noble-metal-free amorphous  $CoMoS_x$ modified CdS core-shell nanowires for dramatically enhanced photocatalytic hydrogen evolution under visible light irradiation. Appl Surf Sci, 2019, 498: 143863
- 274 Shabaev A, Efros AL. 1D exciton spectroscopy of semiconductor nanorods. Nano Lett, 2004, 4: 1821–1825
- 275 Sitt A, Salant A, Menagen G, et al. Highly emissive nano rod-inrod heterostructures with strong linear polarization. Nano Lett, 2011, 11: 2054–2060
- 276 Peng CY, Manning L, Albertson R, *et al.* The tumour-suppressor genes lgl and dlg regulate basal protein targeting in Drosophila neuroblasts. Nature, 2000, 408: 596–600
- 277 Tongying P, Vietmeyer F, Aleksiuk D, *et al.* Double heterojunction nanowire photocatalysts for hydrogen generation. Nanoscale, 2014, 6: 4117–4124

- 278 Wu K, Rodríguez-Córdoba W, Lian T. Exciton localization and dissociation dynamics in CdS and CdS-Pt quantum confined nanorods: Effect of nonuniform rod diameters. J Phys Chem B, 2014, 118: 14062–14069
- 279 Park J, Lee E, Hwang NM, *et al.* One-nanometer-scale size-controlled synthesis of monodisperse magnetic iron oxide nanoparticles. Angew Chem Int Ed, 2005, 44: 2872–2877
- 280 Pileni MP. Self-assemblies of nanocrystals: fabrication and collective properties. Appl Surf Sci, 2001, 171: 1–14
- 281 Wang X, Zhuang J, Peng Q, et al. A general strategy for nanocrystal synthesis. Nature, 2005, 437: 121–124
- 282 Gai Q, Zheng X, Liu W, et al. 2D-2D heterostructured CdS-CoP photocatalysts for efficient H<sub>2</sub> evolution under visible light irradiation. Int J Hydrogen Energy, 2019, 44: 27412–27420
- 283 Liu C, Xiong M, Chai B, et al. Construction of 2D/2D Ni<sub>2</sub>P/CdS heterojunctions with significantly enhanced photocatalytic H<sub>2</sub> evolution performance. Catal Sci Technol, 2019, 9: 6929–6937
- 284 Li C, Han L, Liu R, et al. Controlled synthesis of CdS micro/nano leaves with (0001) facets exposed: enhanced photocatalytic activity toward hydrogen evolution. J Mater Chem, 2012, 22: 23815–23820
- 285 Low J, Cao S, Yu J, *et al.* Two-dimensional layered composite photocatalysts. Chem Commun, 2014, 50: 10768–10777
- 286 Ren D, Liang ZZ, Ng YH, et al. Strongly coupled 2D-2D nanojunctions between P-doped Ni<sub>2</sub>S (Ni<sub>2</sub>SP) cocatalysts and CdS nanosheets for efficient photocatalytic H<sub>2</sub> evolution. Chem Eng J, 2020, 390: 124496
- 287 Cui X, Jiang G, Zhu M, et al. TiO<sub>2</sub>/CdS composite hollow spheres with controlled synthesis of platinum on the internal wall for the efficient hydrogen evolution. Int J Hydrogen Energy, 2013, 38: 9065–9073
- 288 Xu M, Wei Z, Liu J, *et al.* One-pot synthesized visible-light-responsive MoS<sub>2</sub>@CdS nanosheets-on-nanospheres for hydrogen evolution from the antibiotic wastewater: Waste to energy insight. Int J Hydrogen Energy, 2019, 44: 21577–21587
- 289 Yuan W, Zhang Z, Cui X, et al. Fabrication of hollow mesoporous CdS@TiO<sub>2</sub>@Au microspheres with high photocatalytic activity for hydrogen evolution from water under visible light. ACS Sustain Chem Eng, 2018, 6: 13766–13777
- 290 Zheng XL, Song JP, Ling T, *et al.* Strongly coupled nafion molecules and ordered porous CdS networks for enhanced visiblelight photoelectrochemical hydrogen evolution. Adv Mater, 2016, 28: 4935–4942
- 291 Bie C, Zhu B, Xu F, et al. In situ grown monolayer N-doped graphene on CdS hollow spheres with seamless contact for photocatalytic CO<sub>2</sub> reduction. Adv Mater, 2019, 31: 1902868
- 292 Wu K, Wu P, Zhu J, *et al.* Synthesis of hollow core-shell CdS@TiO<sub>2</sub>/Ni<sub>2</sub>P photocatalyst for enhancing hydrogen evolution and degradation of MB. Chem Eng J, 2019, 360: 221–230
- 293 Chen Z, Xu YJ. Ultrathin TiO<sub>2</sub> layer coated-CdS spheres coreshell nanocomposite with enhanced visible-light photoactivity. ACS Appl Mater Interfaces, 2013, 5: 13353–13363
- Yoo I, Kalanur SS, Seo H. A nanoscale p–n junction photoelectrode consisting of an NiO<sub>x</sub> layer on a TiO<sub>2</sub>/CdS nanorod coreshell structure for highly efficient solar water splitting. Appl Catal B-Environ, 2019, 250: 200–212
- 295 Wang M, Cui Z, Yang M, *et al.* Core/shell structured CdS/polydopamine/TiO<sub>2</sub> ternary hybrids as highly active visible-light photocatalysis. J Colloid Interface Sci, 2019, 544: 1–7
- 296 Wu H, Meng S, Zhang J, et al. Construction of two-dimensionally

relative p-n heterojunction for efficient photocatalytic redox reactions under visible light. Appl Surf Sci, 2020, 505: 144638

- 297 Wang Y, Zhang X, Liu Y, *et al.* Crystallinity and phase controlling of g-C<sub>3</sub>N<sub>4</sub>/CdS hetrostructures towards high efficient photocatalytic H<sub>2</sub> generation. Int J Hydrogen Energy, 2019, 44: 30151–30159
- 298 Liu H, Yan T, Jin Z, et al. CoP nanoparticles as cocatalyst modified the CdS/NiWO<sub>4</sub> p-n heterojunction to produce hydrogen efficiently. New J Chem, 2020, 44: 1426–1438
- 299 Zhang Y, Jin Z. Accelerated charge transfer via a nickel tungstate modulated cadmium sulfide p–n heterojunction for photocatalytic hydrogen evolution. Catal Sci Technol, 2019, 9: 1944–1960
- 300 Majhi D, Das K, Mishra A, et al. One pot synthesis of CdS/BiOBr/ Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub>: A novel ternary double Z-scheme heterostructure photocatalyst for efficient degradation of atrazine. Appl Catal B-Environ, 2020, 260: 118222
- 301 Hu T, Li P, Zhang J, et al. Highly efficient direct Z-scheme WO<sub>3</sub>/ CdS-diethylenetriamine photocatalyst and its enhanced photocatalytic H<sub>2</sub> evolution under visible light irradiation. Appl Surf Sci, 2018, 442: 20–29
- 302 Wei W, Tian Q, Sun H, et al. Efficient visible-light-driven photocatalytic H<sub>2</sub> evolution over MoO<sub>2</sub>-C/CdS ternary heterojunction with unique interfacial microstructures. Appl Catal B-Environ, 2020, 260: 118153
- 303 Tang Y, Traveerungroj P, Tan HL, *et al.* Scaffolding an ultrathin CdS layer on a ZnO nanorod array using pulsed electrodeposition for improved photocharge transport under visible light illumination. J Mater Chem A, 2015, 3: 19582–19587
- 304 Ma D, Shi JW, Zou Y, et al. Rational design of CdS@ZnO coreshell structure via atomic layer deposition for drastically enhanced photocatalytic H<sub>2</sub> evolution with excellent photostability. Nano Energy, 2017, 39: 183–191
- 305 Wu H, Zheng Z, Tang Y, *et al.* Pulsed electrodeposition of CdS on ZnO nanorods for highly sensitive photoelectrochemical sensing of copper(II) ions. Sustain Mater Technol, 2018, 18: e00075
- 306 Wang S, Zhu B, Liu M, *et al.* Direct Z-scheme ZnO/CdS hierarchical photocatalyst for enhanced photocatalytic H<sub>2</sub>-production activity. Appl Catal B-Environ, 2019, 243: 19–26
- 307 Hoseini AA, Farhadi S, Zabardasti A, et al. A novel n-type CdS nanorods/p-type LaFeO<sub>3</sub> heterojunction nanocomposite with enhanced visible-light photocatalytic performance. RSC Adv, 2019, 9: 24489–24504
- 308 Han X, Wang D, Guo Z, et al. Excellent visible light absorption by adopting mesoporous SiC in SiC/CdS for enhanced photocatalytic hydrogen generation. mat express, 2019, 9: 65–72
- 309 Arif M, Min Z, Yuting L, et al. A Bi<sub>2</sub>WO<sub>6</sub>-based hybrid heterostructures photocatalyst with enhanced photodecomposition and photocatalytic hydrogen evolution through Z-scheme process. J Industrial Eng Chem, 2019, 69: 345–357
- 310 Zhang Y, Jin Z, Yuan H, et al. Well-regulated nickel nanoparticles functional modified ZIF-67 (Co) derived Co<sub>3</sub>O<sub>4</sub>/CdS p-n heterojunction for efficient photocatalytic hydrogen evolution. Appl Surf Sci, 2018, 462: 213–225
- 311 Xu Q, Zhang L, Yu J, *et al.* Direct Z-scheme photocatalysts: Principles, synthesis, and applications. Mater Today, 2018, 21: 1042–1063
- 312 Li X, Shen R, Ma S, et al. Graphene-based heterojunction photocatalysts. Appl Surf Sci, 2018, 430: 53–107
- 313 Zhong W, Shen S, He M, *et al.* The pulsed laser-induced Schottky junction *via in-situ* forming Cd clusters on CdS surfaces toward efficient visible light-driven photocatalytic hydrogen evolution.

Appl Catal B-Environ, 2019, 258: 117967

- 314 Shang L, Tong B, Yu H, et al. CdS nanoparticle-decorated Cd nanosheets for efficient visible light-driven photocatalytic hydrogen evolution. Adv Energy Mater, 2016, 6: 1501241
- 315 Lang D, Shen T, Xiang Q. Roles of MoS<sub>2</sub> and graphene as cocatalysts in the enhanced visible-light photocatalytic H<sub>2</sub> production activity of multiarmed CdS nanorods. ChemCatChem, 2015, 7: 943–951
- 316 Xu J, Wang L, Cao X. Polymer supported graphene–CdS composite catalyst with enhanced photocatalytic hydrogen production from water splitting under visible light. Chem Eng J, 2016, 283: 816–825
- 317 Kuang P, Sayed M, Fan J, et al. 3D graphene-based H<sub>2</sub>-production photocatalyst and electrocatalyst. Adv Energy Mater, 2020, 10: 1903802
- 318 Xia Y, Cheng B, Fan J, *et al.* Unraveling photoexcited charge transfer pathway and process of CdS/graphene nanoribbon composites toward visible-light photocatalytic hydrogen evolution. Small, 2019, 15: 1902459
- 319 Xia Y, Cheng B, Fan J, et al. Near-infrared absorbing 2D/3D ZnIn<sub>2</sub>S<sub>4</sub>/N-doped graphene photocatalyst for highly efficient CO<sub>2</sub> capture and photocatalytic reduction. Sci China Mater, 2020, 63: 552–565
- 320 Wang Y, Chen J, Liu L, et al. Novel metal doped carbon quantum dots/CdS composites for efficient photocatalytic hydrogen evolution. Nanoscale, 2019, 11: 1618–1625
- 321 Qiu S, Shen Y, Wei G, et al. Carbon dots decorated ultrathin CdS nanosheets enabling *in-situ* anchored Pt single atoms: A highly efficient solar-driven photocatalyst for hydrogen evolution. Appl Catal B-Environ, 2019, 259: 118036
- 322 Ma S, Xu X, Xie J, et al. Improved visible-light photocatalytic H<sub>2</sub> generation over CdS nanosheets decorated by NiS<sub>2</sub> and metallic carbon black as dual earth-abundant cocatalysts. Chin J Catal, 2017, 38: 1970–1980
- 323 Kim YK, Lim SK, Park H, et al. Trilayer CdS/carbon nanofiber (CNF) mat/Pt-TiO<sub>2</sub> composite structures for solar hydrogen production: Effects of CNF mat thickness. Appl Catal B-Environ, 2016, 196: 216–222
- 324 Zhang J, Huang F. Enhanced visible light photocatalytic  $H_2$ production activity of g-C<sub>3</sub>N<sub>4</sub> via carbon fiber. Appl Surf Sci, 2015, 358: 287–295
- 325 Kim YK, Kim M, Hwang SH, *et al.* CdS-loaded flexible carbon nanofiber mats as a platform for solar hydrogen production. Int J Hydrogen Energy, 2015, 40: 136–145
- 326 Gopannagari M, Kumar DP, Park H, et al. Influence of surfacefunctionalized multi-walled carbon nanotubes on CdS nanohybrids for effective photocatalytic hydrogen production. Appl Catal B-Environ, 2018, 236: 294–303
- 327 Li H, Xiao S, Zhou J, et al. A flexible CdS nanorods-carbon nanotubes/stainless steel mesh photoanode for boosted photoelectrocatalytic hydrogen evolution. Chem Commun, 2019, 55: 2741– 2744
- 328 Kim YK, Park H. Light-harvesting multi-walled carbon nanotubes and CdS hybrids: Application to photocatalytic hydrogen production from water. Energy Environ Sci, 2011, 4: 685–694
- 329 Meng A, Zhu B, Zhong B, et al. Direct Z-scheme TiO<sub>2</sub>/CdS hierarchical photocatalyst for enhanced photocatalytic H<sub>2</sub>-production activity. Appl Surf Sci, 2017, 422: 518–527
- 330 Yu W, Zhang S, Chen J, et al. Biomimetic Z-scheme photocatalyst with a tandem solid-state electron flow catalyzing H<sub>2</sub> evolution. J

Mater Chem A, 2018, 6: 15668-15674

- 331 He F, Meng A, Cheng B, et al. Enhanced photocatalytic H<sub>2</sub>-production activity of WO<sub>3</sub>/TiO<sub>2</sub> step-scheme heterojunction by graphene modification. Chin J Catal, 2020, 41: 9–20
- 332 He K, Xie J, Luo X, *et al.* Enhanced visible light photocatalytic  $H_2$  production over Z-scheme  $g-C_3N_4$  nansheets/WO<sub>3</sub> nanorods nanocomposites loaded with Ni(OH)<sub>x</sub> cocatalysts. Chin J Catal, 2017, 38: 240–252
- 333 Low J, Jiang C, Cheng B, *et al.* A review of direct Z-scheme photocatalysts. Small Methods, 2017, 1: 1700080
- 334 Di T, Xu Q, Ho WK, et al. Review on metal sulphide-based Zscheme photocatalysts. ChemCatChem, 2019, 11: 1394–1411
- 335 Zhang L, Hao X, Jian Q, et al. Ferrous oxalate dehydrate over CdS as Z-scheme photocatalytic hydrogen evolution. J Solid State Chem, 2019, 274: 286–294
- 336 Peng J, Shen J, Yu X, et al. Construction of LSPR-enhanced 0D/ 2D CdS/MoO<sub>3</sub>–S-scheme heterojunctions for visible-light-driven photocatalytic H<sub>2</sub> evolution. Chin J Catal, 2021, 42: 87–96
- 337 Ren Y, Zeng D, Ong WJ. Interfacial engineering of graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>)-based metal sulfide heterojunction photocatalysts for energy conversion: A review. Chin J Catal, 2019, 40: 289–319
- 338 Ren D, Zhang W, Ding Y, *et al. In situ* fabrication of robust cocatalyst-free CdS/g-C<sub>3</sub>N<sub>4</sub> 2D-2D step-scheme heterojunctions for highly active H<sub>2</sub> evolution. Sol RRL, 2020, 4: 1900423
- 339 Yang R, Zhu R, Fan Y, et al. Construction of an artificial inorganic leaf CdS-BiVO<sub>4</sub> Z-scheme and its enhancement activities for pollutant degradation and hydrogen evolution. Catal Sci Technol, 2019, 9: 2426–2437
- 340 Low J, Dai B, Tong T, et al. In situ irradiated X-ray photoelectron spectroscopy investigation on a direct Z-scheme TiO<sub>2</sub>/CdS composite film photocatalyst. Adv Mater, 2019, 31: 1802981
- 341 Ge H, Xu F, Cheng B, et al. S-scheme heterojunction TiO<sub>2</sub>/CdS nanocomposite nanofiber as H<sub>2</sub>-production photocatalyst. ChemCatChem, 2019, 11: 6301–6309
- 342 Cui H, Li B, Li Z, et al. Z-scheme based CdS/CdWO<sub>4</sub> heterojunction visible light photocatalyst for dye degradation and hydrogen evolution. Appl Surf Sci, 2018, 455: 831–840
- 343 Yin C, Cui L, Pu T, *et al.* Facile fabrication of nano-sized hollow-CdS@g-C<sub>3</sub>N<sub>4</sub> core-shell spheres for efficient visible-light-driven hydrogen evolution. Appl Surf Sci, 2018, 456: 464–472
- 344 Yu G, Wang X, Cao J, *et al.* Plasmonic Au nanoparticles embedding enhances the activity and stability of CdS for photocatalytic hydrogen evolution. Chem Commun, 2016, 52: 2394–2397
- 345 Oros-Ruiz S, Hernández-Gordillo A, García-Mendoza C, et al. Comparative activity of CdS nanofibers superficially modified by Au, Cu, and Ni nanoparticles as co-catalysts for photocatalytic hydrogen production under visible light. J Chem Technol Biotechnol, 2016, 91: 2205–2210
- 346 Zhou X, Chen H, Sun Y, et al. Highly efficient light-induced hydrogen evolution from a stable Pt/CdS NPs-co-loaded hierarchically porous zeolite beta. Appl Catal B-Environ, 2014, 152: 271–279
- Feng J, An C, Dai L, *et al.* Long-term production of H<sub>2</sub> over Pt/ CdS nanoplates under sunlight illumination. Chem Eng J, 2016, 283: 351–357
- 348 Di T, Cheng B, Ho W, et al. Hierarchically CdS-Ag<sub>2</sub>S nanocomposites for efficient photocatalytic H<sub>2</sub> production. Appl Surf Sci, 2019, 470: 196–204
- 349 Yin J, Zhan F, Jiao T, et al. Facile preparation of self-assembled

MXene@Au@CdS nanocomposite with enhanced photocatalytic hydrogen production activity. Sci China Mater, 2020, 63: 2228–2238

- 350 Ran J, Gao G, Li FT, *et al.*  $Ti_3C_2$  MXene co-catalyst on metal sulfide photo-absorbers for enhanced visible-light photocatalytic hydrogen production. Nat Commun, 2017, 8: 13907
- 351 Li K, Zhang S, Li Y, et al. MXenes as noble-metal-alternative cocatalysts in photocatalysis. Chin J Catal, 2021, 42: 3–14
- 352 Cheng L, Li X, Zhang H, et al. Two-dimensional transition metal MXene-based photocatalysts for solar fuel generation. J Phys Chem Lett, 2019, 10: 3488–3494
- 353 Liu W, Wang X, Yu H, *et al.* Direct photoinduced synthesis of amorphous  $CoMoS_x$  cocatalyst and its improved photocatalytic H<sub>2</sub>-evolution activity of CdS. ACS Sustain Chem Eng, 2018, 6: 12436–12445
- 354 Lu X, Toe CY, Ji F, *et al.* Light-induced formation of MOO<sub>x</sub>S<sub>y</sub> clusters on CdS nanorods as cocatalyst for enhanced hydrogen evolution. ACS Appl Mater Interfaces, 2020, 12: 8324–8332
- 355 Zhang ZW, Li QH, Qiao XQ, et al. One-pot hydrothermal synthesis of willow branch-shaped MoS<sub>2</sub>/CdS heterojunctions for photocatalytic H<sub>2</sub> production under visible light irradiation. Chin J Catal, 2019, 40: 371–379
- 356 Liang Z, Shen R, Ng YH, et al. A review on 2D MoS<sub>2</sub> cocatalysts in photocatalytic H<sub>2</sub> production. J Mater Sci Tech, 2020, 56: 89–121
- 357 Wei Z, Xu M, Liu J, *et al.* Simultaneous visible-light-induced hydrogen production enhancement and antibiotic wastewater degradation using MoS<sub>2</sub>@Zn<sub>x</sub>Cd<sub>1-x</sub>S: Solid-solution-assisted photocatalysis. Chin J Catal, 2020, 41: 103–113
- 358 Chai B, Liu C, Wang C, et al. Photocatalytic hydrogen evolution activity over MoS<sub>2</sub>/ZnIn<sub>2</sub>S<sub>4</sub> microspheres. Chin J Catal, 2017, 38: 2067–2075
- 359 Hu T, Dai K, Zhang J, et al. Noble-metal-free Ni<sub>2</sub>P as cocatalyst decorated rapid microwave solvothermal synthesis of inorganicorganic CdS-DETA hybrids for enhanced photocatalytic hydrogen evolution. Appl Surf Sci, 2019, 481: 1385–1393
- 360 Dai D, Wang L, Xiao N, et al. In-situ synthesis of Ni<sub>2</sub>P co-catalyst decorated Zn<sub>0.5</sub>Cd<sub>0.5</sub>S nanorods for high-quantum-yield photocatalytic hydrogen production under visible light irradiation. Appl Catal B-Environ, 2018, 233: 194–201
- 361 Yuan J, Wen J, Zhong Y, *et al.* Enhanced photocatalytic  $H_2$  evolution over noble-metal-free NiS cocatalyst modified CdS nanorods/g-C<sub>3</sub>N<sub>4</sub> heterojunctions. J Mater Chem A, 2015, 3: 18244–18255
- 362 Song L, Zhang S. A novel cocatalyst of NiCoP significantly enhances visible-light photocatalytic hydrogen evolution over cadmium sulfide. J Industr Eng Chem, 2018, 61: 197–205
- 363 Li S, Wang L, Liu S, et al. In situ synthesis of strongly coupled Co<sub>2</sub>P-CdS nanohybrids: An effective strategy to regulate photocatalytic hydrogen evolution activity. ACS Sustain Chem Eng, 2018, 6: 9940–9950
- 364 Zong X, Han J, Ma G, et al. Photocatalytic H<sub>2</sub> evolution on CdS loaded with WS<sub>2</sub> as cocatalyst under visible light irradiation. J Phys Chem C, 2011, 115: 12202–12208
- 365 Zou Y, Shi JW, Ma D, et al. WS<sub>2</sub>/graphitic carbon nitride heterojunction nanosheets decorated with CdS quantum dots for photocatalytic hydrogen production. ChemSusChem, 2018, 11: 1187–1197
- 366 Moniruddin M, Oppong E, Stewart D, et al. Designing CdS-based ternary heterostructures consisting of co-metal and CoO<sub>x</sub> cocatalysts for photocatalytic H<sub>2</sub> evolution under visible light. Inorg

Chem, 2019, 58: 12325-12333

- 367 Shen R, Xie J, Xiang Q, et al. Ni-based photocatalytic H<sub>2</sub>-production cocatalysts. Chin J Catal, 2019, 40: 240–288
- 368 Zhang H, Dong Y, Zhao S, *et al.* Photochemical preparation of atomically dispersed nickel on cadmium sulfide for superior photocatalytic hydrogen evolution. Appl Catal B-Environ, 2020, 261: 118233
- 369 Meng A, Zhang L, Cheng B, et al. Dual cocatalysts in TiO<sub>2</sub> photocatalysis. Adv Mater, 2019, 31: 1807660
- 370 Huang L, Wang X, Yang J, et al. Dual cocatalysts loaded type I CdS/ZnS core/shell nanocrystals as effective and stable photocatalysts for H<sub>2</sub> evolution. J Phys Chem C, 2013, 117: 11584–11591
- 371 Di T, Zhu B, Zhang J, et al. Enhanced photocatalytic H<sub>2</sub> production on CdS nanorod using cobalt-phosphate as oxidation cocatalyst. Appl Surf Sci, 2016, 389: 775–782
- 372 Ba Q, Jia X, Huang L, et al. Alloyed Pd Ni hollow nanoparticles as cocatalyst of CdS for improved photocatalytic activity toward hydrogen production. Int J Hydrogen Energy, 2019, 44: 5872–5880
- 373 Ba Q, Jia X, Huang L, *et al.* Hollow structured PtNi alloy as cocatalyst of CdS for hydrogen generation under visible light irradiation. Int J Hydrogen Energy, 2019, 44: 28104–28112
- 374 Zhang F, Zhuang HQ, Zhang W, et al. Noble-metal-free CuS/CdS photocatalyst for efficient visible-light-driven photocatalytic H<sub>2</sub> production from water. Catal Today, 2019, 330: 203–208
- 375 Liu G, Zhao G, Zhou W, et al. In situ bond modulation of graphitic carbon nitride to construct p-n homojunctions for enhanced photocatalytic hydrogen production. Adv Funct Mater, 2016, 26: 6822–6829
- 376 Wang X, Yu H, Yang L, et al. A highly efficient and noble metalfree photocatalytic system using Ni<sub>x</sub>B/CdS as photocatalyst for visible light H<sub>2</sub> production from aqueous solution. Catal Commun, 2015, 67: 45–48
- 377 Wen T, Zhang L, Schmitt W. A Mn<sub>13</sub>-cluster based coordination polymer as a co-catalyst of CdS for enhanced visible-light driven H<sub>2</sub> evolution. Dalton Trans, 2018, 47: 10857–10860
- 378 Iqbal S. Spatial charge separation and transfer in L-cysteine capped NiCoP/CdS nano-heterojunction activated with intimate covalent bonding for high-quantum-yield photocatalytic hydrogen evolution. Appl Catal B-Environ, 2020, 274: 119097
- 379 Lian J, Qi Y, Bao Y, *et al.* Reversed configuration of photocatalyst to exhibit improved properties of basic processes compared to conventional one. Sci China Chem, 2020, 63: 771–776
- 380 You F, Wan J, Qi J, et al. Lattice distortion in hollow multi-shelled structures for efficient visible-light CO<sub>2</sub> reduction with a SnS<sub>2</sub>/ SnO<sub>2</sub> junction. Angew Chem Int Ed, 2020, 59: 721–724
- 381 Li J, Liu X, Zhang J. Smart assembly of sulfide heterojunction photocatalysts with well-defined interfaces for direct Z-scheme water splitting under visible light. ChemSusChem, 2020, 13: 2996–3004
- 382 Ai Z, Zhang K, Chang B, et al. Construction of CdS@Ti<sub>3</sub>C<sub>2</sub>@CoO hierarchical tandem p-n heterojunction for boosting photocatalytic hydrogen production in pure water. Chem Eng J, 2020, 383: 123130
- 383 Ning X, Zhen W, Wu Y, et al. Inhibition of CdS photocorrosion by Al<sub>2</sub>O<sub>3</sub> shell for highly stable photocatalytic overall water splitting under visible light irradiation. Appl Catal B-Environ, 2018, 226: 373–383
- 384 Qian L, Hou Y, Yu Z, et al. Metal-induced Z-scheme CdS/Ag/g-C<sub>3</sub>N<sub>4</sub> photocatalyst for enhanced hydrogen evolution under visible light: The synergy of MIP effect and electron mediator of

Ag. Mol Catal, 2018, 458: 43-51

- 385 Peng T, Zhang X, Zeng P, *et al.* Carbon encapsulation strategy of Ni co-catalyst: Highly efficient and stable Ni@C/CdS nanocomposite photocatalyst for hydrogen production under visible light. J Catal, 2013, 303: 156–163
- 386 Xiong J, Liu Y, Cao C, *et al.* An architecture of  $CdS/H_2Ti_5O_{11}$ ultrathin nanobelt for photocatalytic hydrogenation of 4-nitroaniline with highly efficient performance. J Mater Chem A, 2015, 3: 6935-6942
- 387 Hou Y, Laursen AB, Zhang J, et al. Layered nanojunctions for hydrogen-evolution catalysis. Angew Chem Int Ed, 2013, 52: 3621–3625

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**Conflict of interest** The authors declare that they have no conflict of interest.



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## 纳米结构硫化镉光催化分解水产氢综述

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**摘要**太阳能驱动光催化分解水制氢是实现可持续制氢气的一种 有效策略.硫化镉半导体光催化剂基于其较强的可见光响应、适 宜的氧化还原反应带边位置以及优异的电荷传输性能而备受关注. 本文综述了近年来国内外在提高硫化镉基光催化剂制氢性能的设 计、改性和制备等方面的研究进展.首先简要介绍了光催化制氢 的基本概念和机理,阐述了硫化镉光催化制氢的基本性质、重要 进展和瓶颈,综述了该材料的发展前景.随后,重点讨论了硫化镉 基光催化剂光催化分解水产氢的各种改性策略,其中有效的策略 是产生更多的载流子,促进电荷的有效分离,促进界面电荷转移, 加速电荷利用,以及抑制电荷诱导的自光腐蚀.针对每一种改性策 略,都详细讨论了影响光催化剂性能的重要因素和未来潜在的研 究方向.最后介绍了纳米结构硫化镉和硫化镉基纳米复合材料在 光催化分解水产氢中的发展前景和面临的挑战.本综述将为开发 镉基半导体光催化剂提供重要和及时的理论指导,并促进其在太 阳能氢气生产中的应用.