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Review

The roles and mechanism of cocatalysts in photocatalytic water splitting to produce hydrogen

Nan Xiao ^{a,b}, Songsong Li ^b, Xuli Li ^b, Lei Ge ^{a,b,*}, Yangqin Gao ^b, Ning Li ^b^a State Key Laboratory of Heavy Oil Processing, College of New Energy and Materials, China University of Petroleum Beijing, Beijing 102249, China^b Department of Materials Science and Engineering, College of New Energy and Materials, China University of Petroleum Beijing, Beijing 102249, China

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ABSTRACT

Photocatalytic hydrogen (H_2) evolution *via* water splitting over semiconductors has been considered to be one of the most promising strategies for sustainable energy supply in the future to provide non-pollution and renewable energy. The key to efficient conversion of solar-chemical energy is the design of an efficient structure for high charge separation and transportation. Therefore, cocatalysts are necessary in boosting photocatalytic H_2 evolution. To date, semiconductor photocatalysts have been modified by various cocatalysts due to the extended light harvest, enhanced charge carrier separation efficiency and improved stability. This review focuses on recent developments of cocatalysts in photocatalytic H_2 evolution, the roles and mechanism of the cocatalysts are discussed in detail. The cocatalysts can be divided into the following categories: metal/alloy cocatalysts, metal phosphides cocatalysts, metal oxide/hydroxide cocatalysts, carbon-based cocatalysts, dual cocatalysts, Z-scheme cocatalysts and MOFs cocatalysts. The future research and forecast for photocatalytic hydrogen generation are also suggested.

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1. Introduction

Due to the world's heavy reliance on non-renewable, geopolitically sensitive energy sources such as natural gas and coal, coupled with the violent fluctuations in crude oil prices, ensuring alternative clean and renewable energy supplies has never been such urgent [1–6]. The world's primary energy consumption increased by 2.9% in 2018, which is the highest annual growth rate since 2010, almost double of the average annual growth rate in the last 10 years. Our main energy sources still depend on limited and non-renewable fossil fuels, such as oil, natural gas and coal. Besides, the combustion of fossil fuels has led to a series of serious environmental pollution issues, such as air pollution, water pollution and even global warming.

Therefore, it is imperative to develop renewable, clean and environmentally-friendly energy sources. Solar energy is the most tremendous renewable natural resource, which is abundant, cheap and clean [7–11]. H_2 is considered as an important energy in the future, which is mainly due to its cleanness, non-toxicity and high energy density compared to other natural resources. Photocatalytic hydrogen production *via* solar splitting is one of the most promising solutions to address the environmental problems and sustainable clean energy issues.

Since the pioneer work of Fujishima *et al.* [12] on photoelectrochemical water splitting to produce hydrogen (H_2) and oxygen (O_2) separately under light irradiation by using TiO_2 in 1972, semiconductor photocatalytic water splitting to produce H_2 as a potential technology has received extensive attention

* Corresponding author. E-mail: gelei08@sina.com

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and rapid development [11,13–18]. In the past two decades, the semiconductor photocatalysts have been greatly developed by a large number of scholars from various countries and regions. Many photocatalytic materials have been investigated, including metal oxides or sulfides, such as TiO_2 [19–28], CdS [29–38] and ZnCdS [15,39–42], and the metal-free semiconductors such as rGO [43] and $\text{g-C}_3\text{N}_4$ [5,44–54]. However, the photocatalytic activities of the most promising semiconductor photocatalysts are still not quite satisfied due to the easy recombination between charge carriers. In order to suppress the charge recombination, many strategies have been developed for effective separation of electron-hole pairs, including surface loading of cocatalysts [55–57], turning the morphologies [48,58,59], heterojunctions/homojunctions [60–62], molecular design [63–67] and heteroatom doping [5,68]. Cocatalyst loading is an effective strategy to promote the photocatalytic activity of semiconductor photocatalysts, in which way the stability of the photocatalysts, the separation efficiency of the photo-generated charges, the number of exposed active sites and the light harvesting ability could be largely enhanced. Therefore, cocatalysts play an important role in improving the performance of photocatalytic H_2 evolution. Until now, a large number of strategies were developed to modify semiconductor photocatalysts by cocatalysts, such as Type I heterojunction [69,70], Type II heterojunction [61], p-n heterojunction [62,71,72], Schottky-junction [73,74], Z-scheme heterojunction [75–78] and S-scheme heterojunction [14], which have been widely designed to form build-in electric field for boosting the charge carrier separation, thus achieving improved photocatalytic hydrogen production.

In this review, we focus on the roles and mechanisms of cocatalysts developed to date for photocatalytic H_2 evolution, including (1) metals, alloys, metal phosphides, metal oxides, metal hydroxides, metal sulfides, carbon-based, *etc.*, as single cocatalysts for H_2 evolution, (2) the synergetic effect of the dual cocatalysts loading for reduction reaction, (3) the effect of Z-scheme for water splitting, and (4) the improvement of H_2 production by loading MOFs as cocatalysts. We pay attention to the roles and mechanisms of various cocatalyst systems with important and representative research being discussed and summarized.

2. Fundamentals of photocatalysis and roles of cocatalysts

Fig. 1. The mechanism of photocatalytic water splitting in a semiconductor photocatalyst system.

2.1. Fundamentals of photocatalysis

In general, the reaction mechanism of photocatalytic water splitting for H_2 production involves three major steps [79]: (1) absorption of light by semiconductor photocatalysts to generate electron (e^-)-hole (h^+) pairs; (2) charge separation and migration to the surface of semiconductor photocatalysts; and (3) surface reactions for water reduction and oxidation, respectively. The efficiency of photocatalytic H_2 evolution is determined by the kinetics of the above three steps altogether (Eq. 1):

$$\eta = \eta_1 \times \eta_2 \times \eta_3 \quad (1)$$

where η_1 is the efficiency of light absorption, η_2 is the efficiency of charge separation, and η_3 is the efficiency of surface catalytic reaction.

Generally, the semiconductor photocatalyst is composed of vacant conduction band (CB) and filled valence band (VB), which are separated from each other by E_g . The photocatalytic process begins with light absorption, when the photon energy is larger than or equal to the band gap (E_g), photon absorption in the photocatalyst causes electronic transition and generates e^- - h^+ pairs, then the electrons in the VB are excited to the CB, while the holes are left in the VB. The electrons in the CB participate in the reduction reaction to produce H_2 , and the oxidation reaction is driven by the holes in the VB. The minimum band edge of the CB has to be more negative than the redox potential of H^+/H_2 (0 V vs. RHE), while the maximum band edge of the VB should be more positive than the chemical redox potential of $\text{O}_2/\text{H}_2\text{O}$ (Fig. 1). However, if there are no suitable activity sites or reaction center on the surface of the semiconductor photocatalyst, the photogenerated electrons and holes could quickly recombine in the bulk of the semiconductor. According to the previous reports [9,80,81] that the recombination rate of photoinduced electrons and holes in the bulk of the catalysts is very fast (ps to ms). Therefore, the electrons and holes should be quickly captured by the cocatalysts for efficient separation and transfer of photogenerated charges and participate in the reduction reactions on the surface, which is critically important for photocatalytic water splitting.

2.2. Roles of cocatalysts in photocatalytic H_2 evolution system

In photocatalytic H_2 evolution system, the cocatalysts have four pivotal roles in enhancing the activity of the semiconductor photocatalysts (Fig. 2): (1) Cocatalysts can enhance the light

Fig. 2. Functions of cocatalysts in photocatalytic H₂ production.

harvesting. Some plasmon metals (such as Au and Cu) can enhance visible light absorption due to the localized surface plasmon resonance (LSPR) effect [82,83]. (2) Cocatalysts can be effective in facilitating the separation of electron-hole pairs. When a cocatalyst is loaded on the surface of the photocatalysts, the cocatalyst can attract electrons, therefore the separation and transfer of the charge carriers can be enhanced [11,84]. (3) Cocatalysts can provide active sites for the photocatalytic reaction. Most cocatalysts can not only serve as electron sinks, but also provide proton reduction sites [85,86]. (4) Cocatalysts can improve the stability of the photocatalysts. Some metal sulfides can be oxidized easily. After loading cocatalysts, the self-decomposition of sulfides can be suppressed by extracting the photogenerated holes for oxygen evolution reac-

Table 1

The work functions of metals.

Metal	Work function (eV)
Pt	5.65 [109]
Pd	5.2 [110]
Au	5.1 [111]
Ag	4.26 [112]
Ni	5.15 [113]
Co	5.0 [114]

tions [81,87].

3. Single cocatalysts for photocatalytic H₂ evolution

3.1. Metals and alloys

Deposition of metals on the surface of semiconductors is one of the effective ways to improve the photocatalytic performance of photocatalysts. The photogenerated electrons migrate to the metal surface under the action of electric field formed by the relatively low Fermi level of the metal. The schematic of charge transfer for metal/semiconductor under light irradiation due to the existence of the Schottky junction is illustrated in Fig. 3(a). When a metal is in close contact with a semiconductor, Schottky barrier would be formed and resulted in band bending in the semiconductor at the interface of the contact, and the electrons must have a higher energy to over-

Table 2

Summary of metals as cocatalysts in photocatalyst systems for H₂ evolution.

Photocatalyst	Cocatalyst	Light source	Weight (mg)	Solution	Activity	AQY	Year/Ref.
Pt/g-C ₃ N ₄	Pt	300 W Xe lamp	50	200 mL 10 vol% TEOA	318 μmol·h ⁻¹	0.16% (420 nm)	2016 [90]
0.1 wt.% Pt/g-C ₃ N ₄	Pt	300 W Xe lamp (λ≥420 nm)	30	100 mL 10 vol% methanol	473.82 μmol·mg ⁻¹	—	2019 [54]
Pt/g-C ₃ N ₄	Pt	300 W Xe lamp	30	200 mL 10 vol% methanol	42.1 μmol·h ⁻¹	—	2018 [91]
1 wt.% Pt/g-C ₃ N ₄	Pt	300 W Xe lamp (λ≥420 nm)	100	100 mL 10 vol% TEOA	34 μmol·h ⁻¹	—	2015 [92]
Pt/g-C ₃ N ₄	Pt	300 W Xe lamp (λ≥420 nm)	50	80 mL 10 vol% TEOA	571.01 μmol·h ⁻¹ ·g ⁻¹	—	2016 [93]
Pt/g-C ₃ N ₄	Pt	300 W Xe lamp (λ≥420 nm)	100	243 mL 10 vol% TEOA	417 μmol·h ⁻¹ ·g ⁻¹	—	2014 [94]
0.2 wt. %Pt/g-C ₃ N ₄	Pt	300 W Xe lamp	20	50 mL 10 vol% TEOA	4875 μmol·g ⁻¹ ·4h	—	2017 [95]
1 wt.% Pt/g-C ₃ N ₄	Pt	350 W Xe lamp	8	80 mL 10 vol% TEOA	4210.8 μmol·h ⁻¹ ·g ⁻¹	—	2018 [96]
1 wt.% Pd/TiO ₂	Pd	200 W SB-1000P/F lamp (λ≥365 nm)	6.5	20 mL 10 vol% glycerol	47.5 mmol·h ⁻¹ ·g ⁻¹	—	2015 [97]
0.5 wt.% Pd/g-C ₃ N ₄	Pd	300 W Xe lamp (λ≥400 nm)	20	100 mL 10 vol% TEOA	1208.6 μmol·h ⁻¹ ·g ⁻¹	3.8% (420 nm)	2019 [98]
0.5% Ag/g-C ₃ N ₄	Ag	300 W Xe lamp (λ≥400 nm)	50	200 mL 10 vol% methanol	18.09 μmol·h ⁻¹ ·g ⁻¹	—	2016 [100]
20 wt.% Ag/MoS ₂	Ag	300 W Xe lamp	2.1	4.5 mL 0.3 M Na ₂ S/0.3 M Na ₂ SO ₃	179.5 μmol·g ⁻¹	—	2015 [102]
3 wt.% Ag/g-C ₃ N ₄	Ag	300 W Xe lamp	5	70 mL 10 vol% TEOA	2014.2 μmol·h ⁻¹ ·g ⁻¹	—	2016 [103]
2 wt.% Au/g-C ₃ N ₄	Au	300 W Xe lamp (λ≥420 nm)	20	40 mL 2.5 vol% TEOA	540 μmol·h ⁻¹ ·g ⁻¹	1.22% (420 nm)	2018 [104]
Au/TiO ₂	Au	300 W Xe lamp	25	50 mL 20 vol% TEOA	4.92 mmol·h ⁻¹ ·g ⁻¹	—	2018 [24]
Au/TiO ₂	Au	300 W Xe lamp (λ≥420 nm)	10	20 mL 20 vol% methanol	12.4 μmol·h ⁻¹ ·g ⁻¹	—	2018 [107]
Au/g-C ₃ N ₄	Au	300 W Xe lamp (λ≥420 nm)	50	100 mL 10 vol% TEOA	84.1 μmol·h ⁻¹	—	2018 [108]
Zn/g-C ₃ N ₄	Zn	200 W Xe lamp (λ≥420 nm)	200	270 mL 18.5 vol% methanol	59.5 μmol·h ⁻¹	3.2% (420 nm)	2011 [125]
0.5 wt.% Ni/TiO ₂	Ni	100 W SB-100P/F lamp (λ≥365 nm)	6.5	20 mL 5 vol% EtOH	24.3 mmol·h ⁻¹ ·g ⁻¹	—	2015 [119]
10 % Ni/g-C ₃ N ₄	Ni	500 W Xe arc lamp	50	100 mL 10 vol% TEOA	8.41 μmol·h ⁻¹	—	2015 [120]
7.40 % Ni/g-C ₃ N ₄	Ni	300 W Xe lamp	10	10 mL 30 vol% TEOA	4318 μmol·h ⁻¹ ·g ⁻¹	2.1% (400 nm)	2016 [121]
3 wt.% Ni/CdIn ₂ S ₄	Ni	100 W solar simulator	5	10 mL 10 vol% TEOA	1060 μmol·h ⁻¹ ·g ⁻¹	—	2017 [122]
5 wt.% Ni/CdS	Ni	300 W Xe lamp (λ≥400 nm)	100	50 mL 50 vol% lactic acid	3004.8 μmol·h ⁻¹	—	2014 [123]
10 % Co/g-C ₃ N ₄	Co	300 W Xe lamp	20	15 mL 20 vol% TEOA	11.48 μmol·h ⁻¹	5.34% (400 nm)	2018 [124]
2.5% Cu/TiO ₂	Cu	300 W Xe lamp	50	100 mL 20 vol% methanol	6046 μmol·h ⁻¹ ·g ⁻¹	—	2019 [28]
0.3 wt.% Cu/TiO ₂	Cu	300 W Xe lamp (λ≥300 nm)	50	65 mL 20 vol% methanol	20.4 mmol·h ⁻¹ ·g ⁻¹	—	2018 [23]
1 wt.% Cu/Nb ₂ O ₅	Cu	400 W medium pressure halide lamp (λ=360 nm)	200	550 mL 16.7 vol% methanol	1572 μmol·h ⁻¹ ·g ⁻¹	—	2011 [126]

Fig. 3. Schematic of (a) Schottky junction and (b) LSPR effect.

come the barrier [81,88,89]. The photogenerated electrons will transfer from the CB of the semiconductor to the metal through the Schottky barrier until their Fermi levels are equal, and the holes will hold in the VB of the semiconductor, thereby achieving effective separation of e^-h^+ pairs. The metal not only acts as a cocatalyst to separate photogenerated electrons–holes, but also provides an active site for the photocatalytic H_2 evolution. In this section, the application of transition metal phosphides materials as cocatalysts for photocatalytic H_2 production is introduced, and Table 2 and Table 3 summarize the application of metals and alloys as cocatalysts in the photocatalyst system for H_2 evolution.

Several noble-metals such as Pt [54,90–96], Pd [97–99], Ag [100–103] and Au [24,104–108] have been investigated in recent years. Pt, with the largest work function among many noble-metal, (Table 1), is the best cocatalyst for trapping electrons.

In 2016, Li *et al.* [90] reported that isolated single Pt atoms as a new form of cocatalysts deposited on $g-C_3N_4$ to enhance

the photocatalytic H_2 evolution activity. Under visible-light irradiation, bare $g-C_3N_4$ gives a low activity with H_2 evolution rate of $6.5 \mu\text{mol}\cdot\text{h}^{-1}$. While with 0.16 wt.% Pt loading, Pt-CN shows a H_2 generation rate up to $318 \mu\text{mol}\cdot\text{h}^{-1}$. The photocatalytic performance of H_2 production can be improved by adding isolated single Pt atom to the intrinsic change of the $g-C_3N_4$ surface trap state induced by Pt atoms. Zhu *et al.* [54] concluded that the size of Pt co-catalyst can be controlled to form single atoms by inducing a small amount of Pt precursor, which plays a pivotal role in enhancing the photocatalytic performance of $g-C_3N_4$. As shown in Fig. 4, the average size of Pt on $g-C_3N_4$ is less than 0.2 nm after loading 0.1 wt.% Pt. With increasing the loading amount of Pt, the size of Pt clusters is increased. When the size of the Pt clusters is the smallest, the photocatalytic H_2 generation rate of Pt_{0.1}-CN is $473.82 \mu\text{mol}\cdot\text{mg}^{-1}$ under the visible-light irradiation. It is ascribed to the enhanced utilization efficiency of Pt atoms.

Liu *et al.* [96] synthesized Pt/ $g-C_3N_4$ by changing the sequence of adding TEOA on photo-deposition of Pt. The sample named CNS-Pt-A and CNS-Pt-B that TEOA is added into the photocatalytic system after and before photo-deposition of Pt, respectively. Both CNS-Pt-A and CNS-Pt-B show better photocatalytic H_2 production activity as shown in Fig. 5, and the CNS-Pt-A shows a higher photocatalytic H_2 generation rate of $4210.8 \mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$, which is attributed to the formation of coordination complex between TEOA and Pt⁴⁺, inhibiting the photo-reduction of Pt⁴⁺ to metallic Pt.

Metals are modified on the surface of semiconductors to form metal/semiconductor systems, which act as co-catalysts

Table 3

Summary of metal alloys as cocatalysts photocatalyst system for H_2 evolution.

Photocatalyst	Cocatalyst	Light source	Weight (mg)	Solution	Activity	AQY	Year/Ref.
0.2 wt.% Pt _{0.5} Pd _{0.5} / $g-C_3N_4$	Pt _{0.5} Pd _{0.5}	300 W Xe lamp ($\lambda \geq 400$ nm)	50	100 mL 10 vol% TEOA/K ₂ HPO ₄	$1600.8 \mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	5.5% (420 nm)	2019 [127]
1.0 wt.% PtCo/ $g-C_3N_4$	PtCo	300 W Xe lamp ($\lambda \geq 400$ nm)	50	100 mL 10 vol% TEOA	$960 \mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	—	2015 [128]
0.5 wt.% AuPd/ $g-C_3N_4$	AuPd	300 W Xe lamp ($\lambda \geq 400$ nm)	50	100 mL 10 vol% TEOA	$326 \mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	—	2015 [129]
1.0 wt.% AuPd/ $g-C_3N_4$	AuPd	300 W Xe lamp ($\lambda \geq 400$ nm)	50	100 mL 10 vol% TEOA/K ₂ HPO ₄	$107 \mu\text{mol}\cdot\text{h}^{-1}$	—	2017 [130]
AgCu(3)/C ₃ N ₄ NTs	AgCu	300 W Xe lamp ($\lambda \geq 420$ nm)	40	40 mL 10 vol% TEOA	$738 \mu\text{mol}\cdot\text{g}^{-1}$	—	2018 [131]
NiCd/CdS	NiCd	300 W Xe lamp ($\lambda \geq 410$ nm)	20	100 mL 0.1 M Na ₂ S/Na ₂ SO ₃	$11.57 \text{ mmol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	—	2019 [132]
10 wt.% Ni _{0.4} Mo _{0.6} / $g-C_3N_4$	Ni _{0.4} Mo _{0.6}	300 W Xe lamp ($\lambda \geq 420$ nm)	20	100 mL 10 vol% TEOA	$1785 \mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	0.05% (420 nm)	2019 [133]
Ni _{0.8} Co _{0.2} /Zn _{0.75} Cd _{0.25} S	Ni _{0.8} Co _{0.2}	300 W Xe lamp ($\lambda \geq 420$ nm)	50	100 mL 10 vol% TEOA/0.35 M Na ₂ S/0.25 M Na ₂ SO ₃	$211.4 \text{ mmol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	13.3% (365 nm)	2018 [134]
1 wt.% Ni ₁ -Pd ₁₀ /TiO ₂	Ni ₁ -Pd ₁₀	400 W mercury arc UV-vis irradiation	50	5 mL 50 vol% methanol	$1050 \mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	—	2017 [136]
0.5 wt.% Ni ₅ -Au ₁ /TiO ₂	Ni ₅ -Au ₁	300 W Xe lamp	30	3 mL 50 vol% methanol	$937.2 \mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	—	2016 [137]
3.0 wt.% Pt-Ni ₃ /CdS	Pt-Ni ₃	300 W Xe lamp ($\lambda \geq 420$ nm)	100	50 mL 1.0 M (NH ₄) ₂ SO ₃	$48.96 \text{ mmol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	44.0% (420 nm)	2018 [36]
Pt-Ni/ $g-C_3N_4$	Pt-Ni	300 W Xe lamp ($\lambda \geq 420$ nm)	50	100 mL 10 vol% TEOA	$104.7 \mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	—	2018 [138]
0.5 wt.% Ag-2 wt.% Cu/TiO ₂	AgCu	artificial Sun A.M1.5	10	50 mL 10 vol% methanol	$5683 \mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	—	2016 [139]
0.5 wt.% Au ₄ Cu ₁ /CaIn ₂ S ₄	Au ₄ Cu ₁	300 W Xe lamp ($\lambda \geq 420$ nm)	10	100 mL 3.15 g Na ₂ SO ₃ /6.0 g Na ₂ S·9H ₂ O	$452.8 \mu\text{mol}\cdot\text{h}^{-1}$	—	2018 [135]
0.5 wt.% Pt _{0.5} -Au ₁ /TiO ₂	Pt _{0.5} Au ₁	300 W Xe lamp ($\lambda \geq 400$ nm)	20	30 mL 25 vol% methanol	$311 \mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	1.6% (400 nm)	2015 [140]
7% Cu ₆₃ Ni ₃₇ /TiO ₂	Cu ₆₃ Ni ₃₇	Xe lamp	100	100 mL 10 vol% methanol	$0.63 \text{ mmol}\cdot\text{h}^{-1}$	—	2017 [141]
1 wt.% CuNi/rGO	CuNi	300 W Xe lamp	5	70 mL 14.2 vol% lactic acid	$1787 \mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	—	2017 [43]

Fig. 4. Aberration-corrected STEM images of Pt_{0.1}-CN (a) and HRTEM of Pt_{0.3}-CN (b), Pt₁-CN (c), Pt₂-CN (d), and Pt₃-CN (e). Time course of hydrogen evolution over 4 h for Pt_x-CN with different Pt contents (f). From Ref. [54].

to provide active sites and trapping electrons to separate photoinduced electron-hole pairs. When the frequency of the incident photons matches well with the inherent frequency of the free electrons on the surface of metal nanoparticles, which will lead to a collective oscillation, and the metal nanoparticles will have a strong absorption of photon energy, this effect is commonly known as localized surface plasmon resonance (LSPR) as shown in Fig. 2(b) [89,115]. As previously mentioned, the light absorption ability of photocatalyst is an important factor that affects the photocatalytic hydrogen production, the more light that is absorbed, the more photo-generated charges are produced to enhance the rate of photocatalytic H₂ evolution. Au [24,105] and Cu [116,117] are the most popular materials used

for plasmonic cocatalysts to enhance light absorption.

Guo *et al.* [104] reported Au as cocatalyst on g-C₃N₄ nanosheets with Au nanospheres (NSs) and nanorods (NRs) of different plasmon resonance wavelengths. Fig. 6a shows the SEM and TEM images of the Au nanocrystals on g-C₃N₄ nanosheets with Au loading amount of 2.0 wt.%. With the size of the Au nanocrystals increasing, the plasmon peak of the Au/g-C₃N₄ sample moves toward the long wavelength due to the reduction of the effective refractive index of the surrounding environment. The optimal 18 nm-sized Au nanospheres/g-C₃N₄ nanostructure exhibits a superior activity, with the H₂ generation rate reaching 540 μmol·h⁻¹·g⁻¹ under visible light. The introduced plasmonic Au nanocrystals not only enhance the photocatalytic activity, but also endow the hybrid photocatalysts with an extended light absorption range. Meanwhile, the improved H₂ production rates can be attributed to the LSPR effect of Au.

Although noble metal cocatalysts own high photocatalytic activity, their practical applications are limited by some factors such as resource shortages and high prices. Non-noble metals are rich in the earth's crust and some of their properties are similar to noble metals in enhancing the photocatalytic performance. Furthermore, non-noble metals also possess high work function as noble metals (Table 2), therefore non-noble metals play an important role as co-catalysis to trap and transfer electrons in photocatalytic reaction. Recently, non-noble metals such as Zn [118], Ni [119–123] and Co [124] have been utilized to effectively driven photocatalytic water splitting. Among the non-noble metals, the work function of Ni is closest to Pt, even higher than Au, therefore Ni is the most promising substitute for noble metals as co-catalysts for photocatalytic H₂ evolution. In 2016, Dong's group [121] successfully synthesized Ni/g-C₃N₄ photocatalyst, in which the non-noble metal Ni as cocatalyst was loaded on the surface of g-C₃N₄ nanosheets for photocatalytic water splitting under sun-light irradiation. In the absence of cocatalyst, the pure g-C₃N₄ nanosheets showed a low activity of photocatalytic hydrogen evolution due to the strong recombination trend of electrons and holes. When the loading content of Ni was 7.40 wt.%, the rate of H₂ evolution was 4318 μmol·h⁻¹·g⁻¹ with 2.10% AQY at wavelength of 400 nm, and kept stable after 48 h of irradiation. It is worth noting that the content of Ni²⁺ in the photocatalytic system B is the same as that in photocatalytic system A, as shown in Fig. 6a. Comparing with the rate of H₂ evolution, the photocatalytic activity of system A was 2.45 times higher than that of system

Fig. 5. (a) Photocatalytic H₂-production activity of CN-bulk-Pt-A, CN-bulk-Pt-B, CNS-Pt-B, and CNS-Pt-A in 10 vol% TEOA under the irradiation of 350 W Xe lamp; (b) Cyclic H₂-production experiments of CNS-Pt-B and CNS-Pt-A and the corresponding H₂-production rate for the two samples; (c) Diagrammatic sketch of the photoreduction process of Pt with TEOA adding into the system after or before the photo-deposition of Pt. From Ref. [96].

Fig. 6. Characterization and H₂ evolution of the Au nanocrystals/g-C₃N₄ samples. (a) SEM (upper row) and TEM (lower row) images of the Au nanocrystals/g-C₃N₄ samples with an Au loading amount of 2.0 wt.%. The numbers on the top represent the names of the Au nanocrystal samples. (b) Extinction spectra of the Au nanocrystals in aqueous solutions. (c) Absorption spectra of the corresponding hybrid nanostructure samples. (d) H₂ generation rates for the different Au nanocrystals/g-C₃N₄ samples with the same Au loading amount of 2.0 wt.%. (e) Variations of the H₂ evolution rates for the different Au nanocrystals/g-C₃N₄ samples as functions of the Au loading amount. From Ref. [104].

B. The reason for this phenomenon is that Ni²⁺ and TEOA (as sacrifice reagent) could generate a new compound [Ni(TEOA)₂]Cl₂, which acts as the main co-catalyst, not metal Ni in the case of photocatalytic system B. Therefore, non-noble metal Ni could be helpful for the transfer of photogenerated electrons and high efficiency of photocatalytic H₂ evolution.

Metallic copper is common in our lives because of its

earth-abundance and have been used as co-catalyst in different photocatalytic reactions. Some research groups reported that Cu nanoparticles loading on some semiconductors formed Schottky contact. To date, Cheng and co-worker [28] developed a highly efficient photocatalysis system for water splitting by loading metal Cu on TiO₂ microrods. As shown in Fig. 7(a, b), the TiO₂-Cu-2.5 wt.% hybrid photocatalyst exhibited superior

Fig. 7. (a) Photocatalytic H₂ evolution of Cu loaded on TiO₂ at different loading, and (b) average H₂ generation rate. Energy band diagrams of metal Cu and TiO₂, and the proposed electron transfer path in the photocatalytic reaction: (c) before contact and (d) after contact. E_{vac} , vacuum energy; E_v , energy of the valence band maximum; E_c , energy of the conduction band minimum; E_{FS} , Fermi level of the semiconductor; W_s , semiconductor work function; W_m , metal work function; ϕ_{SB} , Schottky barrier. From Ref. [28].

Fig. 8. (a) Photocatalytic hydrogen production for A5/CIS, C5/CIS, C1/A4/CIS and A4C1/CIS composites under visible light irradiation; (b) Schematic illustration for electron transfer mechanism in AuCu bimetallic nanoparticles under visible light irradiation. From Ref. [135].

rate of hydrogen evolution with $6046 \mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$, which is 23 times higher than that of pure TiO₂ microrods. The significant increase in photocatalytic performance is due to the Schottky junction formed between metal Cu and TiO₂ microrods as shown in Fig. 7(c, d). The work function of Cu is larger than that of TiO₂, the e^- would transfer from TiO₂ to Cu. The movement of electrons causes the Fermi levels of metallic Cu and TiO₂ to reach the same level. In the equilibrium state, a depletion layer is formed at the TiO₂-Cu interface, wherein the Cu metal is negatively charged, and TiO₂ is positively charged due to electrostatic induction near its surface. The electric field would be formed between Cu and TiO₂, the photoexcited electrons would be difficult to pass through the Schottky barrier to recombination with holes, so that the electrons and holes could be efficiently separated to improve the rate of H₂ evolution. Therefore, metal Cu which is low-cost and earth-abundant could replace the noble metals as co-catalyst for photocatalytic water splitting.

Similar to mono-metallic, metal alloys such as PtPd [127], PtCo [128], AuPd [129,130], AgCu [131], NiCd [132], NiMo [133] and NiCo [134] have also been synthesized and reported in the field of photocatalytic H₂ evolution, which act as co-catalysts to trap electrons from the semiconductor and improve the charge separation and transfer efficiency [89]. Compared with single-metal, alloy co-catalysts commonly show higher activity in photocatalytic H₂ evolution, which is mainly due to the synergistic effect between the two metals [135]. Bimetallic cocatalysts such as AuCu [135] and AuPd [129,130], which contain plasmonic metals also possess LSPR effect.

In alloy NPs, the activity could be influenced by the different atomic arrangements, as exhibited in Fig. 8(a). Ding and

co-workers [135] reported that the photocatalytic H₂ evolution rate of AuCu alloy nanoparticles/CaIn₂S₄ composite is up to $452.8 \mu\text{mol}\cdot\text{h}^{-1}$, which is 2.2 times higher than the AuCu core-shell structure/CaIn₂S₄ composite. The catalytic mechanism for charge separation is outlined in Fig. 8(b). The photocatalytic performance enhancement of AuCu alloy nanoparticles is better than that of AuCu core-shell structure due to the shorter distance of photoelectrons transfer from CaIn₂S₄ to Au, thus to Cu. Moreover, the existence of Cu shell in AuCu core-shell nanoparticles may decrease the visible absorption of Au core because the incident light can be scattered by Cu shell. Therefore, the AuCu alloy nanoparticles as cocatalyst is better than that of AuCu core-shell structure.

Our group [127] reported that PtPd alloy nanoparticles as cocatalyst were deposited on g-C₃N₄ nanosheets to enhance the photocatalytic H₂ evolution activity under visible-light irradiation as shown in Fig. 9. The 0.2 wt.% Pt_{0.5}Pd_{0.5}/g-C₃N₄ sample presented the highest H₂ evolution activity ($1600.8 \mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$), which is 800 times higher than that of pure g-C₃N₄. When K₂HPO₄ was added to the photocatalytic system, the H₂ production rate of the Pt_{0.5}Pd_{0.5}/g-C₃N₄ composite sample reached $2885.0 \mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$. The AQY of Pt_{0.5}Pd_{0.5}/g-C₃N₄ composite sample at 420 nm was determined to be 5.5%. Therefore, our experimental results demonstrated that PtPd alloy NPs were a promising cocatalyst for g-C₃N₄, which can also be regarded as a potential functional cocatalyst in others semiconductor photocatalysts for enhancement of the photocatalytic H₂ production activities.

The high cost of noble-metals limited their application in industrial scale water splitting for H₂ evolution. Hence, it is necessary to choose a suitable photocatalyst with natural

Fig. 9. (a) Photocatalytic H₂ evolution over PtPd/g-C₃N₄ composite samples with different weight contents of PtPd alloy NPs: (1) Pure g-C₃N₄; (2) 0.1wt.%; (3) 0.2 wt.%; (4) 0.5 wt.%; (5) 1.0 wt.%; (6) 2.0 wt.%; (7) 0.2 wt.% with K₂HPO₄ solution. (b) Photocatalytic H₂ evolution over the bulk 0.2 wt.% Pt_{1-x}Pd_x/g-C₃N₄ composite samples with different Pt/Pd percentage. (c) The photocatalytic H₂ evolution and quantum efficiency in the presence of 0.2 wt.% PtPd/g-C₃N₄ composite sample under 400 nm light irradiation. From Ref. [127].

abundance cocatalyst that constructing an efficient material for water splitting. Non-noble metal elements of Ni or Co show the similar characteristics with noble Pt. Our group [128] reported that PtCo bimetallic alloy as cocatalyst to modified on g-C₃N₄ nanosheets via an in-situ chemical deposition method, which replace part Pt with Co to reduce the high cost. The 1.0 wt.% PtCo/g-C₃N₄ showed the highest rate of photocatalytic H₂ evolution of 960 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$, which is 2.9 times higher than that of pristine bulk PtCo/g-C₃N₄ under visible light irradiation. Similarly, Peng *et al.* [138] found that the PtNi bimetallic alloy decorated on g-C₃N₄ nanotubes could improve the photocatalytic activity, and the H₂ generation rate is 104.7 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$, which is about 47.6 and 1.1 times higher than that of pure g-C₃N₄ nanotubes and Pt/g-C₃N₄, respectively. Hence, PtCo and PtNi bimetallic alloy could replace Pt as a promising cocatalyst for photocatalytic H₂ evolution with better activity and lower cost.

For further cost reductions, the choice of two metals in the alloy are all non-noble metals. In 2018, Zhang's group [134] reported that Ni_{0.8}Co_{0.2} alloy as cocatalysts decorated on Zn_{0.75}Cd_{0.25}S with optimized H₂ evolution rate of 211.4 $\text{mmol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$ and AQY of 13.3% at 365 nm. Besides, the NiCd bimetallic nanoparticle can also be used as cocatalyst to enhance the rate of H₂ evolution with dropping on CdS nanorods which reported by Liu and co-workers [132]. The NiCd/CdS NRs sample exhibited a palpable improved in photocatalytic H₂ production performance, the optimization rate of H₂ evolution was determined to be 11.57 $\text{mmol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$, which is about 64.8, 17.2 and 2.3 times that of pristine CdS NRs, Cd/CdS and Ni/CdS, respectively.

3.2. Metal phosphides

Among the metal-based cocatalysts, metal phosphides are currently broadly studied in photocatalytic fields because of its good stability and high activity. Among the so many developed metal phosphides, metal phosphides composed by the elements of transition metals such as Co, Ni and Fe are getting more research attention. Firstly, phosphorus is abundant in the earth, which is easy to obtain and in low cost. Secondly, compared with other metal-based materials, the transition metal phosphides are easier to synthesize. Thirdly, the P-ligand in the phosphide (namely "the ensemble effect") has a moderate binding strength to hydrogen, which is important for the formation of H₂ molecules and the decrease of H-poisoning effects [142,143]. Typical single transition metal phosphides including CoP [16,41], Co₂P [144], Ni₂P [42], Ni₁₂P₅ [145] Cu₃P [146], FeP [147], *etc.*; multiple transition metal phosphides are mainly NiCoP [148]. In this section, the application of transition metal phosphide materials as cocatalysts for photocatalytic H₂ production is introduced, and Table 4 summarizes the application of non-metals as cocatalysts in photocatalyst system for H₂ evolution.

Han *et al.* [16] have synthesized CoP/g-C₃N₄ photocatalysts by in-situ chemical deposition for enhanced photocatalytic hydrogen production performance. The maximum rate of hydrogen production is 9.2 $\mu\text{mol}\cdot\text{h}^{-1}$. In recent years, our group always committed to explore the transition metal phosphides as cocatalysts for H₂ evolution. Noble-metal-free photocatalyst Co₂P-CdS was synthesized *via* a facile in situ hydrothermal

Table 4
Summary of metal phosphides as cocatalysts in the photocatalyst system for H₂ evolution.

Photocatalyst	Cocatalyst	Light source	Weight (mg)	Solution	Activity	AQY	Year/Ref.
4.0 wt.% WP/CdS	WP	300 W Xe lamp ($\lambda \geq 420$ nm)	50	100 mL 1.0 M (NH ₄) ₂ SO ₃	155.2 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	—	2017 [151]
CdS/Co ₂ P	Co ₂ P	300 W Xe lamp	50	200 mL 10 vol% lactic acid	10.8 $\text{mmol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	—	2016 [152]
1.2 mol% Co ₂ P/CdS	Co ₂ P	300 W Xe lamp ($\lambda \geq 420$ nm)	50	100 mL 0.35 M Na ₂ S/0.25 M Na ₂ SO ₃	0.303 $\text{mmol}\cdot\text{h}^{-1}$	13.88% (420 nm)	2018 [144]
CoP/Zn _{0.5} Cd _{0.5} S	CoP	300 W Xe lamp ($\lambda \geq 420$ nm)	50	100 mL 10 vol% lactic acid	734 $\mu\text{mol}\cdot\text{h}^{-1}$	—	2017 [41]
g-C ₃ N ₄ /CoP-3.4%	CoP	300 W Xe lamp ($\lambda \geq 420$ nm)	10	10 mL 10 vol% TEOA	0.8 $\mu\text{mol}\cdot 2\text{h}^{-1}\cdot\text{g}^{-1}$	—	2017 [153]
3.0 wt.% CoP/g-C ₃ N ₄	CoP	300 W Xe lamp ($\lambda \geq 420$ nm)	50	100 mL 10 vol% TEOA and K ₂ HPO ₄	15.1 $\mu\text{mol}\cdot\text{h}^{-1}$	—	2019 [16]
4% Ni ₂ P/Zn _{0.5} Cd _{0.5} S	Ni ₂ P	300 W Xe lamp ($\lambda \geq 420$ nm)	50	100 mL 0.35 M Na ₂ S/0.25 M Na ₂ SO ₃	1173 $\mu\text{mol}\cdot\text{h}^{-1}$	—	2018 [42]
g-C ₃ N ₄ /Ni ₂ P-3.5 wt.%	Ni ₂ P	300 W high-pressure Xe lamp ($\lambda \geq 420$ nm)	50	100 mL 10 vol% TEOA	474.7 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	3.2% (435 nm)	2018 [154]
g-C ₃ N ₄ /Ni ₂ P-0.48 wt.%	Ni ₂ P	300 W Xe lamp ($\lambda \geq 420$ nm)	10	10 mL 10 vol% TEOA	5.67 $\mu\text{mol}\cdot\text{h}^{-1}$	—	2017 [155]
5 wt.% Ni ₂ P/0.5-Fe ³⁺ -g-C ₃ N ₄	Ni ₂ P	300 W Xe lamp ($\lambda \geq 420$ nm)	100	100 mL 10 vol% TEOA	1891 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	—	2017 [156]
Ni ₂ P/g-C ₃ N ₄	Ni ₂ P	Xe lamp ($\lambda \geq 420$ nm)	2	5 mL 20 vol% TEOA	162 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	—	2017 [149]
0.4 wt.% Ni ₂ P/TiO ₂	Ni ₂ P	300 W Xe lamp ($\lambda \geq 400$ nm)	20	80 mL 50 vol% methanol	9.38 $\text{mmol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	11.6% (360 nm)	2016 [157]
5 wt.% Ni ₁₂ P ₅ /g-C ₃ N ₄	Ni ₁₂ P ₅	300 W high-pressure Xe lamp ($\lambda \geq 420$ nm)	60	150 mL 10 vol% TEOA	535.7 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	4.67% (420 nm)	2017 [145]
5 wt.% FeP/CdS	FeP	30×3 W LED ($\lambda \geq 420$ nm)	1	10 mL 10 vol% lactic acid	202000 $\mu\text{mol}\cdot 5\text{h}^{-1}\cdot\text{g}^{-1}$	35% (520 nm)	2016 [147]
g-C ₃ N ₄ /Fe ₃ P-0.08	Fe ₃ P	300 W Xe lamp ($\lambda \geq 420$ nm)	10	10 mL 10 vol% TEOA	166.4 $\mu\text{mol}\cdot 2\text{h}^{-1}\cdot\text{g}^{-1}$	—	2017 [150]
10 wt.% Cu ₃ P/g-C ₃ N ₄	Cu ₃ P	300 W Xe lamp ($\lambda \geq 420$ nm)	50	80 mL 15 vol% TEOA	159.41 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	—	2018 [146]
NiCoP/g-C ₃ N ₄	NiCoP	300 W Xe lamp ($\lambda \geq 420$ nm)	50	80 mL 10 vol% TEOA	1709.3 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	9.4% (420 nm)	2017 [148]

Fig. 10. Schematic of photocatalysis by Co₂P-CdS composites. (a) Illustration of combination between metal Co₂P (Co, blue; P, purple) and semiconductor CdS (S, yellow; Cd, dull yellow). (b) Calculated work function and band bending of metal Co₂P and CdS. From Ref. [144].

method [144]. The Co₂P-CdS sample with a loading ratio of 1.2 mol% Co₂P gave the highest H₂ production rate of 0.303 mmol·h⁻¹, after further introduction of K₂HPO₄ as sacrificial agent, the H₂ production rate reached 0.356 mmol·h⁻¹, and the AQE of the Co₂P-decorated CdS sample is about 13.88% at 420 nm. The application of Co₂P as co-catalyst has significantly improved the photocatalytic H₂ evolution performance of CdS. When CdS and Co₂P form intimate contact, the electrons transfer from Co₂P to CdS, which leads to a downward bending of the energy bands of CdS, the separation and transfer of photo charges can be boosted as a result of the band bending formed at the interface, which leads to a dramatically enhanced performance of photocatalytic H₂ production (Fig. 10).

Sun *et al.* [149] tested the performance of three different crystalline phases of Ni₂P, Ni₁₂P₅, and Ni₃P as cocatalysts to hybridize with g-C₃N₄ for photocatalytic H₂ generation in 2017. As shown in Fig. 11, all three phases of Ni_xP_y work as eximious cocatalysts for enhancement of visible light H₂ generation with g-C₃N₄. The highest H₂ generation activities by achieved with 5 wt.% Ni₂P/g-C₃N₄ was 0.162 mmol·h⁻¹·g⁻¹, which was approximately 34 times of the amount obtained on pure g-C₃N₄, and the rate was close to 5 wt.% Pt/g-C₃N₄ (0.168 mmol·h⁻¹·g⁻¹). In addition, the photocatalyst exhibited favorable stability after 9 hours illumination under visible light irradiation.

Dong's group [150] reported that noble-metal-free iron phosphide (Fe_xP) cocatalyst decorated graphitic carbon nitride (g-C₃N₄) as photocatalysts by two-step hydrothermal and phosphidation method for the highly efficient and stable H₂ evolution from water splitting under visible light irradiated. The g-C₃N₄/Fe_xP-0.08 showed the optimal rate of photocatalytic H₂ generation, the rate reached up to 166.4 μmol·h⁻¹·g⁻¹, which was about 277 and 139 times that over pristine g-C₃N₄

and g-C₃N₄/FeOOH precursor, respectively. The Fe_xP as cocatalyst significantly accelerates the separation and transfer of photogenerated charges which lead to the highly efficient photocatalytic H₂ evolution activity of g-C₃N₄.

In 2017, Qin *et al.* [148] synthesized NiCoP core/shell NPs as cocatalyst by a solid-state phosphorization reaction. NiCoP@NiCo-Pi/g-C₃N₄ exhibited much higher hydrogen production rate than Ni₂P@NiCo-Pi/g-C₃N₄ and CoP@NiCo-Pi/g-C₃N₄, which demonstrated better performance of NiCoP cocatalysts for photocatalytic H₂ evolution than the single transition metal phosphides.

3.3. Metal oxides and hydroxides

Several metal oxides such as TiO₂ [158–161], CuO [22,162–165], Cu₂O [49,166,167] and NiO [168] are well known as cocatalysts for photocatalytic H₂ production. Table 5 summarizes the application of metal oxides and hydroxides as cocatalyst in the photocatalyst system for H₂ evolution. Recently, Tan *et al.* [160] reported the nanostructured

Fig. 11. (a) Photocatalytic H₂ generation rates for g-C₃N₄, Pt/g-C₃N₄, and Ni₂P/g-C₃N₄ (5 wt.% Ni₂P). (b) Recycle of H₂ generation on Ni₂P/g-C₃N₄ (5 wt.% Ni₂P). From Ref. [149].

Table 5Summary of metal oxides and hydroxides as cocatalysts in the photocatalyst systems for H₂ evolution.

Photocatalyst	Cocatalyst	Light source	Weight (mg)	Solution	Activity	AQY	Year/Ref.
TiO ₂ /g-C ₃ N ₄	TiO ₂	300 W Xe lamp (λ≥420 nm)	100	100 mL 10 vol% TEOA	513 μmol·h ⁻¹ ·g ⁻¹	0.31%	2018 [160]
B-TiO ₂ /g-C ₃ N ₄	B-TiO ₂	300 W Xe lamp (λ≥420 nm)	50	100 mL 10 vol% TEOA	808.97 μmol·h ⁻¹ ·g ⁻¹	—	2019 [161]
0.330% C-TiO ₂ /g-C ₃ N ₄	C-TiO ₂	300 W Xe lamp (λ≥420 nm)	50	80 mL 10 vol% TEOA	5.728 mmol·5h ⁻¹ ·g ⁻¹ 52.395 mmol·64h ⁻¹ ·g ⁻¹	6.2% (420 nm)	2017 [159]
2.0 wt. % TiO ₂ /g-C ₃ N ₄	TiO ₂	3 W UV-LEDs (λ≥420 nm)	50	80 mL 25 vol% methanol	5.6 μmol·h ⁻¹	3.25% (420 nm)	2016 [158]
0.4% Bi ₂ O ₃ /TiO ₂	Bi ₂ O ₃	natural solar light	5	50 mL 5 vol% glycerol	26.02 mmol·h ⁻¹ ·g ⁻¹	—	2017 [179]
0.83 wt.% Ag ₂ O/g-C ₃ N ₄	Ag ₂ O	300 W Xe lamp (λ≥420 nm)	100	100 mL 10 vol% TEOA	33.04 μmol·h ⁻¹	—	2015 [170]
2.5 mol% Cu ₂ O/TiO ₂	Cu ₂ O	500 W Xe lamp (λ≥420 nm)	a certain amount	450 mL 10 vol% methanol	2048.25 μmol·h ⁻¹ ·g ⁻¹	4.32% (365 nm)	2015 [167]
10% CuO/TiO ₂	CuO	500 W Xe lamp	100	100 mL 25 vol% methanol	8.23 mmol·h ⁻¹ ·g ⁻¹	—	2013 [22]
0.9 mol% Cu ₂ O/TiO ₂	Cu ₂ O	300 W Xe lamp (λ≥320 nm)	50	40 mL 0.05 M glycerol	318 μmol·h ⁻¹	28.6% (365 nm)	2013 [166]
0.05 wt.% Cu ₂ O/g-C ₃ N ₄	Cu ₂ O	300 W Xe lamp (λ≥420 nm)	100	180 mL 10 vol% TEOA	241.3 μmol·h ⁻¹ ·g ⁻¹	—	2014 [49]
0.25 wt.% NiO/TiO ₂	NiO	300 W Xe lamp	50	80 mL 25 vol% methanol	337 μmol·h ⁻¹ ·g ⁻¹	1.7% (365 nm)	2015 [168]
1.3 wt.% CuO/TiO ₂	CuO	3 W UV-LEDs (λ=365 nm)	80	80 mL 0.1 M glycerol	2061 μmol·h ⁻¹ ·g ⁻¹	13.4% (365 nm)	2011 [162]
23 mol% Ni(OH) ₂ /CdS	Ni(OH) ₂	300 W Xe lamp (λ≥420 nm)	50	80 mL 25 vol% TEOA	5084 μmol·h ⁻¹ ·g ⁻¹	28% (420 nm)	2011 [171]
0.23 mol % Ni(OH) ₂ /TiO ₂	Ni(OH) ₂	3 W UV-LEDs (λ=365 nm)	50	80 mL 25 vol% methanol	3056 μmol·h ⁻¹ ·g ⁻¹	12.4% (365 nm)	2011 [19]
0.5 mol% Ni(OH) ₂ /g-C ₃ N ₄	Ni(OH) ₂	350 W Xe lamp (λ≥400 nm)	50	80 mL 10 vol% TEOA	7.6 μmol·h ⁻¹	1.1% (420 nm)	2013 [46]
Ni(OH) ₂ /CdS	Ni(OH) ₂	300 W Xe lamp (λ≥420 nm)	100	50 mL 1 M (NH ₄) ₂ SO ₃	40.18 mmol·h ⁻¹ ·g ⁻¹	66.1% (420 nm)	2019 [180]
0.34 mol% Cu(OH) ₂ /g-C ₃ N ₄	Cu(OH) ₂	300 W Xe lamp (λ≥400 nm)	100	80 mL 25 vol% methanol	48.7 μmol·h ⁻¹ ·g ⁻¹	—	2014 [181]
0.29 mol% Cu(OH) ₂ /TiO ₂	Cu(OH) ₂	3 W UV-LEDs (λ=365 nm)	50	80 mL 0.09 M ethylene glycol	3418 μmol·h ⁻¹ ·g ⁻¹	13.9% (365 nm)	2011 [182]
0.5 mol% Co(OH) ₂ /TiO ₂	Co(OH) ₂	300 W Xe lamp (UV-visible light)	50	100 mL 25 vol% methanol	746.93 μmol·h ⁻¹ ·g ⁻¹	—	2017 [169]
Zn-Cr-LDH/g-C ₃ N ₄	Zn-Cr-LDH	300 W Xe lamp (λ≥420 nm)	—	10 vol% TEOA	155.7 μmol·h ⁻¹ ·g ⁻¹	—	2018 [178]
CdSe/Zn-Cr-LDH	Zn-Cr-LDH	300 W Xe lamp (λ≥420 nm)	50	100 mL 0.1 M Na ₂ S/0.1 M Na ₂ SO ₃	2196 μmol·h ⁻¹ ·g ⁻¹	51.3% (420 nm)	2015 [177]
2 mol% Ni-Co-LDH/40 wt.% P-CdS	Ni-Co-LDH	300 W Xe lamp (λ≥420 nm)	50	100 mL 10 vol% lactic acid	8.665 mol·h ⁻¹ ·g ⁻¹	14.0% (420 nm)	2019 [183]

g-C₃N₄/TiO₂ was synthesized by controlling the growth of nanoscale g-C₃N₄ on TiO₂ NPs *via* one step vapor deposition method. The CN/TiO₂-24 composite shows the greatest H₂ evolution rate of 513 μmol·g⁻¹·h⁻¹. Under visible light irradiation, the visible-light-excited electrons in the CB of g-C₃N₄ can transfer to the CB of TiO₂, the photoinduced charge could be efficiently separated, and therefore improve the photocatalytic H₂ evolution of the CN/TiO₂-24 composite.

For transition metal oxides, CuO and Cu₂O have also been proven to be beneficial for photocatalytic H₂ production. Wang and co-worker [167] reported that Cu₂O loading on TiO₂ displayed 14.48 times larger photocatalytic H₂ evolution activity than pure P25. Yu's group [162] found CuO can act as an effective cocatalyst to improve the photocatalytic H₂ production

activity of TiO₂. When the loading content of CuO in the photocatalyst was increased to 1.3 wt.%, the rate of H₂ evolution reached 2061 μmol·h⁻¹·g⁻¹ with an AQY of 13.4% at 420 nm. The quantum size effect of CuO influences the electron transfer and its valence band edges, which enhance the photocatalytic activity. As shown in Fig. 12(a, b), the bulk CuO has a less negative potential than H⁺/H₂ potential. As the quantum size of CuO increases, the band gap decreases and the CB and VB edges are also shifted to the positions which permit transfer of photo-generated electrons, facilitating the interfacial electron transfer from CuO to H⁺ in the solution for photocatalytic H₂ evolution.

In 2015, Wu *et al.* [170] synthesized Ag₂O/g-C₃N₄ *via* facial hydrothermal reaction, the composite photocatalyst shows efficient properties for hydrogen evolution from water splitting

Fig. 12. (a) Schematic illustration for the charge transfer and separation in CuO-TiO₂ under UV light. (b) Energy levels of the conduction and valence band edges vs normal hydrogen electrode (NHE, at pH 0) for TiO₂ and CuO with various size (the quantum size effect is reflected by the band gap increase). From Ref. [162]. (c) Schematic illustration for the charge transfer and separation in plate-like Co(OH)₂/TiO₂ nanosheets system; (d) Proposed mechanism for photocatalytic H₂ production under UV-Visible light irradiation. From Ref. [169].

under visible light irradiation, in which the rate of hydrogen evolution is $33.04 \mu\text{mol}\cdot\text{h}^{-1}$. For the mechanism, the Ag₂O as a cocatalyst plays an important role in charges transferred of photocatalytic progress. The reason relies on the relative position of CB and VB between g-C₃N₄ and Ag₂O, in which the CB of Ag₂O is lower than the redox potential of H^+/H_2 , so that the photogenerated electrons of g-C₃N₄ cannot be transferred to the CB of Ag₂O, which could be used to photocatalytic hydrogen evolution reaction. While the photogenerated holes in the VB of g-C₃N₄ can be transferred to the VB of Ag₂O, and the holes are consumed by TEOA. Thereby achieving the purpose of charge orientation separation.

Inspired by the research of NiO modified TiO₂, Yu's group reported that Ni(OH)₂ as cocatalysts decorated on TiO₂ [19], g-C₃N₄ [46] and CdS [171] for enhanced photocatalytic H₂ production activity which was synthesized by a simple precipitation reaction. Ni(OH)₂ is an outstanding and universal material as cocatalysts for photocatalytic water splitting under visible-light irradiation. The rate of H₂ evolution even is higher than Pt as cocatalyst deposited on CdS.

Our group [169] reported that plate-like Co(OH)₂ was incorporated onto the surface of TiO₂ nanosheets as an effective cocatalyst to increase the rate of H₂ production for water splitting. The sample of 0.5 mol% Co(OH)₂/TiO₂ shows a maximum hydrogen rate with $746.93 \mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$, which is 20 times higher than pure TiO₂ nanosheets, along with a good stability for photocatalytic H₂ evolution upon continuous irradiation of 14 h. As shown in Fig. 12(c, d), the reason for photocatalytic performance improvement is the plate-like Co(OH)₂ act as electron collector to facilitate the migration of electron from TiO₂ to the plate-like Co(OH)₂, and reduce partial Co 2p to Co

atoms, the as-formed Co⁰ species can work as a co-catalyst, therefore improve the separation efficiency and lifetime of the photoexcited electrons and holes.

The layered double hydroxide (LDH) can be represented by the general formula $[\text{M}^{2+}_{1-x}\text{M}^{3+}_x(\text{OH})_2](\text{A}^{n-})_{x/n}\cdot m\text{H}_2\text{O}$, where M²⁺ and M³⁺ are divalent and trivalent metal cations respectively and Aⁿ⁻ is the interlayer anion compensating for the positive charge of the brucite-like layers [172–176]. LDHs materials have been studied in photocatalysis due to their low cost, high photocatalytic activity and controllable electronic structure. For photocatalytic water splitting H₂ evolution, Zhang *et al.* [177] synthesized CdSe/ZnCr-LDH nanohybrids *via* an electrostatically derived self-assemble process, which exhibited a high photocatalytic hydrogen generation rate of $2196 \mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$ with an AQY of 51.3% for H₂ generation under visible-light irradiation. The ZnCr-LDH as cocatalyst was also applied with g-C₃N₄, which is effective in enhancing the photocatalytic hydrogen generation activity, the H₂ production rate reached $155.7 \mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$. ZnCr-LDH acts as an important role in improving the activity of photocatalytic hydrogen production by water splitting. As shown in Fig. 13, the electrons transfer from the CB of g-C₃N₄ to the lower-lying CB of ZnCr-LDH, the holes in the VB of ZnCr-LDH move to the upper-lying VB of g-C₃N₄, leading to an efficient separation of electrons and holes [178].

3.4. Metal sulfides

To date, many metal sulfides, such as MoS₂ [30,184–188], NiS [45,51,184,189], Cu_xS [190–196], Co₃S₄ [197], FeS [198], Ag₂S [199], Bi₂S₃ [200], WS₂ [201], Co₃Mo₇S [15] and NiMoS [202,203], have been reported in photocatalytic H₂ evolution

Fig. 13. Schematic model for the band structure of the ZnCr-LDH/g-C₃N₄ nanohybrids. From Ref. [178].

reaction. MoS₂ is an efficient cocatalyst on variety of semiconductor photocatalysts. Meng's group [184] load MoS₂ on ZnIn₂S₄ *via* hydrothermal method. Loading MoS₂ on ZnIn₂S₄ as a cocatalyst improved the rate of H₂ evolution by up to 28 times. In 2016, Li and co-worker [55] reported on the synthesis of novel bilayer junctions by assembling metallic MoS₂ monolayers selectively and chemically on oxygen-deficient (Bi₁₂O₁₇) end-faces of Bi₁₂O₁₇Cl₂ monolayers *via* oxygen-vacancy (OV) chemistry. Under visible light irradiation, the photocatalytic H₂ evolution rate reached 33 mmol·h⁻¹·g⁻¹ with an AQY of 36% at 420 nm. Furthermore, the band structures of Bi₁₂O₁₇Cl₂ and MoS₂ were shown in Fig. 14, Bi₁₂O₁₇Cl₂ in the photoexcited Bi₁₂O₁₇Cl₂-MoS₂ generated electrons and transferred from Bi₁₂O₁₇Cl₂ to MoS₂ in photocatalytic H₂ evolution process. In addition, in Bi₁₂O₁₇Cl₂, internal electric field can drive electrons to (Bi₁₂O₁₇) end-faces and the holes to (Cl₂) end-faces, achieving the atomic-level steering of charge separation.

Very recently, Xu *et al.* [188] found that MoS₂ could be facilely modulated through phosphorus doping, which can act as a cocatalyst and embedded onto the CdS nanorod for not only facilitating the separation of the charge carriers, but also promoting the separation efficiency of the charge carriers. The 3 wt.% CdS/P-MoS₂ sample exhibited a higher photocatalytic hydrogen evolution rate of 8.86 mmol·h⁻¹·g⁻¹ with the AQY of 32.4% at 420 nm.

In most reports, the NiS cocatalysts are generally decorated on semiconductors to synthesize hybrid photocatalysts. The NiS/g-C₃N₄ heterojunction was formed by one-step calcination method [189], hydrothermal method [45] and ion-exchange

procedure [51]. All of the photocatalysts exhibited good photocatalytic hydrogen production performance in TEOA solution under visible light illumination, which is 250 times and 56 times higher than pure g-C₃N₄, respectively. This remarkable enhancement in the photocatalytic activity resulted from NiS cocatalyst, which acted as an important role in the NiS/g-C₃N₄ photocatalyst by boosting the electron separation and transfer from the CB g-C₃N₄ to the surface NiS, the reactions are presented in equations (2) and (3):

Furthermore, NiS was also decorated on TiO₂ [21], CdS [204,205] and CdZnS [206] to enhance the catalytic activity.

The CuS/ZnS photocatalyst was prepared *via* a simple hydrothermal and cation exchange reaction between ZnS[en]_{0.5} nanosheets and Cu(NO₃)₂ by Zhang in 2011 [191]. The optimal CuS loading content on ZnS is 2 mol% and the corresponding rate of H₂ production is 4147 μmol·h⁻¹·g⁻¹ with an AQY of 20% at 420 nm. As shown in Fig. 15(a), the photoinduced interfacial charge transfer (IFCT) from the ZnS VB to CuS causes partial reduction of CuS to Cu₂S, the holes in the VB of ZnS could be consumed by the sacrificial agents. The IFCT will retard the recombination of photoinduced electrons and holes due to the space separation and lead to H₂ evolution. The CuS/Cu₂S acts as an electron sink and cocatalyst to boost the separation and transfer of electrons from ZnS VB to CuS/Cu₂S, where H⁺ is reduced to H₂. The steps of electron transfer in this catalytic H₂ evolution process under visible light irradiation are listed as the following equations:

In 2017, Zhang and co-workers [190] reported that a self-optimizing bifunctional core-shell CdS/Cu₂S heterojunction was synthesized *via* solvothermal method for photocatalytic hydrogen evolution under visible light irradiation in which the Cu₂S acts as cocatalyst. Compared with pure CdS, the rate of photocatalytic H₂ production has improved almost 25 times, the maximum rate of hydrogen production reached 14.4 mmol·h⁻¹·g⁻¹ with an AQY of 19.5% at 420 nm. Fig. 15(b, c) illustrated the mechanism for photocatalytic H₂ production by

Fig. 14. (a) Band alignments in Bi₁₂O₁₇Cl₂ and MoS₂. Schematic illustration of the crystal structure of Bi₁₂O₁₇Cl₂-MoS₂ (b) and of the charge flow processes within Bi₁₂O₁₇Cl₂-MoS₂, including the electron-hole separation within Bi₁₂O₁₇Cl₂ (c) and the interfacial electron transfer from Bi₁₂O₁₇Cl₂ to MoS₂ along the Bi-S bonds (d). From Ref. [55].

Fig. 15. (a) Schematic illustration for visible light induced interfacial charge transfer from the VB of ZnS to the CuS clusters in CuS/ZnS system as the proposed mechanism for photocatalytic H_2 production. From Ref. [191] (b) Schematic illustration of light-driving self-optimizing process on CdS/Cu₂S core-shell hybrid. (c) Schematic illustration of photocatalytic HER process on Cu@CdS/Cu₂S core-shell hybrid. From Ref. [190].

Fig. 16. (a) Photocatalytic performance of typical photocatalytic materials before and after a-CoMoS_x modification. (b) Schematic diagram illustrating the photocatalytic H_2 -evolution mechanism of a-CoMoS_x/CdS photocatalysts: (1) the rapid capture of photogenerated electrons by a-CoMoS_x; (2) the effective transfer of photogenerated electrons from the capture sites to active sites; (3) the efficient interfacial H_2 -evolution reactions on the a-CoMoS_x active sites. From Ref. [207].

CdS/Cu₂S. Under visible light irradiation, e^-h^+ pairs were generated in CdS core, partial photo-electrons participate in H_2 evolution, while the others reduce Cu₂S into Cu⁰. The electrons transfer from the CB of CdS to Cu₂S/Cu⁰, the Cu₂S acts as active sites for photocatalytic H_2 production, while the light-reduced Cu⁰ accelerates the separation process of photo-generated electrons and holes by forming heterojunction.

In recent years, many studies have reported that the bimetallic sulfide play an important role in enhancing the photocatalytic H_2 evolution. Yu's group [207] found that the CoMoS co-catalyst could significantly improve the H_2 production activity of CdS photocatalyst, the rate of photocatalytic H_2 evolution is 178.5 $\mu\text{mol}\cdot\text{h}^{-1}$, which is higher than that of pure CdS, MoS₂/CdS and Co/CdS by 26.3, 3.1 and 7.5 times, respectively. Furthermore, the CoMoS co-catalyst acts as a universal cocatalyst to improve the photocatalytic H_2 evolution activity of other semiconductors, such as TiO₂ and g-C₃N₄, their corresponding rate of is shown in Fig. 16. The exceptional visible light photocatalytic H_2 evolution performance is due to the presence of CoMoS, which acts as an efficient cocatalyst to prompt the transportation of the electrons for H_2 production, the detail process is described as the following 3 steps: (1) under visible light irritation, the CoMoS first work as an electron capturer to prompt the transportation of the electrons from the CB of CdS; (2) then play as an electron transfer mediator to efficiently transport the electrons; (3) finally serves as the activity site for

H_2 production to boost the rate of photo-reduction of water.

Similar to MoS₂, Cu_xS, NiS and CoMoS_x, there are also many diverse metal sulfide cocatalysts which can decorated on semiconductors to effectively increase photocatalytic H_2 -evolution activity, such as Ag₂S [199], Bi₂S₃ [200], NiMoS [202,203], Co₃Mo₇S [15], Zn_{0.23}Cd_{0.77}S [208] and ZnIn₂S₄ [209], the application of metal sulfide co-catalysts for photocatalytic H_2 evolution is summarized in Table 6.

3.5. Carbon-based materials

Common cocatalysts are mostly metal or their compounds loaded on semiconductor photocatalysts. However, metal-free carbon nanomaterials, which have many unique properties to be applications in the photocatalysts field, such as large work function, excellent electron receptors, large surface area and novel morphologies. In addition, they are very cheap, stable, abundant in earth and non-toxic. Many studies have shown that carbon-based materials can be used as an effective cocatalyst or an excellent conductor cocatalyst to enhance the activity of catalytic hydrogen production. Carbon-based materials including carbon quantum dots (CQDs) [27,211–213], graphene [116,214,215] and carbon nanotube (CNT) [50,216–221], and carbon-based material can act as cocatalysts in photocatalytic hydrogen production process, the related researches were summarized and showed in Table 7.

The QCDs were extensively studied due to some superior performances include the long-term stability, tunable size and band gap and size dependent photoluminescence. In 2018, Wang and co-workers [213] prepared tubular QCD-implanted

g-C₃N₄ heterostructures (CCTs) *via* thermal polymerization of freeze-dried urea and QCDs precursor. The photocatalyst exhibited efficient photocatalytic activity with a high H₂ evolution rate of 3538.3 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$ under visible-light irradiation and

Table 6

Summary of metal sulfide as cocatalysts in the photocatalyst systems for H₂ evolution.

Photocatalyst	Cocatalyst	Light source	Weight (mg)	Solution	Activity	AQY	Year/Ref.
3 wt.% CdS/P-MoS ₂	MoS ₂	300 W Xe lamp ($\lambda \geq 420$ nm)	5	50 mL 0.35 M Na ₂ S/0.25 M Na ₂ SO ₃	8.86 $\text{mmol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	32.4% (420 nm)	2019 [188]
6 wt.% MoS ₂ /Cu-ZnIn ₂ S ₄	MoS ₂	300 W Xe lamp ($\lambda \geq 420$ nm)	50	250 mL 0.1 M ascorbic acid	5463 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	13.6% (420 nm)	2017 [187]
0.5 wt.% MoS ₂ /g-C ₃ N ₄	MoS ₂	300 W Xe lamp ($\lambda \geq 420$ nm)	50	120 mL 25 vol% methanol	867.6 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	—	2018 [185]
1 wt.% MoS ₂ /ZnIn ₂ S ₄	MoS ₂	300 W Xe lamp ($\lambda \geq 420$ nm)	80	80 mL 12.5 vol% lactic acid	343 $\mu\text{mol}\cdot\text{h}^{-1}$	3.85% (420 nm)	2017 [186]
2 wt.% CdS/MoS ₂	MoS ₂	300 W Xe lamp ($\lambda \geq 420$ nm)	20	80 mL 10 vol% lactic acid	493.1 $\mu\text{mol}\cdot\text{h}^{-1}$	28.5% (420 nm)	2017 [30]
60 wt.% MoS ₂ /TiO ₂	MoS ₂	300 W Xe lamp ($\lambda \geq 320$ nm)	4	80 mL 0.35 M Na ₂ S/0.25 M Na ₂ SO ₃	1.68 $\text{mmol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	—	2015 [210]
0.375 wt.% MoS ₂ /ZnIn ₂ S ₄	MoS ₂	300 W Xe lamp ($\lambda \geq 420$ nm)	100	150 mL 10 vol% lactic acid	8.047 $\text{mmol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	—	2014 [184]
MoS ₂ /Bi ₁₂ O ₁₇ Cl ₂	MoS ₂	300 W Xe lamp ($\lambda \geq 420$ nm)	10	80 mL 0.3M ascorbic acid	33 $\text{mmol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	36% (420 nm)	2016 [55]
NiS/g-C ₃ N ₄	NiS	300 W Xe lamp ($\lambda \geq 420$ nm)	50	80 mL 15 vol% TEOA	29.68 $\mu\text{mol}\cdot\text{h}^{-1}$	—	2018 [189]
1.5 mol % NiS/g-C ₃ N ₄	NiS	300 W Xe lamp ($\lambda \geq 420$ nm)	100	100 mL 10 vol% TEOA	44.77 $\mu\text{mol}\cdot\text{h}^{-1}$	—	2014 [51]
1.1% NiS/C ₃ N ₄	NiS	300 W Xe lamp ($\lambda \geq 420$ nm)	100	100 mL 15 vol% TEOA	48.2 $\mu\text{mol}\cdot\text{h}^{-1}$	1.1% (420 nm) 1.9% (440 nm)	2013 [45]
7 mol % NiS/TiO ₂	NiS	300 W Xe lamp	200	100 mL 30 vol% lactic acid	698 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	—	2012 [21]
NiS/CdS	NiS	300 W Xe lamp ($\lambda \geq 420$ nm)	300	100 mL 30 vol% lactic acid	2.18 $\text{mmol}\cdot\text{h}^{-1}$	51.3% (420 nm)	2010 [204]
NiS/CdS	NiS	300 W Xe lamp ($\lambda \geq 400$ nm)	100	110 mL 1.22M lactic acid	5.98 $\text{mmol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	69.9% (420 nm)	2018 [205]
0.01% g-C ₃ N ₄ /WS ₂	WS ₂	300 W Xe lamp ($\lambda \geq 420$ nm)	50	80 mL 25 vol% methanol	101 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	—	2015 [201]
30% CdS/Cu ₂ S	Cu ₂ S	300 W Xe lamp ($\lambda \geq 420$ nm)	20	80 mL 10 vol% lactic acid/0.5 M K ₂ HPO ₄	14.4 $\text{mmol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	19.5% (420 nm)	2017 [190]
2 mol % CuS/ZnS	CuS	350 W Xe lamp ($\lambda \geq 420$ nm)	50	50 mL 0.35 M Na ₂ S/0.25 M Na ₂ SO ₃	4147 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	20% (420 nm)	2011 [191]
2 wt.% CuS/g-C ₃ N ₄	CuS	300 W Xe lamp ($\lambda \geq 420$ nm)	50	200 mL 20 vol% TEOA	17.2 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	—	2017 [192]
3 wt.% CuS/Zn _{0.8} Cd _{0.2} S	CuS	500 W Xe lamp	200	200 mL 0.35 M Na ₂ S/0.25 M Na ₂ SO ₃	2792 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	37.6% (420 nm)	2013 [194]
3 mol % CuS/CdS	CuS	500 W Xe lamp	200	200 mL 0.35 M Na ₂ S/0.25 M Na ₂ SO ₃	332 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	—	2013 [195]
1 wt.% CuS/TiO ₂	CuS	500 W Xe lamp	50	80 mL 50 vol% methanol	570 $\mu\text{mol}\cdot\text{h}^{-1}$	—	2013 [196]
Cu ₂ S/CdS-0.05	Cu ₂ S	300 W Xe lamp ($\lambda \geq 420$ nm)	200	190 mL 0.35 M Na ₂ S/0.25 M Na ₂ SO ₃	400.1 $\mu\text{mol}\cdot\text{h}^{-1}$	9.5% (420 nm)	2015 [193]
5% Ag ₂ S/g-C ₃ N ₄	Ag ₂ S	12 W UV-LEDs ($\lambda \geq 420$ nm)	50	50 mL 25 vol% methanol	10 $\mu\text{mol}\cdot\text{h}^{-1}$	—	2014 [199]
6 wt.% Bi ₂ S ₃ /TiO ₂	Bi ₂ S ₃	UV Hg pen-lamp $\lambda = 254$ nm	50	200 mL 50 vol% methanol	2460 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	—	2016 [200]
g-C ₃ N ₄ @ZnIn ₂ S ₄	ZnIn ₂ S ₄	300 W Xe lamp ($\lambda \geq 420$ nm)	50	50 mL 20 vol% TEOA	2.78 $\text{mmol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	3.80% (420 nm)	2018 [209]
10% Co ₃ Mo ₇ S/Cd _{0.5} Zn _{0.5} S	Co ₃ Mo ₇ S	300 W Xe lamp ($\lambda \geq 420$ nm)	50	100 mL 0.35 M Na ₂ S/0.25 M Na ₂ SO ₃	188.65 $\mu\text{mol}\cdot\text{h}^{-1}$	16.72% (420 nm)	2019 [15]
Cu _{1.94} S/Zn _{0.23} Cd _{0.77} S	Zn _{0.23} Cd _{0.77} S	300 W Xe lamp ($\lambda \geq 420$ nm)	20	50 mL 0.1 M Na ₂ S/0.1 M Na ₂ SO ₃	7735 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	26.4% (420 nm)	2016 [208]
3 wt.% NiMoS/CdS	NiMoS	300 W Xe lamp ($\lambda \geq 420$ nm)	5	20 mL 15 vol% lactic acid	185.4 $\text{mmol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	21.82% (420 nm)	2017 [203]
1% NiMoS/CdS	NiMoS	300 W Xe lamp	50	60 mL 0.35 M Na ₂ S/0.25 M Na ₂ SO ₃	24 $\text{mmol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	17.3% (435 nm)	2016 [202]
CoMoS/CdS	CoMoS	300 W Xe lamp ($\lambda \geq 420$ nm)	50	80 mL 10 vol% lactic acid	178.5 $\mu\text{mol}\cdot\text{h}^{-1}$	—	2018 [207]

Table 7Summary of carbon-based materials as cocatalysts photocatalyst system for H₂ evolution.

Photocatalyst	Cocatalyst	Light source	Weight (mg)	Solution	Activity	AQY	Year/Ref.
10 wt. % CNNS/CQDs	CQDs	1000 W Xe lamp ($\lambda \geq 420$ nm)	10	10 mL 20 vol% methanol	219.5 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	0.024% (700 nm) 0.034% (808 nm)	2015 [211]
10 wt. % CDs/g-C ₃ N ₄	CDs	3 W LEDs ($\lambda \geq 355$ nm)	50	80 mL 10 vol% lactic acid	183.0 $\mu\text{mol}\cdot\text{h}^{-1}$	—	2017 [212]
CQDs/TiO ₂	CQDs	300 W Xe lamp	20	60 mL 20 vol% methanol	7.9 $\mu\text{mol}\cdot\text{h}^{-1}$	—	2019 [27]
CCTs/CQDs	CQDs	300 W Xe lamp ($\lambda \geq 400$ nm)	50	60 mL 20 vol% methanol	3538.3 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	10.94% (420 nm)	2018 [213]
1.0 wt. % graphene/g-C ₃ N ₄	graphene	350 W Xe lamp ($\lambda \geq 400$ nm)	80	80 mL 25% methanol	451 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	2.6%	2011 [214]
Cu ₂ O/RGO-2 wt.%	RGO	300 W Hg lamp ($\lambda \geq 400$ nm)	20	20 mL 20 vol% methanol	64.3 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	—	2019 [215]
0.1 wt.% MWCNT-TiO ₂	MWCNT	Mercury Vapour (Hg) lamp (200–800 nm)	5	50 mL 5 vol% glycerol	8.8 $\text{mmol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	—	2018 [216]
Zn _{0.83} Cd _{0.17} S/CNTs-0.25 wt.%	CNTs	500 W Xe lamp	1	40 mL 0.1 M Na ₂ S/0.02 M Na ₂ SO ₃	5.41 $\text{mmol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	—	2014 [217]
CNT@Ni ₃ S ₂	CNT	300 W Xe lamp ($\lambda \geq 420$ nm)	50	100 mL 15 vol% TEOA and 200 mg ErY	5.32 $\text{mmol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	11.1% (420 nm)	2012 [218]
0.25 wt.% CNT/Cd _{0.1} Zn _{0.9} S	CNT	300 W Xe lamp ($\lambda \geq 420$ nm)	50	80 mL 0.35 M Na ₂ S/0.25 M Na ₂ SO ₃	78.2 $\mu\text{mol}\cdot\text{h}^{-1}$	7.9% (420 nm)	2012 [219]
0.2 wt.% CNT/g-C ₃ N ₄	CNT	300 W Xe lamp ($\lambda \geq 420$ nm)	100	100 mL 10 vol% TEOA	39.4 $\mu\text{mol}\cdot\text{h}^{-1}$	—	2014 [50]
CNT/g-C ₃ N ₄	CNT	10 LED lamps ($\lambda \geq 420$ nm)	100	50 mL 10 vol% TEOA	654.8 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	37.9% (420 nm)	2017 [220]
Zn _{0.83} Cd _{0.17} S/CNTs	CNT	500 W Xe lamp	10	40 mL 0.1 M Na ₂ S/0.02 M Na ₂ SO ₃	6.03 $\text{mmol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	—	2013 [221]

AQY was 10.94% at 420 nm. The integration of CQDs into CCTs optimizes the morphology and band structure, increases visible light absorption and reduces the energy barrier, thus improving the photocatalytic efficiency for H₂ evolution. Tang's group [211] reported the CQDs decorated g-C₃N₄ nanosheets *via* hydrothermal method. The photocatalytic H₂ evolution ability was tremendously improved by loading 10 wt.% CQDs as a cocatalyst. This study showed that CQDs/g-C₃N₄ displayed a maximum photocatalytic H₂ evolution rate of 219.5 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$ (UV-Vis) and 50.5 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$ (Vis). In addition, the 10 wt.% CQDs/g-C₃N₄ has an AQY of 0.024% at 700 nm and 0.034% under 808 nm laser, the wavelength dependence of EQE clearly shows the extended active range toward the NIR region derived from the higher content CQD loading. The broadband absorption and high photocatalytic activity originate from the interaction of spectral and electronic spectrum, coupling these interactions helps to promote the wide range absorption and photoinduced charge separation. Very recently, Sui *et al.* [27] found that the CQDs modified TiO₂ with a majority of (001) facet *via* a facile method. The CQDs/TiO₂-001 exhibited a superior photocatalytic H₂ evolution ability. CQDs loading on the surface of TiO₂-001 plays an important role of electron reservoir to trap photogenerated electron, which not only promotes efficient separation of electron-hole pairs, but also prevents the recombination of the photogenerated electron-hole pairs.

Graphene (GO), a two-dimensional macromolecular sheet of carbon atoms with a honeycomb structure, which has a wide applications in photocatalysis due to the outstanding performance with high thermal conductivity, excellent mobility of

charge carriers and extremely high specific surface area [222–224]. Yu's group [214] reported the fabrication of graphene/g-C₃N₄ by combined impregnation-chemical reduction strategy. The optimal graphene content was 1.0 wt.% and the corresponding photocatalytic H₂ evolution rate was 451 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$. The graphene acted as an acceptor of the photo-generated electrons, which could enhance the photocatalytic H₂ evolution under visible light irradiation. Zhang *et al.* [116] reported an in-site process for preparation of Cu NPs on rGO nanosheet. The Cu/rGO composite exhibited superior photocatalytic H₂ evolution activity which possesses a hydrogen evolution rate of 59 $\text{mmol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$ in lactic acid solution under visible light irradiation. Significantly, the Cu/rGO composite still have hydrogen production rate of 2.76 and 1.96 $\text{mmol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$ with the wavelength of 800 nm and 900 nm, respectively. The rGO co-catalyst acts as an electron mediator for enhancing the photoinduced carrier separation efficiency and promote the restrain of e^-h^+ recombination. To date, Zhang *et al.* [215] have prepared Cu₂O-RGO heterojunction with oxygen vacancy through hydrothermal method. Compared with pure Cu₂O, the rate of 2 wt.% Cu₂O-RGO heterojunction photocatalytic H₂ evolution was 64.3 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$, which was 5 times higher than that of pure Cu₂O (12.8 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$). The RGO as co-catalyst loading on Cu₂O to form heterojunction could enhance a broader absorbance under visible light and promote a faster electron transfer, which lead to the improved photocatalytic H₂ production activity.

Recently, Reddy and co-workers [216] prepared CNT/TiO₂ has enhanced photocatalytic H₂ evolution. After loading CNT on TiO₂, the photocatalytic H₂ evolution rate could be increased

Fig. 17. (a) Schematic illustration of the formation of Ni₃S₂ ultrathin nanosheets supported on CNT backbone (CNT@Ni₃S₂) by a multi-step conversion route: (I) uniform coating of a silica layer on CNT; (II) in-situ formation of nickel silicate shell on the silica layer; and (III) chemical conversion of nickel silicate into Ni₃S₂ to form CNT@Ni₃S₂ with simultaneous elimination of the intermediate silica layer. (b) Schematic illustration of photocatalytic H₂ production over the CNT@Ni₃S₂ structure. From Ref. [218].

from 1.3 to 8.8 mmol·h⁻¹·g⁻¹. Yu *et al.* [219] investigation revealed that the CNT could serve as a highly efficient co-catalyst for Cd_{0.1}Zn_{0.9}S to promote the photocatalytic H₂ production under visible-light irradiation. The optimum rate of H₂ evolution is 78.2 μmol·h⁻¹ with an AQY of 7.9% at 420 nm, exceeding that of pure Cd_{0.1}Zn_{0.9}S by more than 3.3 times. Chen's group [50] found that introduce 0.2 wt.% CNT into g-C₃N₄ could enhance its photocatalytic activity for H₂ evolution under visible-light irradiation, the highest H₂ evolution rate is 39.4 μmol·h⁻¹, which is 2.4 times higher than the value obtained with pure g-C₃N₄. In 2012, Lou's group [218] reported that CNT@Ni₃S₂ nanostructures for photocatalytic H₂ evolution which composed of Ni₃S₂ nanosheets grown on carbon nanotube (CNT) backbone *via* multi-step transformation route, the synthesis procedure of CNT@Ni₃S₂ nanostructures is shown in Fig. 17. Under visible light irradiation, the rate of photocatalytic H₂ evolution is 5.32 mmol·h⁻¹·g⁻¹ with an AQY of 11.1% at 420 nm, which is superior to pure Ni₃S₂. The high photocatalytic hydrogen production activity is due to the sensitization effect of ErY for effective visible light absorption, which would then be transformed into excited states. The photoexcited electrons in ErY are quickly transferred to the Ni₃S₂ nanosheets due to the presence of the CNT backbone. Then the protons partake in the reduction reaction to product H₂ on Ni₃S₂ (Fig. 17). In this photocatalytic system, CNT not only acts as co-catalyst to collect and transfer electrons, but also provides the active sites for H₂ evolution.

4. Dual cocatalysts for photocatalytic H₂ evolution

4.1. Randomly distributed

Efficient charge separation is an effective way to improve the photocatalytic hydrogen evolution performance. The hydrogen production efficiency of water splitting over single photocatalyst is limited by the rapid recombination of photoexcited charge carriers. Cocatalyst loading can effectively accelerate the surface reaction to promote the water splitting process [225]. The electron-hole pairs are separated under the light irradiation, and the photoexcited electrons are the main active species that are used to reduce the proton to H₂. Various reductive cocatalysts have been broadly studied to transport electrons to water protons. Noble metals such as Pt and Pd with higher work function and lower impedance are usually primary candidates to act as reductive cocatalysts to transfer the electrons to protons. The higher work function equally to the lower Fermi level results in the separated electrons inclines to the noble metals, while the lower impedance can insure a faster electron mobility, which can prompt the photoinduced electrons transfer to the water proton. However, noble metals are suffering from high cost and low abundance in the earth. The emergence of various non-noble species has played an important role in the development of reductive cocatalyst. The nucleus on photocatalytic H₂ production are concentrated on the half reduction reaction of water splitting. The holes are unnecessary factor to charge separation. Oxidative cocatalyst, such as some metal oxides, CoO_x, IrO₂ *etc.*, has a tendency to capture holes, while reductive cocatalysts acting as electrons trapping agents to pull photoinduced electrons away from the photogenerated charges [29,226–228]. The applications of dual-cocatalysts photocatalyst systems for H₂ evolution are summarized in Table 8.

In 2016, Yu's group [229] reported that synergistic effect of dual amorphous cocatalysts, in which the Ti(IV)-hole cocatalyst and Ni(II)-electron cocatalyst were loaded on CdS to improve the photocatalytic H₂ evolution activity under visible light irradiation. The maximum photocatalytic H₂ evolution rate is 3437.95 μmol·h⁻¹·g⁻¹, which is 2.1 times higher than that of pure CdS. The reason for the high performance is that when both of Ti(IV) and Ni(II) cocatalysts are simultaneously modified on the CdS surface, the Ni(II) cocatalyst can first act as an effective trapping site to accept the electrons, and then act as the reduction active site to boost the H₂ production reactions on the surface, while the Ti(IV) cocatalyst act as hole cocatalyst to quickly transfer the holes and boot the oxidation reaction (Fig. 18).

Wang *et al.* [230] reported the co-loading of graphene quantum dots (GQDs) and PdS dual cocatalysts on ZnCdS surface by hydrothermal and in-situ chemical deposition method for efficient photocatalytic H₂ evolution. The GQDs/ZnCdS/PdS hybrids exhibited the highest H₂ evolution rate of 517 μmol·h⁻¹ with an AQY of 22.4% at 420 nm, which were 15, 7 and 1.7 times higher than that of pure ZnCdS, GQDs/ZnCdS and ZnCdS/PdS, respectively.

Li's group [32] synthesized ternary structured photocatalyst which is composed by co-loading dual earth-abundant cocatalysts of metallic carbon black (CB) and NiS₂ on CdS *via* solvothermal and impregnation method. The superior photocatalytic H₂ evolution activity of CdS/CB/NiS₂ is 166.7 μmol·h⁻¹. As

Table 8Summary of dual-cocatalyst photocatalyst systems for H₂ evolution.

Photocatalyst	Cocatalyst	Light source	Weight (mg)	Solution	Activity	AQY	Year/Ref.
Pt/TiO ₂ /CdS/Co ₃ O ₄	Pt/Co ₃ O ₄	300 W Xe lamp ($\lambda \geq 420$ nm)	30	0.2 M Na ₂ S and Na ₂ SO ₃	2000 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	—	2017 [231]
Pt@CdS/1%PdS	Pt/PdS	300 W Xe lamp ($\lambda \geq 400$ nm)	10	50 mL 0.1 M Na ₂ S/ 0.1 M Na ₂ SO ₃	144.8 $\text{mmol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	11.65% (420 nm)	2018 [234]
0.019 wt.% CoO _x /TiO ₂ /0.046 wt.% Pt	CoO _x /Pt	300 W Xe lamp	35	200 mL 15 vol% methanol	275.9 $\mu\text{mol}\cdot\text{h}^{-1}$	—	2016 [235]
Ni(II)-Ti(IV)/CdS	Ni(II)-Ti(IV)	350 W Xe lamp ($\lambda \geq 420$ nm)	50	80 mL 0.35 M Na ₂ S/0.25 M Na ₂ SO ₃	3437.95 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	—	2016 [229]
GQDs/ZnCdS/PdS	GQDs/PdS	300 W Xe lamp ($\lambda \geq 420$ nm)	50	100 mL 0.5 M Na ₂ S/Na ₂ SO ₃	517 $\mu\text{mol}\cdot\text{h}^{-1}$	22.4% (420 nm)	2018 [230]
CdS/CB/NiS ₂	CB/NiS ₂	300 W Xe lamp ($\lambda \geq 420$ nm)	50	80 mL 0.25 M Na ₂ S/Na ₂ SO ₃	166.7 $\mu\text{mol}\cdot\text{h}^{-1}$	—	2017 [32]
15 wt.% MoS ₂ -Mn _{0.2} Cd _{0.8} S/MnS	MoS ₂ /MnS	300 W Xe lamp ($\lambda \geq 420$ nm)	50	50 mL 0.35 M Na ₂ S/ 0.25 M Na ₂ SO ₃	995 $\mu\text{mol}\cdot\text{h}^{-1}$	30.2% (420 nm)	2019 [236]
ZnO-ZnS/graphene	graphene	300 W Xe lamp	50	100 mL 40 vol% glycerol	1070 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	—	2018 [237]
CdS/Au/g-C ₃ N ₄	CdS/Au	Xe lamp ($\lambda \geq 420$ nm)	100	60 mL 17 vol% methanol	19.02 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	—	2015 [238]
CsTaWO ₆ /Au/g-C ₃ N ₄	Au/g-C ₃ N ₄	300 W Xe lamp	50	100 mL 20 vol% methanol	9.16 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	—	2015 [239]
g-C ₃ N ₄ /Pt-TiO ₂ (70:30)	Pt/TiO ₂	300 W Xe lamp ($\lambda \geq 420$ nm)	100	200 mL 10 vol% TEOA	178 $\mu\text{mol}\cdot\text{h}^{-1}$	—	2012 [44]
g-C ₃ N ₄ /Pt/GO-0.5%	Pt/GO	300 W Xe lamp ($\lambda \geq 420$ nm)	50	100 mL 20 vol% TEOA/50 mg Eosin Y	3.82 $\text{mmol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	9.7% (420 nm)	2018 [240]
2 wt.% Ni/NiO/g-C ₃ N ₄	Ni/NiO	300 W Xe lamp ($\lambda \geq 420$ nm)	50	100 mL 10 vol% TEOA	10 $\mu\text{mol}\cdot\text{h}^{-1}$	—	2015 [241]
Ni/Ni(OH) ₂ /CdS	Ni/Ni(OH) ₂	300 W Xe lamp ($\lambda \geq 400$ nm)	100	100 mL 30 vol% metha- nol	373.5 $\mu\text{mol}\cdot\text{h}^{-1}$	—	2015 [242]
5 wt.% CuS/5 wt.% NiS/TiO ₂	CuS/NiS	500 W Xe lamp	50	80 mL 50 vol% methanol	80 $\mu\text{mol}\cdot\text{h}^{-1}$	—	2014 [243]
Ni/CdS/g-C ₃ N ₄	Ni/CdS	300 W Xe lamp ($\lambda \geq 420$ nm)	100	100 mL 10 vol% TEOA	1258.7 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	—	2016 [244]
TiO ₂ /Au/CdS	Au/CdS	300 W Xe lamp ($\lambda \geq 420$ nm)	100	0.1 M Na ₂ S/0.1 M Na ₂ SO ₃	1.81 $\text{mmol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	—	2016 [245]
TiO ₂ /Au/CdS	Au/CdS	300 W Xe lamp ($\lambda \geq 400$ nm)	25	100 mL 0.1 M Na ₂ S/ 0.1 M Na ₂ SO ₃	0.76 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	—	2016 [246]
ZnS/CuS/CdS	CuS/CdS	150 W Xe lamp	100	150 mL 60mM Na ₂ S	837.6 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	—	2014 [247]
TiO ₂ -Ni(OH) ₂ /CNT/CdS	CNT/CdS	300 W Xe lamp ($\lambda \geq 400$ nm)	50	230 mL 8.7% lactic acid	12 $\text{mmol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	—	2017 [248]
Cu@CuO-g-C ₃ N ₄ /MCM-41	Cu@CuO /MCM-41	125 W mercury ($\lambda \geq 400$ nm)	20	20 mL 17 vol% methanol	750 $\mu\text{mol}\cdot 2\text{h}^{-1}$	24.8%	2016 [249]
Cu-Cu ₂ O-CuO/TiO ₂	Cu-Cu ₂ O- CuO	300 W Xe lamp	40	40 mL 10 vol% methanol	12779 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	—	2013 [250]
0.5% Cr ₂ O ₃ /TNS/MoS ₂	MoS ₂	300 W Xe lamp ($\lambda \geq 400$ nm)	50	80 mL 15 vol% TEOA	217 $\mu\text{mol}\cdot\text{h}^{-1}$	—	2018 [251]

illustrated in Fig. 19(a), under visible light irradiation, the electrons are excited from the VB to the CB of CdS, then the electrons move to the carbon black due to its intimate interface contact and matched work functions, in which the carbon black acts as an electron mediator to transfer the collected electrons to the H₂ evolution active sites on NiS₂ owing to its excellent electrical conductivity and carrier mobility properties, leading to the effective separation and transfer of the electron-hole pairs. The effective separation of electron-hole pairs is the key factor in improving the photocatalytic hydrogen production activity.

4.2. Orientated distributed

The charge separation can be further promoted by loading reductive and oxidative cocatalysts [232]. The rational design of spatially-separated dual cocatalysts on photocatalysts has aroused an increasing attention. In most cases, the cocatalysts were randomly distributed on the surface of semiconductors, resulting in a random flow of the photogenerated electrons and holes and severe charges recombination. Li's group [233] reported an Pt-PdS/CdS photocatalyst in 2009. Visi-

ble-light-driven hydrogen production with the rational simultaneously design of oxidative and reductive cocatalysts could further enhance the photocatalytic activity. Wang *et al.* [231] have demonstrated the efficiency of Pt/TiO₂/CdS/Co₃O₄ in hierarchical structure, Pt and Co₃O₄ species were spatially decorated on the inner and outer surface of the TiO₂/CdS heterojunction shell. Its hydrogen production rate is 2000 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$ under visible light irradiation, which is over 540 times higher than that of TiO₂/CdS double-shelled hollow spheres under the same conditions. The outstanding H₂ evolution rate can be attributed to the efficient separation of photo-generated carriers, transportation and interface reaction. The ultrathin shell thickness could contribute to the fast electron transportation and the synergistic effect of the separately loaded dual cocatalysts (Fig. 19(b)).

Sun *et al.* [234] synthesized a novel hollow porous CdS photocatalyst with Pd and PdS nanoparticles spatially distributed on the inner and outer surfaces by using microporous zeolites as a hard template. The Pd@CdS/PdS sample exhibits superior visible-light-driven photocatalytic H₂ evolution rate up to 144.8 $\text{mmol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$. This is the highest values among all of the reported CdS-based catalysts. This synthetic approach may be

Fig. 18. Graphical illustration for the synthesis and photocatalytic mechanism of various samples: (a) CdS, (b) Ti(IV)/CdS, (c) Ni(II)/CdS, and (d) Ti(IV)-Ni(II)/CdS. From Ref. [229].

used to fabricate other highly efficient catalysts with spatially

Fig. 19. (a) Proposed photocatalytic H₂ evolution and charge transfer mechanisms of CdS/CB/NiS₂ composite photocatalysts under visible-light irradiation [32]; Illustration of the (b) structure and (c) reaction procedure of double-shelled hollow sphere photocatalyst. From Ref. [231].

Fig. 20. The proposed mechanism for photocatalytic hydrogen production mediated by CoO_x/TiO₂/Pt. (a) The reaction process. (b) Band structure of the photocatalysts. (c) Synthetic process for TiO₂/Pt and CoO_x/TiO₂/Pt photocatalysts by template-assisted ALD. (d) TEM and (e) HRTEM images of the CoO_x/TiO₂/Pt samples (inset in (d), expanded view of the rectangular area; inset in (f), fast Fourier transform (FFT) of crystalized TiO₂ film). (j) Atomic-resolution HAADF-STEM image of the CoO_x/TiO₂/Pt samples. (h–k) STEM image and EDS mapping profiles of the rectangular area in panel (h) for (h) titanium, (i) oxygen, (j) platinum, and (k) cobalt. One ALD cycle for Pt and CoO_x. From Ref. [235].

separated cocatalysts. Furthermore, the remarkably enhanced H₂ evolution rate can be result from the spatially separated reaction sites in the Pd@CdS/PdS sample, in which the metallic Pd pulls the photoexcited electrons away from CdS while PdS pushes the holes for more thorough oxidation of the sacrificial agent.

In 2016, Zhang and co-worker [235] reported that CoO_x/TiO₂/Pt photocatalysts produced by template-assisted atomic layer deposition for photocatalytic hydrogen evolution with CoO_x and Pt dual cocatalysts. Fig. 20 showed the reaction process of CoO_x/TiO₂/Pt photocatalysts with porous hollow TiO₂ nanotubes as a semiconductor, which the Pt and CoO_x deposited on the inner and outer surfaces of the nanotubes, respectively. The highest rate of 0.019 wt.% CoO_x/TiO₂/0.046 wt.% Pt photocatalysts is 275.9 μmol·h⁻¹, which is almost 5 times higher than that of porous hollow TiO₂ nanotubes. The spatially separated dual Pt and CoO_x cocatalysts not only facilitate electron-hole separation but also provide the activity sites for photocatalytic H₂ evolution on the surface.

5. Z-scheme cocatalysts for photocatalytic H₂ evolution

5.1. Redox mediator Z-scheme photocatalyst system

An artificial Z-scheme photocatalyst system was inspired by the natural photocatalytic process, which was first reported by

Fig. 21. Schematic illustration of the (a) redox mediator Z-scheme system, (b) all-solid-state Z-scheme system, and (c) direct Z-scheme system.

Bard in 1979 [252]. The schematic illustration of the redox-mediator Z-scheme system is shown in Fig. 21(a), there is no direct contact between the two semiconductors in the Z-scheme system, and the charge carrier transfer is achieved by ion redox shuttles in solution. Both the two semiconductors are photoexcited and generate e^-/h^+ pairs in their CB and VB under light irradiation, respectively. And then the photogenerated e^- in the CB of PS II is transferred to the VB of PS I via D/A pairs. Finally, h^+ in the VB of PS II participate in oxidation reaction and e^- in the CB of PS I participate in reduction reaction on the surface of photocatalysts, respectively. Commonly used D/A pairs are IO_3^-/I^- [253], $\text{Fe}^{3+}/\text{Fe}^{2+}$ [254, 255], I_3^-/I^- [256], $\text{NO}_3^-/\text{NO}_2^-$ [257], $[\text{Co}(\text{phen})_3]^{3+/2+}$ and $[\text{Co}(\text{bpy})_3]^{2+}$ [258].

In 2016, Ma and co-workers [256] reported a Z-scheme of $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ and co-loading with Pt to generate H_2 , in which triiodide/iodide (I_3^-/I^-) redox couple were used as a shuttle electron mediator. Kudo's group [258] found a Z-scheme system was constructed using a $\text{Ru}/\text{BaTa}_2\text{O}_6:\text{Ir},\text{La}$ H_2 evolving photocatalyst combined with a $[\text{Co}(\text{bpy})_3]^{2+}$ as electron mediator. The redox potential of $[\text{Co}(\text{bpy})_3]^{2+}$ was reported as 0.32 V, and the value was not affected by pH. Due to the doping of Ir, the wide band gap material has a wider visible light absorption range. Yang *et al.* [259] revealed a carbon nanodots(CNDs)/ WO_3 Z-scheme to improve the photocatalytic performance with IO_3^-/I^- as shuttle redox mediator. As shown in Fig. 22, photogenerated e^-/h^+ pairs tend to recombine, and only a little of them participates in the photocatalytic reactions, which results in low photocatalytic activity. For the Z-scheme system, the photogenerated electrons transferred from the CB of WO_3 to the VB of CNDs through IO_3^-/I^- as shuttle redox mediator. Therefore the e^- reduce H^+ to H_2 in the CB of CNDs. Because of the existence of the IO_3^-/I^- , the e^-/h^+ pairs could be

effectively separated without direct contact between the two semiconductors, thereby improving the photocatalytic activity of water splitting.

5.2. All-solid-state photocatalyst system

However, the redox-mediator Z-scheme photocatalytic system has some drawbacks. Namely, the redox mediator-induced back reactions are thermodynamically favorable, and can easily occur because the photogenerated electrons and holes with strong redox power are consumed by the shuttle redox ion pairs. In addition, the light-shielding effect, feasibility confined in solution systems and solution pH sensitivity could be limited its application in the field of photocatalytic water splitting. Thus, all-solid-state Z-scheme photocatalytic system attracted some scientific attentions.

Different from the photocatalytic mechanism of the redox-mediator Z-scheme, in the solid-state Z-scheme photocatalytic system, the two semiconductors are directly contacted via conductor as electron mediator (such as Au [260,261], RGO [31,262] and MWCNT [263]) to form Ohmic contacts with low contacting resistance. As shown in Fig. 21(b), both the photogenerated electrons in the CB of PS II and photogenerated holes in the VB of PS I transfer to the electron mediator and recombine with each other, leaving electrons in the CB of PS I and holes in the VB of PS II, which are mostly reserved for the targeting reduction and oxidation reactions, respectively. For the solid-state Z-scheme photocatalytic system, the distance of electrons transfer is reduced due to the presence of electron mediator, therefore reducing the recombine of the photogenerated e^-/h^+ pairs. Without the D/A pairs, the solid-state Z-scheme photocatalytic system can work not only in the liquid phase, but also in the gas phase. However, when the electron mediator is noble metal, the development of the solid-state Z-scheme photocatalytic systems are limited by the expensive cost and shielding effect [264]. Table 9 shows the applications of all-solid-state Z-scheme photocatalytic system in hydrogen evolution applications.

In 2016, Ma's group [265] reported sandwich-structured Z-scheme $\text{g-C}_3\text{N}_4\text{-Au-CdZnS}$ nanoparticles system for visible light photocatalytic hydrogen evolution with $24.6 \text{ mmol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$ hydrogen yield. Attribute to the Z-scheme charge-carrier transfer mechanism, Au is used as the electron transfer mediator between $\text{g-C}_3\text{N}_4$ and CdZnS , which improves the photocatalytic performance of the composite. Au acts as an electron tran-

Fig. 22. Schematic diagram of the Z-scheme photocatalytic mechanism of CNDs/ WO_3 photocatalyst. From Ref. [259].

Table 9Summary of all-solid-state Z-scheme photocatalyst systems for H₂ evolution.

Photocatalyst	Mediator	Cocatalyst	Light source	Weight (mg)	Solution	Activity	AQY	Year/Ref.
CdS-Au _x -ZnO	Au	ZnO	300 W Xe lamp ($\lambda \geq 420$ nm)	20	80 mL Na ₂ S/Na ₂ SO ₃	102.9 $\mu\text{mol}\cdot\text{h}^{-1}$	9.6 % (420 nm)	2018 [267]
Cd _{0.5} Zn _{0.5} S/RGO/CN-4 0%	RGO	Cd _{0.5} Zn _{0.5} S	300 W Xe lamp ($\lambda \geq 420$ nm)	30	100 mL 0.1 M Na ₂ S/0.1 M Na ₂ SO ₃	39.24 $\text{mmol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	37.88% (420 nm)	2018 [262]
CdS/3 wt.% Ag/15 wt.% g-C ₃ N ₄	Ag	g-C ₃ N ₄	300 W Xe lamp ($\lambda \geq 420$ nm)	50	100 mL 10 vol% TEOA	1376.0 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	—	2018 [268]
Zn _{0.5} Cd _{0.5} S-MWCNT-TiO ₂	MWCNT	Zn _{0.5} Cd _{0.5} S	500 W Xe lamp	30	100 mL 0.1 M Na ₂ S/0.1 M Na ₂ SO ₃	21.9 $\mu\text{mol}\cdot\text{h}^{-1}$	—	2017 [263]
NiTiO ₃ /Ag/g-C ₃ N ₄	Ag	NiTiO ₃	300 W Xe lamp	4	40 mL 10 vol% TEOA	3351 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	—	2019 [269]
Ti ₃ C ₂ @CdS/MoS ₂	CdS	Ti ₃ C ₂	300 W Xe lamp ($\lambda \geq 420$ nm)	30	100 mL 20% lactic acid	8.47 $\text{mmol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	—	2019 [270]
g-C ₃ N ₄ /Au/CdZnS	Au	CdZnS	150 W Xe lamp ($\lambda \geq 420$ nm)	100	100 mL 0.35 M Na ₂ S/0.25 M Na ₂ SO ₃	24.6 $\text{mmol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	—	2016 [265]
Cd _{0.8} Zn _{0.2} S/Au/g-C ₃ N ₄	Au	Cd _{0.8} Zn _{0.2} S	300 W Xe lamp ($\lambda \geq 420$ nm)	50	100 mL 0.1M glucose	123 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	—	2017 [260]
Au@CdS/U-WO ₃	Au	CdS	300 W Xe lamp ($\lambda \geq 420$ nm)	20	100 mL 2.34 g Na ₂ S/3.78 g Na ₂ SO ₃	1.39 $\text{mmol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	3.45% (420 nm)	2015 [271]
CdS-Au-HCNS	Au	CdS	300 W Xe lamp ($\lambda \geq 420$ nm)	20	100 mL 10 vol% TEOA	277 $\mu\text{mol}\cdot\text{h}^{-1}$	8.7% (420 nm)	2015 [272]
TiO ₂ /WO ₃ @MoS ₂	TiO ₂	MoS ₂	300 W Xe lamp	50	65 mL 38.5% methyl alcohol	273.69 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	—	2018 [273]
MoO ₃ /1T-MoS ₂ /g-C ₃ N ₄	1T-MoS ₂	g-C ₃ N ₄	300 W Xe lamp ($\lambda \geq 420$ nm)	10	20 mL 10 vol% TEOA	513.0 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	—	2018 [266]
CdS/RGO/g-C ₃ N ₄	RGO	CdS	350 W Xe lamp ($\lambda \geq 400$ nm)	20	50 mL 10% lactic acid	676.5 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	36.5% (400 nm)	2017 [31]
TiO ₂ /WO ₃ /Au	Au	TiO ₂	300 W Xe lamp ($\lambda \geq 400$ nm)	50	65 mL 38.5% methyl alcohol	269.63 $\mu\text{mol}\cdot\text{h}^{-1}$	—	2017 [261]

sition mediator that induces the recombination of photogenerated electrons in CdZnS to the photogenerated holes in g-C₃N₄. Except noble metals, metal sulfide and oxides with significant conductivity have been employed as electron-mediator between the photocatalysts in Z-scheme system. Wang and his co-worker [266] reported a novel composite photocatalyst by sandwiching metallic 1T-phase MoS₂ nanosheets between MoO₃ and g-C₃N₄ for the first time, in which the metallic 1T-phase MoS₂ nanosheets act as electron mediator between MoO₃ and g-C₃N₄ to construct an all-solid-state Z-scheme photocatalytic system, and the photocatalytic H₂ evolution rate reaches to 513.0 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$ under visible light irradiation. In addition, non-metal with significant conductivity such as reduced graphene oxide (RGO) have also been used as electron mediator to enhance the photocatalytic hydrogen evolution. Xue *et al.* [262] constructed ternary Cd_{0.5}Zn_{0.5}S/RGO/g-C₃N₄ all-solid-state Z-scheme *via* two-step method and obtained an H₂ evolution rate of 39.24 $\text{mmol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$ with an AQE of 37.88% at 420 nm. The enhanced photocatalytic hydrogen evolution performance can be ascribed to the synergistic effect between Cd_{0.5}Zn_{0.5}S nanospheres and g-C₃N₄ nanosheets in the existence of RGO, which plays a decisive role in the ternary system by acting as a mediator for charge carriers between the two semiconductors.

5.3. Direct Z-scheme photocatalyst system

Although the electron mediators play an important role in transferring electrons between PS I and PS II, there are several adverse effects, such as metal-based electron mediators might affect light absorption, and Au could cause SPR effect, which

would have great influence on the activity of the photocatalyst. Hence, mediator-free Z-scheme photocatalyst was constructed in 2013, Yu *et al.* [47] first proposed the concept of a direct Z-scheme photocatalyst. Although the band structures of direct Z-scheme photocatalyst systems are similar to the Type-II heterostructures, the electron transfer path between the two semiconductors is completely different. As schematically illustrated in Fig. 21(c), the direct Z-scheme photocatalyst system was constituted by two closely contacted semiconductors, the electrons directly transfer across the interface for the CB of PS I to the VB of PS II without any mediator, and then participate in the redox reaction occurred on the surface of photocatalysts. As a result, the direct Z-scheme photocatalyst system has a strong redox ability for driving the photocatalytic reactions and spatially separated reductive and oxidative active sites. The application of direct Z-scheme photocatalyst system for H₂ production is summarized in Table 10. Yu's group [274] reported a novel TiO₂/NiS core-shell direct Z-scheme nanostructure hybrid for photocatalytic H₂ production with the rate of 655 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$. As shown in Fig. 23, when the two semiconductors form an ohmic contact, a built-in electric field is formed at the interface between TiO₂ and NiS, the electrons in the CB of TiO₂ will recombine with the holes in the VB of NiS. The photogenerated electrons in the CB of NiS would effectively reduce H₂O to produce H₂. Meanwhile, the holes in the VB of TiO₂ oxidize the sacrificial agent of methyl. The TiO₂/NiS direct Z-scheme could effective separate electron-hole pairs to promote photocatalytic hydrogen production.

To date, Liu's group [275] conducted studies on the Bi₂WO₆/CdS Z-scheme photocatalyst system and obtained a photocatalytic H₂ evolution rate of 1223.364 $\mu\text{mol}\cdot\text{h}^{-1}$ with AQY

Table 10Summary of direct Z-scheme photocatalyst systems for H₂ evolution.

Photocatalyst	Cocatalyst	Light source	Weight (mg)	Solution	Activity	AQY	Year/Ref.
Bi ₂ WO ₆ /CdS	CdS	300 W Xe lamp ($\lambda \geq 420$ nm)	20	100 mL 25% methanol	1223.364 $\mu\text{mol}\cdot\text{h}^{-1}$	1.4% (420 nm)	2019 [275]
TiO ₂ /CdS	CdS	350 W Xe lamp	50	80 mL 25% methanol	51.4 $\mu\text{mol}\cdot\text{h}^{-1}$	—	2017 [33]
5%WO ₃ /CdS-DETA	WO ₃	300 W Xe lamp ($\lambda \geq 400$ nm)	50	100 mL 0.35 M Na ₂ S/ 0.25 M Na ₂ SO ₃	15522 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	—	2018 [35]
0.5%CdS/CdWO ₄	CdS	300 W Xe lamp	10	100 mL 0.35 M Na ₂ S/ 0.25 M Na ₂ SO ₃	2400 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	—	2018 [34]
anatase/rutile TiO ₂	Pt	350 W Xe lamp ($\lambda \geq 365$ nm)	50	80 mL 20% methanol	324 $\mu\text{mol}\cdot\text{h}^{-1}$	20.9% (365 nm)	2014 [280]
BCN-TiO ₂	Pt	300 W Xe lamp ($\lambda \geq 420$ nm)	50	100 mL 20 vol% TEOA	19.7 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	—	2017 [281]
10 wt.% WO ₃ /g-C ₃ N ₄	WO ₃	300 W Xe lamp ($\lambda \geq 420$ nm)	100	100 mL 10 vol% TEOA	1853 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	—	2018 [282]
15% WO ₃ /g-C ₃ N ₄	WO ₃	350 W Xe lamp	50	80 mL 20% methanol	982 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	—	2019 [14]
C ₃ N ₄ /W ₁₈ O ₄₉	W ₁₈ O ₄₉	300 W Xe lamp ($\lambda \geq 400$ nm)	50	120 mL 10 vol% TEOA	8597 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	39.1% (420 nm)	2017 [283]
WO ₃ /C ₃ N ₄	Ni(OH) _x	300 W Xe lamp ($\lambda \geq 400$ nm)	50	80 mL 15 vol% TEOA	576 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	—	2017 [284]
g-C ₃ N ₄ /WO ₃	Pt	300 W Xe lamp	50	80 mL 10 vol% TEOA	3.12 mmol·h ⁻¹ ·g ⁻¹	—	2017 [285]
g-C ₃ N ₄ /Bi ₄ NbO ₈ Cl (molar ratio 3:1)	Pt	300 W Xe lamp ($\lambda \geq 420$ nm)	100	50 mL 10 vol% lactic acid	287.71 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	2.02% (420 nm)	2018 [286]
TiO ₂ /NiS	NiS	350 W Xe lamp	50	80 mL 20% methanol	655 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	—	2018 [274]
1% Bi ₂ MoO ₆ /CdSe-DETA	Pt	300 W Xe lamp ($\lambda \geq 420$ nm)	50	100 mL 0.35 M Na ₂ S/ 0.25 M Na ₂ SO ₃	5.92 mmol·h ⁻¹ ·g ⁻¹	27.3% (420 nm)	2019 [278]
20 wt.% CdS/WO ₃	Pt	500 W Xe lamp ($\lambda \geq 400$ nm)	50	lactic acid	2900 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	—	2014 [277]
Zn _{0.5} Cd _{0.5} S/ZnO	Zn _{0.5} Cd _{0.5} S	300 W Xe lamp	20	100 mL 0.75 M Na ₂ S/ 1.05 M Na ₂ SO ₃	28.6 mmol·h ⁻¹ ·g ⁻¹	—	2018 [287]
WO _{3-x} /Zn _{0.3} Cd _{0.7} S	Zn _{0.3} Cd _{0.7} S	300 W Xe lamp ($\lambda \geq 420$ nm)	100	100 mL 0.1 M Na ₂ S/ 0.1 M Na ₂ SO ₃	352.1 $\mu\text{mol}\cdot\text{h}^{-1}$	7.3% (420 nm)	2017 [288]
g-C ₃ N ₄ /Ag ₂ CrO ₄	Pt	300 W Xe lamp ($\lambda \geq 420$ nm)	50	100 mL 25% methanol/10 mM NaHCO ₃	902.1 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	23.1% (420 nm)	2018 [279]
10 wt.% WO ₃ /g-C ₃ N ₄	Pt	300 W Xe lamp ($\lambda \geq 420$ nm)	40	40 mL 10 vol% TEOA	110 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	—	2014 [289]
CdS/ZnO	Pt	225 W Xe lamp	10	25 mL 0.75 M Na ₂ S/ 1.05 M Na ₂ SO ₃	22.12 mmol·h ⁻¹ ·g ⁻¹	—	2017 [276]

of 1.4% at 420 nm. The H₂ production rate was significantly higher than the one produced by using pure Bi₂WO₆ or CdS photocatalysts (Fig. 24). The excellent photocatalytic performance is due to the intrinsic properties of the direct Z-scheme Bi₂WO₆/CdS photocatalyst system, which replaces the electron mediator with an ohmic contact to shorten the distance of electron transfer, and thus improves the separation of electrons and holes. Pt acts as dual cocatalyst to improve the H₂ evolution activity in the photocatalyst system, because of the enhanced charge separation of photogenerated charge carriers and the efficient photocatalytic H₂ production. Pt is also applicable to other direct Z-scheme systems and acts as a cocatalyst to promote the activity of photocatalytic H₂ [276–279].

Fig. 23. Schematic illustration of TiO₂ and NiS direct Z-scheme heterojunction (a) before and (b) after contact along with the charge transfer and separation in TN10 under UV-visible light irradiation. From Ref. [274].

6. MOFs cocatalysts for photocatalytic H₂ evolution

Metal organic frameworks (MOFs) are well known as porous materials consisting of metal nodes and organic ligands with unique catalytic natures [290,291]. MOFs have been often used as electrocatalysts and photocatalysts because of their high design flexibility, large specific surface area and tunable porous channels, which are available for exposing numerous active sites to drive the redox reactions and shorten the transfer distance of photoexcited carriers to the pore surface [292]. In addition, MOF-derived materials have been found to serve as precursors for porous semiconductor materials, which includes metal phosphide, metal oxides, carbon materials and metal sulfides *via* facile thermal treatment, phosphorization and sulfidation process [293–296]. The as-prepared MOF-based materials can not only maintain the initial structural features of MOF materials that ensures the mono-dispersion of metals centers, but also improve the conductivity property of the materials. Thus, tremendous efforts have been made to explore MOF-derived materials in photocatalytic water splitting.

MOF-based materials as cocatalysts in the hydrogen evolution half-reaction system can serve various metal ions, and facilitate the doping of C and N to the MOF-derived semiconductors, and more important they can provide high surface areas to expose numerous active sites.

UiO-66 as a representative stable MOF owns intrinsic photocatalytic H₂ evolution activity. Jiang's group [297] has syn-

Fig. 24. (a) Comparison of photocatalytic H₂ evolution over Bi₂WO₆, pristine CdS nanowires and Bi₂WO₆/CdS (1-BW/Cd, 2-BW/Cd, 3-BW/Cd and 4-BW/Cd) from aqueous solution containing 25% methanol by volume; (b) and (c) Schematic photocatalytic decomposition and photocatalytic H₂ evolution mechanism over Bi₂WO₆/CdS in Z-scheme photocatalytic system under visible-light illumination. From Ref. [275].

Fig. 25. Synthetic Process for CdS/UiO-66 Composites. From Ref. [297]

thesized the composite of CdS-decorated UiO-66 that not only has taken the advantage of both CdS and MOF, but also avoid the drawbacks of each component. CdS/UiO-66 (Fig. 25) exhibits high H₂ production activity for water splitting of H₂ evolution under visible light irradiation, the key contribution of the composite is that CdS has the capability to adsorb visible light and UiO-66 provides a large surface area to disperse the CdS on the MOF surface, so that providing more adsorption sites and photocatalytic reaction centers. ZnIn₂S₄@NH₂-MIL-125(Ti) nanocomposites were obtained by a simple solvothermal method and ZnIn₂S₄ nanosheets were also highly dispersed on the surface of NH₂-MIL-125 (Ti) MOF [298]. The composite displayed higher photocatalytic performance towards H₂ production and process stability during the photocatalytic reactions under visible light irradiation. In addition, the g-C₃N₄/MOF (Fig. 26) heterojunctions that were synthesized by combined MOFs (UiO-66) also displayed outstanding photocatalytic performance toward H₂ production, as well as CO₂ reduction and organic pollutants degradation [299]. Interestingly, crystalline and porous covalent organic frameworks (COFs) and metal-organic frameworks (MOFs) materials are amazing combinations in the field of photocatalytic H₂ evolution. Zhang *et al.* [300] have successfully synthesized MOF/COF (Fig. 27) hybrid materials with high surface area, porous framework and high crystallinity by integrating COF (TpPa-1-COF) with stable MOF (NH₂-UiO-66). Especially, the resulting NH₂-UiO-66/TpPa-1-COF (4:6) exhibits excellent photocatalytic H₂ production rate of 23.41 mmol·g⁻¹·h⁻¹. This design will provide a new path to construct efficient photocatalysts for hydrogen evolution.

MOF-derived metal sulfides can also be well used as cocata-

lysts for photocatalysts. Kumar *et al.* [301] have incorporated MOF-derived hollow structure of Co₄S₃ with CdS particles (Fig.

Fig. 26. (a) Schematic illustration of decorating g-C₃N₄ on UiO-66 octahedrons via annealing process. Increasing the g-C₃N₄ amount leads to higher coverage of g-C₃N₄ on UiO-66 octahedrons. SEM images of (b) UiO-66, (c) UG-10 and (d) UG-50. (e) XRD patterns of g-C₃N₄, UiO-66, UG-10, UG-30 and UG-50 hybrid photocatalysts. (f) The histogram showing the H₂ production rate over UG-x samples (x = 10, 30 and 50). The H₂ production rate was taken from the first 4 h photocatalytic reaction. The H₂ production rate over pristine UiO-66 and g-C₃N₄ was also included for comparison. The inset shows the long term H₂ production over UG-50 sample. (g) The stable state PL spectra of UG-x (x = 10, 30 and 50). (h) The schematic illustration of possible mechanism. From Ref. [299].

Fig. 27. (a) Schematic illustration of the synthesis of $\text{NH}_2\text{-UiO-66/TpPa-1-COF}$ hybrid material; (b) Mechanism schematic of $\text{NH}_2\text{-UiO-66/TpPa-1-COF}$ (4:6) hybrid material. From Ref. [300].

28) via a facile wet chemical method. The optimized $\text{Co}_4\text{S}_3/\text{CdS}$ composites exhibited superior photocatalytic performance and the H_2 evolution rate is $12,360 \mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$. The high catalytic performance can be ascribed to the abundant active sites and onion slice-type hollow structure in MOF-derived Co_4S_3 , which were beneficial for effective separation and transfer of photo-induced charge carriers and boosting the surface shuttling properties.

Metal phosphide has been considered to be the most interesting co-catalysts with unique charging nature (positive charged in metal and negative charged in phosphorous [302,303] for water splitting, especially for HER. Xu *et al.* [304] have constructed $\text{Fe}_2\text{P}/\text{Ni}_2\text{P}$ -modified $\text{g-C}_3\text{N}_4$ photocatalysts, in which the C, N co-doped $\text{Fe}_2\text{P}/\text{Ni}_2\text{P}$ cocatalyst was derived from $\text{NH}_2\text{-MIL-101(Fe)}/\text{Ni(OH)}_2$. The $\text{g-C}_3\text{N}_4$ nanosheets were deposited on the surface of Ni(OH)_2 anchored $\text{NH}_2\text{-MIL-101(Fe)}$ MOF matrix and then were phosphidized. The photocatalyst showed excellent H_2 evolution rate of $13.81 \text{ mmol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$, which was contributed to the hollow polyhedrons structure that facilitated the efficient charges separation and transfer

between the interface of $\text{g-C}_3\text{N}_4$, $\text{CN}/\text{Fe}_2\text{P}$ and Ni_2P . Kumar *et al.* [305] also utilized nickel phosphide (Ni_2P) as cocatalysts to modify CdS , which is derived from metal-organic framework (Ni-MOF) (Fig. 29). The optimized composite material exhibited better photocatalytic activity than Pt loaded CdS .

Metal oxide nanostructures are considered to be the most important photocatalysts due to its low cost, low toxicity and high stability. Lin's group [20] have developed a system of $\text{Fe}_2\text{O}_3/\text{TiO}_2$ (Fig. 30) with MIL-101(Fe) as template and Fe precursor and then calcined in air to decompose the core. This material shows interesting photophysical performance due to its ability to split water under visible light irradiation. In addition, the MOF templating synthesis procedure can be well modulated by modified varying the MOF and coating materials. Yao's group [306] also incorporated small amounts of uniform GO in MOF templated iron oxide ($\alpha\text{-Fe}_2\text{O}_3$ and $\gamma\text{-Fe}_2\text{O}_3$), the heterojunction resulted in highly promoted photo-induced charge separation and transportation for synergistic effect between the reduced graphene and iron oxide. As a consequence, the as-prepared maghemite-carbonaceous composite showed

Fig. 28. Schematic representation of material preparation: synthesis of Co-MOFs, synthesis of cobalt sulfide derived from Co-metal-organic framework and synthesis of $\text{Co}_4\text{S}_3/\text{CdS}$ composite. From Ref. [301].

Fig. 29. Synthesis of Ni-BTC MOFs, nickel phosphides derived from Ni-BTC metal-organic frameworks, and $\text{Ni}_2\text{P}/\text{CdS}$ composite. From Ref. [305].

Table 11

Summary of MOF-based cocatalysts for photocatalytic HER in recent publications.

Photocatalyst	Irradiation	Solvent	H ₂ evolution rate	Stability test	Ref.
CdS/MIL-101(Cr)	Visible-light	Lactic acid	1.1 mmol·h ⁻¹ ·g ⁻¹	5 h	[308]
1TMoS ₂ /MIL-125-NH ₂	UV-Vis light	N/A	2.094 mmol·h ⁻¹ ·g ⁻¹	72 h	[309]
g-C ₃ N ₄ /UiO-66/Ni ₂ P	5 W LED white light	TEOA	0.2 mmol·h ⁻¹ ·g ⁻¹	20 h	[312]
Ni ₂ P/CdS	Simulated solar	Lactic acid	33.48 mmol·h ⁻¹ ·g ⁻¹	25 h	[305]
MoS ₂ @TiO ₂	UV-Vis light	TEOA	10.046 mmol·h ⁻¹ ·g ⁻¹	30 h	[310]
Cu ₂ O@C ₃ N	UV-Vis light	EDTA	0.018 mmol·27 h ⁻¹ ·g ⁻¹	N/A	[311]
Co ₃ O ₄ /TiO ₂	UV-Vis light	SED	7 mmol·h ⁻¹ ·g ⁻¹	N/A	[313]
MoS ₂ -ZnS	UV-Vis light	TEOA	0.411 mmol·h ⁻¹ ·g ⁻¹	N/A	[314]
Ni _x Mo _{1-x} S ₂ /MOF-5@g-C ₃ N ₄	UV-Vis light	TEOA	0.319 mmol·h ⁻¹ ·g ⁻¹	5 h	[315]
Co ₄ S ₃ /CdS	UV-Vis light	Lactic acid	12.36 mmol·h ⁻¹ ·g ⁻¹	65 h	[301]

an ideal photocatalytic H₂ evolution rate of 318 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$.

Porous Pt-doped heterojunction, Pt-ZnO-Co₃O₄, Pt-ZnS-CoS' and Pt-Zn₃P₂-CoP (Fig. 31) can be obtained *via* facile oxidation, sulfurization and phosphorization treatment of ZnCo-zeolitic-imidazolate-framework (ZnCo-ZIF) and then doped Pt nanoparticles. The composite exhibits excellent photocatalytic performance towards H₂ production by water splitting, which is attributed to the porous structures of the MOF

materials that can significantly enhance the light adsorption and afford abundant active sites. In addition, suitable band matching in heterojunctions facilitates the efficient photo-induced charge separation and transportation [307].

Apart from the abovementioned works, Table 11 summarizes other recently published MOF-based photocatalysts for photocatalytic HER, including pristine MOF-based materials, CdS/MIL-101(Cr) [308], 1TMoS₂/MIL-125-NH₂ [309], MOF-derived materials, MoS₂@TiO₂ [310], Cu₂O@C₃N [311], etc.

7. Summary and outlook

In the past decade, semiconductor-based photocatalytic hydrogen production has grown tremendously to be more efficient in converting solar energy into chemical energy. A high performance photocatalytic H₂ evolution reaction generally requires high charge separation and effectually charge transportation, which are necessary for loading cocatalysts. In this review, we summarized the research progress on several cocatalysts for photocatalytic hydrogen production in the past decade. It has been proved that integrating these cocatalysts with semiconductors to construct specific structures can significantly improve the photocatalytic activity for H₂ evolution. For comparison, TableS 2–11 summarize the latest developments in photocatalytic H₂ evolution over various kinds of cocatalysts including single, dual, Z-scheme and MOFs.

The cocatalysts have been extensively investigated in photocatalytic H₂ evolution to rapidly trap electrons from the bulk of the semiconductors, which results in efficient separation of charge carriers and suppressed recombination of e^-h^+ pairs. Additionally, the cocatalysts could supply active sites for water reduction and reduce the surface activation energy to catalyze the surface chemical reactions. Further, the cocatalysts usually possess good electrical conductivity, which could boost efficient transfer of charge carriers.

At present, the cocatalysts used in photocatalytic hydrogen evolution systems has evolved from noble-metals to transition metals and alloys and from single systems to complex systems to enhance the production of H₂ evolution. In the above transitions, researchers have achieved a great progress in the field of photocatalytic hydrogen production *via* water spilling. However, the matching relationship between cocatalysts and photo-

Fig. 30. (a) H₂ produced by Fe₂O₃@TiO₂ in 20/1 v/v H₂O/TEA at various time points over 48 h, with a 420 nm filter. The inset shows the amount of H₂ produced over this time period. (b) UV-vis diffuse reflectance spectra of Fe₂O₃@TiO₂, a physical mixture of Fe₂O₃ and TiO₂, Fe₂O₃ alone, and TiO₂ alone. The inset shows a photograph of dispersions of MIL-101 (1), MIL-101@TiO₂ (2), Fe₂O₃@TiO₂ (3), Fe₂O₃@TiO₂/Pt (4), Fe₂O₃ (5), and TiO₂ (6) in ethanol. (c) MOF-templated synthesis of Fe₂O₃@TiO₂ by coating MIL-101 with TiO₂ followed by calcination, and its use for photocatalytic hydrogen production after depositing Pt particles. From Ref. [20].

Fig. 31. (a) SEM and (b) TEM images of ZnO-Co₃O₄; (c) SEM and (d) TEM images of ZnS-CoS; (e) SEM and (f) TEM images of Zn₃P₂-CoP; TEM images of (g) Pt-ZnO-Co₃O₄, (h) Pt-ZnS-CoS, and (i) Pt-Zn₃P₂-CoP. (j) The schematic illustration of the fabrication of Pt-ZnO-Co₃O₄, Pt-ZnS-CoS, and Pt-Zn₃P₂-CoP photocatalysts. From Ref. [307].

Graphical Abstract

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The roles and mechanism of cocatalysts in photocatalytic water splitting to produce hydrogen

Nan Xiao, Songsong Li, Xuli Li, Lei Ge *, Yangqin Gao, Ning Li
China University of Petroleum

The roles and mechanism of cocatalysts, extended light harvest, enhanced charge carrier separation efficiency and improved stability are summarized to offer a conceptual basis for designing and developing highly efficient photocatalytic H₂-evolution cocatalysts.

catalysts is still needed to be further studied. We believe that with the continuous development of new cocatalysts and the further development of the related theories, the efficiency of solar photocatalytic hydrogen production will continue to increase, and the photocatalytic hydrogen production system will also achieve a greater development.

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光催化分解水制氢反应中助催化剂的作用及机理

肖楠^{a,b}, 李松松^b, 李旭力^b, 戈磊^{a,b,*}, 高旻钦^b, 李宁^b

^a中国石油大学(北京)重质油国家重点实验室, 新能源与材料学院, 北京102249

^b中国石油大学(北京)新能源与材料学院, 材料科学与工程系, 北京1022449

摘要: 近年来, 随着一次能源过度消耗所带来的能源和环境问题日益突出, 开发廉价、可持续的清洁能源备受关注。光催化分解水制氢可利用太阳能普遍率高和几乎免费等特点制取燃烧热值高、燃烧产物无污染的氢气能源。自从1972年日本的Fujishima教授和Honda教授首次发现TiO₂单晶电极光催化分解水可以产生氢气以来, 光催化制氢被认为是实现可持续制氢最有潜力的方法之一。有效地将太阳能转换为化学能的关键是设计高效的电荷分离和运输结构。然而, 现有的大多数半导体光催化剂因缺少活性位点、光生载流子易复合等缺点而无法达到较高的转换效率。因此, 如何提高半导体光催化产氢的转换效率是现阶段面对的重要问题。在众多解决方法中, 助催化剂的引入可以为光催化制氢反应增加活性位点, 促进光生载流子的有效分离, 进而有效地提高半导体光催化产氢速率。本文总结了多种不同类型的助催化剂应用于光催化产氢研究的最新进展, 详细讨论了助催化剂在增强光吸收、提供活性位点、增加催化剂稳定性和促进电荷分离等方面的作用, 阐明了助催化剂在光催化分解水制氢中的反应机理, 同时还提出了光催化制氢的未来研究和预测。

本文将助催化剂分为以下几种类别进行讨论: (1)单一助催化剂, 包括金属/合金、金属氧化物/氢氧化物、金属磷化物、金属硫化物、碳基材料等助催化剂材料; (2)双助催化剂; (3)Z-Scheme助催化剂; (4)MOFs助催化剂。近年来, 助催化剂材料在光催化产氢中应用的发展趋势从当初价格昂贵的贵金属趋于价格相对低廉的非贵金属, 从单一体系趋于更复杂的体系。虽然现阶段关于助催化剂与基底之间的匹配还需要进一步研究, 但我们相信随着技术的发展, 这些问题都可以迎刃而解。希望在不久的将来, 可以精确设计和构建出具有高效光催化产氢活性的催化剂体系, 开发出更多新的可再生清洁能源, 从而缓解能源紧缺和环境恶化等棘手问题。

关键词: 助催化剂; 光催化; 析氢; 电荷分离; 分解水

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*通讯联系人. 电子信箱: gelei08@sina.com

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