



# Recent Advances in Semiconductor Heterojunctions and Z-Schemes for Photocatalytic Hydrogen Generation

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## Abstract

The formation of semiconductor heterojunctions and Z-schemes is still a very prominent and efficient strategy of materials chemists to extend the absorption range of semiconductor combinations. Moreover, the spatial separation of photoexcited charge carriers and thereby the reduction of their recombination ultimately lead to increased photocatalytic activities. The present article reviews recent trends in semiconductor heterojunctions and Z-schemes with a focus on hydrogen generation and water splitting, exhibiting specific needs for charge carrier separation. We also included recent material trends, i.e. 2D/2D combinations, direct Z-schemes, MOFs and COFs, and combinations with upconversion materials.

**Keywords** Charge separation · Heterojunctions · Z-scheme · Photocatalysis · Hydrogen

## 1 Introduction

With an estimated market of 100 million metric tons, hydrogen ( $H_2$ ) is an important basic chemical in industry and technology [1]. The worldwide most important process involving  $H_2$  is the production of ammonia for the production of nitrogen-based fertilisers. Steam reforming of natural gas is by far the most dominant process employed to produce  $H_2$  [2]. The literature describes and labels  $H_2$  cleanness by different colours, the three main being grey, blue, and green. The “colour” of  $H_2$  is determined by the source or additional technology utilised to produce the gas [3]. Since 96% of the overall  $H_2$  is based on fossil fuels and mainly synthesised by steam reforming/water–gas shift reactions, a vast majority of  $H_2$  is considered to be

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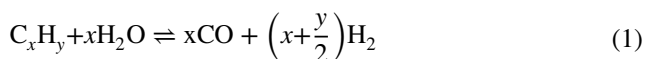
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a polluting type of H<sub>2</sub>, labelled grey H<sub>2</sub> [2–4]. Blue H<sub>2</sub> combines grey H<sub>2</sub> feedstocks with carbon capture and storage (CCS) technologies [4]. Whilst CCS technologies might defer climate change problems and buy time, H<sub>2</sub> production without the emission of greenhouse gases (green H<sub>2</sub>) is considered to be the solution for decarbonising many large-scale chemical synthesis processes [4–6]. Promising technologies like fuel cells, the injection of H<sub>2</sub> in blast furnaces and several other technologies will need further research but rely first and foremost on the large-scale production of green H<sub>2</sub> [7–9]. An example of an environmentally friendly way to produce green H<sub>2</sub> is photocatalytic water splitting. Challenges like low solar-to-H<sub>2</sub> efficiencies as well as rare and expensive co-catalysts are yet to be solved [6]. Based on 50 years of materials research, this field has developed multiple strategies that will be essential to further improve photocatalysts in the future. Recent developments and improvements using two of these strategies—namely heterojunctions and Z-schemes—will be summarised in this review.

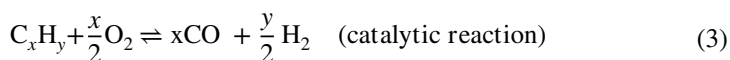
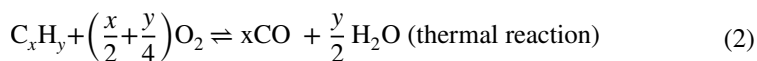
## 2 State of Research

### 2.1 H<sub>2</sub> Production and H<sub>2</sub> Economy

H<sub>2</sub> can be produced from a wide range of resources using different feedstocks, pathways and technologies, including renewable resources and fossil fuels [3]. Steam reforming is by far the most dominant process employed to produce H<sub>2</sub> for industrial purposes. This method uses a mix of light hydrocarbons with methane being the dominant one. In the case of natural gas, a desulphurisation step is necessary to convert sulphur into H<sub>2</sub>S, which is then adsorbed and removed. For the actual steam reforming, the gas mix of high-temperature steam and desulphurised feed is exposed to a nickel-based catalyst at high pressure. Depending on the process design, temperature ranges of 750–900 °C and pressure ranges of 3–25 bar are used to convert hydrocarbon and steam into synthesis gas consisting of a mix of CO and H<sub>2</sub> [2]:



The steam-reforming reaction (reaction (1)) for the formation of CO and H<sub>2</sub> is endothermic and therefore requires heat. External heating can be avoided or reduced by using a compact design and the exothermic partial oxidation of the feedstock (reaction (2) and (3)) [2]:



However, efficient heat recovery is essential to enable an economic operation of the process. The H<sub>2</sub>:CO ratio in the resulting synthesis gas can be adjusted via the

water–gas shift reaction (reaction (4)), which is exothermic for the formation of CO<sub>2</sub> and H<sub>2</sub> and allows lower temperatures than the steam reforming reaction [2].



Depending on the subsequent use, the gas mix is subjected to separation processes like pressure swing adsorption (PSA), membrane processes, or methanation of left-over CO.

According to reactions (1) and (4), steam reforming can produce up to four units of H<sub>2</sub> gas for each unit of methane. While natural gas is the most common feedstock for steam reforming, other fossil fuels can usually be converted to lighter hydrocarbons. Gasification can be applied to all solid and liquid carbon-containing feedstocks, including biomass. As a result, the gasification of coal has a significant contribution to global greenhouse gas emissions considering the coal-based production of ammonia and methanol [2, 10].

Only a small amount of the overall produced H<sub>2</sub> stems from electrochemical processes. Nonetheless, electrolysis might be a key technology since it allows the production of pure H<sub>2</sub> from water while using electrical energy from renewable energy sources like wind power or photovoltaic. One distinguishes between alkaline, PEM (proton-exchange membrane), and high-temperature electrolysis. Alkaline electrolysis is a well-established production method reaching high overall efficiencies in the order of 70–80%. At temperatures between 60 and 90 °C, H<sub>2</sub> is co-generated with oxygen (O<sub>2</sub>) [2]. Water splitting electrolytic processes are closely related to the respective fuel cell technology. High-temperature electrolysis, for example, uses the principles of inverted solid oxide fuel cells (SOFC). The energy required for the process is partially supplied as heat, leading to a lower electricity consumption compared to the other mentioned processes [2, 11].

In comparison, the price of electricity and natural gas largely defines the competitiveness between steam reforming and electrolysis. The production of H<sub>2</sub> via alkaline electrolysis is often considerably more expensive than the production by steam reforming [2, 11].

While electrolysis is a well-known method to purposely produce H<sub>2</sub>, other chemical or electrolytic processes produce H<sub>2</sub> as a side product. One example is the electrolytic production of chlorine. Common processes use membrane or diaphragm cells and produce H<sub>2</sub> at the cathode. In this context, the co-production of H<sub>2</sub> is often seen as a waste of energy and a safety hazard. Therefore, present developments aim at process modifications that reduce or eliminate H<sub>2</sub> co-production. O<sub>2</sub> depolarised cathodes are, for example, used since the beginning of this millennium. Here, O<sub>2</sub> is reduced together with water to hydroxide ions, which enables a reduction in cell voltages of up to 30% [2, 12, 13].

H<sub>2</sub> is used for fertiliser production, petrochemical refining, metal work, food processing, power generator cooling in power plants, and semiconductor manufacturing [3]. Hence, H<sub>2</sub> is a basic substance for many industrial processes in the twenty-first century. Additionally, the term “H<sub>2</sub> economy” is often used to describe ideas and challenges about a future economy heavily relying on H<sub>2</sub> [4, 14–17]. The concept of H<sub>2</sub> economy was originally created by John Bockris in the 1970s. It described a

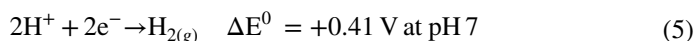
vision in which  $H_2$  is produced via water electrolysis, transported via pipelines and eventually converted back to electricity in fuel cells [18]. The idea of using  $H_2$  as a fuel dates back to the beginnings of fuel cell developments by W.R. Grove in 1839. Even science fiction writings from the nineteenth century discussed  $H_2$ /water as an energy source (Jules Verne, “The Mysterious Island”) [14]. Nowadays, there are still different opinions on whether  $H_2$ -based technologies will play a major role in a certain sector or will be outperformed by other technologies. Nevertheless, recurring statements about the future role of  $H_2$  and its production are found in literature. While publications from the early 2000s still partially discuss a  $H_2$  economy based on fossil fuels, nuclear reactors and renewable energy sources, publications from the last decade focus mainly on green  $H_2$  [4, 14]. Green  $H_2$  is seen as a solution to decarbonise many large-scale chemical synthesis processes [4]. It is also seen as an energy carrier and a storage medium for the intermittency of many renewable resources [15]. In this context, decentralisation and microgrids are discussed [4]. At the same time,  $H_2$  is often no longer evaluated in isolation but in conjunction with various alternatives. The term “ $H_2$  economy” may therefore be misleading but illustrates that (green)  $H_2$  will play an important role to enable a society supported entirely by renewable energy [4, 14–17].

## 2.2 Photocatalytic Water Splitting

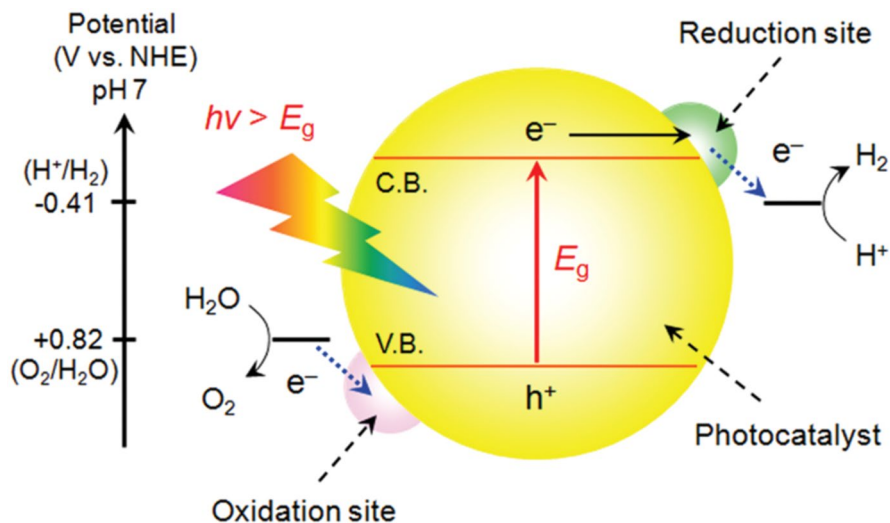
With growing attention being paid to reducing greenhouse gas emissions, renewable resources rapidly gain potential as a clean source to produce renewable  $H_2$  as a carbon-emissions-free energy carrier [3]. Solar energy can be seen as the most abundant renewable energy source. Therefore,  $H_2$  production from solar energy is considered to be a promising solution for sustainable energy [19].

Semiconductor materials can convert sunlight energy into chemical energy by catalysing the formation of chemical bonds. Thus, generating  $H_2$  and  $O_2$  by performing photocatalytic water splitting is intensely investigated [20–23]. A semiconductor absorbs sunlight when the energy of the incident photon is equal to or larger than the band gap ( $E_g$ ). An electron is thereby excited from the valence band (VB) into the conduction band (CB) of the semiconductor (Fig. 1). Together with the remaining hole in the VB, an exciton is formed [20].

The photoexcited electron can be used to reduce protons to  $H_2$  if the CB minimum has a more negative potential than the electrochemical potential of reaction (5). Similarly, the photogenerated hole in the VB can perform the electrochemical oxidation of water to  $O_2$  if the maximum of the VB is more positive than the electrochemical potential of reaction (6) [20, 23]:



Compared to the  $H_2$  evolution reaction (HER), the  $O_2$  evolution reaction (OER) is comparatively more complex because this reaction requires a four-electron oxidation



**Fig. 1** Schematic energy diagram of photocatalytic water splitting; oxidation site and reduction site might refer to co-catalysts discussed in the next section. Reprinted with permission from [24] © 2010 American Chemical Society

step combined with the removal of four protons to form a relatively weak oxygen–oxygen bond [25]. The overall water splitting reaction is an uphill reaction with a positive shift in Gibbs free energy (+237 kJ/mol). Therefore, water splitting is thermodynamically a photosynthetic reaction [26]. In theory, the minimum band gap energy ( $E_g$ ) of the semiconductor should be 1.23 eV (approximately equivalent to a wavelength of 1000 nm). Due to energy losses, kinetic overpotentials are needed; thus, the  $E_g$  of a single semiconductor should lie in the range of 1.5–2.5 eV [23].

It is known that the CB potential of a semiconductor material in aqueous solutions usually exhibits a pH dependence according to the following equation [23]:

$$E_{CB} = E_{CB}^0(\text{pH } 0) - 0.059 \text{ pH}$$

Since the redox potentials of water show the same linear dependence with a slope of 0.059 V per pH, band edge positions of the semiconductor usually cannot be shifted relative to the redox potentials of water by changing the pH value [23].

## 2.3 Strategies for the Improvement of Photocatalysts

### 2.3.1 Single Absorber, Co-catalysts and Sacrificial Agents

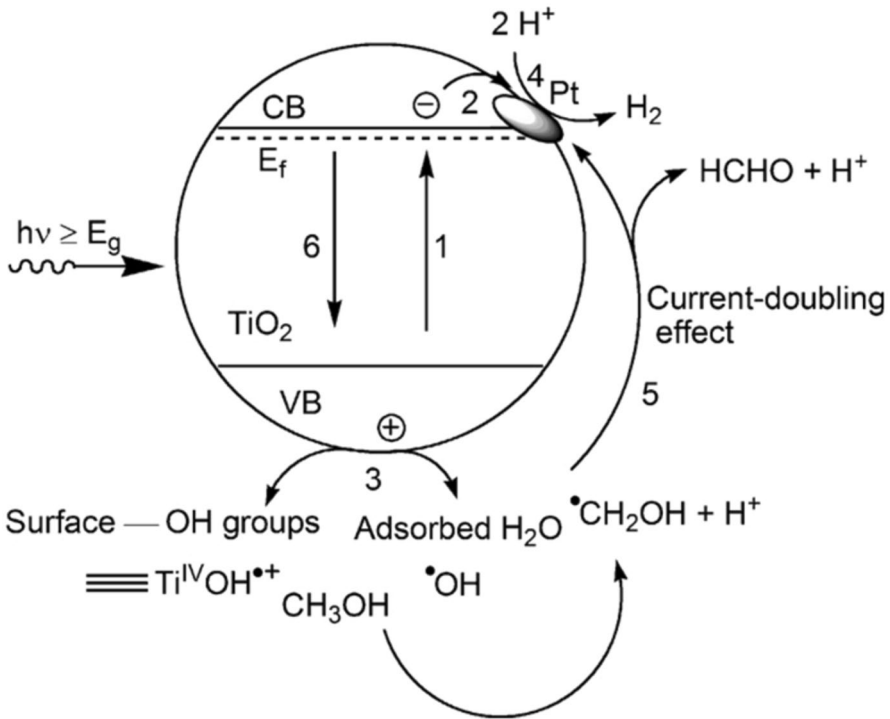
So far, many semiconductors have been found to be capable of producing  $\text{H}_2$  or  $\text{O}_2$  under light irradiation [23, 27, 28]. Thereby, metal oxide semiconductors can usually be divided into two classes: materials containing metal cations with  $d^0$  configuration and those with  $d^{10}$  configuration [6, 23]. Many recent research activities are focused on composite materials, but single absorbers are still investigated. This

is due to newly discovered materials or known materials that are back in the focus of research. One example is  $\text{SrTiO}_3$  which experienced a renaissance due to new insights into defect engineering and the electronic structure of doped  $\text{SrTiO}_3$  [6, 29–31].

Charge carrier recombination limits photocatalytic efficiencies in many photocatalytic systems but especially for undecorated semiconductors used as photocatalysts. Increasing the crystallinity of a photocatalyst can reduce recombination. Defects and grain boundaries are related to interband and surface states, which act as traps for holes. Therefore, increasing the crystallinity can result in higher photocatalytic efficiencies [20]. Another possibility to prevent charge carrier recombination is charge separation. One popular strategy is the use of co-catalysts often applied as nanoparticles on the surface of a semiconductor photocatalyst. The Fermi energy of the metal nanoparticle is usually lower than that of the semiconductor, facilitating electron transfer from the semiconductor to the metal via a Schottky contact [20]. Usually noble metal nanoparticles such as rhodium, palladium, platinum or gold are used. Noble metals serve as electron sinks, thus spatially separating the electron from the photoexcited hole in VB of the semiconductor [20, 32]. Besides noble metals as co-catalysts for the reduction reaction, other materials like metal oxides ( $\text{RuO}_2$ ,  $\text{NiO}$ ,  $\text{CuO/Cr}_2\text{O}_3$ ,  $\text{Rh}_{2-y}\text{Cr}_y\text{O}_3$ ), metal sulphides ( $\text{MoS}_2$ ) and molecular co-catalysts have been investigated [20, 32–35]. For the oxidation reaction, metal oxides such as  $\text{RuO}_2$  and  $\text{IrO}_2$  are used. Efforts are being made to use more earth-abundant alternatives for both the reduction and the oxidation reaction [20, 32]. Charge carrier separation due to co-catalysts can also stabilise certain photocatalysts since some sulphides, oxysulphides, oxynitrides and nitride semiconductors are known for their photoinstability, which is usually due to photocorrosion. Therefore, loading of oxidation cocatalysts like PdS can protect semiconductors that tend to be oxidised by photogenerated holes [32, 36].

As already mentioned, the reduction and oxidation of water is a complex multi-step reaction involving four electrons. Thus, photocatalytic water splitting is a rather inefficient process and far away from large-scale industrial applications. Using electron donors can improve the  $\text{H}_2$  production as holes are scavenged by these molecules. Additionally, charge carrier recombination can be reduced and the back reaction to water is suppressed because  $\text{O}_2$  is not produced [37]. Various organic and inorganic compounds (alcohols, organic acids, hydrocarbons, sulphides and sulphites) are being employed as hole scavengers/electron donors [28, 37]. Methanol is one of the most frequently used sacrificial agents. Nonetheless, the application of methanol is highly debatable for environmental reasons even if the substance is derived from biomass. Furthermore, molecular  $\text{H}_2$  formation in systems using sacrificial agents should not be called water splitting. The term water splitting should only be used when pure water is used as solvent and reactant, without any additional reagents [6]. Acting as an electron donor, methanol reacts irreversibly with the photogenerated VB holes (Fig. 2) [37]. In the overall methanol decomposition reaction (not shown in Fig. 2), methanol can be stepwise oxidised to carbon dioxide [38].

Similarly, sacrificial electron acceptors can be used to support the oxidation of water. Silver cations,  $\text{Ag}^+$ , are employed by a vast majority of research groups. The photocatalytic formation of molecular  $\text{O}_2$  is accompanied by the reduction of  $\text{Ag}^+$



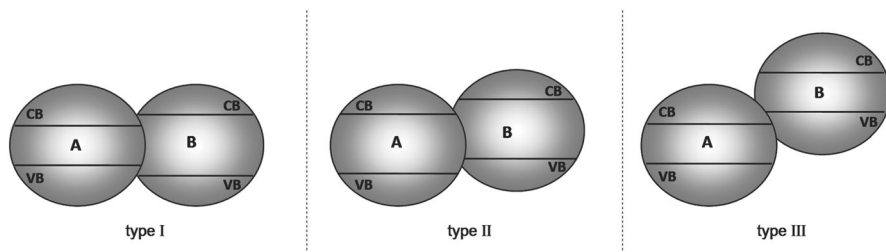
**Fig. 2** Schematic representing the proposed steps for the photocatalytic molecular H<sub>2</sub> production from aqueous methanol solution, (1) photogeneration of charge carriers, e<sup>-</sup> and h<sup>+</sup>; (2) trapping of e<sup>-</sup> by Pt islands; (3) first oxidation step of CH<sub>3</sub>OH by either trapped hole or hydroxyl radical,  $\cdot OH$ ; (4) reduction of H<sup>+</sup>; (5) formation of HCHO through e<sup>-</sup> injection into the conduction band of TiO<sub>2</sub> or to the Pt islands (current-doubling); (6) recombination channel. Reprinted with permission from [39] © 2011 Elsevier

and thereby accompanied by the deposition of metallic silver nanocontacts. The optical changes and changes in catalytic activity arising from this deposition should always be discussed [37].

### 2.3.2 Heterojunctions

Key issues for improving photocatalytic activity are improved light absorption, high crystallinity, large surface areas, and effective charge separation. Furthermore, suitable band positions are needed, as well as earth-abundant elements and high chemical stability of the photocatalyst [20]. A composite photocatalyst system consisting of two or more semiconductors allows different favourable properties from each participating compound to be combined, extending the absorption range of the visible spectrum, reducing photoexcited electron hole recombination and increasing the photo-corrosion stability, thus improving water splitting efficiency [40–43].

Heterojunctions formed by two semiconductors can be classified into three different types depending on the band position (Fig. 3).



**Fig. 3** Different types of semiconductor heterojunctions. Reprinted with permission from [20] © 2013 Wiley-VCH

In type I heterojunctions, material A has a smaller band gap than material B. Due to a more negative CB and a more positive VB of material B, holes and electrons transfer from material B to material A. An example of a type I heterojunction is  $\text{TiO}_2/\text{Fe}_2\text{O}_3$  where photogenerated electron and hole flow occurs from  $\text{TiO}_2$  to  $\text{Fe}_2\text{O}_3$  [40, 44, 45]. A type I heterojunction yields therefore no improvement to charge carrier separation and thus, in theory, no improvement in photocatalytic activity. Due to many wide band gap semiconductors known and limitations in valence band and conduction band positions, type I heterojunctions are common when composite materials consist of a small band gap and a wide band gap semiconductor [20, 40, 46].

In type II heterojunctions, the CB position of material B is more negative than that of material A, while material A has a more positive VB position. As a result, electrons and holes transfer in opposite directions, which leads to improved charge carrier separation, reduced recombination probability, increased charge carrier lifetimes, and, in the end, to improved photocatalytic activity. Most of the examples of composite photocatalysts described in the literature are type II heterojunctions. A  $\text{WO}_3/\text{BiVO}_4$  heterojunction is one example of this type of system [20, 40, 47].

In type III heterojunctions the charge carrier transfer is the same as in type II semiconductors, but the band positions are further set off. Due to the band position, these systems are also called broken-gap situations [20]. A BP/ $\text{ReS}_2$  system (BP = black phosphorus) is one example of this type. In general, type III heterojunctions are rather rarely reported but for example discussed for electronic applications [48].

**2.3.2.1 Recent Trends in Heterojunction Photocatalysts** Tremendous efforts have been dedicated to the development of type II heterojunction photocatalysts due to their ability to separate photogenerated electrons and holes. However, in the past few years, a trend towards Z-schemes (next section) can be observed. Broad review articles discussing improvements in heterojunction photocatalysts have usually been written in 2017 or earlier [20, 47, 49, 50]. Recent review articles are rare and heterojunctions are rather discussed in articles that only cover one specific material. However, there are recent trends that are worth mentioning.

Photocatalysts made of 2D materials are of particular interest due to their electrical and optical properties. Type II heterojunctions based on 2D materials have been



designed and studied as efficient photocatalysts theoretically and experimentally [51–55]. Hua et al., for example, reported a 2D  $\text{La}_2\text{Ti}_2\text{O}_7/\text{In}_2\text{S}_3$  type II heterojunction [52]. The intimate contact of the two layers was realised by strong Coulomb static forces due to inverse zeta potentials of both components. The strong interaction between the two layers and the type II heterojunction co-promoted the charge separation, resulting in  $\text{H}_2$  production rates 3.5 times higher than pristine  $\text{In}_2\text{S}_3$  and 18 times higher than the physical mixture of both components [51, 52]. Although type II heterojunctions can separate photoinduced charges efficiently,  $p$ - $n$  heterojunctions can separate the charges even faster with the aid of internal electric fields [51].

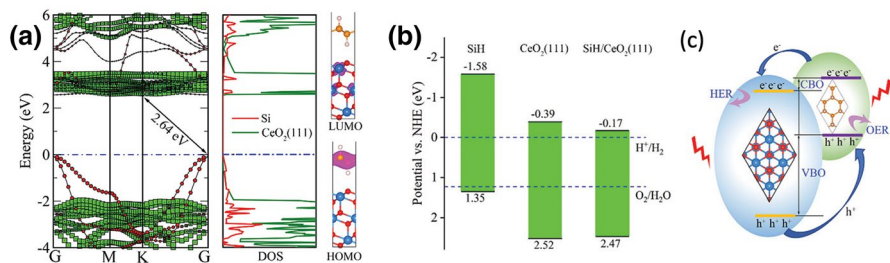
In 2018, Qin et al. constructed a  $p$ - $n$  heterojunction by attaching  $p$ -type  $\text{Cu}_3\text{P}$  nanoparticles to the surface of  $n$ -type  $\text{g-C}_3\text{N}_4$ . The photocatalyst exhibited 95 times higher hydrogen evolution activity from 10 vol% triethanolamine (TEOA) solution than bare  $\text{g-C}_3\text{N}_4$  with an apparent quantum efficiency of 2.6% at 420 nm [56]. Two years later, a  $\text{MoS}_2/\text{Bi}_2\text{O}_3$   $p$ - $n$  heterojunction for overall water splitting was described.  $\text{Bi}_2\text{O}_3$  nanorods were anchored on  $\text{MoS}_2$  microflowers. As a result,  $\text{H}_2$  evolution rates increased by a factor of ten [57].

Qin et al. prepared a 2D/2D  $\text{g-C}_3\text{N}_4/\text{ZnIn}_2\text{S}_4$  heterojunction photocatalyst [58]. The improved photocatalytic performance ( $6.095 \text{ mmol g}^{-1} \text{ h}^{-1}$  using triethanolamine as sacrificial agent) was attributed to the larger contact area and sulphur vacancies that acted as active sites for trapping electrons, which led to elongated charge lifetimes. Furthermore, the vacancies shortened the band gap, enhancing the absorption of visible light. Van der Waals (vdW) forces acted as an intermolecular driving force for charge carrier transport. This was considered to be an alternative route for enhancing  $\text{H}_2$  evolution efficiency since heterojunctions are therefore not restricted by the lattice matching of the component materials [58].

A similar approach was used by Zeng et al. for theoretical description of a  $\text{SiH}/\text{CeO}_2(111)$  type II heterojunction [59]. Both components were chosen because of a  $< 1\%$  lattice mismatch. The staggered band structure (Fig. 4) demonstrates that  $\text{SiH}/\text{CeO}_2(111)$  is a type II vdW heterojunction, which effectively promotes the separation of photogenerated hole-electron pairs and should improve its photocatalytic activity.

The band gap of the  $\text{SiH}/\text{CeO}_2(111)$  heterojunction is 2.64 eV and thus smaller than the band gap of the  $\text{SiH}$  monolayer and  $\text{CeO}_2(111)$ . Light absorption of the composite material should be significantly extended into the visible light wavelength range compared to that of pure  $\text{CeO}_2(111)$ , and oxygen vacancies on the surface of  $\text{CeO}_2(111)$  can also enhance its visible light absorption performance. Moreover, valence band maximum (VBM) and conduction band minimum (CBM) potentials meet the requirements of water splitting (Fig. 4) [59]. Simulations like these might help to synthesise deliberately chosen composite materials in the future.

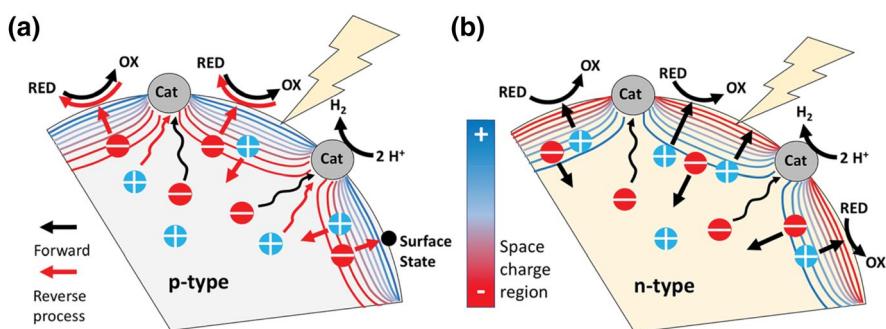
Deep investigations might explain and solve problems that have limited the performance of (heterojunction) photocatalysts in the past. For example, it is known that certain  $p$ -type materials can be used as photocathode materials for  $\text{H}_2$  evolution, but only show low activity as photocatalysts. Zhao et al. investigated  $p$ -type gallium phosphide to better understand this limitation [60].  $\text{H}_2$  evolution rates could be inversely correlated with the standard reduction potential of the used donors (KI,



**Fig. 4** **a** Electronic structure of the SiH/CeO<sub>2</sub>(111) heterojunction. The projected band structure (left panel), partial density of states (PDOS, middle panel), as well as the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) (right panel). The green squares and red circles in the left panel represent the CeO<sub>2</sub>(111) and SiH constituents, respectively. The Fermi level is set to zero. **b** Calculated VBM and CBM potentials versus normal hydrogen electrode (NHE) of SiH, CeO<sub>2</sub>(111), and SiH/CeO<sub>2</sub>(111) heterojunction. The upper and lower blue dashed lines stand for the proton reduction potential (H<sup>+</sup>/H<sub>2</sub>) and O<sub>2</sub> reduction potential (O<sub>2</sub>/H<sub>2</sub>O) for water splitting with values of 0 and 1.23 eV (pH 0), respectively. **c** Schematic diagram of charge transfer between SiH/CeO<sub>2</sub>(111) heterojunction layers. Reprinted with permission from [59] © 2021 Royal Society of Chemistry

K<sub>4</sub>[Fe(CN)<sub>6</sub>], Na<sub>2</sub>SO<sub>3</sub>; more reducing donors give lower rates). Due to a depletion layer at the *p*-type gallium phosphide/electrolyte interface, photogenerated electrons are directed away from the cocatalyst (here Ni<sub>2</sub>P) toward the sacrificial donors and surface states (Fig. 5).

The electrons react with the surface states or with the oxidised form of the sacrificial electron donor (e.g. triiodide is reduced to iodide). As a result, electrons deep inside the *p*-type semiconductor must reach the cocatalyst by diffusion. This is a slow process because electrons are the minority carriers with a short lifetime. According to surface photovoltage measurements, the depletion layer had a barrier



**Fig. 5** Depletion layer and charge carrier movement in illuminated **a** *p*-type and **b** *n*-type semiconductor/co-catalyst configurations in aqueous solutions of a reducing sacrificial agent. Straight arrows indicate drift and wavy arrows indicate diffusion. Minority carriers (holes for *n*-type SC and electrons for *p*-type SC) generated inside the depletion layer are attracted to the surface and away from the proton reduction co-catalyst (Cat). For *p*-type semiconductors this promotes the back reaction (red arrows) and for *n*-type semiconductors the forward reaction (black arrows). Reprinted with permission from [60] © 2021 Royal Society of Chemistry

height of up to 0.45 eV for  $\text{Na}_2\text{SO}_3$ . Findings like these explain basic observations in semiconductor photocatalysis and might play a key role in the development of *p*-type and composite photocatalysts [60].

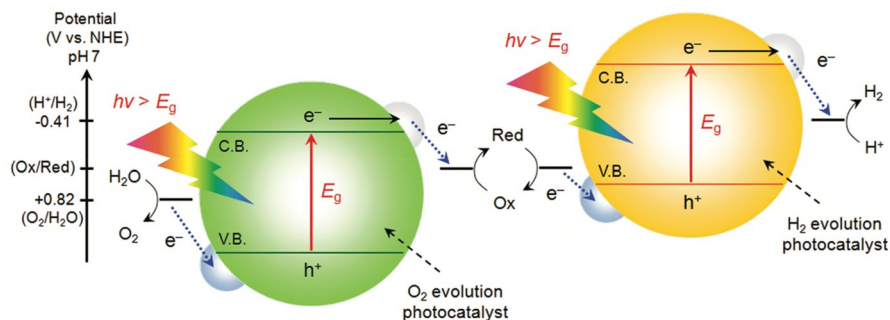
In recent years, the number of examples for heterojunctions with three type of absorber materials has significantly increased. One of the earliest examples for such a triple heterojunction was the combination of anatase- $\text{TiO}_2$ /rutile- $\text{TiO}_2$ / $\text{WO}_3$  [61]. Instead of  $\text{WO}_3$ , Huang et al. used carbon nitride in combination with anatase- $\text{TiO}_2$  and rutile- $\text{TiO}_2$ , increasing the visible light absorption further for  $\text{H}_2$  and  $\text{O}_2$  evolution [62]. Other triple absorber heterojunctions reported including  $\text{TiO}_2$  are for example  $\text{Fe}_2\text{TiO}_5/\text{Fe}_2\text{O}_3/\text{TiO}_2$  [63],  $\text{Ag}_2\text{O}/\text{Fe}_2\text{O}_3/\text{TiO}_2$  [64], and  $\text{Bi}_2\text{O}_3/\text{C}_3\text{N}_4/\text{TiO}_2$  [65].

An interesting example is the combination of  $\text{CoP}/\text{CdS}/\text{WS}_2$ , containing no oxide at all forming a *p-n-n* heterojunction for  $\text{H}_2$  generation [66]. The apparent quantum efficiency at  $\lambda = 420$  nm was reported to be 1.34%; unfortunately, no oxidation product was confirmed in pure water. Containing two other sulphide materials,  $\text{ZnS}/\text{CdS}/\text{TaON}$  heterojunctions were reported to show 14 times higher  $\text{H}_2$  evolution activity (from sulphide/sulphite solutions) compared to  $\text{CdS}/\text{TaON}$ , in the absence of noble-metal co-catalysts and an optimum amount of  $\text{ZnS}$  of 6 wt% [67]. Overall,  $839.6 \mu\text{mol h}^{-1} \text{g}^{-1}$  could be reached under AM 1.5G illumination; no quantum efficiencies were reported. Since  $\text{ZnS}$  has quite a large band gap compared to  $\text{CdS}$  and  $\text{TaON}$ ,  $\text{ZnS}$  might act as a hole sink/co-catalyst rather than an absorber in such a system.  $\text{CdS}$  on the other hand is very prominent for its ideal band gap for water splitting but well-known photocorrosion issues. In combination with  $\text{Bi}_{20}\text{TiO}_{32}$  and  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ , it was reported as ternary heterojunction for  $\text{H}_2$  evolution recently [68]. Photocatalytic  $\text{H}_2$  production (from aqueous methanol solution) of up to  $\text{H}_2$  production  $1890 \mu\text{mol g}^{-1} \text{h}^{-1}$  under 250-W xenon lamp ( $\lambda > 400$  nm) illumination was reported, with strongly increased activities compared to  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ,  $\text{CdS}$ , or  $\text{Bi}_{20}\text{TiO}_{32}/\text{Bi}_4\text{Ti}_3\text{O}_{12}$ . However, not a heterojunction behaviour but a scheme involving a type I bridged coupled Z-scheme system was proposed to explain the observed activities. Z-schemes will be covered in the following section.

### 2.3.3 Z-Schemes

Z-schemes use two different semiconductors and typically a reversible donor/acceptor pair, a so-called shuttle redox mediator (Fig. 6). This system is inspired by natural photosynthesis in green plants, where photosystems I and II harvest 700 and 680-nm photons, respectively [69].

A traditional Z-scheme photocatalyst was first proposed by Bard in 1979 [70]. Since then, redox couple mediated Z-schemes have attracted considerable attention. In contrast to heterojunctions, the semiconductors are usually not in direct contact to each other but electronically coupled via the redox mediator (the next section will concentrate on solid Z-schemes). Thus, semiconductors can be combined that can only perform either water reduction or oxidation due to their band potential [69]. For example,  $\text{WO}_3$ , which does not have the ability to reduce  $\text{H}^+$ , is capable of producing  $\text{O}_2$  from an aqueous solution containing appropriate electron acceptors under

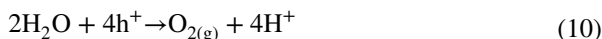
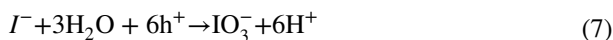


**Fig. 6** Schematic energy diagram of photocatalytic water splitting for a two-step photoexcitation system. Reprinted with permission from [24] © 2010 American Chemical Society

visible light and acts as an effective building block for  $O_2$  evolution in Z-scheme water splitting [69].

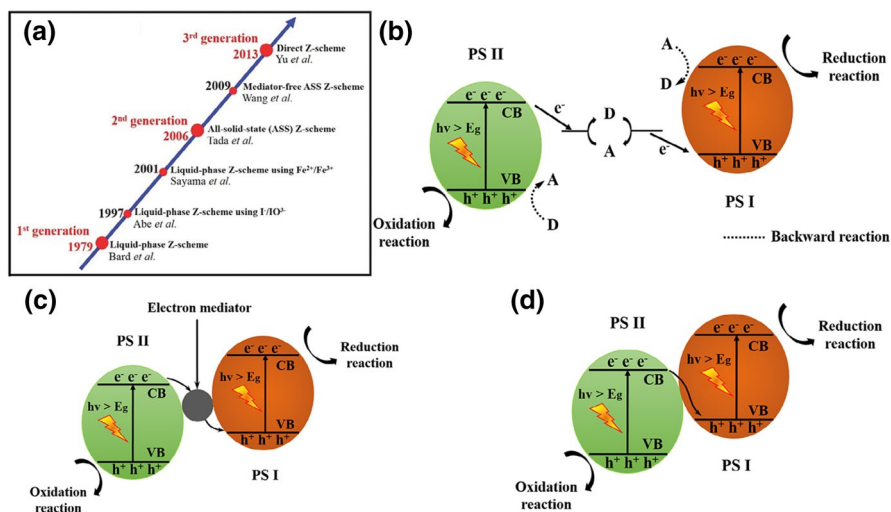
The redox mediator is an essential component in the Z-scheme water splitting system because it transfers electrons from an  $O_2$  evolution photocatalyst to a  $H_2$  evolution catalyst. Therefore, the flow of charge carriers is reversed in Z-schemes compared to the above mentioned heterojunctions of two semiconductors [6]. The process leads to spatially separated, high-redox-capacity electrons and holes in the  $H_2$  evolving photocatalyst and the  $O_2$  evolving photocatalyst, respectively.

The most employed redox couples are  $Fe^{3+}/Fe^{2+}$  and  $IO_3^-/I^-$ , which both have unique characters affecting the efficiency of Z-scheme water splitting. The following reactions describe a water splitting system using the  $IO_3^-/I^-$  couple as a mediator [69]:



Taking the  $IO_3^-/I^-$  couple, there is a dependence of activity on the concentration of the redox mediator. With increasing the concentration of  $I^-$ , the efficiency of the  $I^-$  oxidation by VB holes in a  $H_2$  evolution photocatalyst is enhanced, while the oxidation reaction in the  $O_2$  evolution site is suppressed because of competitive oxidation of  $I^-$  by photogenerated holes in the VB of the  $O_2$  evolution photocatalyst. Hence, using NaI as an initiator, there is a volcano-type trend between the concentration of NaI and Z-scheme activity in most cases [69, 71–73].

An  $Fe^{2+}/Fe^{3+}$  redox system is limited to acidic conditions because iron ions undergo precipitation (iron hydroxide) in neutral and basic conditions. The



**Fig. 7** **a** The roadmap of the evolution of the Z-scheme photocatalytic system from the first generation to the third generation. **b** Schematic illustration of electron transfer in a traditional Z-scheme photocatalytic system (PS I-A/D-PS II), where A and D represent the electron acceptor and donor, respectively. **c** Schematic illustration of electron transfer in an all-solid-state Z-scheme photocatalytic system with an electron mediator (PS I-EM-PS II), where EM represents the electron mediator that provides an electron transport channel. **d** Schematic illustration of electron transfer in a direct Z-scheme photocatalytic system without any electron mediator (PS I-PS II). Reprinted with permission from [78] © 2020 Wiley-VCH

IO<sub>3</sub><sup>-</sup>/I<sup>-</sup> couple can be employed in a wider range of pH values but also shows a pH dependence [69].

Apart from their role of shuttling electrons, redox mediators show multiple side effects in Z-scheme water splitting. One example is that I<sup>-</sup> ions apparently undergo adsorption onto the surface of Pt, used as a co-catalyst, forming an iodine layer which suppresses the backward reaction of water formation [69, 74]. A similar behaviour was reported for the Fe<sup>2+</sup>/Fe<sup>3+</sup> redox mediator. Water formation and the reduction of Fe<sup>3+</sup> are efficiently suppressed by adsorption of [Fe(SO<sub>4</sub>)(H<sub>2</sub>O)<sub>5</sub>]<sup>+</sup> and/or [Fe(OH)(H<sub>2</sub>O)<sub>5</sub>]<sup>2+</sup> on Pt surfaces [69, 75]. Although the backward reaction of water formation on Pt is not completely suppressed by adsorbed iron species, further studies revealed that Ru does not suffer from water formation. Using Ru as a co-catalyst, the reduction of Fe<sup>3+</sup> by H<sub>2</sub> and the oxidation of Fe<sup>2+</sup> by O<sub>2</sub> are also suppressed [69, 76].

However, traditional Z-scheme photocatalysts have further drawbacks. Noteworthy are light-shielding effects by the redox mediator, slow charge carrier transfer rates limited by diffusion of ion pairs, and, as already mentioned, limitations because of pH sensitivity. Moreover, redox mediators are often unstable and tend to deactivate, which results in decreased reaction rates [77]. In addition, the photogenerated electrons in the CB of the photocatalysts I (PS I) and holes in the VB of photocatalysts II (PS II) with strong redox ability can also be consumed by the redox mediator (Fig. 7). This is called backward reaction and again has a negative impact on the photocatalysis [78, 79]. Several attempts have been made

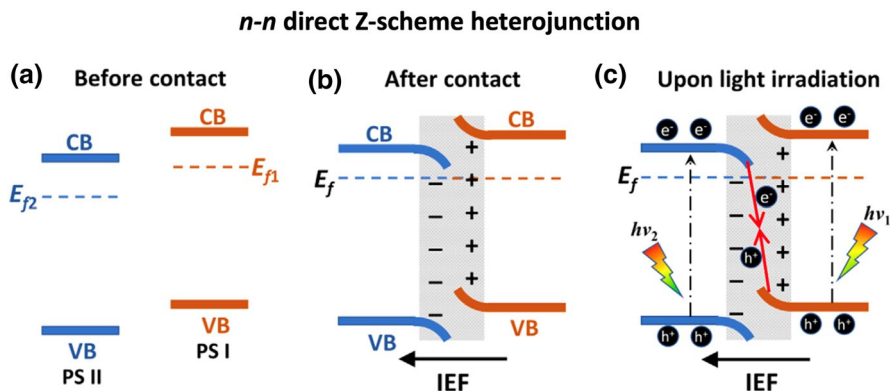
to overcome these drawbacks. The historical evolution of Z-scheme photocatalysts is shown in Fig. 7.

**2.3.3.1 All-Solid-State Z-Schemes, Direct Z-Schemes** In 2006, Tada et al. proposed the concept of an all-solid-state Z-scheme heterojunction. The CdS-Au-TiO<sub>2</sub> system used gold as a solid-state electron mediator [80]. As shown in Fig. 7c, the photocatalytic system consists of two semiconductors and a solid-state electron mediator between two semiconductors with an intimate contact. The intimate contact between the mediator and both semiconductors favours the interfacial charge carrier transfer [77, 78]. Commonly used solid-state electron mediators are noble metal (such as Au, Ag, Cu, Pt) shells/nanoparticles and graphene and carbon nanotubes. When the two semiconductors are excited by light irradiation, the photogenerated electrons in the CB of PS II can recombine with the photogenerated holes in the VB of PS I with the help of the electron mediator because of low contact resistances with both semiconductors [78, 81].

All-solid-state Z-schemes eliminate the aforementioned backward reactions and the long-term stability issues of redox mediators in traditional Z-schemes. Furthermore, it can be applied in liquid and gas phases because of the solid conductor [77, 78]. Light-shielding effects can be reduced compared to traditional Z-scheme photocatalytic systems, but effective light utilisation might be hindered by light absorption from the electron mediator. These conductors might also act as co-catalysts instead of charge-transfer shuttles. Therefore, intimate contact and carefully designed sandwiched structures are necessary, which is synthetically challenging. Additionally, the use of rare and noble metals limits practical applications of all-solid-state Z-schemes [77, 78, 82].

In 2013, a direct Z-scheme heterojunction (g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub>) without using any electron mediator was reported by Yu et al. [83]. In contrast to the traditional Z-scheme system, the backward reactions were significantly suppressed because of the absence of redox mediators. The shielding effect caused by redox mediators/charge carrier mediators can also be reduced [77].

Analogous to the all-solid-state Z-scheme, the directly contacted semiconductors are both excited by light irradiation, and the photogenerated electrons in the CB of PS II can recombine with the holes in the VB of PS I. As a result, the photogenerated electrons in CB of PS I and photogenerated holes in the VB of PS II are spatially separated and maintain their strong redox capability [78]. A work function difference between the two semiconductors is a pre-requisite for the Z-scheme charge transfer mode. PS I must have higher CB and VB positions and a smaller work function (higher Fermi level) than PS II. When both semiconductors are in contact, an electron transfer from PS I to PS II takes place due to Fermi level equilibration (c.f. the *n-n* type direct Z-scheme in Fig. 8). Thus, the PS I side is positively charged, whereas the PS II side is negatively charged. Hence, an internal electric field (IEF) as well as band bending occurs. PS II energy band edges bend downwards because the accumulation of electrons and PS I energy band edges bends upwards because of decreased electron density [77, 82]. The IEF, the extra potential barrier induced by band bending, and Coulomb repulsion



**Fig. 8** Schematic of *n-n* type heterojunction: **a** before contact, **b** after contact, and **c** formation of direct Z-scheme charge transfer upon light irradiation.  $E_f$  and IEF stand for Fermi level and internal electric field, respectively. Reprinted with permission from [82] © 2021 Elsevier

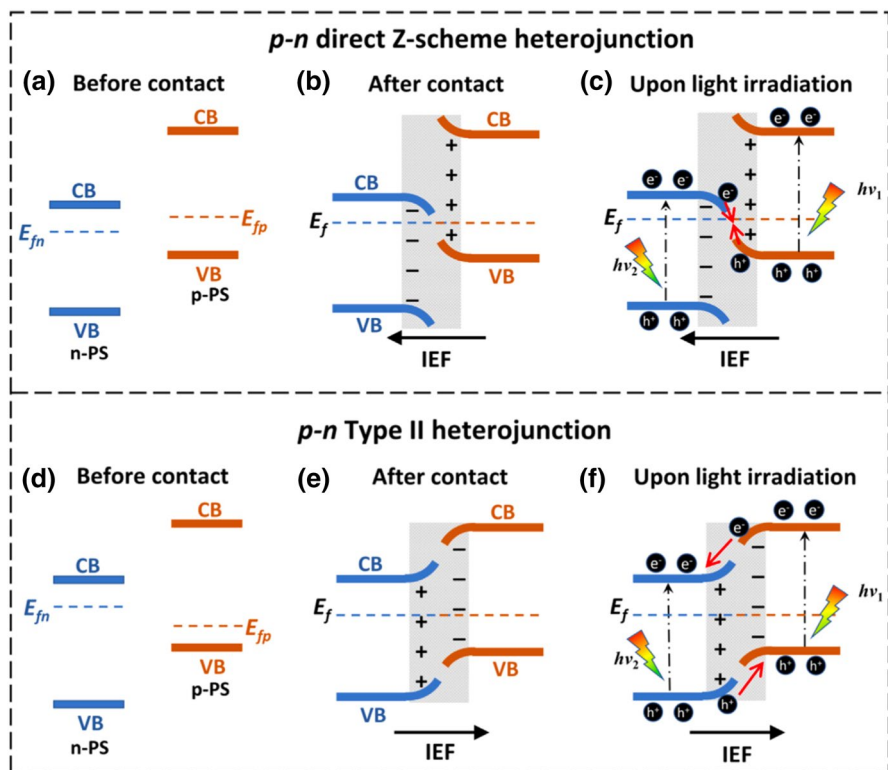
hinder photogenerated electrons from transferring from PS I CB to PS II CB. This also applies to the photogenerated holes in PS II VB [77].

A similar process occurs in the construction of a *p-n* type direct Z-scheme. However, when the Fermi level of a *p*-type semiconductor (*p*-PS) is lower than that of an *n*-type semiconductor (*n*-PS), a type II heterojunction is formed. The energy band edges are bent in an inverted fashion at their interface (Fig. 9). Therefore, under light irradiation, photogenerated electrons move from *p*-PS to *n*-PS and holes in the opposite way driven by the IEF. The requirement for Fermi levels is easily met in *n-n* type heterojunctions but very hard to fulfil in *p-n* heterojunctions because of the huge band offset (Fig. 9). Hence, most direct Z-schemes are made of *n-n* heterojunctions [82].

Known *p-n* type direct Z-schemes are for example  $\text{CuInS}_2\text{-WO}_3$ ,  $\text{CuAl}_2\text{O}_4\text{-Bi}_2\text{WO}_6$ , and  $\text{Cu}_2\text{O-TiO}_2$  [82, 84–86].

The band alignment configuration in Z-scheme heterojunctions is similar to that of type II heterojunctions, but their charge transfer mechanisms are different. To investigate the exact charge transfer process, various methods can and should be used. Several methods have been reported: self-confirmation by photocatalytic reaction products and radical species; selective photodeposition of a noble metal; in situ irradiated x-ray photoelectron spectroscopy (XPS) analysis; surface photovoltage (SPV) technique; time-resolved diffuse reflectance (TDR) spectroscopic analysis [78]. Sometimes, photo-corrosion effects are reduced, which can be a hint for a Z-scheme mechanism (e.g. in composite materials containing CdS) [87].

The investigation of charge transfer processes is essential to describe the photocatalytic activity in a given system and to improve photocatalysts in the future. As mentioned before, heterojunctions and Z-schemes can show undesired charge transfers and backward reactions. We would like to mention that the term S-scheme (step scheme) was also introduced and is mainly synonymously used with direct Z-schemes [88–90]. In this article, the term direct Z-scheme instead of S-scheme is used.



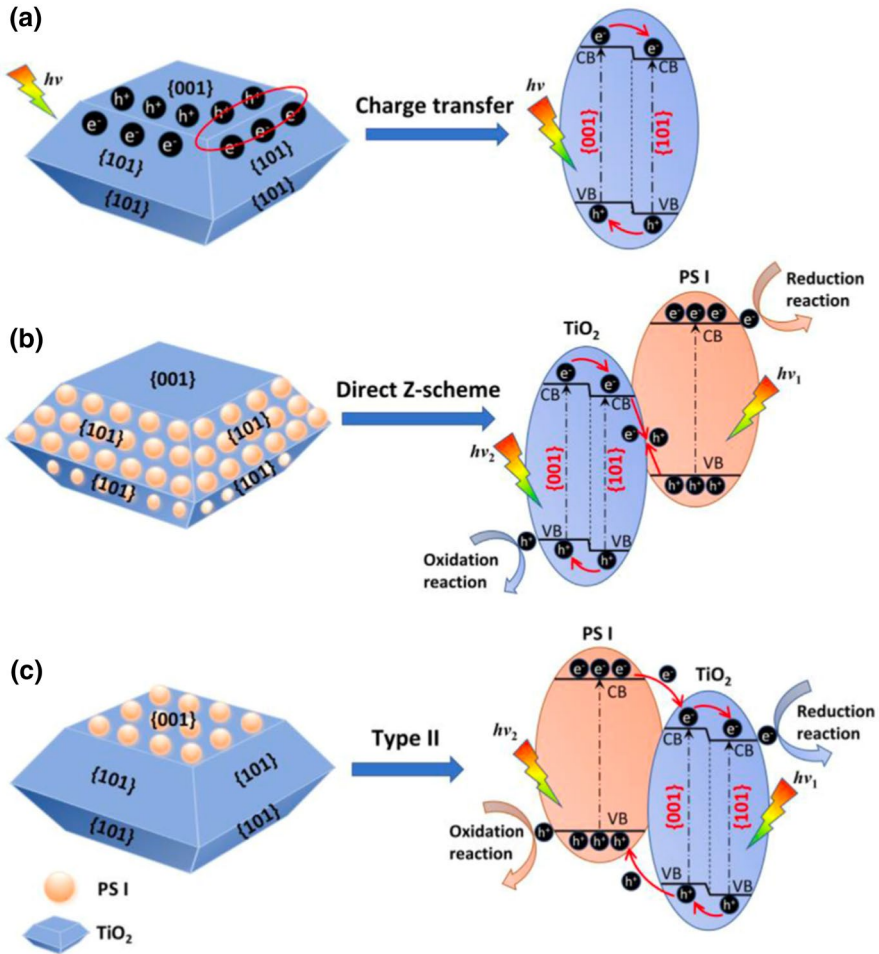
**Fig. 9** Schematic of **a–c** *p-n* direct Z-scheme heterojunction and **d–f** *p-n* type II heterojunction. Reprinted with permission from [82] © 2021 Elsevier

**2.3.3.2 Facets and Regulation of Charge Flow Direction** Facet design has been discussed many times for various photocatalysts [91, 92]. Direct Z-schemes can also be constructed and improved through facet design. Here, charge flow directions and the recombination of photogenerated charges at interfaces can be regulated [82]. The co-exposed  $\{0\ 0\ 1\}$  and  $\{1\ 0\ 1\}$  facets of anatase  $\text{TiO}_2$ , for example, would form a “surface heterojunction” as shown in Fig. 10a. Due to different band structures and band edge positions, photogenerated electrons and holes would transfer to  $\{1\ 0\ 1\}$  and  $\{0\ 0\ 1\}$  facets, respectively [82, 93].

Anchoring a suitable semiconductor with a smaller work function (higher Fermi level) on the  $\{1\ 0\ 0\}$  facet of  $\text{TiO}_2$ , would lead to the formation of a Z-scheme (Fig. 10b). In contrast, if said semiconductor is deposited on  $\{0\ 0\ 1\}$  facets, a type II heterojunction will be formed instead [82]. In 2015, a facet-induced direct Z-scheme between  $\text{TiO}_2$   $\{1\ 0\ 1\}$  and  $\text{g-C}_3\text{N}_4$  was realised by Huang et al. [94].

Jiang et al. used chemical deposition and photodeposition to regulate the electron flow direction in  $\text{g-C}_3\text{N}_4/\text{CdS}$  composite materials [95]. In the photodeposition case, a type II heterojunction was constructed because CdS was selectively



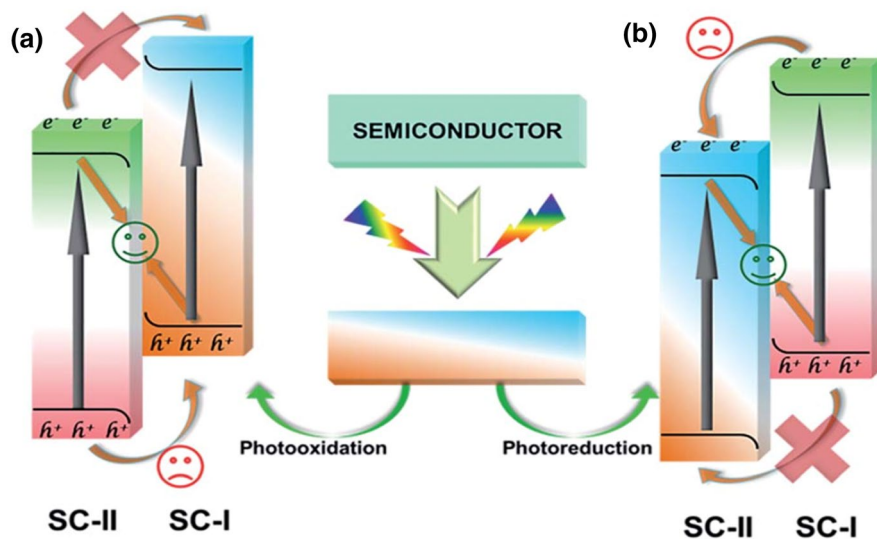


**Fig. 10** Charge transfer **a** at the edge of a single TiO<sub>2</sub> nanocrystal, **b** in a direct Z-scheme, and **c** in a type II TiO<sub>2</sub>-based heterojunctions induced by facet design. Reprinted with permission from [82] © 2021 Elsevier

deposited at the electron transfer site of g-C<sub>3</sub>N<sub>4</sub>, resulting in a photogenerated electron transfer from g-C<sub>3</sub>N<sub>4</sub> to CdS. Using a chemical deposition technique, CdS was randomly deposited onto g-C<sub>3</sub>N<sub>4</sub>, which resulted in a Z-scheme charge transfer mechanism [95].

The same group showed in 2019 that deliberate construction of direct Z-scheme photocatalysts was possible by photodeposition [96]. Two routes to construct direct Z-schemes were proposed via photooxidation and photoreduction (Fig. 11).

When g-C<sub>3</sub>N<sub>4</sub> was selected as SC-I, Fe<sub>2</sub>O<sub>3</sub> as SC-II was selectively deposited on hole-rich sites of g-C<sub>3</sub>N<sub>4</sub> through photooxidation (Fig. 11a). When CdS was selected as SC-I, it was selectively deposited on electron rich sites of SC-II (TiO<sub>2</sub>) (Fig. 11b)



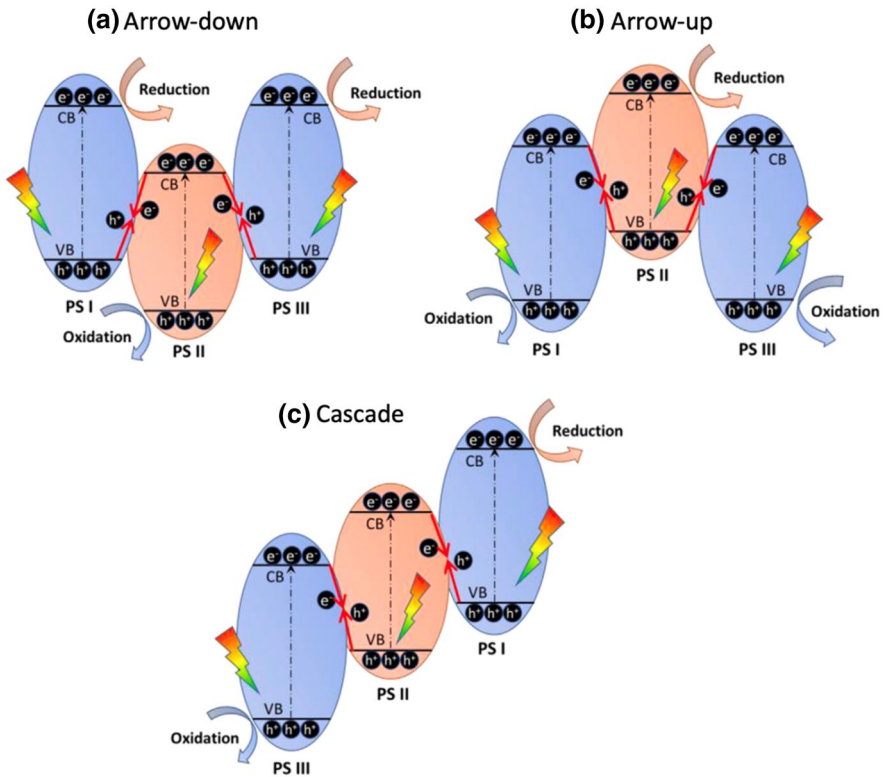
**Fig. 11** The construction routes of direct Z-scheme photocatalysts through photodeposition: **a** photodeposition of SC-II (e.g.  $\text{Fe}_2\text{O}_3$ ) on SC-I (e.g.  $\text{g-C}_3\text{N}_4$ ) through photooxidation; **b** photodeposition of SC-I (e.g.  $\text{CdS}$ ) on SC-II (e.g.  $\text{TiO}_2$ ) through photoreduction (SC=semiconductor). Reprinted with permission from [96] © 2019 Royal Society of Chemistry

[96]. In the future, further investigations might allow to transfer this approach to other materials. A foundation would be extensive investigations of electron- and hole-rich sites and the deliberate construction of these sites for different materials.

**2.3.3.3 Dual Direct Z-Schemes** Direct Z-schemes can also be built from a combination of three semiconductors. These photocatalysts are usually called “dual Z-schemes” or “ternary Z-schemes” [82]. One advantage of these systems is the better spatial separation of reduction and oxidation reactions which occurs on nonadjacent semiconductors. As a result, recombination rates can be reduced or, in other words, the lifetime of photogenerated charge carriers can be prolonged [82, 97, 98]. Furthermore, a broader light absorption spectrum is achievable [98].

Li et al. divide dual direct Z-schemes into three categories (Fig. 12). According to the shape formed by the position of conduction bands and valence bands relative to each other, these systems are called arrow-down, arrow-up, and cascade dual Z-schemes [82].

In an arrow-down system, the electrons in the CB of PS II combine with holes in the VBs of PS I and PS III. Therefore, the electrons at the CBs of PS I and PS III participate in the reduction reaction while the holes in the VB of PS II participate in the oxidation reaction. In an arrow-up photocatalyst, the band positions are inverted compared to the former described system. Therefore, the reduction takes place at PS II while oxidation takes place at PS I and PS III. In a cascade dual Z-scheme, the electrons in the CB and holes in the VB of PS II combine with the holes in the VB of PS I and electrons in the CB of PS III, respectively [82].

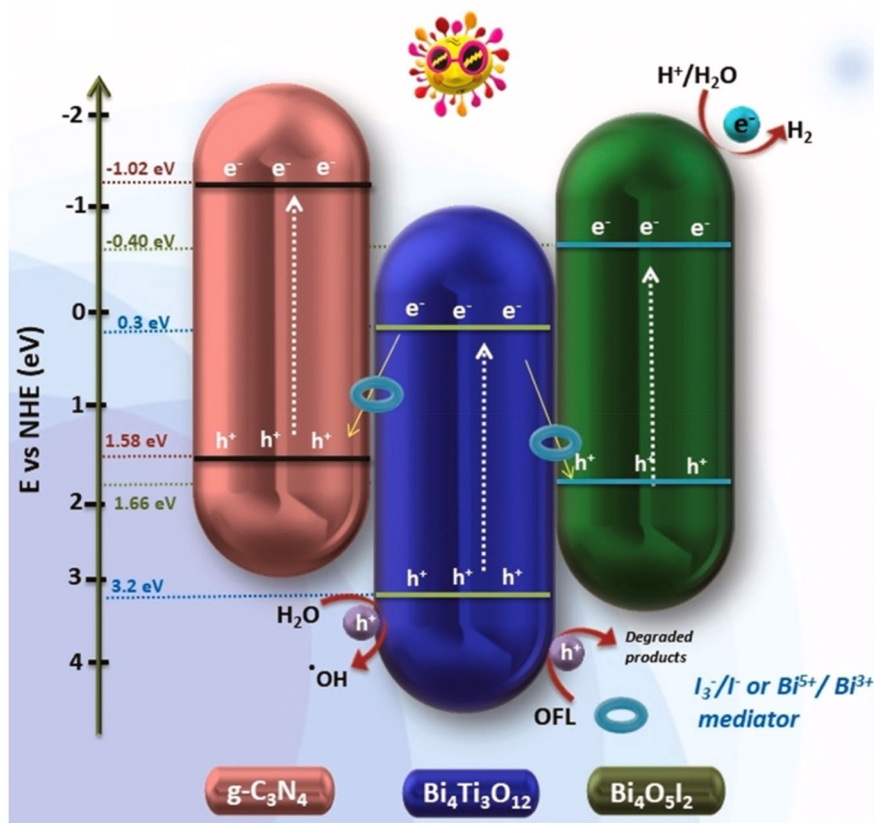


**Fig. 12** Band alignments in three types of dual direct Z-schemes: **a** arrow-down, **b** arrow-up, and **c** cascade. Reprinted with permission from [82] © 2021 Elsevier

All three types of dual Z-schemes have been realised in the past few years. An arrow-down dual Z-scheme was demonstrated by Xue et al. in the form of a  $g\text{-C}_3\text{N}_4/\text{Bi}_2\text{WO}_6/\text{AgI}$  combination [99]. An arrow-up dual Z-scheme was reported by Zheng et al. for a  $\text{Co}_3\text{O}_4@\text{CoO}/g\text{-C}_3\text{N}_4$  combination [100]. In 2019, Wang et al. reported a  $g\text{-C}_3\text{N}_4/\text{Zn}_2\text{SnO}_4\text{N}/\text{ZnO}$  cascade dual Z-scheme [97].

Unfortunately, none of these three systems were tested for water splitting or  $\text{H}_2$  evolution reactions. In the past 3–4 years, more and more dual direct Z-schemes have been reported aiming at  $\text{H}_2$  evolution. Recently, Kumar et al. reported a  $g\text{-C}_3\text{N}_4/\text{Bi}_4\text{Ti}_3\text{O}_{12}/\text{Bi}_4\text{O}_5\text{I}_2$  arrow-down dual Z-scheme for photocatalytic antibiotic degradation and  $\text{H}_2$  production (Fig. 13) [101].

XPS measurements confirmed that the double Z-scheme mechanism is facilitated or mediated by in-built redox mediators  $\text{Bi}^{5+}/\text{Bi}^{3+}$  and  $\text{I}_3^-/\text{I}^-$  or  $\text{IO}_3^-/\text{I}^-$ . Thus, a complicated dual direct Z-scheme assisted by redox mediators was constructed. Aside from antibiotic degradation, the system was also tested for photocatalytic  $\text{H}_2$  evolution in pure water and in solutions containing triethanolamine (TEOA,  $6.7 \cdot 10^{-5}$  M) reaching  $24.12 \text{ mmol g}^{-1} \text{ h}^{-1}$  and  $69 \text{ mmol g}^{-1} \text{ h}^{-1}$ , respectively (Table 1 in the Appendix).

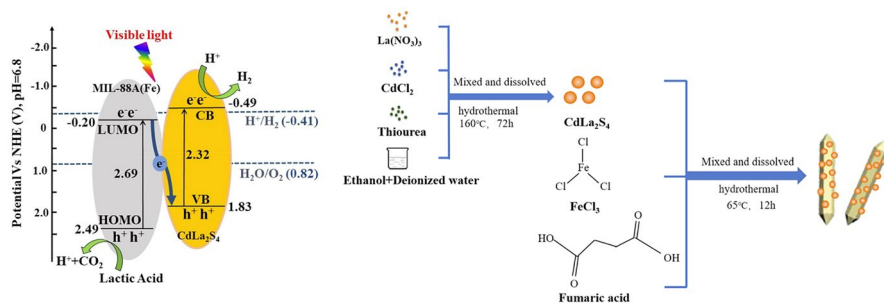


**Fig. 13** Photocatalytic mechanism for  $\text{H}_2$  evolution and pollutant degradation by dual Z-scheme mechanism. Reprinted with permission from [101] © 2021 Elsevier

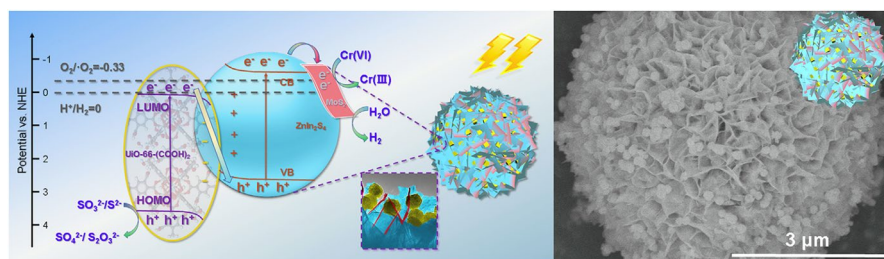
Another ternary structure for photocatalytic  $\text{H}_2$  evolution reported by Dong et al. used a  $\text{ZnO}/\text{ZnS}/\text{g-C}_3\text{N}_4$  cascade dual Z-scheme. The composite displayed specific surface areas of  $76.6 \text{ m}^2 \text{ g}^{-1}$  and reached a  $\text{H}_2$  evolution rate of  $0.3 \text{ mmol g}^{-1} \text{ h}^{-1}$  using sacrificial agents ( $\text{Na}_2\text{S}$  and  $\text{Na}_2\text{SO}_3$ ) but no co-catalysts [102].

In summary, dual direct Z-schemes are a recent trend and further reports focusing on  $\text{H}_2$  evolution reactions and water splitting are expected for the future. Nevertheless, these structures suffer from the limitation of material availability to achieve suitable band alignments [82]. Also, complex synthesis protocols and even more challenging charge transfer analyses are necessary to optimise and understand these systems.

**2.3.3.4 Z-Schemes with MOFs and COFs** Metal organic frameworks (MOFs) are one-, two-, or three-dimensional coordination networks consisting of metal ions/clusters linked together by organic linker molecules. MOFs have received growing attention in the construction of direct Z-schemes. Advantages like tuneable



**Fig. 14** Band alignments in the CdLa<sub>2</sub>S<sub>4</sub>/MIL-88A(Fe) Z-scheme (left) and synthesis process of the composite (right). Reprinted with permission from [104] © 2019 Elsevier



**Fig. 15** Proposed photocatalytic Z-scheme mechanism (left) and field-emission scanning electron microscope (FESEM) image of the UiO-66-(COOH)<sub>2</sub>/ZnIn<sub>2</sub>S<sub>4</sub> (yellow/blue) photocatalyst decorated with MoS<sub>2</sub> co-catalyst (red) (right). Reprinted with permission from [106] © 2019 Elsevier

composition and light-harvesting property, high surface areas, and controllable pore sizes make MOFs attractive in applications of photocatalysis [82, 103]. The visible light photocatalytic performance of pure MOFs is quite poor. However, in direct Z-schemes significant improvements have been reported [82, 104–106]. Various morphologies are easily achievable, which enables the use of 3D, 2D, and 1D structures in direct Z-schemes. Chen et al. constructed a direct Z-scheme by anchoring CdLa<sub>2</sub>S<sub>4</sub> nanoparticles on 1D MIL-88A(Fe) micro-rods (Fig. 14). The nanocomposite obtained high H<sub>2</sub> evolution rates of up to 7.678 mmol g<sup>-1</sup> h<sup>-1</sup> using a 20 wt% content of MIL-88A(Fe). Moreover, the CdLa<sub>2</sub>S<sub>4</sub>/MIL-88A(Fe) composite exhibited high durability during the photocatalytic H<sub>2</sub> evolution [104].

The high photocatalytic activity mainly contributed to the formed Z-scheme structure [104].

In 2019, a 3D hierarchical structure of a UiO-66-(COOH)<sub>2</sub>/ZnIn<sub>2</sub>S<sub>4</sub> Z-scheme was reported [106]. Here, UiO-66-(COOH)<sub>2</sub> nanoparticles were decorated in the interweaving petal nanosheets of ZnIn<sub>2</sub>S<sub>4</sub> microspheres, while co-catalyst MoS<sub>2</sub> nanosheets were folded at the edge of these interweaving petals as shown in Fig. 15.

The optimised photocatalyst showed high H<sub>2</sub> evolution rates of 18.794 mmol g<sup>-1</sup> h<sup>-1</sup>, which was about 15.3 times higher than the H<sub>2</sub> evolution rate of pure ZnIn<sub>2</sub>S<sub>4</sub>.

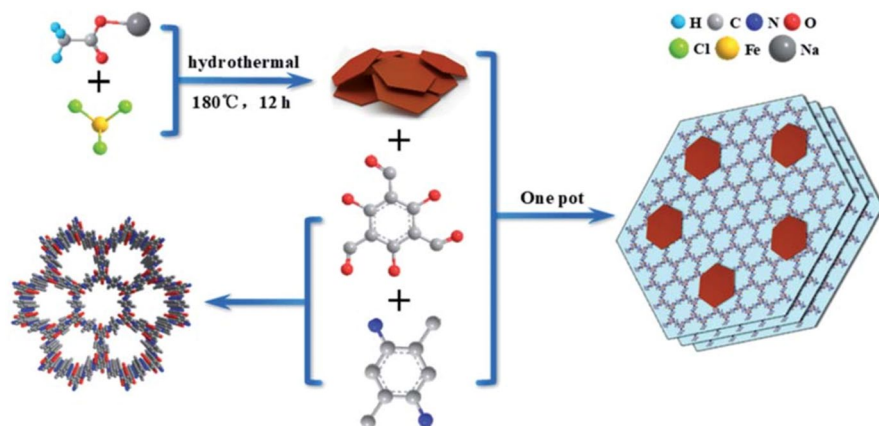
Overall, only a small group of MOFs are suitable for H<sub>2</sub> evolving or water splitting photocatalytic applications since most MOFs are known to become unstable if exposed to moisture/water. However, > 40 MOFs are known to show enhanced water stability (amongst others MIL-100, MIL-101, UiO-66, Zn-DMOF, DUT-67) [107]. Considering possible morphologies and composite materials containing MOFs, there still seems to be potential for stable and low-cost direct Z-schemes in the future.

Covalent organic frameworks (COFs) are crystalline covalent polymers with a high surface area. These porous materials with tuneable topology and functionalities have gathered significant interest among researchers in the field of photocatalysis [108, 109]. The moderate band gap and the presence of extended  $\pi$ -conjugated electronic networks enable visible-light responsive ability and possibilities for bandgap engineering. Therefore, COFs and COF-linked hybrid materials are used as photocatalysts for H<sub>2</sub> production. Due to the stability of covalent bonds compared to coordinate bonds in MOFs, COFs are known to exhibit high stability in various solvents even under harsh acidic, basic, oxidative, or reductive conditions. However, a majority of reported photocatalytic COFs are based on imine, hydrazone, or azine linkages and are considered unstable for extended photocatalysis in water [108]. Currently, only a few COF materials have been investigated for photocatalytic H<sub>2</sub> evolution or water splitting. Nonetheless, there has been considerable progress regarding stability and photocatalytic activity in the past few years. One example is sulfone-containing COFs reported in 2018 by Wang et al. [110]. These covalent organic frameworks are based on a benzobis(benzothiophene sulfone) moiety and are stable for at least 50 h in water under visible light irradiation. Using ascorbic acid (0.1 M) as a sacrificial electron donor and Pt as a co-catalyst (8 wt%), H<sub>2</sub> evolution rates of up to 10.1 mmol g<sup>-1</sup> h<sup>-1</sup> were obtained (300 W Xe light source). Without the addition of co-catalyst, still significant rates of up to 1.32 mmol g<sup>-1</sup> h<sup>-1</sup> were reported [110]. Their internal pore structure could be decorated with nanoparticles/quantum dots, making these COFs a platform for developing hybrid photocatalysts.

In 2020, a COF-based noble-metal-free Z-scheme (TpPa-2-COF/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) was reported for the first time [111]. The transfer of photogenerated electrons from the CB of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> to the VB of the TpPa-2-COF was confirmed, and the effectiveness of the Z-scheme structure attributed to the tight integration between the metal oxide and the COF. As illustrated in Fig. 16, the hybrid material was synthesised by a simple one-pot synthesis using  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, 1,3,5-triformylphloroglucinol and 2,5-dimethyl-*p*-phenylenediamine.

The co-catalyst free Z-scheme showed H<sub>2</sub> evolution rates of up to 3.77 mmol g<sup>-1</sup> h<sup>-1</sup>, which is about 53 times higher than that of the parent TpPa-2-COF and the same conditions and even better than that with a Pt (2 wt%) co-catalyst [111].

Compared to MOFs, COFs are still “young”, but their cheap synthesis, tuneable pores, and other characteristics like visible-light absorption make them attractive for the application as photocatalysts. Hybrids with metal-oxides have already



**Fig. 16** Schematic illustration of the synthesis of an  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/TpPa-2-COF hybrid material. Reprinted with permission from [111] © 2020 Royal Society of Chemistry

demonstrated significant performance improvements [82]. Hybrid materials based on already optimised COFs from recent publications might lead to even higher photocatalytic activity.

**2.3.3.5 Coupling Surface Plasmon Resonance (SPR) Effect into Direct Z-Scheme Systems** Another strategy to improve photocatalytic activity is coupling surface plasmon resonance (SPR) into direct Z-schemes. SPR is the collective oscillation of electrons that are in resonance with the oscillating electric field of incident light [112]. Resonances near the visible or near IR range can enhance the light absorption ability of the photocatalytic system. In addition, SPR-induced hot plasmon electrons or SPR-enhanced localised electromagnetic fields can boost the charge separation near the interfaces between the SPR material and the semiconductor [82, 113, 114]. Well-known materials are noble metals (Ag and Au) and heavily doped semiconductors (H<sub>x</sub>WO<sub>3</sub>, W<sub>18</sub>O<sub>49</sub> and BiO<sub>2-x</sub>) [82].

Among these materials, noble metals are most commonly used for application in photocatalysis. The Schottky junction supplies an internal electric field between the noble metal and the semiconductor, which improves the interfacial charge transfer. Localised surface plasmon resonances (LSPR) can enhance solar light absorption. Both features can lead to significant enhancement of the photo-reactivity [82, 113]. This was described, for example, in TiO<sub>2</sub>/Au/WO<sub>3</sub> or TiO<sub>2</sub>/Ag/Cu<sub>2</sub>O Z-schemes for H<sub>2</sub> generation [115, 116]. Other examples or Z-scheme couples with LSPR for photocatalytic H<sub>2</sub> generation include TiO<sub>2</sub>/Pt/WO<sub>3</sub> [117], TiO<sub>2</sub>/Au/CdS [118], C<sub>3</sub>N<sub>4</sub>/Au/TiO<sub>2</sub> [119], C<sub>3</sub>N<sub>4</sub>/Ag/NiTiO<sub>3</sub> [120], C<sub>3</sub>N<sub>4</sub>/Ag/SnS<sub>2</sub>

[121], SrTiO<sub>3</sub>/C<sub>3</sub>N<sub>4</sub>/Ag/Fe<sub>3</sub>O<sub>4</sub> [122], and C<sub>3</sub>N<sub>4</sub>/Ag/CdS [123]. In contrast, for a Ag/C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> system, a SPR-enhanced heterojunction was reported, with Ag not acting as electron mediator simultaneously [124].

Xie et al. combined modified C<sub>3</sub>N<sub>4</sub> (NCN-CN<sub>x</sub>) with gold nanoparticles and CuInS<sub>2</sub> to achieve photocatalytic hydrogen evolution from water/triethanolamine, reaching 4.28 mmol h<sup>-1</sup> g<sup>-1</sup> at wavelengths > 550 nm [125]. Interestingly, surface photovoltage spectroscopy was additionally used to confirm the SPR effect and the synergistic effects of SPR and Z-scheme mechanism.

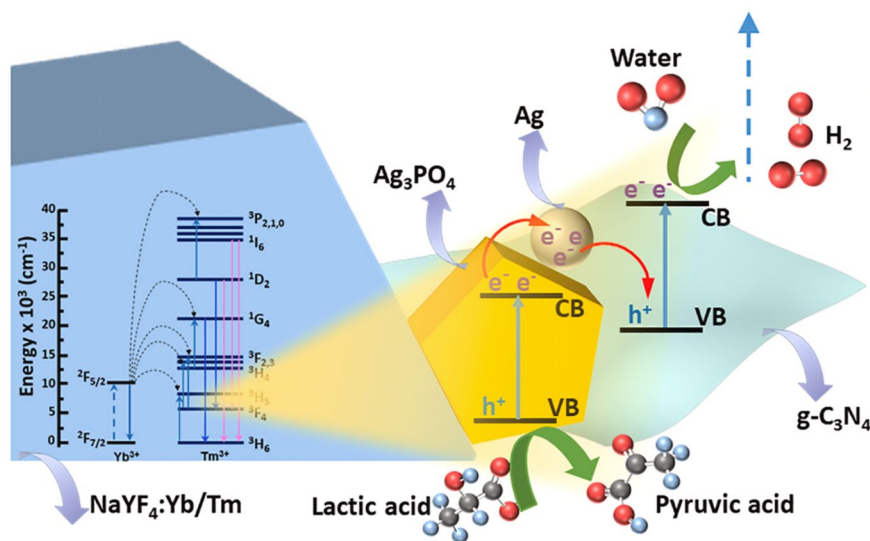
Modulating the stoichiometric ratio of certain semiconductors is also used to improve light absorption abilities since it can increase the free-charge density and lead to LSPR arising from collective oscillations of the excess free-charges on the semiconductor surface [126]. Blue W<sub>18</sub>O<sub>49</sub> is a nonstoichiometric tungsten oxide with a bandgap of 3.0 eV and exhibits LSPR absorption in both the vis and NIR region because of abundant oxygen vacancies on its surface. Zhang et al. used this material to synthesise a g-C<sub>3</sub>N<sub>4</sub>/W<sub>18</sub>O<sub>49</sub> plasmonic Z-scheme photocatalyst, which could harvest photon energies spanning from the UV to the near IR region [126]. A wavelength range of 450–900 nm electrons near the Fermi level of W<sub>18</sub>O<sub>49</sub> reached the high-energy surface plasmon state and became plasmonic “hot electrons”, which then could partly transfer to the conduction band of g-C<sub>3</sub>N<sub>4</sub>. The system reached H<sub>2</sub> evolution rates of up to 3.04 mmol g<sup>-1</sup> h<sup>-1</sup> when triethanolamine (15 vol%) was used as sacrificial agent.

Although considerable progress has been made in plasmonic metal-based and nonmetal-based photocatalysts, challenges remain such as low utilisation of hot carriers, uncovered mechanisms of hot carrier-driven reactions, and the exploration of novel (nonmetallic) plasmonic materials. Therefore, the full potential of plasmonic materials for efficient photocatalytic systems is yet to be realised [127].

**2.3.3.6 Upconversion Photoluminescence (UCPL) Materials in Z-Schemes** Besides the (L)SPR materials, most direct Z-scheme photocatalysts can only utilise the light energy in the UV and visible region. These materials' inability to utilise light from the near IR (NIR) region is an impediment in the progressive photocatalysis research since NIR light constitutes the maximum portion of solar energy (approximately 50%) [128]. Therefore, efficient full-spectrum-activated (UV–Vis–NIR) photocatalysts have gained a lot of attention. An attractive strategy is to integrate non-linear UCPL materials in direct Z-scheme systems [82, 129].

UCPL materials exhibit a multi-photon-assisted anti-Stokes excitation mechanism, which enables the conversion of low energy (NIR) photons into radiation of UV and visible light [130]. Rare-earth-based lanthanide-doped materials, such as Yb<sup>3+</sup>- and Er<sup>3+</sup>-doped NaYF<sub>4</sub>, are popular UCPL substances [82]. Unfortunately, rare earth-doped upconversion materials generally suffer from low upconversion efficiency due to small absorption cross sections and low energy transfer efficiencies [131]. In doped NaYF<sub>4</sub>, the upconversion characteristics entirely depend on





**Fig. 17** Schematic representation of the photocatalytic  $\text{H}_2$  evolution mechanism of  $\text{g-C}_3\text{N}_4/\text{Ag}_3\text{PO}_4$  Z-scheme photocatalyst under the sunlight illumination using Yb/Tm-doped  $\text{NaYF}_4$  as an UCPL material and lactic acid as a sacrificial agent. Reprinted with permission from [128] © 2021 Elsevier

the selection of dopants [132]. Yb/Tm-doped  $\text{NaYF}_4$ , for example, exhibits several UV–visible upconversion emission peaks that fall under the absorption range of semiconductor photocatalysts. Recently, this material has been used by Murali et al. for a NIR-activated  $\text{g-C}_3\text{N}_4/\text{Ag}_3\text{PO}_4$  Z-scheme [128]. The mechanism behind the NIR-light utilised photocatalytic  $\text{H}_2$  production is shown in Fig. 17.

The NIR photons in solar irradiation excite  $\text{Yb}^{3+}$  ions in the  $\text{NaYF}_4$  host from the ground state ( $^2\text{F}_{7/2}$ ) to the excited state ( $^2\text{F}_{5/2}$ ). These excited  $\text{Yb}^{3+}$  ions act as sensitizers and populate higher energy levels of  $\text{Tm}^{3+}$  ions. Non-radiative relaxation of  $\text{Tm}^{3+}$  ions populates several other of its energy levels. The energy is then transferred to the  $\text{g-C}_3\text{N}_4/\text{Ag}_3\text{PO}_4$  via Förster resonance energy transfer (FRET). The absorption of additional energy by the UV–visible  $\text{g-C}_3\text{N}_4/\text{Ag}_3\text{PO}_4$  Z-scheme spurs the number of free charges. In this particular system,  $\text{Ag}^0$  comprised in  $\text{Ag}_3\text{PO}_4$  additionally acts as a channel between both semiconductors [128].

Yb/Tm-doped  $\text{NaYF}_4/\text{Ag}_3\text{PO}_4$  was also combined with black phosphorus for another Z-scheme/UCPL heterostructure [133]. Interestingly, a laser source (980 nm) was used as light source to prove the NIR upconversion;  $0.146 \text{ mmol g}^{-1} \text{ h}^{-1} \text{ H}_2$  evolution from aqueous glycerol solution (50 vol%) could be achieved, with 0.077% apparent quantum efficiency at 980 nm.

$\text{TiO}_2$  was also used in combination with other semiconductors and UCPL materials for photocatalytic  $\text{H}_2$  evolution. Together with  $\text{g-C}_3\text{N}_4$  and carbon quantum dots, photocatalytic water splitting was achieved in a 2:1 ratio at a maximum  $\text{H}_2$  evolution rate of

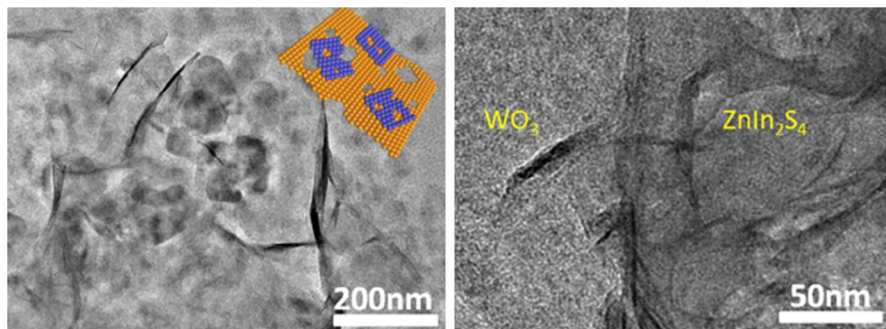
$6.497 \mu\text{mol h}^{-1} \text{g}^{-1}$  under 300 W Xe illumination ( $>400 \text{ nm}$ ) [134]. Therein, the carbon quantum dots are supposed to have a dual function as upconversion material and catalyst for  $\text{H}_2\text{O}_2$  decomposition, therefore facilitating oxygen evolution and water splitting.

Iron-doped  $\text{TiO}_2$  combined with vanadium-doped  $\text{Ta}_2\text{O}_5$  and  $\text{Er}^{3+}:\text{YAlO}_3$  as UCPL were applied for photocatalytic  $\text{H}_2$  generation from aqueous methanol solutions, including decoration with gold nanoparticles [135].  $\text{Er}^{3+}:\text{YAlO}_3$  was used as UCPL agent from visible-light to ultraviolet-light to be able to excite the wide band gap oxides with visible light, and a Z-scheme was established by the dopants resulting in a  $\text{TiO}_2\text{-Fe}^{3+}/\text{V}^{5+}\text{-Ta}_2\text{O}_5$  redox cycle system. By irradiation with a 300-W Xe lamp and a cut-off filter,  $\text{H}_2$  evolution activity of approximately  $32 \mu\text{mol h}^{-1} \text{g}^{-1}$  was shown in visible light.

These examples show that the combination of UCPL materials and Z-schemes or heterojunctions is another promising method to enhance the sunlight absorption of semiconductor photocatalyst systems for  $\text{H}_2$  generation and water splitting. More efforts are however needed to optimize the FRET to the semiconductors to improve the overall solar-to- $\text{H}_2$  efficiency.

**2.3.3.7 2D/2D Z-Schemes** Among the various developed photocatalysts, 2D materials are receiving increasing attention because of their unique physical and chemical properties [136]. Compared with bulk photocatalysts, 2D photocatalysts have a higher specific surface area due to their planar structure and ultralow thickness. Additionally, more surface atoms can provide more adsorption and active sites for photocatalytic reactions [78]. Constructing 2D/2D Z-scheme heterojunctions can combine the respective advantages of 2D materials and Z-scheme systems.

Zhu et al. fabricated a 2D/2D BP/ $\text{BiVO}_4$  Z-scheme (BP = black phosphorus) and realised overall water splitting [137, 138]. Thin BP and  $\text{BiVO}_4$  were hybridised by electrostatic interactions. In both photocatalytic  $\text{H}_2$  and  $\text{O}_2$  production processes, the 2D/2D Z-scheme exhibited better photocatalytic activities than BP and  $\text{BiVO}_4$  alone.  $\text{H}_2$  and  $\text{O}_2$  production rates of  $0.16 \text{ mmol g}^{-1} \text{h}^{-1}$  and  $0.102 \text{ mmol g}^{-1} \text{h}^{-1}$ , respectively, and an apparent quantum efficiency of 0.89% were realised [137, 138].



**Fig. 18** TEM images of the 2D/2D  $\text{ZnIn}_2\text{S}_4/\text{WO}_3(10 \text{ wt}\%)$  Z-scheme. Reprinted with permission from [139] © 2019 Elsevier

Li et al. prepared a Janus sulphur vacancy-rich  $\text{ZnIn}_2\text{S}_4/\text{WO}_3$  Z-scheme [139]. The Janus bilayer was fabricated via electrostatic self-assembly by adding  $\text{WO}_3$  nanosheets into the precursor of  $\text{ZnIn}_2\text{S}_4$ . TEM images of the 2D/2D  $\text{ZnIn}_2\text{S}_4/\text{WO}_3$  (10 wt%) composite are shown in Fig. 18.

Vacancy-rich  $\text{ZnIn}_2\text{S}_4$  was chosen because the sulphur vacancies significantly promoted  $\text{H}_2$  production due to optimised charge separation and light utilisation. The Z-scheme photocatalyst obtained  $\text{H}_2$  evolution rates of up to  $7.81 \text{ mmol g}^{-1} \text{ h}^{-1}$ , which was about 20.8 and 1.69 times higher than those of  $\text{ZnIn}_2\text{S}_4$  and  $\text{Pt-ZnIn}_2\text{S}_4$ . In addition, the loading of NiS quantum dots as co-catalyst could further improve the photocatalytic  $\text{H}_2$  production, which reached  $11.09 \text{ mmol g}^{-1} \text{ h}^{-1}$ . This is the highest photocatalytic activity toward visible-light-driven  $\text{H}_2$  evolution among the family of  $\text{ZnIn}_2\text{S}_4$  materials reported so far.

In addition to the previous examples, 2D/2D Z-schemes were also reported for  $\text{g-C}_3\text{N}_4/\text{Fe}_2\text{O}_3$  [140],  $\text{g-C}_3\text{N}_4/\text{WO}_3$  [141],  $\text{g-C}_3\text{N}_4/\text{BiVO}_4$  [142],  $\text{Zn}_{0.67}\text{Cd}_{0.33}\text{S}/\text{Cu}_2\text{S}$  [143],  $\text{Zn}_x\text{Cd}_{1-x}\text{S}/\text{ZnO}$  [144],  $\text{g-C}_3\text{N}_4/\text{La}_2\text{Ti}_2\text{O}_7$  [145], and several other composite materials. Some of these 2D/2D Z-schemes are listed in Table 1 in the appendix.

More than 3000 papers on 2D/2D Z-scheme photocatalyst have been published, more than 700 of them in 2021 alone (data from SciFinder<sup>®</sup>). Research on 2D/2D composites is therefore a major trend in the field of Z-scheme photocatalysis, which cannot be fully covered in this review. Interested readers are referred to other excellent reviews [78, 146–149].

### 3 Comparison, Trends, and Conclusion

Considering heterojunctions and Z-schemes reported in the last 5 years, high  $\text{H}_2$  evolution rates were achieved, for example, for  $\text{CdLa}_2\text{S}_4/\text{MIL-88}(\text{Fe})$  ( $7.678 \text{ mmol g}^{-1} \text{ h}^{-1}$ ) [104],  $\text{g-C}_3\text{N}_4/\text{CdS}$  ( $10.89 \text{ mmol g}^{-1} \text{ h}^{-1}$ ) [150],  $\text{g-C}_3\text{N}_4/\text{Ag}_3\text{PO}_4$  ( $23.56 \text{ mmol g}^{-1} \text{ h}^{-1}$ ) [128],  $\text{CoTiO}_3/\text{UiO-66}$  ( $26.545 \text{ mmol g}^{-1} \text{ h}^{-1}$ ) [151],  $\text{CdS}/(\text{Au}/\text{TiO}_2)$  ( $47.6 \text{ mmol g}^{-1} \text{ h}^{-1}$ ) [118],  $\text{CdS}/\text{BiVO}_4$  ( $23$  and  $57 \text{ mmol g}^{-1} \text{ h}^{-1}$ ) [87, 152],  $\text{g-C}_3\text{N}_4/\text{Bi}_4\text{Ti}_3\text{O}_{12}/\text{Bi}_4\text{O}_5\text{I}_2$  ( $69 \text{ mmol g}^{-1} \text{ h}^{-1}$ ) [101],  $\text{CdS}/\text{ZnO}$  ( $98.82 \text{ mmol g}^{-1} \text{ h}^{-1}$ ) [153], and several other photocatalytic systems (Table 1 in the Appendix).

Unfortunately, these values are not comparable because of differences in measurement setups, light sources, intensity, filters, co-catalysts, and several other factors.  $\text{H}_2$  evolution rates from > 50 publications have been evaluated and are listed in Table 1 in the appendix. Nevertheless, we hope that the readers of this article find it useful to compare some parameters used for hydrogen production in literature recently. Some of the production rates are very high and could also be a result of normalising the given rate in the publication to the used catalyst mass. Furthermore, high rates were often reported when low catalyst weights (<20 mg) were used [139, 152, 153]. This may indicate that rather small setups were used or that weighing errors can lead to incorrect production rates. In some cases, no production rates were given, and we had to estimate hydrogen production rates from graphical depictions [128, 154, 155]. It is

moreover well known that in photocatalysis the observed rates should not be normalized to the photocatalyst mass because of scattering and shadowing effects leading to non-linear correlation of photocatalyst mass and activity [156].

Therefore, no particular heterojunction or Z-scheme can be seen as superior based on stated  $H_2$  evolution rates. However, composite materials containing CdS,  $BiVO_4$ , or g- $C_3N_4$  often show high photocatalytic activity when combined with a suitable second semiconductor. Furthermore, new strategies like 2D/2D Z-schemes, the use of upconversion photoluminescent materials, or deliberate syntheses led to enhanced  $H_2$  production rates.

A benchmark was set in 2016 by Wang et al. who presented a photocatalyst sheet with a Z-scheme charge carrier transfer based on La- and Rh-codoped  $SrTiO_3$  and Mo-doped  $BiVO_4$  embedded into a gold layer [157]. A solar-to- $H_2$  energy conversion of 1.1% and an apparent quantum yield of > 30% for pure water splitting was reported. Unfortunately, only in one third of the reviewed publications were apparent quantum yields stated. Values for solar-to- $H_2$  energy conversion are also only given for a few cases.

Since different sacrificial agents (MeOH, TEOA, lactic acid, NaS,  $Na_2SO_3$ , etc.) and different concentrations of sacrificial agents were used to enhance  $H_2$  production rates, this caused additional problems for good comparability. Here, the need for sacrificial agents is viable for mechanistic studies and should be avoided when the aim to maximise hydrogen production is discussed.

In 2015, Horst Kisch discussed that apparent quantum yields cannot be compared in a quantitative way. Clear standards are needed to make apparent quantum yields and evolution rates to some extent comparable. Kisch proposed that *optimal rates* should be measured in one unique photoreactor at a given lamp intensity [158]. Common standards, including a standard photoreactor, are needed in the field of photocatalysis and will be inevitable at some point. These standards will not be perfectly suitable for every photocatalyst, but standardised measurements could establish a better comparability.

In terms of materials, in the past 5 years a clear trend toward direct Z-schemes has been recognisable. Heterojunctions have been discussed extensively for decades and are still prominent in photocatalysis research, but nowadays more attention is paid to Z-schemes because of their stronger redox capabilities. Z-schemes are now in the third generation, called direct Z-schemes, and have lost several of the drawbacks of their predecessors (redox mediated Z-schemes and all-solid-state Z-schemes) such as backward reactions and light-shielding problems.

Various new heterojunctions and Z-schemes have been reported in the last years. Overall, a number of trends can be identified that also leave room for new approaches and ideas:

Nanoparticles, nanosheets, and other 0D, 1D, 2D, or 3D structures are commonly used in all kinds of photocatalysts and in (direct) Z-schemes. However, mesoporous Z-schemes are rarely reported. In some of these reports, the mesoporous structure is not even discussed or further investigated [159, 160]. High specific surface areas,

enhanced diffusion of reactants, and improved charge carrier transfer (for example because of an “antenna mechanism” [39]) would make mesoporous Z-schemes promising photocatalysts. Obviously, one mesoporous semiconductor (PS I or PS II) would not be capable of being in intimate contact with a bulk material since the contact area would be significantly reduced because of the pores. Two-dimensional materials such as nanosheets might even block pores, which would take away the advantages of a mesoporous semiconductor. Therefore, careful material design of macroporous/mesoporous heterojunctions might be a way to partially maintain a porous structure and achieve sufficient contact between two semiconductors. Another approach would be core-shell Z-schemes with a porous or incomplete outer shell. This might be a promising strategy, especially for semiconductors in the core that are prone to corrosion or other effects.

The 2D/2D type Z-schemes are probably the most interesting trend in Z-scheme photocatalysis research. Nonetheless, their synthesis is challenging, and large-scale synthesis protocols are lacking so far. Furthermore, 2D structures are mostly reserved to layered semiconductors. Effective synthetic methods need to be developed to produce 2D photocatalysts from non-layered semiconductors, as has been done for SrTiO<sub>3</sub> for example [161].

In general, intimate contact seems to be crucial for Z-scheme charge carrier transport. Typical mechanical/physical methods, such as ball-milling, grinding, or simple mixing of the materials, are frequently used. However, composites assembled by these methods have no intimate interface and both semiconductors are easily detached from each other. Strong interaction is favoured by in-situ growth strategies, hydrothermal and solvothermal treatment, solid-state synthesis, ion-exchange, and electrospinning [77].

Interestingly, chemical deposition of a semiconductor was used to deliberately construct Z-schemes (g-C<sub>3</sub>N<sub>4</sub>/CdS) while photodeposition led to the formation of a type II heterojunction [95]. It is worth mentioning that the type II heterojunction exhibited higher photocatalytic activity. Deliberate construction of Z-schemes is also possible using photooxidation and photoreduction [96]. These techniques might be applicable to other semiconductors such as CeO<sub>2</sub> in case of photooxidation and a variety of metal sulphides for photoreduction.

The field of photocatalysis has experienced a revival of certain materials. Doped SrTiO<sub>3</sub>, for example, was intensively studied for many years and was used in the probably most prominent example for a Z-scheme (SrTiO<sub>3</sub>:La,Rh/Au/BiVO<sub>4</sub>:Mo) [157]. The question therefore arises as to the extent to which other semiconductors could be optimised for improved charge carrier transfer in Z-schemes and heterojunctions. Oxygen/sulphur vacancies and mid gap states have been used in several Z-schemes [58, 145, 162–164]. Intrinsic defects and doping strategies could be applied to other semiconductors to further improve charge carrier transport in direct Z-schemes.

Black phosphorous is another semiconductor that research has focused on recently. For example, a black/red phosphorus multiphase heterojunction has been

prepared and tested for water splitting [154, 155]. Furthermore, supported black phosphorus nanosheets as H<sub>2</sub>-evolving photocatalyst achieved 5.4% energy conversion efficiency, demonstrating the potential of black phosphorus-based materials [165].

Apart from improving existing Z-schemes by doping and new combinations of known semiconductors, new material classes have been introduced. Metal organic frameworks (MOFs) and more recently covalent organic frameworks (COFs) have been used in Z-scheme photocatalysts [104–106, 111, 151]. Other continuing trends are localised surface plasmon resonances (LSPR) and upconversion photoluminescent (UCPL) materials to improve the light absorption of photocatalysts in the visible and near IR range.

In summary, heterojunction and (direct) Z-scheme photocatalysts with multiple semiconductor combinations are still highly investigated in photocatalysis research for hydrogen generation, with different materials strategies addressing varying issues including light absorption over broad wavelength range and charge carrier separation. New types of materials classes such as MOFs and COF and 2D materials are included in heterojunctions and Z-schemes more frequently. Both remain extremely promising material designs and present unique advantages over single material photocatalysts for hydrogen generation; the recent trends and developments have been presented in this work. Although promising approaches such as the application of LSPR and UCPL materials as well as new material combinations, new syntheses, sophisticated morphologies, and improved doping strategies will inevitably make photocatalytic systems more complex, the increase in complexity is and will be the result of knowledge-based improvements [6] developing new and better absorber combinations for hydrogen generation, which might allow, one day, the large-scale production of green H<sub>2</sub> from photocatalytic water splitting.

## Appendix

**Table 1** Recent heterojunction (red) and Z-scheme (blue) photocatalytic systems for H<sub>2</sub> evolution (light colour) or water splitting (dark colour), respectively

Catalyst: Z-scheme (P-I or S-II); Heterojunction (higher CB lower CB)	Band-gap (eV/eV)	Catalyst amount	Cocatalyst, molar ratio (wt. %)	Synthesis of the composite material	Light source	Yield/production rate	Sacrificial agents, volume	Apparent quantum efficiency (AQE)	Comment	Ref./year
BCN/TiO <sub>2</sub>	2.72/3.21	50 mg	Pt, -	ball milling	300 W Xe lamp (λ > 420 nm)	0.093 mmol h <sup>-1</sup> H <sub>2</sub> → 0.06 mmol g <sup>-1</sup> h <sup>-1</sup> H <sub>2</sub>	20 vol.% triethanolamine (TEOA), 100 ml	-	absorbed state Z-scheme with a O <sub>2</sub> vacancy layer as contact interface; no details of Pt amounts as co-catalyst given	[162] 2018
CdLa <sub>2</sub> S <sub>4</sub> -MIL-89(Fr)	2.32/2.69	50 mg	-	hydrothermal	300 W Xe lamp (λ > 420 nm)	7.678 mmol g <sup>-1</sup> h <sup>-1</sup> H <sub>2</sub>	10 vol.% ethanedioic acid, 100 ml	10.3% at 420 nm	Z-scheme containing a metal organic framework (MOF); H <sub>2</sub> evolution rate almost 8 times higher than that of pristine CdLa <sub>2</sub> S <sub>4</sub>	[104] 2020
CdS/Bi <sub>2</sub> VO <sub>4</sub> /Bi <sub>2</sub> VO <sub>4</sub>	2.52/4.02/3.96	100 mg	-	combustion, hydrothermal	250 W Xe lamp (λ > 400 nm)	1.890 mmol g <sup>-1</sup> h <sup>-1</sup> H <sub>2</sub>	MeOH, 80 ml	-	type I bridged coupled Z-scheme electron migration	[88] 2022
CdS/BiVO <sub>4</sub>	2.2/2.5	10 mg	Pt, 0.5	precipitation	300 W Xe lamp (λ > 420 nm)	CdS: 0.11 mmol h <sup>-1</sup> H <sub>2</sub> CdS-BiVO <sub>4</sub> : 0.57 mmol h <sup>-1</sup> H <sub>2</sub> → 57 mmol g <sup>-1</sup> h <sup>-1</sup> H <sub>2</sub>	25 vol.% MeOH, 50 ml	20.6% at 420 nm	CdS nanoparticles on BiVO <sub>4</sub> nanowires	[152] 2017
CdS/BiVO <sub>4</sub>	2.25/2.4	50 mg	Pt, 2	hydrothermal	320 W Xe lamp (λ > 420 nm)	CdS: 0.034 mmol h <sup>-1</sup> H <sub>2</sub> CdS/BiVO <sub>4</sub> : 1.153 mmol h <sup>-1</sup> H <sub>2</sub> → 23 mmol g <sup>-1</sup> h <sup>-1</sup> H <sub>2</sub>	20 vol.% lactic acid/ 1 M Na <sub>2</sub> SO <sub>4</sub> , 200 ml	-	CdS nanoparticles on BiVO <sub>4</sub> nanowires, 10% performance fading over 10 hours in lactic acid solution	[87] 2017
CdS/ZnO	2.28/3.0	100 mg	-	chemical deposition	300 W Xe lamp	with increased oxygen vacancies: 1.329 mmol g <sup>-1</sup> h <sup>-1</sup> H <sub>2</sub> without increased oxygen vacancies: 0.584 mmol g <sup>-1</sup> h <sup>-1</sup> H <sub>2</sub>	0.1 M Na <sub>2</sub> S and 0.1 M Na <sub>2</sub> SO <sub>4</sub> , 270 ml	with increased oxygen vacancies: 19.01% at 380 nm without increased oxygen vacancies: 12.94% at 380 nm	oxygen vacancies promote the direct Z-scheme transfer process	[163] 2017
CdS(Au)/TiO <sub>2</sub>	2.4/3.26	50 mg	- (Au)	stirring	300 W Xe lamp	47.6 mmol g <sup>-1</sup> h <sup>-1</sup> H <sub>2</sub>	0.25 M Na <sub>2</sub> S and 0.35 M Na <sub>2</sub> SO <sub>4</sub> , 100 ml	9.83% at 450 nm	SPE effect and internal electron transfer ability, depending on the size of Au nanoparticles	[118] 2021
CdS/TiO <sub>2</sub>	2.4/3.2	50 mg	-	ionic layer adsorption and reaction (ILAR)	150 W Xe lamp	0.0514 mmol h <sup>-1</sup> H <sub>2</sub> → 1.028 mmol g <sup>-1</sup> h <sup>-1</sup> H <sub>2</sub>	25 vol.% MeOH, 80 ml	-	CdS nanoparticles on TiO <sub>2</sub> microspheres	[166] 2017
CdS/WS <sub>2</sub>	2.17/1.79	50 mg	- (Co/P, WS <sub>2</sub> )	hydrothermal	300 W Xe lamp (λ > 420 nm)	0.0692 mmol h <sup>-1</sup> H <sub>2</sub>	-, 100 ml H <sub>2</sub> O	1.34% at 420 nm	p-n junction heterojunction (decorated with Co/P) as oxidation product confirmed in pure water	[66] 2019
CdS/ZnO	2.4/3.2	10 mg	Pt/PdS, -	atomic layer deposition (ALD)	225 W Xe lamp (320 nm < λ < 780 nm)	71.39 mmol g <sup>-1</sup> h <sup>-1</sup> for Pt co-catalyst 98.82 mmol g <sup>-1</sup> h <sup>-1</sup> for PdS co-catalyst 11.36 mmol g <sup>-1</sup> h <sup>-1</sup> without co-catalyst	0.35 M Na <sub>2</sub> S and 0.25 M Na <sub>2</sub> SO <sub>4</sub> , 100 ml	-	CdS@ZnO core-shell structure, extremely high H <sub>2</sub> production rates	[153] 2017
CdSe/CdS	0.89/2.4	20 mg	-	solvothermal	300 W Xe lamp (AM 1.5)	1.06 mmol g <sup>-1</sup> h <sup>-1</sup> H <sub>2</sub>	Na <sub>2</sub> S and Na <sub>2</sub> SO <sub>4</sub> (unknown conc.)	-	hollow structure might allow multiple reflections	[161] [168] 2017
CdTe/Cd <sub>3</sub> (SO <sub>4</sub> ) <sub>2</sub> (OH) <sub>2</sub>	2.36/2.67	20 mg	-	hydrothermal	300 W Xe lamp (λ > 420 nm)	0.5309 mmol h <sup>-1</sup> H <sub>2</sub> → 26.545 mmol g <sup>-1</sup> h <sup>-1</sup> H <sub>2</sub>	10 vol.% MeOH, 20 ml	-	p-n heterojunction containing a metal organic framework (MOF); unclear H <sub>2</sub> evolution rate	[151] 2020
CdSe/g-C <sub>3</sub> N <sub>4</sub>	1.75/2.73	50 mg	-	hydrothermal	300 W Xe lamp (λ > 420 nm)	1.290 mmol g <sup>-1</sup> h <sup>-1</sup> H <sub>2</sub>	10 vol.% TEOA and 0.25 M Na <sub>2</sub> S and 0.2 M Na <sub>2</sub> SO <sub>4</sub> , 10 ml	-	Z-scheme verification via deposition of Pt on electron rich sites	[169] 2017
Co-PPH/VO <sub>2</sub>	1.6/2.8	100 mg	-	ball-milling	150 W Xe lamp	0.0047 mmol g <sup>-1</sup> h <sup>-1</sup> H <sub>2</sub> 0.0023 mmol g <sup>-1</sup> h <sup>-1</sup> O <sub>2</sub>	0.5 M Na <sub>2</sub> HPO <sub>4</sub> / NaH <sub>2</sub> PO <sub>4</sub> , 80 ml	-	co-catalyst free water splitting	[170] 2018

Table 1 (continued)

Cu <sub>2</sub> S <sub>2</sub> /MS	0.772.12	1 mg	MnO <sub>2</sub> -	cation exchange	300 W Xe lamp	0.209 mmol g <sup>-1</sup> h <sup>-1</sup> H <sub>2</sub> ; 0.036 mmol g <sup>-1</sup> h <sup>-1</sup> O <sub>2</sub>	~ 6 ml H <sub>2</sub> O	5.5 % at 420 nm	non-stoichiometric ratio of H <sub>2</sub> O <sub>2</sub> , probably due to reactive O <sub>2</sub> species; possible additional contribution by surface plasmons of Cu <sub>2</sub> S	[171], [172] 2017
Cu <sub>2</sub> S <sub>2</sub> /MS	0.772.12	1 mg	-	cation exchange	300 W Xe lamp	0.718 mmol g <sup>-1</sup> h <sup>-1</sup> H <sub>2</sub>	0.35 M Na <sub>2</sub> S and 0.22 M Na <sub>2</sub> SO <sub>3</sub> , 6 ml	18.8 % at 420 nm	possible additional contribution by surface plasmons of Cu <sub>2</sub> S	[171], [172] 2017
Fe <sub>3</sub> O <sub>4</sub> @TiO <sub>2</sub> @TiO <sub>2</sub>	2.02.13.0	50 mg	-	combustion	300 W Xe lamp	0.370 mmol g <sup>-1</sup> h <sup>-1</sup> H <sub>2</sub>	10 vol.% TEOA, 100 ml	-	double type II cascade heterojunction	[63] 2020
g-C <sub>3</sub> N <sub>4</sub> /Ag <sub>2</sub> O <sub>2</sub>	2.772.46	5 mg	Ag <sub>2</sub> -	stirring	300 W Xe lamp (AM 1.5, near IR filter)	23.56 mmol g <sup>-1</sup> h <sup>-1</sup> H <sub>2</sub> ; AM 1.5; approx. 13 mmol g <sup>-1</sup> h <sup>-1</sup> H <sub>2</sub> ; near IR: approx. 9 mmol g <sup>-1</sup> h <sup>-1</sup> H <sub>2</sub>	10 % lactic acid, 50 ml	-	Na <sub>2</sub> Y <sub>2</sub> F <sub>10</sub> disks used for upconverting photoluminescence; near IR active photocatalyst	[123]
g-C <sub>3</sub> N <sub>4</sub> @TiO <sub>2</sub> /BiOCl (PS I/PS II/PS III)	2.702.80.2.66	40 mg	-	stirring/ hydrothermal	500 W Xe lamp (λ > 420 nm)	pure water; 24.12 mmol g <sup>-1</sup> h <sup>-1</sup> H <sub>2</sub> ; with TEOA; 69 mmol g <sup>-1</sup> h <sup>-1</sup> H <sub>2</sub>	pure water or 6.7 · 10 <sup>-6</sup> M TEOA, 100 ml	-	complicated dual direct Z-scheme assisted by redox mediators	[101] 2021
g-C <sub>3</sub> N <sub>4</sub> /Ag <sub>2</sub> O/CdS	2.462.32	50 mg	-(Ag)	hydrothermal	350 W Xe lamp (λ > 420 nm)	1.376 mmol g <sup>-1</sup> h <sup>-1</sup> H <sub>2</sub>	10 % lactic acid, 100 ml	-	SPR effect	[122] 2018
g-C <sub>3</sub> N <sub>4</sub> /CdS	2.72.4	300 mg	Pt, 0.4 mg	stirring	350 W Xe lamp (λ > 420 nm)	10.89 mmol g <sup>-1</sup> h <sup>-1</sup> H <sub>2</sub>	0.01 M Na <sub>2</sub> S and 0.05 M Na <sub>2</sub> SO <sub>3</sub> , 100 ml	-	CdS@g-C <sub>3</sub> N <sub>4</sub> ; duration of illumination unclear	[150] 2017
g-C <sub>3</sub> N <sub>4</sub> /Ag <sub>2</sub> O g-C <sub>3</sub> N <sub>4</sub> /CdS	2.872.30	10 mg	Pt, 1	stirring (photodepos.) / hydrothermal (chemical depos.)	300 W Xe lamp (λ > 420 nm)	5.69 mmol g <sup>-1</sup> h <sup>-1</sup> H <sub>2</sub> (photodepos.) 1.49 mmol g <sup>-1</sup> h <sup>-1</sup> H <sub>2</sub> (chemical depos.)	0.05 M Na <sub>2</sub> S and 0.1 M Na <sub>2</sub> SO <sub>3</sub> , 100 ml	10.3 % at 420 nm 3.8 % at 420 nm (chemical depos.)	photodepos. leads to type II heterojunction (higher photocatalytic activity) chemical depos. leads to Z-scheme (lower photocatalytic activity)	[95] 2018
NiCN/CN <sub>x</sub> (Au)/CdSe	2.71.6	10 mg	(Au), Pt	stirring	300 W Xe lamp (λ > 550 nm)	full spectra; 10.72 mmol g <sup>-1</sup> h <sup>-1</sup> H <sub>2</sub> ; with filter; 4.28 mmol g <sup>-1</sup> h <sup>-1</sup> H <sub>2</sub>	10 vol.% TEOA, 100 ml	-	synergistic effects of SPR and Z-scheme mechanism	[123] 2021
g-C <sub>3</sub> N <sub>4</sub> /Cu <sub>2</sub> P	2.72.1.50	20 mg	-	precipitation + solid state reaction	300 W Xe lamp (λ > 420 nm)	0.284 mmol g <sup>-1</sup> h <sup>-1</sup> H <sub>2</sub>	10 vol.% TEOA, 80 ml	2.6 % at 420 nm	p-n junction; H <sub>2</sub> production rate 95 times higher than pure g-C <sub>3</sub> N <sub>4</sub>	[50] 2018
g-C <sub>3</sub> N <sub>4</sub> /Ag <sub>2</sub> O/TiO <sub>2</sub>	2.61.2.18	4 mg	-(Ag)	stirring	300 W Xe lamp	3.331 mmol g <sup>-1</sup> h <sup>-1</sup> H <sub>2</sub>	10 vol.% TEOA, 40 ml	-	synergistic effects of SPR and Z-scheme mechanism	[120] 2019
g-C <sub>3</sub> N <sub>4</sub> /Ag <sub>2</sub> O/SrS	2.862.28	100 mg	-(Ag)	hydrothermal	500 W Xe lamp (λ > 420 nm)	1.1045 mmol g <sup>-1</sup> h <sup>-1</sup> H <sub>2</sub>	0.25 M Na <sub>2</sub> S and 0.35 M Na <sub>2</sub> SO <sub>3</sub> , 100 ml	-	Z-scheme plasmonic photocatalyst with 3D flower-like SrS microspheres on the 2D Ag <sub>2</sub> O/Cu <sub>2</sub> N <sub>4</sub> nanosheets	[121] 2021
g-C <sub>3</sub> N <sub>4</sub> /Ag <sub>2</sub> O/Fe <sub>3</sub> O <sub>4</sub>	2.73.14	50 mg	(Ag), Pt, 2	wet-impregnation, calcination	300 W Xe lamp	without Pt: 2.0088 mmol g <sup>-1</sup> h <sup>-1</sup> H <sub>2</sub> ; with Pt: 4.200 mmol g <sup>-1</sup> h <sup>-1</sup> H <sub>2</sub>	10 vol.% TEOA, 55 ml	-	g-C <sub>3</sub> N <sub>4</sub> /SrFeO <sub>3</sub> junction bridged with Ag <sub>2</sub> O/Cu <sub>2</sub> N <sub>4</sub> nanoparticles; SPR effect	[122] 2018
g-C <sub>3</sub> N <sub>4</sub> (Au)/TiO <sub>2</sub>	2.73.2	10 mg	-(Au)	stirring, hydrothermal	300 W Xe lamp (λ > 420 nm)	0.129 mmol g <sup>-1</sup> h <sup>-1</sup> H <sub>2</sub>	10 vol.% TEOA, 20 ml	-	SPR effects of Au; enhanced light utilization of carbon doped TiO <sub>2</sub> hollow spheres	[173] 2017
g-C <sub>3</sub> N <sub>4</sub> /TiO <sub>2</sub>	2.73.19	10 mg	(Ag), Pt, 1.0	stirring, calcination	350 W Xe lamp (λ > 400 nm)	6.4 mmol in 4 h (non-linear course)	10 vol.% TEOA, 10 ml	-	SPR effect	[124] 2019
g-C <sub>3</sub> N <sub>4</sub> /TiO <sub>2</sub>	2.93.2	50 mg	Pt, 1.0	suspension, calcination	350 W Xe lamp	4.128 mmol g <sup>-1</sup> h <sup>-1</sup> H <sub>2</sub>	10 vol.% TEOA, 100 ml	-	3D TiO <sub>2</sub> microflowers on 2D g-C <sub>3</sub> N <sub>4</sub> nanosheets; Z-scheme charge transfer presumed only based on potential barriers	[174] 2019



Table 1 (continued)

$\text{Fe}_2\text{O}_3/\text{TiO}_2$	2.7632	12.5 mg	PE, 0.5 on TiO <sub>2</sub>	calcination	300 W Xe lamp ( $\lambda > 400$ nm)	visible light: 1.07 mmol g <sup>-1</sup> h <sup>-1</sup> ; full sun: ca. 6.33 mmol g <sup>-1</sup> h <sup>-1</sup>	10 vol% TEOA, 80 ml	-	targeted charge transfer gap	[175] 2019
$\text{Fe}_2\text{O}_3/\text{TiO}_2$ ( $\text{Fe}:\text{Ti}=10:1$ )	3.93, 203.03	50 mg	P, 1	mixing, heating	300 W Xe lamp / 300 W Hg lamp ( $\lambda > 400$ nm)	simulated sunlight: 0.151 mmol g <sup>-1</sup> h <sup>-1</sup> ; visible light: 0.089 mmol g <sup>-1</sup> h <sup>-1</sup>	10 vol% MeOH, 33 ml	-	further experiments regarding oxygen evolution	[176] 2020
$\text{Fe}_2\text{O}_3/\text{TiO}_2$ (NaCl: TiO <sub>2</sub> )	2.6244	50 mg	-	sonication, thermal annealing	300 W Xe lamp	0.089 mmol g <sup>-1</sup> h <sup>-1</sup>	10 vol% TEOA, 100 ml	-	Fe <sup>3+</sup> self-doped TiO <sub>2</sub> (g-C <sub>3</sub> N <sub>4</sub> ) <sub>2</sub> hollow core-shell structure	[177] 2020
$\text{Fe}_2\text{O}_3/\text{TiO}_2$	2.732	50 mg	-	hydrothermal	300 W Xe lamp ( $\lambda > 400$ nm)	0.0065 mmol g <sup>-1</sup> h <sup>-1</sup>	~ 100 ml	-	carbon quantum dots with upconversion fluorescence for improved visible light utilization and H <sub>2</sub> O absorption	[174] 2018
$\text{Fe}_2\text{O}_3/\text{TiO}_2/\text{ZnO}$	2.7359	5 mg	PE, 1.0	sol-gel	320 W Xe lamp with solar filter (AM 1.5)	3.04 mmol g <sup>-1</sup> h <sup>-1</sup>	15 vol% TEOA, 10 ml	-	ternary photocatalytic ZnO:Fe hydrothermal photocatalyst. VIS/NIR absorption due to LSPR	[126] 2017
$\text{Fe}_2\text{O}_3/\text{TiO}_2/\text{ZnO}$	1.83229	50 mg	P, 3	sol-gel	300 W Xe lamp ( $\lambda > 420$ nm)	0.095 mmol g <sup>-1</sup> h <sup>-1</sup>	20 vol% TEOA, 10 ml	12.9 % at 400 nm 9.8 % at 420 nm	2D/2D (g-C <sub>3</sub> N <sub>4</sub> /phthalocyanine) sulphur vacancies-mediated light absorption & trapping electrons	[181] 2020
$\text{Fe}_2\text{O}_3/\text{TiO}_2/\text{ZnO}$ (95:1:5 PS: Fe)	2.73, 673.37	100 mg	-	stirring	300 W Xe lamp	0.301 mmol g <sup>-1</sup> h <sup>-1</sup>	0.25 M NaCl and 0.25 M Na <sub>2</sub> SO <sub>4</sub> , 100 ml	-	stud direct ZnO:Fe. title analysis of charge transfer mechanism	[102] 2017
$\text{Fe}_2\text{O}_3/\text{TiO}_2/\text{ZnO}$	2.25382	60 mg	P, 2	ultra-sonication under oxidation	300 W Xe lamp ( $\lambda > 400$ nm)	0.159 mmol g <sup>-1</sup> h <sup>-1</sup>	0.05 M NaCl and 0.05 M Na <sub>2</sub> SO <sub>4</sub> , 100 ml	-	Type II as heterojunction. ZnO is in the photocatalytic reaction in a photocatalytic manner	[151] 2019
$\text{Fe}_2\text{O}_3/\text{TiO}_2$	1.82.81	50 mg	-	hydrothermal	300 W Xe lamp ( $\lambda > 420$ nm)	0.010 mmol g <sup>-1</sup> h <sup>-1</sup>	-	-	no O <sub>2</sub> production rate stated	[157] 2020
$\text{Fe}_2\text{O}_3/\text{TiO}_2$	1.893.56	50 mg	P, 3	hydrothermal	300 W Xe lamp	0.622 mmol g <sup>-1</sup> h <sup>-1</sup>	0.3 M titanium C, 100 ml	4.6 % at 350 nm	MeO <sub>2</sub> nanoparticles on hollow CaTiO <sub>3</sub> cubes	[178] 2020
$\text{Fe}_2\text{O}_3/\text{TiO}_2$	1.41/2.91	50 mg	P, 2	milling	300 W Xe lamp	0.577 mmol g <sup>-1</sup> h <sup>-1</sup>	25 vol% MeOH, 120 ml	-	polye MeO <sub>2</sub> quantum dots on ox-type Fe <sub>2</sub> O <sub>3</sub> nanorods	[179] 2018
$\text{Fe}_2\text{O}_3/\text{TiO}_2/\text{ZnO}$	2.372.41	10 mg	-	mixing	5 W LED	1.712 mmol over 5 h → 34.20 mmol g <sup>-1</sup> h <sup>-1</sup>	10 vol% P <sub>2</sub> lactate acid, 30 ml	-	ZnO:Fe containing a metal-organic framework (MOF)	[100] 2020
$\text{Fe}_2\text{O}_3/\text{TiO}_2$	1.423.46	50 mg	P, 1	hydrothermal	300 W Xe lamp (AM 1.5 filter)	0.191 mmol g <sup>-1</sup> h <sup>-1</sup>	9.00 vol% MeOH, 55 ml	-	material with Fe <sup>3+</sup> and oxygen vacancies that are more efficient higher photochemical activity	[104] 2019
$\text{Fe}_2\text{O}_3/\text{TiO}_2$	1.923.2	50 mg	-	hydrothermal and electrospinning	350 W Xe lamp / 250 W Hg lamp	0.655 mmol g <sup>-1</sup> h <sup>-1</sup> ; (Xe lamp)	20 vol% methanol, 80 ml	-	core shell hybrid Fe <sub>2</sub> O <sub>3</sub> nanoparticles on electrospun TiO <sub>2</sub> nanofibers, more than ten times using methanol and O <sub>2</sub> is presented as evidence for water splitting	[180] 2018
$\text{Fe}_2\text{O}_3/\text{TiO}_2$	0.712.45	15 mg	-	stirring, high-speed centrifugation	10 W laser (980 nm)	0.146 mmol g <sup>-1</sup> h <sup>-1</sup>	50 vol% glycerol, 100 ml (other sacrificial agents were tested)	0.077 % at 980 nm	NaCl <sub>2</sub> ·6H <sub>2</sub> O·Fe <sup>3+</sup> used for upconverting photoluminescence, near IR active photocatalyst	[133] 2019
$\text{Fe}_2\text{O}_3/\text{TiO}_2$	0.72.39	5 mg	-	mechanical mixing	320 W Xe lamp ( $\lambda > 420$ nm)	0.16 mmol g <sup>-1</sup> h <sup>-1</sup> ; 0.102 mmol g <sup>-1</sup> h <sup>-1</sup> O <sub>2</sub>	~ 8 ml H <sub>2</sub> O	0.89 % at 420 nm	water splitting on a 2D heterostructure	[132] 2018
$\text{Fe}_2\text{O}_3/\text{TiO}_2/\text{ZnO}$	1.274.96	2 mg	Cu, Fe, Ni, Cu	sol-gel	LED light (120-10 W, $\lambda > 420$ nm)	0.33 mmol g <sup>-1</sup> h <sup>-1</sup> without co-catal. 3 mmol g <sup>-1</sup> h <sup>-1</sup> Fe <sup>3+</sup> H <sub>2</sub> with Cu co-catal.	~ 6 ml H <sub>2</sub> O	1.21 % at 420 nm	oxidation species: H <sub>2</sub> O (combined to the combination of two hydroxyl radicals)	[154], [155] 2018
$\text{Fe}_2\text{O}_3/\text{TiO}_2$	2.032	unclear (fixed on Si subs.)	-	ALD	300 W Xe lamp	0.400 mmol g <sup>-1</sup> h <sup>-1</sup>	20 vol% MeOH, 25 ml	-		[181] 2018
$\text{Fe}_2\text{O}_3/\text{TiO}_2$	3.123.85	100 mg	Au, +	ultrasound, calcination	300 W Xe lamp (visible light filter), cut-off wavelength: not given	~ 1159 mmol g <sup>-1</sup> h <sup>-1</sup> over 5 h → 0.023 mmol g <sup>-1</sup> h <sup>-1</sup>	MeOH, +	-	Fe <sup>3+</sup> /YAO in upconversion luminescence (light filter) visible light is ultraviolet-light. ZnO:Fe established by a TiO <sub>2</sub> ·Fe <sup>3+</sup> /YAO's roles cycle system	[135] 2018
$\text{Fe}_2\text{O}_3/\text{TiO}_2$	3.22.8	50 mg	Au, up to 0.45 wt%	electrospinning	300 W Xe lamp	0.2696 mmol h <sup>-1</sup> ; → 5.038 mmol g <sup>-1</sup> h <sup>-1</sup>	20 vol% MeOH, 70 ml	-	enhanced activity attributed to synergistic effect of Fe <sup>3+</sup> ions and SPR	[111] 2017
$\text{Fe}_2\text{O}_3/\text{TiO}_2/\text{WO}_3$	3.22.8	50 mg	(Fe), Au	electrospinning	300 W Xe lamp	0.242 mmol g <sup>-1</sup> h <sup>-1</sup>	20 vol% MeOH, 45 ml	-	plasma-enhanced charged separation	[117] 2017
$\text{Fe}_2\text{O}_3/\text{TiO}_2/\text{ZnO}$ ( $\text{Fe}:\text{Ti}:\text{Zn}$ )	2.04/2.07	10 mg	-	sol-gel	300 W Xe lamp ( $\lambda > 420$ nm)	3.77 mmol g <sup>-1</sup> h <sup>-1</sup>	0.1 M phosphate-buffered saline (PBS) at pH = 7 containing 100 mg sodium ascorbate, 50 ml	0.157 % at 450 nm	first reported coordination organic framework (COF) based ZnO:Fe	[111] 2020
$\text{Zn}_0.9\text{Fe}_0.1\text{O}$	3.50 to 2.79	25 mg	-	hydrothermal sulfidation/oxidation	300 W Xe lamp ( $\lambda > 420$ nm)	38.93 mmol g <sup>-1</sup> h <sup>-1</sup>	0.1 NaCl and 0.1 M Na <sub>2</sub> SO <sub>4</sub> , 100 ml	40.93 % at 420 nm	oxide: ZnO:Fe layer double hydroxide (LDH)	[144] 2018
$\text{Zn}_0.9\text{Fe}_0.1\text{O}$	2.5232	100 mg	PE, 0.1	calcination	300 W Xe lamp ( $\lambda > 420$ nm)	without PE: 25.18 mmol g <sup>-1</sup> h <sup>-1</sup> ; with PE: 37.79 mmol g <sup>-1</sup> h <sup>-1</sup>	0.1 NaCl and 0.1 M Na <sub>2</sub> SO <sub>4</sub> , 100 ml	without PE: 48.5 % at 420 nm with PE: 62.1 % at 420 nm	extremely high AQE, oxygen vacancies enhance light absorption	[182] 2017
$\text{ZnO}/\text{Fe}_2\text{O}_3/\text{TiO}_2/\text{ZnO}$	2.643.62	40 mg	Me <sub>2</sub> S, 2	sol-gel	300 W Xe lamp	18.794 mmol g <sup>-1</sup> h <sup>-1</sup>	0.70 M NaCl and 0.5 M Na <sub>2</sub> SO <sub>4</sub> , 100 ml	-	ZnO:Fe containing a metal-organic framework (MOF). ZnO:Fe charge transfer for only based on produced species and Fermi levels	[106] 2020
$\text{ZnO}/\text{Fe}_2\text{O}_3/\text{WO}_3$	2.372.58	5 mg	NiS, quantum dots	mixing/refluxing	300 W Xe lamp	without NiS: 7.81 mmol g <sup>-1</sup> h <sup>-1</sup> ; with NiS: 11.09 mmol g <sup>-1</sup> h <sup>-1</sup>	10 vol% lactic acid, 40 ml	72 % at 420 nm	Juno sulphur vacancy rich ZnO:Fe. highest activity among the family of ZnO:Fe materials	[139] 2019
$\text{ZnO}/\text{Fe}_2\text{O}_3/\text{TiO}_2$	~ 2.42.71	100 mg	-	sol-gel	300 W Xe lamp with solar filter (AM 1.5) cut-off filter ( $\lambda > 420$ nm)	0.8396 mmol g <sup>-1</sup> h <sup>-1</sup>	0.35 M NaCl and 0.25 M Na <sub>2</sub> SO <sub>4</sub> , 100 ml	-	14 times higher Fe <sub>2</sub> O <sub>3</sub> evolution activity compared to CdTe/TiO <sub>2</sub>	[67] 2019
$\text{ZnO}/\text{Fe}_2\text{O}_3/\text{TiO}_2$	2.143.05	50 mg	Au, 2	hydrothermal	320 W Xe lamp (500 nm $\lambda > 400$ nm)	3.34 mmol g <sup>-1</sup> h <sup>-1</sup> H <sub>2</sub> and O <sub>2</sub> with a ratio of 2 : 1	~ 50 ml H <sub>2</sub> O	-	SPR enhanced ZnO:Fe: core-shell TiO <sub>2</sub> /ZnO:Fe: core-shell nanorods, no O <sub>2</sub> production rate stated	[183] 2019

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## Declarations

**Conflict of interest** On behalf of all authors, the corresponding author states that there is no conflict of interest.

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## References

1. Brown D (2016) US and world hydrogen production—2014. CryoGas Int, Lexington
2. Ausfelder F, Bazzanella A (2016) Hydrogen in the chemical industry. *Hydrog Sci Eng Mater Process Syst Technol* 10:19–40
3. Dawood F, Anda M, Shafiqullah GM (2020) Hydrogen production for energy: an overview. *Int J Hydrogen Energy* 45:3847–3869
4. Oliveira AM, Beswick RR, Yan Y (2021) A green hydrogen economy for a renewable energy society. *Curr Opin Chem Eng* 33:100701. <https://doi.org/10.1016/j.coche.2021.100701>
5. Haszeldine RS (2009) Carbon capture and storage: how green can black be? *Science* (80–) 325:1647–1652. <https://doi.org/10.1126/science.1172246>
6. Marschall R (2021) 50 years of materials research for photocatalytic water splitting. *Eur J Inorg Chem* 2021:2435–2441. <https://doi.org/10.1002/ejic.202100264>
7. Edwards PP, Kuznetsov VL, David WIF, Brandon NP (2008) Hydrogen and fuel cells: towards a sustainable energy future. *Energy Policy* 36:4356–4362. <https://doi.org/10.1016/j.enpol.2008.09.036>
8. Thomas JM, Edwards PP, Dobson PJ, Owen GP (2020) Decarbonising energy: the developing international activity in hydrogen technologies and fuel cells. *J Energy Chem* 51:405–415. <https://doi.org/10.1016/j.jechem.2020.03.087>
9. Yilmaz C, Wendelstorf J, Turek T (2017) Modeling and simulation of hydrogen injection into a blast furnace to reduce carbon dioxide emissions. *J Clean Prod* 154:488–501. <https://doi.org/10.1016/j.jclepro.2017.03.162>
10. Bicer Y, Dincer I, Vezina G, Raso F (2017) Impact assessment and environmental evaluation of various ammonia production processes. *Environ Manage* 59:842–855
11. Ursua A, Gandia LM, Sanchis P (2011) Hydrogen production from water electrolysis: current status and future trends. *Proc IEEE* 100:410–426
12. Moussallem I, Pinnow S, Wagner N, Turek T (2012) Development of high-performance silver-based gas-diffusion electrodes for chlor-alkali electrolysis with oxygen depolarized cathodes. *Chem Eng Process Process Intensif* 52:125–131. <https://doi.org/10.1016/j.cep.2011.11.003>
13. Kayfeci M, Keçebaş A, Bayat M (2019) Chapter 3—hydrogen production. In: Calise F, D'Accadia MD, Santarelli M et al (eds) Solar hydrogen production. Academic Press, London, pp 45–83
14. Penner SS (2006) Steps toward the hydrogen economy. *Energy* 31:33–43. <https://doi.org/10.1016/j.energy.2004.04.060>
15. Clark WW, Rifkin J (2006) A green hydrogen economy. *Energy Policy* 34:2630–2639. <https://doi.org/10.1016/j.enpol.2005.06.024>

16. Brandon NP, Kurban Z (2017) Clean energy and the hydrogen economy. *Philos Trans R Soc A Math Phys Eng Sci* 375:20160400
17. Ball M, Weeda M (2015) The hydrogen economy—vision or reality? *Int J Hydrog Energy* 40:7903–7919
18. Bockris JO (1972) A hydrogen economy. *Science* (80–) 176:1323
19. Koumi Ngoh S, Njomo D (2012) An overview of hydrogen gas production from solar energy. *Renew Sustain Energy Rev* 16:6782–6792. <https://doi.org/10.1016/j.rser.2012.07.027>
20. Marschall R (2014) Semiconductor composites: strategies for enhancing charge carrier separation to improve photocatalytic activity. *Adv Funct Mater* 24:2421–2440. <https://doi.org/10.1002/adfm.201303214>
21. Takanabe K (2017) Photocatalytic water splitting: quantitative approaches toward photocatalyst by design. *ACS Catal* 7:8006–8022. <https://doi.org/10.1021/acscatal.7b02662>
22. Li Y, Tsang SCE (2020) Recent progress and strategies for enhancing photocatalytic water splitting. *Mater Today Sustain* 9:100032
23. Li X, Yu J, Low J et al (2015) Engineering heterogeneous semiconductors for solar water splitting. *J Mater Chem A* 3:2485–2534
24. Maeda K, Domen K (2010) Photocatalytic water splitting: recent progress and future challenges. *J Phys Chem Lett* 1:2655–2661. <https://doi.org/10.1021/jz1007966>
25. Kanan MW, Nocera DG (2008) In situ formation of an oxygen-evolving catalyst in neutral water containing phosphate and Co<sup>2+</sup>. *Science* (80–) 321:1072–1075
26. Osterloh FE (2017) Photocatalysis versus photosynthesis: a sensitivity analysis of devices for solar energy conversion and chemical transformations. *ACS Energy Lett* 2:445–453. <https://doi.org/10.1021/acsenergylett.6b00665>
27. Kudo A, Miseki Y (2009) Heterogeneous photocatalyst materials for water splitting. *Chem Soc Rev* 38:253–278. <https://doi.org/10.1039/b800489g>
28. Chen X, Shen S, Guo L, Mao SS (2010) Semiconductor-based photocatalytic hydrogen generation. *Chem Rev* 110:6503–6570. <https://doi.org/10.1021/cr1001645>
29. Moss B, Wang Q, Butler KT et al (2021) Linking in situ charge accumulation to electronic structure in doped SrTiO<sub>3</sub> reveals design principles for hydrogen-evolving photocatalysts. *Nat Mater* 20:511–517. <https://doi.org/10.1038/s41563-020-00868-2>
30. Modak B, Ghosh SK (2015) Exploring the role of La codoping beyond charge compensation for enhanced hydrogen evolution by Rh–SrTiO<sub>3</sub>. *J Phys Chem B* 119:11089–11098. <https://doi.org/10.1021/acs.jpcc.5b02906>
31. Zhao ZV, Goncalves R, Barman KS et al (2019) Electronic structure basis for enhanced overall water splitting photocatalysis with aluminum doped SrTiO<sub>3</sub> in natural sunlight. *Energy Environ Sci* 12:1385–1395. <https://doi.org/10.1039/C9EE00310J>
32. Yang J, Wang D, Han H, Li CAN (2013) Roles of cocatalysts in photocatalysis and photoelectrocatalysis. *Acc Chem Res* 46:1900–1909
33. Maeda K, Lu D, Teramura K, Domen K (2008) Direct deposition of nanoparticulate rhodium–chromium mixed-oxides on a semiconductor powder by band-gap irradiation. *J Mater Chem* 18:3539–3542. <https://doi.org/10.1039/B808484J>
34. Maeda K, Ohno T, Domen K (2011) A copper and chromium based nanoparticulate oxide as a noble-metal-free cocatalyst for photocatalytic water splitting. *Chem Sci* 2:1362–1368. <https://doi.org/10.1039/C1SC00177A>
35. Zong X, Yan H, Wu G et al (2008) Enhancement of photocatalytic H<sub>2</sub> evolution on CdS by loading MoS<sub>2</sub> as cocatalyst under visible light irradiation. *J Am Chem Soc* 130:7176–7177. <https://doi.org/10.1021/ja8007825>
36. Yan H, Yang J, Ma G et al (2009) Visible-light-driven hydrogen production with extremely high quantum efficiency on Pt–PdS/CdS photocatalyst. *J Catal* 266:165–168. <https://doi.org/10.1016/j.jcat.2009.06.024>
37. Schneider J, Bahnemann DW (2013) Undesired role of sacrificial reagents in photocatalysis. *J Phys Chem Lett* 4:3479–3483. <https://doi.org/10.1021/jz4018199>
38. Kawai T, Sakata T (1980) Photocatalytic hydrogen production from liquid methanol and water. *J Chem Soc Chem Commun* 20:694–695
39. Kandiell TA, Dillert R, Robben L, Bahnemann DW (2011) Photonic efficiency and mechanism of photocatalytic molecular hydrogen production over platinumized titanium dioxide from aqueous methanol solutions. *Catal Today* 161:196–201. <https://doi.org/10.1016/j.cattod.2010.08.012>

40. Afroz K, Moniruddin M, Bakranov N et al (2018) A heterojunction strategy to improve the visible light sensitive water splitting performance of photocatalytic materials. *J Mater Chem A* 6:21696–21718. <https://doi.org/10.1039/C8TA04165B>
41. Sun K, Jing Y, Li C et al (2012) 3D branched nanowire heterojunction photoelectrodes for high-efficiency solar water splitting and H<sub>2</sub> generation. *Nanoscale* 4:1515–1521. <https://doi.org/10.1039/C2NR11952H>
42. Hou Y, Zuo F, Dagg A, Feng P (2012) Visible light-driven  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanorod/graphene/BiV<sub>1-x</sub>MoxO<sub>4</sub> core/shell heterojunction array for efficient photoelectrochemical water splitting. *Nano Lett* 12:6464–6473. <https://doi.org/10.1021/nl303961c>
43. Xiang Q, Yu J, Jaroniec M (2011) Preparation and enhanced visible-light photocatalytic H<sub>2</sub>-production activity of graphene/C<sub>3</sub>N<sub>4</sub> composites. *J Phys Chem C* 115:7355–7363. <https://doi.org/10.1021/jp200953k>
44. Nasir SNFM, Ullah H, Ebadi M et al (2017) New insights into Se/BiVO<sub>4</sub> heterostructure for photoelectrochemical water splitting: a combined experimental and DFT study. *J Phys Chem C* 121:6218–6228. <https://doi.org/10.1021/acs.jpcc.7b01149>
45. Lou Z, Li F, Deng J et al (2013) Branch-like hierarchical heterostructure ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub>): a novel sensing material for trimethylamine gas sensor. *ACS Appl Mater Interfaces* 5:12310–12316. <https://doi.org/10.1021/am402532v>
46. Watanabe MO, Yoshida J, Mashita M et al (1985) Band discontinuity for GaAs/AlGaAs heterojunction determined by C-V profiling technique. *J Appl Phys* 57:5340–5344
47. Moniz ASJ, Shevlin AS, James Martin D et al (2015) Visible-light driven heterojunction photocatalysts for water splitting—a critical review. *Energy Environ Sci* 8:731–759. <https://doi.org/10.1039/C4EE03271C>
48. Shim J, Oh S, Kang D-H et al (2016) Phosphorene/rhenium disulfide heterojunction-based negative differential resistance device for multi-valued logic. *Nat Commun* 7:13413. <https://doi.org/10.1038/ncomms13413>
49. Wang H, Zhang L, Chen Z et al (2014) Semiconductor heterojunction photocatalysts: design, construction, and photocatalytic performances. *Chem Soc Rev* 43:5234–5244
50. Low J, Yu J, Jaroniec M et al (2017) Heterojunction photocatalysts. *Adv Mater* 29:1601694
51. Wang Z, Lin Z, Shen S et al (2021) Advances in designing heterojunction photocatalytic materials. *Chin J Catal* 42:710–730. [https://doi.org/10.1016/S1872-2067\(20\)63698-1](https://doi.org/10.1016/S1872-2067(20)63698-1)
52. Hua E, Jin S, Wang X et al (2019) Ultrathin 2D type-II pn heterojunctions La<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>/In<sub>2</sub>S<sub>3</sub> with efficient charge separations and photocatalytic hydrogen evolution under visible light illumination. *Appl Catal B Environ* 245:733–742
53. Kumar R, Das D, Singh AK (2018) C<sub>2</sub>N/WS<sub>2</sub> van der Waals type-II heterostructure as a promising water splitting photocatalyst. *J Catal* 359:143–150
54. Wang B, Yuan H, Chang J et al (2019) Two dimensional InSe/C<sub>2</sub>N van der Waals heterojunction as enhanced visible-light-responsible photocatalyst for water splitting. *Appl Surf Sci* 485:375–380
55. Zhang X, Chen A, Zhang Z et al (2019) Rational design of C<sub>2</sub>N-based type-II heterojunctions for overall photocatalytic water splitting. *Nanoscale Adv* 1:154–161
56. Qin Z, Wang M, Li R, Chen Y (2018) Novel Cu<sub>3</sub>P/g-C<sub>3</sub>N<sub>4</sub> pn heterojunction photocatalysts for solar hydrogen generation. *Sci China Mater* 61:861–868
57. Khalid NR, Israr S, Tahir MB, Iqbal T (2020) Highly efficient Bi<sub>2</sub>O<sub>3</sub>/MoS<sub>2</sub> pn heterojunction photocatalyst for H<sub>2</sub> evolution from water splitting. *Int J Hydrog Energy* 45:8479–8489
58. Qin Y, Li H, Lu J et al (2020) Synergy between van der Waals heterojunction and vacancy in ZnIn<sub>2</sub>S<sub>4</sub>/g-C<sub>3</sub>N<sub>4</sub> 2D/2D photocatalysts for enhanced photocatalytic hydrogen evolution. *Appl Catal B Environ* 277:119254
59. Zeng J, Xu L, Luo X et al (2021) A novel design of SiH/CeO<sub>2</sub> (111) van der Waals type-II heterojunction for water splitting. *Phys Chem Chem Phys* 23:2812–2818. <https://doi.org/10.1039/D0CP05238H>
60. Zhao Z, Willard EJ, Dominguez JR et al (2019) Depletion layer controls photocatalytic hydrogen evolution with p-type gallium phosphide particles. *J Mater Chem A* 7:18020–18029. <https://doi.org/10.1039/C9TA05879F>
61. Papp J, Soled S, Dwight K, Wold A (1994) Surface acidity and photocatalytic activity of TiO<sub>2</sub>, WO<sub>3</sub>/TiO<sub>2</sub>, and MoO<sub>3</sub>/TiO<sub>2</sub> photocatalysts. *Chem Mater* 6:496–500. <https://doi.org/10.1021/cm00040a026>

62. Zhou B-X, Ding S-S, Wang Y et al (2020) Type-II/type-II band alignment to boost spatial charge separation: a case study of g-C<sub>3</sub>N<sub>4</sub> quantum dots/a-TiO<sub>2</sub>/r-TiO<sub>2</sub> for highly efficient photocatalytic hydrogen and oxygen evolution. *Nanoscale* 12:6037–6046. <https://doi.org/10.1039/D0NR00176G>
63. Bhoi YP, Fang F, Zhou X et al (2020) Single step combustion synthesis of novel Fe<sub>2</sub>TiO<sub>5</sub>/α-Fe<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> ternary photocatalyst with combined double type-II cascade charge migration processes and efficient photocatalytic activity. *Appl Surf Sci* 525:146571. <https://doi.org/10.1016/j.apsusc.2020.146571>
64. Galedari M, Mehdipour Ghazi M, Mirmasoomi SR (2021) Novel visible-driven Ag<sub>2</sub>O/Fe<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> nano sized hetero-structured photocatalyst: synthesis, characterization and photo-degradation of tetracycline. *Chem Eng Res Des* 170:248–255. <https://doi.org/10.1016/j.cherd.2021.04.008>
65. Ke T, Shen S, Yang K, Lin D (2022) In situ fabrication of Bi<sub>2</sub>O<sub>3</sub>/C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub>@C photocatalysts for visible-light photodegradation of sulfamethoxazole in water. *Appl Surf Sci* 580:152302. <https://doi.org/10.1016/j.apsusc.2021.152302>
66. Zhong Y, Wu Y, Chang B et al (2019) A CoP/CdS/WS<sub>2</sub> p–n–n tandem heterostructure: a novel photocatalyst for hydrogen evolution without using sacrificial agents. *J Mater Chem A* 7:14638–14645. <https://doi.org/10.1039/C9TA03721G>
67. An L, Han X, Li Y et al (2019) ZnS–CdS–TaON nanocomposites with enhanced stability and photocatalytic hydrogen evolution activity. *J Sol-Gel Sci Technol* 91:82–91. <https://doi.org/10.1007/s10971-019-05009-z>
68. Das K, Bariki R, Majhi D et al (2022) Facile synthesis and application of CdS/Bi<sub>20</sub>TiO<sub>32</sub>/Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> ternary heterostructure: a synergistic multi-heterojunction photocatalyst for enhanced endosulfan degradation and hydrogen evolution reaction. *Appl Catal B Environ* 303:120902. <https://doi.org/10.1016/j.apcatb.2021.120902>
69. Maeda K (2013) Z-scheme water splitting using two different semiconductor photocatalysts. *ACS Catal* 3:1486–1503. <https://doi.org/10.1021/cs4002089>
70. Bard AJ (1979) Photoelectrochemistry and heterogeneous photo-catalysis at semiconductors. *J Photochem* 10:59–75. [https://doi.org/10.1016/0047-2670\(79\)80037-4](https://doi.org/10.1016/0047-2670(79)80037-4)
71. Abe R, Sayama K, Sugihara H (2005) Development of new photocatalytic water splitting into H<sub>2</sub> and O<sub>2</sub> using two different semiconductor photocatalysts and a shuttle redox mediator IO<sub>3</sub><sup>-</sup>/I<sup>-</sup>. *J Phys Chem B* 109:16052–16061
72. Abe R, Higashi M, Domen K (2011) Overall water splitting under visible light through a two-step photoexcitation between TaON and WO<sub>3</sub> in the presence of an iodate-iodide shuttle redox mediator. *ChemSuschem* 4:228–237
73. Maeda K, Higashi M, Lu D et al (2010) Efficient nonsacrificial water splitting through two-step photoexcitation by visible light using a modified oxynitride as a hydrogen evolution photocatalyst. *J Am Chem Soc* 132:5858–5868. <https://doi.org/10.1021/ja1009025>
74. Abe R, Sayama K, Arakawa H (2003) Significant influence of solvent on hydrogen production from aqueous I<sub>3</sub><sup>-</sup>/I<sup>-</sup> redox solution using dye-sensitized Pt/TiO<sub>2</sub> photocatalyst under visible light irradiation. *Chem Phys Lett* 379:230–235
75. Kato H, Sasaki Y, Iwase A, Kudo A (2007) Role of iron ion electron mediator on photocatalytic overall water splitting under visible light irradiation using Z-scheme systems. *Bull Chem Soc Jpn* 80:2457–2464
76. Sasaki Y, Iwase A, Kato H, Kudo A (2008) The effect of co-catalyst for Z-scheme photocatalysis systems with an Fe<sup>3+</sup>/Fe<sup>2+</sup> electron mediator on overall water splitting under visible light irradiation. *J Catal* 259:133–137
77. Xu Q, Zhang L, Yu J et al (2018) Direct Z-scheme photocatalysts: principles, synthesis, and applications. *Mater Today* 21:1042–1063. <https://doi.org/10.1016/j.mattod.2018.04.008>
78. Liu X, Zhang Q, Ma D (2021) Advances in 2D/2D Z-scheme heterojunctions for photocatalytic applications. *Sol RRL* 5:2000397. <https://doi.org/10.1002/solr.202000397>
79. Li H, Tu W, Zhou Y, Zou Z (2016) Z-Scheme photocatalytic systems for promoting photocatalytic performance: recent progress and future challenges. *Adv Sci* 3:1500389
80. Tada H, Mitsui T, Kiyonaga T et al (2006) All-solid-state Z-scheme in CdS–Au–TiO<sub>2</sub> three-component nanojunction system. *Nat Mater* 5:782–786
81. Zhou P, Yu J, Jaroniec M (2014) All-solid-state Z-scheme photocatalytic systems. *Adv Mater* 26:4920–4935

82. Li X, Garlisi C, Guan Q et al (2021) A review of material aspects in developing direct Z-scheme photocatalysts. *Mater Today* 47:75–107. <https://doi.org/10.1016/j.mattod.2021.02.017>
83. Yu J, Wang S, Low J, Xiao W (2013) Enhanced photocatalytic performance of direct Z-scheme g-C<sub>3</sub>N<sub>4</sub>-TiO<sub>2</sub> photocatalysts for the decomposition of formaldehyde in air. *Phys Chem Chem Phys* 15:16883–16890. <https://doi.org/10.1039/C3CP53131G>
84. Li H, Ba G, Liang Z et al (2019) Construction of direct all-solid-state Z-scheme p-n copper indium disulfide/tungsten oxide heterojunction photocatalysts: function of interfacial electric field. *J Colloid Interface Sci* 555:72–81. <https://doi.org/10.1016/j.jcis.2019.07.073>
85. Zhang J, Xin J, Shao C et al (2019) Direct Z-scheme heterostructure of p-CuAl<sub>2</sub>O<sub>4</sub>/n-Bi<sub>2</sub>WO<sub>6</sub> composite nanofibers for efficient overall water splitting and photodegradation. *J Colloid Interface Sci* 550:170–179. <https://doi.org/10.1016/j.jcis.2019.04.099>
86. Aguirre ME, Zhou R, Eugene AJ et al (2017) Cu<sub>2</sub>O/TiO<sub>2</sub> heterostructures for CO<sub>2</sub> reduction through a direct Z-scheme: protecting Cu<sub>2</sub>O from photocorrosion. *Appl Catal B Environ* 217:485–493. <https://doi.org/10.1016/j.apcatb.2017.05.058>
87. Zhou FQ, Fan JC, Xu QJ, Min YL (2017) BiVO<sub>4</sub> nanowires decorated with CdS nanoparticles as Z-scheme photocatalyst with enhanced H<sub>2</sub> generation. *Appl Catal B Environ* 201:77–83
88. Xu Q, Zhang L, Cheng B et al (2020) S-scheme heterojunction. *Photocatalyst Chem* 6:1543–1559. <https://doi.org/10.1016/j.chempr.2020.06.010>
89. Zhang L, Zhang J, Yu H, Yu J (2022) Emerging S-scheme photocatalyst. *Adv Mater* 1:2107668. <https://doi.org/10.1002/adma.202107668>
90. Fu J, Xu Q, Low J et al (2019) Ultrathin 2D/2D WO<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> step-scheme H<sub>2</sub>-production photocatalyst. *Appl Catal B Environ* 243:556–565
91. Liu G, Jimmy CY, Lu GQM, Cheng H-M (2011) Crystal facet engineering of semiconductor photocatalysts: motivations, advances and unique properties. *Chem Commun* 47:6763–6783
92. Bai S, Wang L, Li Z, Xiong Y (2017) Facet-engineered surface and interface design of photocatalytic materials. *Adv Sci* 4:1600216
93. Yu J, Low J, Xiao W et al (2014) Enhanced photocatalytic CO<sub>2</sub>-reduction activity of anatase TiO<sub>2</sub> by coexposed 001 and 101 facets. *J Am Chem Soc* 136:8839–8842
94. Huang Z, Sun Q, Lv K et al (2015) Effect of contact interface between TiO<sub>2</sub> and g-C<sub>3</sub>N<sub>4</sub> on the photoreactivity of g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> photocatalyst: (001) vs (101) facets of TiO<sub>2</sub>. *Appl Catal B Environ* 164:420–427. <https://doi.org/10.1016/j.apcatb.2014.09.043>
95. Jiang W, Zong X, An L et al (2018) Consciously constructing heterojunction or direct Z-scheme photocatalysts by regulating electron flow direction. *ACS Catal* 8:2209–2217. <https://doi.org/10.1021/acscatal.7b04323>
96. Jiang W, Qu D, An L et al (2019) Deliberate construction of direct Z-scheme photocatalysts through photodeposition. *J Mater Chem A* 7:18348–18356. <https://doi.org/10.1039/C9TA05607F>
97. Wang M, Tan G, Ren H et al (2019) Direct double Z-scheme O<sub>g</sub>-C<sub>3</sub>N<sub>4</sub>/Zn<sub>2</sub>SnO<sub>4</sub>N/ZnO ternary heterojunction photocatalyst with enhanced visible photocatalytic activity. *Appl Surf Sci* 492:690–702
98. Zhu M, Liu Q, Chen W et al (2017) Boosting the visible-light photoactivity of BiOCl/BiVO<sub>4</sub>/N-GQD ternary heterojunctions based on internal Z-scheme charge transfer of N-GQDs: simultaneous band gap narrowing and carrier lifetime prolonging. *ACS Appl Mater Interfaces* 9:38832–38841
99. Xue W, Huang D, Li J et al (2019) Assembly of AgI nanoparticles and ultrathin g-C<sub>3</sub>N<sub>4</sub> nanosheets codecorated Bi<sub>2</sub>WO<sub>6</sub> direct dual Z-scheme photocatalyst: an efficient, sustainable and heterogeneous catalyst with enhanced photocatalytic performance. *Chem Eng J* 373:1144–1157
100. Zheng J, Zhang L (2019) Designing 3D magnetic peony flower-like cobalt oxides/g-C<sub>3</sub>N<sub>4</sub> dual Z-scheme photocatalyst for remarkably enhanced sunlight driven photocatalytic redox activity. *Chem Eng J* 369:947–956
101. Kumar A, Sharma G, Kumari A et al (2021) Construction of dual Z-scheme g-C<sub>3</sub>N<sub>4</sub>/Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub>/Bi<sub>4</sub>O<sub>3</sub>I<sub>2</sub> heterojunction for visible and solar powered coupled photocatalytic antibiotic degradation and hydrogen production: boosting via I-/I<sub>3</sub><sup>-</sup> and Bi<sup>3+</sup>/Bi<sup>5+</sup> redox mediators. *Appl Catal B Environ* 284:119808
102. Dong Z, Wu Y, Thirugnanam N, Li G (2018) Double Z-scheme ZnO/ZnS/g-C<sub>3</sub>N<sub>4</sub> ternary structure for efficient photocatalytic H<sub>2</sub> production. *Appl Surf Sci* 430:293–300
103. Liu J, Chen L, Cui H et al (2014) Applications of metal-organic frameworks in heterogeneous supramolecular catalysis. *Chem Soc Rev* 43:6011–6061

104. Chen Q, Li J, Cheng L, Liu H (2020) Construction of CdLa<sub>2</sub>S<sub>4</sub>/MIL-88A(Fe) heterojunctions for enhanced photocatalytic H<sub>2</sub>-evolution activity via a direct Z-scheme electron transfer. *Chem Eng J* 379:122389. <https://doi.org/10.1016/j.cej.2019.122389>
105. Li M, Li J, Jin Z (2020) 0D/2D spatial structure of CdxZn1-xS/Ni-MOF-74 for efficient photocatalytic hydrogen evolution. *Dalt Trans* 49:5143–5156. <https://doi.org/10.1039/D0DT00271B>
106. Mu F, Cai Q, Hu H et al (2020) Construction of 3D hierarchical microarchitectures of Z-scheme UiO-66-(COOH)2/ZnIn<sub>2</sub>S<sub>4</sub> hybrid decorated with non-noble MoS<sub>2</sub> cocatalyst: a highly efficient photocatalyst for hydrogen evolution and Cr(VI) reduction. *Chem Eng J* 384:123352. <https://doi.org/10.1016/j.cej.2019.123352>
107. Liu B, Vikrant K, Kim K-H et al (2020) Critical role of water stability in metal–organic frameworks and advanced modification strategies for the extension of their applicability. *Environ Sci Nano* 7:1319–1347
108. You J, Zhao Y, Wang L, Bao W (2021) Recent developments in the photocatalytic applications of covalent organic frameworks: a review. *J Clean Prod* 291:125822
109. Pachfule P, Acharjya A, Roeser J et al (2018) Diacetylene functionalized covalent organic framework (COF) for photocatalytic hydrogen generation. *J Am Chem Soc* 140:1423–1427
110. Wang X, Chen L, Chong SY et al (2018) Sulfone-containing covalent organic frameworks for photocatalytic hydrogen evolution from water. *Nat Chem* 10:1180–1189
111. Zhang Y-P, Tang H-L, Dong H et al (2020) Covalent-organic framework based Z-scheme heterostructured noble-metal-free photocatalysts for visible-light-driven hydrogen evolution. *J Mater Chem A* 8:4334–4340. <https://doi.org/10.1039/C9TA12870K>
112. Li H, Zhang L (2017) Photocatalytic performance of different exposed crystal facets of BiOCl. *Curr Opin Green Sustain Chem* 6:48–56. <https://doi.org/10.1016/j.cogsc.2017.05.005>
113. Wang M, Ye M, Iocozzia J et al (2016) Plasmon-mediated solar energy conversion via photocatalysis in noble metal/semiconductor composites. *Adv Sci* 3:1600024. <https://doi.org/10.1002/adv.201600024>
114. Yuan L, Weng B, Colmenares JC et al (2017) Multichannel charge transfer and mechanistic insight in metal decorated 2D–2D Bi<sub>2</sub>WO<sub>6</sub>–TiO<sub>2</sub> cascade with enhanced photocatalytic performance. *Small* 13:1702253. <https://doi.org/10.1002/sml.201702253>
115. Gao H, Zhang P, Zhao J et al (2017) Plasmon enhancement on photocatalytic hydrogen production over the Z-scheme photosynthetic heterojunction system. *Appl Catal B Environ* 210:297–305. <https://doi.org/10.1016/j.apcatb.2017.03.050>
116. Fu J, Cao S, Yu J (2015) Dual Z-scheme charge transfer in TiO<sub>2</sub>–Ag–Cu<sub>2</sub>O composite for enhanced photocatalytic hydrogen generation. *J Mater* 1:124–133. <https://doi.org/10.1016/j.jmat.2015.02.002>
117. Zhao J, Zhang P, Wang Z et al (2017) Direct evidence of multichannel-improved charge-carrier mechanism for enhanced photocatalytic H<sub>2</sub> evolution. *Sci Rep* 7:16116. <https://doi.org/10.1038/s41598-017-12203-y>
118. Zhao H, Li C-F, Hu Z-Y et al (2021) Size effect of bifunctional gold in hierarchical titanium oxide-gold-cadmium sulfide with slow photon effect for unprecedented visible-light hydrogen production. *J Colloid Interface Sci* 604:131–140. <https://doi.org/10.1016/j.jcis.2021.06.167>
119. Zou Y, Shi J-W, Ma D et al (2017) Fabrication of g-C<sub>3</sub>N<sub>4</sub>/Au/C-TiO<sub>2</sub> hollow structures as visible-light-driven Z-scheme photocatalysts with enhanced photocatalytic H<sub>2</sub> evolution. *ChemCatChem* 9:3752–3761. <https://doi.org/10.1002/cctc.201700542>
120. Kim S-R, Jo W-K (2019) Application of a photostable silver-assisted Z-scheme NiTiO<sub>3</sub> nanorod/g-C<sub>3</sub>N<sub>4</sub> nanocomposite for efficient hydrogen generation. *Int J Hydrogen Energy* 44:801–808. <https://doi.org/10.1016/j.ijhydene.2018.11.014>
121. Zhao W, Li Y, Zhao P et al (2021) Novel Z-scheme Ag-C<sub>3</sub>N<sub>4</sub>/SnS<sub>2</sub> plasmonic heterojunction photocatalyst for degradation of tetracycline and H<sub>2</sub> production. *Chem Eng J* 405:126555. <https://doi.org/10.1016/j.cej.2020.126555>
122. Kumar A, Rana A, Sharma G et al (2018) High-performance photocatalytic hydrogen production and degradation of levofloxacin by wide spectrum-responsive Ag/Fe<sub>3</sub>O<sub>4</sub> bridged SrTiO<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> plasmonic nanojunctions: joint effect of Ag and Fe<sub>3</sub>O<sub>4</sub>. *ACS Appl Mater Interfaces* 10:40474–40490. <https://doi.org/10.1021/acsami.8b12753>
123. Qian L, Hou Y, Yu Z et al (2018) Metal-induced Z-scheme CdS/Ag/g-C<sub>3</sub>N<sub>4</sub> photocatalyst for enhanced hydrogen evolution under visible light: the synergy of MIP effect and electron mediator of Ag. *Mol Catal* 458:43–51. <https://doi.org/10.1016/j.mcat.2018.07.027>

124. Geng R, Yin J, Zhou J et al (2019) In situ construction of Ag/TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> heterojunction nanocomposite based on hierarchical co-assembly with sustainable hydrogen evolution. *Nanomaterials* 10:1. <https://doi.org/10.3390/nano10010001>
125. Zhang R, Wang H, Li Y et al (2021) Investigation on the photocatalytic hydrogen evolution properties of Z-scheme Au NPs/CuInS<sub>2</sub>/NCN-CN x composite photocatalysts. *ACS Sustain Chem Eng* 9:7286–7297. <https://doi.org/10.1021/acssuschemeng.1c01234>
126. Zhang Z, Huang J, Fang Y et al (2017) A Nonmetal plasmonic Z-scheme photocatalyst with UV- to NIR-driven photocatalytic protons reduction. *Adv Mater* 29:1606688. <https://doi.org/10.1002/adma.201606688>
127. Li J, Lou Z, Li B (2021) Nanostructured materials with localized surface plasmon resonance for photocatalysis. *Chin Chem Lett*. <https://doi.org/10.1016/j.ccllet.2021.07.059>
128. Murali G, Vattikuti SVP, Kshetri YK et al (2021) Near-infrared-activated Z-scheme NaYF<sub>4</sub>: Yb/Tm@ Ag<sub>3</sub>PO<sub>4</sub>/Ag@ g-C<sub>3</sub>N<sub>4</sub> photocatalyst for enhanced H<sub>2</sub> evolution under simulated solar light irradiation. *Chem Eng J* 421:129687
129. Kumar A, Kumar A, Chand H, Krishnan V (2022) Upconversion nanomaterials for photocatalytic applications. *Upconversion nanophosphors*. Elsevier, New York, pp 391–406
130. Duan C, Liang L, Li L et al (2018) Recent progress in upconversion luminescence nanomaterials for biomedical applications. *J Mater Chem B* 6:192–209
131. Sun Q-C, Mundoor H, Ribot JC et al (2014) Plasmon-enhanced energy transfer for improved upconversion of infrared radiation in doped-lanthanide nanocrystals. *Nano Lett* 14:101–106
132. Chen G, Qiu H, Prasad PN, Chen X (2014) Upconversion nanoparticles: design, nanochemistry, and applications in theranostics. *Chem Rev* 114:5161–5214. <https://doi.org/10.1021/cr400425h>
133. Zhang Y, Wang L, Park SH et al (2019) Single near-infrared-laser driven Z-scheme photocatalytic H<sub>2</sub> evolution on upconversion material@Ag<sub>3</sub>PO<sub>4</sub>@black phosphorus. *Chem Eng J* 375:121967. <https://doi.org/10.1016/j.cej.2019.121967>
134. Pan J, You M, Chi C et al (2018) The two dimension carbon quantum dots modified porous g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> nano-heterojunctions for visible light hydrogen production enhancement. *Int J Hydrogen Energy* 43:6586–6593. <https://doi.org/10.1016/j.ijhydene.2018.02.067>
135. Wang G, Ma X, Wei S et al (2018) Highly efficient visible-light driven photocatalytic hydrogen production from a novel Z-scheme Er<sub>3+</sub>:YAlO<sub>3</sub>/Ta<sub>2</sub>O<sub>5</sub>-V<sup>5+</sup>//Fe<sub>3+</sub>-TiO<sub>2</sub>/Au coated composite. *J Power Sources* 373:161–171. <https://doi.org/10.1016/j.jpowsour.2017.11.005>
136. Tan C, Cao X, Wu X-J et al (2017) Recent advances in ultrathin two-dimensional nanomaterials. *Chem Rev* 117:6225–6331
137. Zhu M, Sun Z, Fujitsuka M, Majima T (2018) Z-scheme photocatalytic water splitting on a 2D heterostructure of black phosphorus/bismuth vanadate using visible light. *Angew Chem* 130:2182–2186. <https://doi.org/10.1002/ange.201711357>
138. Zhu M, Sun Z, Fujitsuka M, Majima T (2018) Z-scheme photocatalytic water splitting on a 2D heterostructure of black phosphorus/bismuth vanadate using visible light. *Angew Chem Int Ed* 57:2160–2164. <https://doi.org/10.1002/anie.201711357>
139. Li Z, Hou J, Zhang B et al (2019) Two-dimensional Janus heterostructures for superior Z-scheme photocatalytic water splitting. *Nano Energy* 59:537–544
140. Xu Q, Zhu B, Jiang C et al (2018) Constructing 2D/2D Fe<sub>2</sub>O<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> direct Z-scheme photocatalysts with enhanced H<sub>2</sub> generation performance. *Sol Rrl* 2:1800006
141. Liu D, Zhang S, Wang J et al (2019) Direct Z-scheme 2D/2D photocatalyst based on ultrathin g-C<sub>3</sub>N<sub>4</sub> and WO<sub>3</sub> nanosheets for efficient visible-light-driven H<sub>2</sub> generation. *ACS Appl Mater Interfaces* 11:27913–27923
142. Xie H, Zhao Y, Li H et al (2019) 2D BiVO<sub>4</sub>/g-C<sub>3</sub>N<sub>4</sub> Z-scheme photocatalyst for enhanced overall water splitting. *J Mater Sci* 54:10836–10845
143. Shi J, Li S, Wang F et al (2019) In situ topotactic formation of 2D/2D direct Z-scheme Cu<sub>2</sub>S/Zn<sub>0.67</sub>Cd<sub>0.33</sub>S in-plane intergrowth nanosheet heterojunctions for enhanced photocatalytic hydrogen production. *Dalt Trans* 48:3327–3337
144. Shi J, Li S, Wang F et al (2018) In situ topotactic fabrication of direct Z-scheme 2D/2D ZnO/ZnxCd1-xS single crystal nanosheet heterojunction for efficient photocatalytic water splitting. *Catal Sci Technol* 8:6458–6467. <https://doi.org/10.1039/C8CY01884G>
145. Wang K, Jiang L, Wu X, Zhang G (2020) Vacancy mediated Z-scheme charge transfer in a 2D/2D La<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>/gC<sub>3</sub>N<sub>4</sub> nanojunction as a bifunctional photocatalyst for solar-to-energy conversion. *J Mater Chem A* 8:13241–13247



146. Zhu B, Cheng B, Fan J et al (2021) g-C<sub>3</sub>N<sub>4</sub>-based 2D/2D composite heterojunction photocatalyst. *Small Struct* 2:2100086. <https://doi.org/10.1002/sstr.202100086>
147. Qin M-Z, Fu W-X, Guo H et al (2021) 2D/2D heterojunction systems for the removal of organic pollutants: a review. *Adv Colloid Interface Sci* 297:102540. <https://doi.org/10.1016/j.cis.2021.102540>
148. Su Q, Li Y, Hu R et al (2020) Heterojunction photocatalysts based on 2D materials: the role of configuration. *Adv Sustain Syst* 4:2000130. <https://doi.org/10.1002/advs.202000130>
149. Su J, Li G, Li X, Chen J (2019) 2D/2D heterojunctions for catalysis. *Adv Sci* 6:1801702. <https://doi.org/10.1002/advs.201801702>
150. Liu L, Hu P, Cui W et al (2017) Increased photocatalytic hydrogen evolution and stability over nano-sheet g-C<sub>3</sub>N<sub>4</sub> hybridized CdS core@shell structure. *Int J Hydrog Energy* 42:17435–17445. <https://doi.org/10.1016/j.ijhydene.2017.02.171>
151. Subudhi S, Paramanik L, Sultana S et al (2020) A type-II interband alignment heterojunction architecture of cobalt titanate integrated UiO-66-NH<sub>2</sub>: a visible light mediated photocatalytic approach directed towards Norfloxacin degradation and green energy (Hydrogen) evolution. *J Colloid Interface Sci* 568:89–105
152. Zou L, Wang H, Wang X (2017) High efficient photodegradation and photocatalytic hydrogen production of CdS/BiVO<sub>4</sub> heterostructure through Z-scheme process. *ACS Sustain Chem Eng* 5:303–309. <https://doi.org/10.1021/acssuschemeng.6b01628>
153. Ma D, Shi J-W, Zou Y et al (2017) Rational design of CdS@ZnO core-shell structure via atomic layer deposition for drastically enhanced photocatalytic H<sub>2</sub> evolution with excellent photostability. *Nano Energy* 39:183–191. <https://doi.org/10.1016/j.nanoen.2017.06.047>
154. Liu F, Shi R, Wang Z et al (2019) Direct Z-scheme hetero-phase junction of black/red phosphorus for photocatalytic water splitting. *Angew Chem* 131:11917–11921
155. Liu F, Shi R, Wang Z et al (2019) Direct Z-scheme hetero-phase junction of black/red phosphorus for photocatalytic water splitting. *Angew Chem Int Ed* 58:11791–11795. <https://doi.org/10.1002/anie.201906416>
156. Kramm UI, Marschall R, Rose M (2019) Pitfalls in heterogeneous thermal, electro- and photocatalysis. *ChemCatChem* 11:2563–2574. <https://doi.org/10.1002/cctc.201900137>
157. Wang Q, Hisatomi T, Jia Q et al (2016) Scalable water splitting on particulate photocatalyst sheets with a solar-to-hydrogen energy conversion efficiency exceeding 1%. *Nat Mater* 15:611–615. <https://doi.org/10.1038/nmat4589>
158. Kisch H (2015) *Semiconductor photocatalysis*. Wiley, New York
159. Abd-Rabboh HSM, Benaissa M, Hamdy MS et al (2021) Synthesis of an efficient, and recyclable mesoporous BiVO<sub>4</sub>/TiO<sub>2</sub> direct Z-scheme heterojunction by sonochemical route for photocatalytic hydrogen production and photodegradation of rhodamine B dye in the visible region. *Opt Mater (Amst)* 114:110761. <https://doi.org/10.1016/j.optmat.2020.110761>
160. Guan R, Zhai H, Li J et al (2020) Reduced mesoporous TiO<sub>2</sub> with Cu<sub>2</sub>S heterojunction and enhanced hydrogen production without noble metal cocatalyst. *Appl Surf Sci* 507:144772. <https://doi.org/10.1016/j.apsusc.2019.144772>
161. Maček Kržmanc M, Daneu N, Čontala A et al (2021) SrTiO<sub>3</sub>/Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> nanoheterostructural platelets synthesized by topotactic epitaxy as effective noble-metal-free photocatalysts for pH-neutral hydrogen evolution. *ACS Appl Mater Interfaces* 13:370–381. <https://doi.org/10.1021/acsaami.1c16253>
162. Xing X, Zhu H, Zhang M et al (2018) Interfacial oxygen vacancy layer of a Z-scheme BCN–TiO<sub>2</sub> heterostructure accelerating charge carrier transfer for visible light photocatalytic H<sub>2</sub> evolution. *Catal Sci Technol* 8:3629–3637. <https://doi.org/10.1039/C8CY01035H>
163. Xie YP, Yang Y, Wang G, Liu G (2017) Oxygen vacancies promoted interfacial charge carrier transfer of CdS/ZnO heterostructure for photocatalytic hydrogen generation. *J Colloid Interface Sci* 503:198–204. <https://doi.org/10.1016/j.jcis.2017.05.006>
164. Liu J, Tao Z, Xie H et al (2019) Facial construction of defected NiO/TiO<sub>2</sub> with Z-scheme charge transfer for enhanced photocatalytic performance. *Catal Today* 335:269–277. <https://doi.org/10.1016/j.cattod.2018.11.055>
165. Tian B, Tian B, Smith B et al (2018) Supported black phosphorus nanosheets as hydrogen-evolving photocatalyst achieving 5.4% energy conversion efficiency at 353 K. *Nat Commun* 9:1397. <https://doi.org/10.1038/s41467-018-03737-4>
166. Meng A, Zhu B, Zhong B et al (2017) Direct Z-scheme TiO<sub>2</sub>/CdS hierarchical photocatalyst for enhanced photocatalytic H<sub>2</sub>-production activity. *Appl Surf Sci* 422:518–527. <https://doi.org/10.1016/j.apsusc.2017.06.028>

167. Qiu B, Zhu Q, Du M et al (2017) Efficient solar light harvesting CdS/Co9S8 hollow cubes for Z-scheme photocatalytic water splitting. *Angew Chem* 129:2728–2732. <https://doi.org/10.1002/ange.201612551>
168. Qiu B, Zhu Q, Du M et al (2017) Efficient solar light harvesting CdS/Co9S8 hollow cubes for Z-scheme photocatalytic water splitting. *Angew Chem Int Ed* 56:2684–2688. <https://doi.org/10.1002/anie.201612551>
169. Li X, Xie K, Song L et al (2017) Enhanced photocarrier separation in hierarchical graphitic-C<sub>3</sub>N<sub>4</sub>-supported CuInS<sub>2</sub> for noble-metal-free Z-scheme photocatalytic water splitting. *ACS Appl Mater Interfaces* 9:24577–24583. <https://doi.org/10.1021/acsami.7b06030>
170. Rauf A, Ma M, Kim S et al (2018) Mediator-and co-catalyst-free direct Z-scheme composites of Bi<sub>2</sub>WO<sub>6</sub>-Cu<sub>3</sub>P for solar-water splitting. *Nanoscale* 10:3026–3036
171. Yuan Q, Liu D, Zhang N et al (2017) Noble-metal-free janus-like structures by cation exchange for Z-scheme photocatalytic water splitting under broadband light irradiation. *Angew Chem* 129:4270–4274. <https://doi.org/10.1002/ange.201700150>
172. Yuan Q, Liu D, Zhang N et al (2017) Noble-metal-free janus-like structures by cation exchange for Z-scheme photocatalytic water splitting under broadband light irradiation. *Angew Chem Int Ed* 56:4206–4210. <https://doi.org/10.1002/anie.201700150>
173. Zou Y, Shi JW, Ma D et al (2017) Fabrication of g-C<sub>3</sub>N<sub>4</sub>/Au/C-TiO<sub>2</sub> hollow structures as visible-light-driven Z-scheme photocatalysts with enhanced photocatalytic H<sub>2</sub> evolution. *ChemCatChem* 9:3752–3761
174. Wang J, Wang G, Wang X et al (2019) 3D/2D direct Z-scheme heterojunctions of hierarchical TiO<sub>2</sub> microflowers/g-C<sub>3</sub>N<sub>4</sub> nanosheets with enhanced charge carrier separation for photocatalytic H<sub>2</sub> evolution. *Carbon N Y* 149:618–626. <https://doi.org/10.1016/j.carbon.2019.04.088>
175. Cai H, Wang B, Xiong L et al (2019) Orienting the charge transfer path of type-II heterojunction for photocatalytic hydrogen evolution. *Appl Catal B Environ* 256:117853
176. Zhou BX, Ding SS, Wang Y et al (2020) Type-II/type-II band alignment to boost spatial charge separation: A case study of g-C<sub>3</sub>N<sub>4</sub> quantum dots/a-TiO<sub>2</sub>/r-TiO<sub>2</sub> for highly efficient photocatalytic hydrogen and oxygen evolution. *Nanoscale* 12:6037–6046. <https://doi.org/10.1039/d0nr00176g>
177. Pan J, Dong Z, Wang B et al (2019) The enhancement of photocatalytic hydrogen production via Ti<sub>3+</sub> self-doping black TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> hollow core-shell nano-heterojunction. *Appl Catal B Environ* 242:92–99
178. Jiang E, Song N, Che G et al (2020) Construction of a Z-scheme MoS<sub>2</sub>/CaTiO<sub>3</sub> heterostructure by the morphology-controlled strategy towards enhancing photocatalytic activity. *Chem Eng J* 399:125721. <https://doi.org/10.1016/j.cej.2020.125721>
179. Liu Y, Zhang H, Ke J et al (2018) 0D (MoS<sub>2</sub>)/2D (g-C<sub>3</sub>N<sub>4</sub>) heterojunctions in Z-scheme for enhanced photocatalytic and electrochemical hydrogen evolution. *Appl Catal B Environ* 228:64–74. <https://doi.org/10.1016/j.apcatb.2018.01.067>
180. Xu F, Zhang L, Cheng B, Yu J (2018) Direct Z-scheme TiO<sub>2</sub>/NiS core-shell hybrid nanofibers with enhanced photocatalytic H<sub>2</sub>-production activity. *ACS Sustain Chem Eng* 6:12291–12298
181. Liang Y-H, Liao M-W, Mishra M, Perng T-P (2019) Fabrication of Ta<sub>3</sub>N<sub>5</sub>ZnO direct Z-scheme photocatalyst for hydrogen generation. *Int J Hydrogen Energy* 44:19162–19167. <https://doi.org/10.1016/j.ijhydene.2018.07.117>
182. Guo H-L, Du H, Jiang Y-F et al (2017) Artificial photosynthetic Z-scheme photocatalyst for hydrogen evolution with high quantum efficiency. *J Phys Chem C* 121:107–114. <https://doi.org/10.1021/acs.jpcc.6b10013>
183. Zhang W, Hu Y, Yan C et al (2019) Surface plasmon resonance enhanced direct Z-scheme TiO<sub>2</sub>/ZnTe/Au nanocorn cob heterojunctions for efficient photocatalytic overall water splitting. *Nanoscale* 11:9053–9060

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