

Chapter 26

Hybridized Nanomaterials for Enhancing Photocatalytic Activity in Solar Fuel Production



Özlem Kap, Nesrin Horzum, and Canan Varlikli

Abstract Meeting the increasing demand for energy and clean water, access to these resources has become an essential requirement of modern human life. Nanohybrid material engineering is significant for the development of functional materials which can be used as photocatalyst. By optimizing the size, shape, and surface properties of such nanostructures, the photocatalytic process in terms of ensuring sustainable resource supply can be improved. The hybrid nanomaterials aim to obtain a high visible light absorption and low charge recombination resulting in a superior efficiency of photocatalytic reactions. The application areas which benefit from such nanohybrid materials are the filtration and degradation of organic pollutants and the photochemical hydrogen production for solar water splitting. This chapter describes in detail the nanohybrid materials including metal oxides, carbon-based materials, metal sulfides, metal–organic frameworks, and transition metal phosphides as well as bandgap tuning based on these structures, which affect the efficiency of photocatalysis.

Keywords Photocatalytic activity • Energy conversion • Photocatalytic degradation • Nanohybrid materials • Heterostructure • Solar fuel

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26.1 Introduction

The non-renewable energy resources reserve mainly constituted of fossil fuels have a limited source and might be run out in the near future, causing an energy crisis [121]. Besides, the pollutant gases have produced by these fossil resources threaten global life due to contamination of air and climate change [38, 159]. Therefore, it has become important to improve the use of renewable resources which can supply the energy demand of the world. While the sources such as wind, biomass, hydro, geothermal, which have all renewable energy potential, have a strong production performance, the solar energy potential is relatively high, and it differs from the others remarkably given the capacity [193].

In recent years, the production of fuels such as hydrogen, methanol, and methane produced by converting solar energy into chemical energy has become a very rational approach to meet the energy demand and to cope with the environmental challenges. Photoelectrochemical (PEC) water splitting and CO₂ reduction is performed by using different semiconductor nanostructures as a photocatalyst to perform the solar-to-fuel conversion. Figure 26.1a shows the primary mechanism of water splitting by using a semiconductor photocatalyst. This mechanism works as follows: when a photocatalyst exposed the light which is greater or equal to its bandgap energy, absorbs the photons. Thus electrons and holes are formed bounded by Coulomb forces on the valance band and conduction band, respectively [233]. The semiconductor utilizes a proton to excite an electron from valance band to the conduction band in an excited state. The exposed light excites the electrons into the conduction band by leaving behind the holes in the valance band, as seen in Fig. 26.1b. An oxidation–reduction reaction proceeds during the exposure of the light. The charge carriers dissociate in a catalyst–liquid interface to produce hydrogen and oxygen from water molecules. However, one of the challenges during

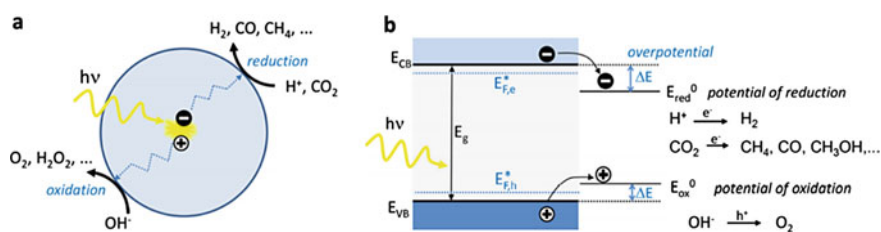


Fig. 26.1 **a** Photocatalytic processes on semiconductor nanomaterial involving photoexcitation and formation of electron–hole pair in the nanomaterial. The charges separately diffuse to the surface, where they can participate in reduction and oxidation reactions, respectively; **b** Energy diagram of the same process for a semiconductor with conduction band minimum located at E_{CB} and valence band maximum at E_{VB} , separated by a bandgap E_g . The overpotentials, ΔE , shown in blue, provide the driving force for the transfer of the charges to the electron acceptor (reduction) and donor (oxidation) molecules. the Fermi levels of the electrons and the holes are elevated to so-called quasi-Fermi levels, corresponding to Fermi levels under illumination (from Ref. [233] with permission from American Chemical Society)

the reaction is that the electrons and holes recombine on the catalyst surface, which resulted in low conversion efficiency.

In order to increase the photoconversion efficiency of the semiconductor nanomaterials, some methods used have led to the emergence of different strategies. These strategies may involve changing the shape, size, composition, and thus the active surface sites of the semiconductor photocatalysis [15]. It may involve doping method, surface functionalization, or forming a new interface with different nanomaterials as a heterostructure [190]. Therefore, the electronic band structure of the material would differ, and the solar-to-fuel efficiency would result in various efficiency depending on the bandgap engineering of the material. The required minimum energy transfer to achieve water splitting should be 1.23 eV per electron, according to Nernst's equation [254]. Thus, the photocatalyst to be used must absorb solar light photon energy greater than 1.23 eV. In a photoanode to conduct the oxygen evolution reaction (OER), the valence band must be more positive than the O_2/H_2O potential. In contrast, in a photocathode, the hydrogen evolution reaction (HER) would be conducted with more negative potential than the H^+/H_2 potential [227]. The band edge positions of different materials are shown in Fig. 26.2.

The requirement to perform an effective PEC water splitting and to commercialize it is to increase light-to-energy conversion efficiency. Until today, studies have been carried out on the development of low-priced, non-toxic, stable, and efficient semiconductor materials that can absorb the light in the visible region of the electromagnetic spectrum. It should be noted that the solar light, which is a green energy source by itself, is also included in the scope of green energy in the many synthesis methods of photocatalysts used to harvest it.

Many literature studies, in which all configurable and hybrid combinations of nanomaterials have been investigated using as a photocathode or photoanode in overall solar water splitting reaction to increase efficiency as a photocatalyst. This book chapter focuses on recent studies on solar-to-fuel conversion because of the

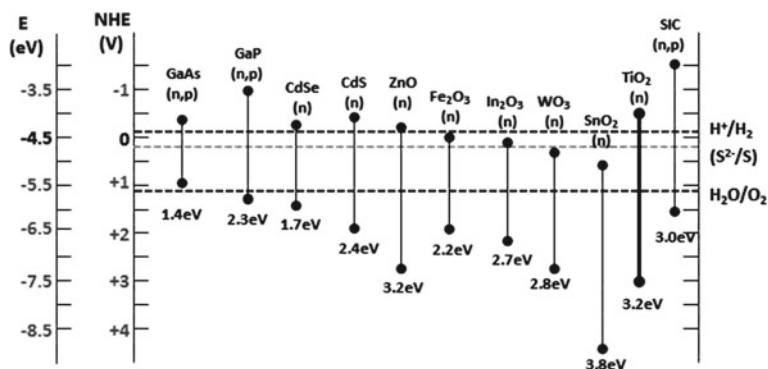


Fig. 26.2 Band edge positions of semiconductors and their relevance with photocatalytic H_2 generation

highly efficient nanomaterials such as metal oxides, metal–organic frameworks, carbon-based materials, metal sulphides, and phosphides which have been used mostly for photoelectrochemical water splitting applications. The factors which reduce the efficiency of solar conversion will be discussed based on the electron–hole recombination, limited photon absorption, and charge separation efficiency for the mentioned nanomaterials. This chapter has been evaluated for water splitting and CO₂ reduction application of the nanomaterials, however, it should be noted that the same structures can also be used for photocatalytic degradation application.

26.2 Metal Oxides

In this section, we aim to focus on the use of hybridized metal oxide nanomaterials in the study of photocatalysis for hydrogen generation from water splitting, pollutant degradation, and greenhouse gas reduction. Nanostructured metal oxides are ideal photocatalysts due to their high surface area, reactive sites, bandgap, and morphology [116, 213]. The metal oxide first remembered as a photocatalyst is titanium dioxide (TiO₂) with its non-toxicity, chemical stability, and high photocatalytic activity. However, one disadvantage is the wide bandgap (3.2 eV) that makes TiO₂ only sensitive to the ultraviolet (UV) region [48]. Another disadvantage is the fast electron–hole recombination and its relatively poor charge-carrying ability, resulting in low quantum efficiencies [96, 169]. Several approaches have been used to modify TiO₂ materials to overcome these disadvantages. Not only morphological modifications such as the production of TiO₂ nanomaterials with larger surface area, but also chemical modifications which include metal, non-metal, metal–non-metal, metal oxide doping, immobilization of TiO₂ on secondary substrates, and the use of nanomaterials as TiO₂ support, composite fabrication with semi-conductors have been applied to increase photocatalytic activity. In this context, some studies which have been conducted in recent years are classified in Table 26.1.

Doping is one of the frequently used methods to increase the photocatalytic activity of TiO₂ by reducing the bandgap and constructing new energy levels. The proper amount of doping will reduce the recombination of photogenerated charges, but when used excessively, they act as a recombination center [5]. One of the favorite metal doping for TiO₂ semiconductor is iron which is non-toxic, inexpensive, and earth-abundant element. Because the ionic radius of iron is very close to the TiO₂ lattice parameter [306], in this case, it can also be doped easily. However, the iron doping process requires precise control during synthesis. Xu et al. showed that the photocatalytic performance of Fe-doped TiO₂ varies depending on the method of synthesis, iron precursor, and iron concentration which cause the changes in porosity, particle size, and morphology [291]. The CH₄ formation yield was 0.23 μmol g⁻¹ h⁻¹ under visible light illumination for Fe-doped TiO₂. Its specific surface area and bandgap were 275 m² g⁻¹, 2.75 eV, respectively. Fe-TiO₂-500 was synthesized via one-step hydrothermal method at 500 °C. BET

Table 26.1 The chemical modification classification for TiO₂

Chemical modifications			
Metal doping	Bimetal doping	Metal oxide doping	Metal/non-metal doping
Silver (Ag) [69], Aluminium (Al) [191] Cobalt (Co) [307] Chromium (Cr) [170] Copper (Cu) [41] Erbium (Er) [226] Gallium (Ga) [152] Lanthanum (La) [145] Magnesium (Mg) [179] Molybdenum (Mo) [115] Manganese (Mn) [236] Nickel (Ni) [110] Niobium (Nb) [173] Palladium (Pd) [212] Platinum (Pt) [39] Rhodium (Rh) [108] Ruthenium (Ru) [4] Antimony (Sb) [133] Tin (Sn) [228] Strontium (Sr) [326] Terbium (Tb) [274] Vanadium (V) [194] Tungsten (W) [137] Ytterbium (Y) [14] Zinc (Zn) [104] Zirconium (Zr) [46]	Au–Ag [304] Bi–Y [76] Cu–Ni [160] Cu–Zn [160] Fe–Ni [240] Ni–Bi [183] Ni–Cr [218] Ni–Si [129] Mn–Zn [276] Er–W [113] La–Nb [75] Rh–Sb [106] Sn–La [343] Sr–Rh [184] Zr–Ag [180] Zr–Pd [46] Nanomaterials supported on TiO₂ Ag nanoparticles [332] Au nanoparticles [187] Au–Pd nanoparticles [42] Bi nanoparticles [333] Cu nanoparticles [210] CuO nanoparticles [312] Pd–Au nanoparticles [224] PdCoNi nanoparticles [24] Pt nanoparticles [234] Pt–Pb nanoparticles [9] SnO ₂ nanostructures [256]	Cu ₂ O [296] Fe ₂ O ₃ [177] MoO ₃ [109] NiO [112] PdO [105] PtO [174] SnO ₂ [83] WO ₃ [66] V ₂ O ₅ [198] ZnO [189] ZrO ₂ [157] Hybrid TiO₂ nanostructures Graphitic carbon nitride (g-C ₃ N ₄)–Pt–TiO ₂ [313] TiO ₂ supported MOF-199 derived Cu–Cu ₂ O nanoparticles [158] g-C ₃ N ₄ nanosheet hybridized N-doped TiO ₂ nanofibers [77] TiO ₂ /FeMnP core/shell nanorod [216] Pd-decorated hierarchical TiO ₂ constructed from the MOFs NH ₂ -MIL-125(Ti) [300] Cu/TiO ₂ /Ti ₃ C ₂ T _x [192] NH ₂ -MIL-125(Ti)/TiO ₂ [309] Cu/TiO ₂ core–shell heterostructures derived from Cu-MOF [176] TiO ₂ nanorod mats surface sensitized by cobalt ZIF-67 [56] Fe ₂ TiO ₅ –TiO ₂ [321] MOF-derived TiO ₂ photoanodes sensitized with quantum dots (CdSe@CdS) [221] Ru species supported on MOF-derived N-doped TiO ₂ /C hybrids [299]	Fe–N [54] Ag–N [316] K–Na–Cl [45] Non-metal doping Carbon (C) [130] Nitrogen (N) [107] Phosphorus (P) [171] Sulfur (S) [197] Selenium (Se) [287] Fluorine (F) [17] Chlorine (Cl) [270] Bromine (Br) [265] Iodine (I) [215] N–S [58] C–N–S [51] TiO₂ supported on secondary substances Activated carbon fibers (ACFs) [64] Carbon nanotubes (CNTs) [10] Graphitic carbon nitride (g-C ₃ N ₄) [229] Graphene [79] Graphene oxide [249] Silica [196] Aluminium silicate [95] Zeolite [315] Biochar [317] Poly(methyl methacrylate) nanofibers [134] Poly(styrene-co-vinylphosphonic acid) fibers [88]

specific surface area was 202 m^2 , and the bandgap was of 2.42 eV . The bandgap and porosity reduced by the changing the synthesis condition, which results in an increase of the CH_4 formation rate as $0.47 \mu\text{mol g}^{-1} \text{ h}^{-1}$.

The concentration of metal doping affects the photocatalytic activity of doped- TiO_2 since the metal doping may tune the anatase–rutile transformation during the synthesis [5]. Anatase is the indirect bandgap semiconductor, whereas rutile is direct bandgap semiconductor. Indirect bandgap anatase exhibits a longer lifetime of photoexcited electrons and holes. It has been shown that anatase has the lightest effective mass, which helps the fastest migration of photogenerated electrons and holes from the inside to surface of anatase TiO_2 by lowering the recombination rate of photogenerated charge carriers. Therefore, anatase TiO_2 has a higher photocatalytic activity than rutile TiO_2 [319].

Rutile and anatase have a band of 3.0 and 3.2 eV , respectively. Ding et al. have formed a heterojunction with these two phases, and the internal electric field has been built with two different work functions of anatase and rutile. They showed that the heterophase junction constructed by using TiO_2 nanobelt increases photocatalytic activity [49]. Figure 26.3 is a schematic illustration of the photocatalytic mechanism owing to the heterophase junction. Moreover, the O_2 production rate was investigated with increasing calcination temperature. The highest O_2 evolution rate of $0.352 \text{ mmol h}^{-1} \text{ g}^{-1}$ was obtained due to the formation of anatase/rutile heterophase junctions connections at $900 \text{ }^\circ\text{C}$. TiO_2 nanobelt calcinated at $600, 700, 800 \text{ }^\circ\text{C}$ were pure anatase, at $1000 \text{ }^\circ\text{C}$ was of pure rutile, and the O_2 evolution rate is $0.09, 0.124, 0.16$ and $0.198 \text{ mmol h}^{-1} \text{ g}^{-1}$, respectively. Thus, constructed anatase/rutile heterophase junctions enhanced carrier separation efficiency and carrier recombination suppress.

Some non-metallic element dopings which are most commonly used in the literature have been listed in Table 26.1. Non-metallic doping increases the light absorption in the visible region of TiO_2 , enhancing the electron–hole separation, but again they act as recombination centers due to the formed oxygen vacancies [5]. However, it was stated that the performance of the non-metallic doping could not enhance the photocatalytic activity as much as metallic doping [96]. The advantage

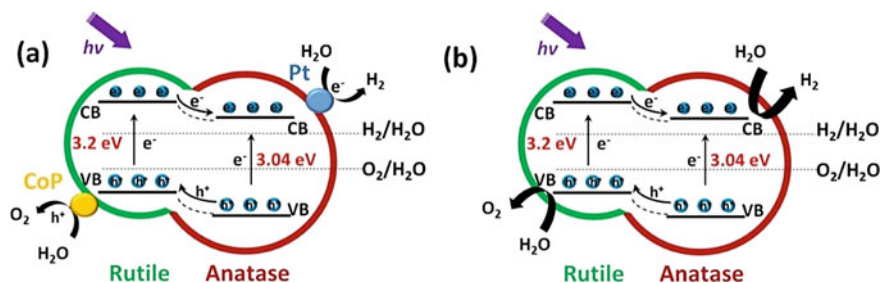


Fig. 26.3 Schematic illustration of the photocatalytic mechanism of the rutile/anatase heterophase junction **a** with and without Pt/CoP cocatalysts (Reprinted from Ref. [49] with permission from Elsevier)

of the non-metallic doping to metals does not act as electron traps, and they have been used to improve photocatalytic activity by using this feature [298].

The p-states of the non-metallic elements mix with the O-2p states of TiO₂ which causes redshift on the valance band and the bandgap decreases. Nitrogen is one of the most frequently used as dopants for TiO₂. Likewise, C doped TiO₂ also enables the formation of new energy levels above the valance band, so the lower absorption spectrum shifts to the higher wavelengths [12]. F-doped TiO₂ is another non-metal doping element, and they occupy the oxygen vacancies which are in the lattice rather than doping into the TiO₂. Thus, electron-hole recombination sites are reduced by fluorine. Moreover, Du et al. stated that the reason why F doping decreases photocatalytic activity is that element F causes surface fluorination, not doping [55]. A very high photocatalytic activity has been obtained by the F doping method by using Mesoporous mesocellular foams as support for fluorine atoms in a study. In order to increase the substitution of these atoms, the vacuum activation method was used to boost the oxygen vacancies in TiO₂, thus yielding Ti³⁺-F lattice structures.

The F-doped catalyst exhibits high photocatalytic activity and stability for H₂ evolution under solar light irradiation with an AM 1.5 air mass filter. The success of the technique attributed to the decrease of recombination sites by high concentration F doping and the synergistic effect between lattice Ti³⁺-F and surface Ti³⁺-F [289]. Other single metal oxides used for photocatalytic applications other than TiO₂ include ZnO [57, 87, 93], CeO₂ [85], CuO [203], Cu₂O [283], SnO₂ [186, 225], Fe₂O₃ [82], NiO [139], MoO₃ [205, 344], WO₃ [217], ZrO₂ [68], Ag₂O [268], Bi₂O₃ [266], In₂O₃ [90]. Besides defect engineering strategies such as surface hydrogenation, metal reduction, and thermal treatment to create oxygen vacancies, heterostructure engineering is considered to be another effective way of obtaining photocatalysts with improved efficiencies [11]. For example, metal catalysts (Au, Pt, Pd, Cu) and bimetallic catalysts (Au-M (M=La, Ni, Cu, Fe, Cr, Y), Pt-Cu, Pd-Cu) are supported on various single and dual metal oxides to enhance the light absorption capacity under UV light due to the Schottky barrier and SPR [40]. The photocatalytic activity of the metal oxides can be improved by not only changing the morphology (i.e., obtaining nanostructures with a core/shell structure) but also using binary metal oxides (ZnO/V₂O₅ [8], ZnO/In₂O₃ [43], CeO₂ supported on SiO₂ fibers [89], Fe₂O₃/TiO₂ [16], Fe₂O₃/WO₃ [178], ZnO Nanorod/ α -Fe₂O₃ [251], NiO/V₂O₅ [175], Bi₂O₃-BiFeO₃ [163], SnO₂/ZnO [341], WO₃-BiVO₄ nanostructures [120]) with higher oxygen mobility over the surface, visible light activity. Besides precious metals decorated binary metal oxides, ternary metal oxide nano-photocatalysts (CuO/CeO₂/ZnO [151] Bi₂O₃/Bi₂SiO₅/SiO₂ microspheres [320]) with more efficient photocatalytic performance have been studied. Moreover, QDs, carbon nanotubes, g-C₃N₄ are used as sensitizers for photocatalytic metal oxide structures such as ZnO/CdS [3], ZnO/CdTe [156], MoO₃-MWCNT [219] ZrO₂/g-C₃N₄ [94], etc. An important class of metal oxide catalysts in green energy production is perovskite oxides (such as titanate-based perovskites; ATiO₃ (A=Ba, Ca, Co, Cu, Fe, Mg, Mn, Ni, Pb, Sr, Zn), tantalite-based; KTaO₃, NaTaO₃, and other-metal-based perovskite oxide photocatalysts like BaZrO₃, LaFeO₃, and LaMnO₃ because of their excellent absorption, bandgap tunability, and water splitting [185].

26.3 Carbon-Based Nanomaterials

26.3.1 Graphene-Based Nanomaterials

Graphene (G) consists of a single layer of sp^2 hybridized carbon atoms, arranged in a 2D honeycomb lattice. In addition to being the thinnest material known, it is also the most robust material with a 1GPa Young' modulus [117]. Graphene synthesis can be carried out either by the top-down approach via mechanical, chemical, or electrochemical exfoliation methods or by the bottom-up approach via chemical vapor deposition and chemical synthesis methods [20]. In Table 26.2, the methods used to synthesize graphene-based structures are summarized, additively, the synthesis methods of composite structures have also been shown.

Graphene has drawn attention in solar fuel applications due to excellent properties such as high stability, large specific surface area, the strong adsorption capacity, high thermal and electrical conductivity [6]. The high surface area contributes to the stabilization of the metal NPs, metal oxide, and quantum dot structures because the expanded π orbitals of G overlap with the d orbitals of the metallic structures [6]. Thus, it can be seen from the literature studies shown in Table 26.2; the formed heterojunction contributes to the photocatalytic conversion efficiently.

A well-known structure among various graphene derivatives is graphene oxide (GO) which is obtained by the oxidation of graphene. Contrary to the hydrophobic nature of graphene, GO containing hydrophilic functional groups (hydroxyl, carbonyl, carboxyl, epoxide) eliminates the problem of aggregation in aqueous solutions [47]. GO has low electrical conductivity; however, it is increased by the reduction of GO [21]. In a study, Zhu et al. used Ag NPs, CdS NRs, and reduced graphene oxide(rGO) composite material as photocatalyst for CO_2 reduction [345]. According to the result, it was determined that CO_2 adsorption capacity of CdS was $5.01 \text{ cm}^3 \text{ g}^{-1}$, while rGO-CdS and Ag-rGO-CdS were 6.60 and $6.02 \text{ cm}^3 \text{ g}^{-1}$, respectively. Increased adsorption indicates the positive contribution of RGO's high electrical conductivity, p-p conjugation between the rGO and CO_2 , higher surface area ($46.2 \text{ m}^2 \text{ g}^{-1}$) and large surface active sites. Moreover, both Ag and RGO act as the electron acceptor, which expedite in the CO_2 reduction reaction.

The degree of the reduction of GO can change the bandgap of the material, which is essential in the photocatalytic applications [2]. The optical band gap obtained by incorporation of G/GO into different materials is shown in Table 26.2. It has been reported in the studies the existence of G or GO resulted in narrowed the bandgap [74, 102, 141, 201, 220, 231, 242, 269, 335]. As a result of the bandgap calculation with the Tauc plot analysis, Sorcar et al. found that doped GO amount with 0.25, 0.50, or 0.75 ml to the reduced blue titania (RBT) reduced the bandgap to 2.61, 2.41, 2.22 eV, respectively, which was 2.68 eV for pure RBT [231]. While the produced C_2H_6 and CH_4 amount increased for 0.25 and 0.50 doping, and it decreased compared to the two for 0.75 doping. Similarly, Wang et al. detected CH_4

Table 26.2 Typical photocatalytic H₂-production systems of graphene-based nanomaterials

Catalyst	Synthesize-preparation method	Optical bandgap (eV)	Application	Products/Activity ($\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$)	References
Graphene/TiO ₂ /Mo	Sol-gel for composite	2.62	Decomposition of methylene blue	–	[102]
Graphene/TiO ₂	Drop-casting for graphene film on FTO-glass/magnetron sputtering, thermal treatment for composite	–	Photoelectrochemical (PEC) water splitting	–	[252]
PbBiO ₂ Br/GO	Hydrothermal synthesis for composite	2.40	Removal of CO ₂ , crystal violet dye and 2-hydroxybenzoic acid	CH ₄ /1.193	[141]
TiO ₂ /GO/rGO	Electrochemical anodization for TiO ₂ , UV-A radiation for reduction of GO, reflux process for GO and rGO functionalization	–	Photocatalytic reduction of CO ₂	CO ₂ /760 $\mu\text{mol}\cdot\text{g}^{-1}$	[204]
Defective Graphene/NiO/Ni NPs	Pyrolysis for graphene, thermal treatment for composite	–	Photoassisted CO ₂ reduction by H ₂	CH ₄ /642.66	[165]
Graphene/UIO-66-NH ₂	Hydrothermal synthesis and microwave-irradiation induced solvothermal synthesis for composite	2.64	CO ₂ photo-reduction under visible-light	CO ₂ /42.6 μmol	[269]
rGO/CdS/ZnO	In-situ growth	2.12	Synthesis of the efficient hybrids for photocatalytic or PEC hydrogen generation	H ₂ /0.79 $\mu\text{mol}\cdot\text{cm}^{-2}\cdot\text{h}^{-1}$	[335]
N-doped defective graphene/RhCrOx /STO:Al	Pyrolysis for graphene, impregnation for composite	–	Produce a hybrid material for efficient photocatalyst	H ₂ /6375 O ₂ /3080	[167]

(continued)

Table 26.2 (continued)

Catalyst	Synthesize-preparation method	Optical bandgap (eV)	Application	Products/Activity ($\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$)	References
rGO/Rh ₂ O ₃ /Rh NPs	Hummers method for GO, Hydrothermal, thermal treatment for composite	–	CO ₂ photoreduction	CH ₄ /814.38	[101]
Graphene/Cu ₂ O	Pyrolysis for graphene	–	CO ₂ reduction	H ₂ /2031 $\mu\text{mol cm}^{-2} \text{h}^{-1}$	[91]
rGO/TiO ₂	Reflux and vacuum thermal treatment for composite	2.36	Photocatalytic reduction of CO ₂ into solar fuel	CH ₄ /12.75	[220]
N-doped rGO/TiO ₂ /ZnFe ₂ O ₄	Hummers method for graphene oxide, hydrothermal synthesis for composite	2.98	Degradation of reactive Yellow 86 and methanol oxidation	H ₂ /2481	[242]
Graphene/CeO ₂ /CuO/QDs	Calcination for graphene	1.75 (CuO-G) 2.70 (CeO ₂ -G)	Synthesis highly efficient material for solar-driven hydrogen production	–	[201]
rGO/CoFe ₂ O ₄ /TiO ₂	Hummers method for GO, Ultrasound-assisted wet impregnation for composite	3.20 (TiO ₂ -G) 1.38 (CoFe ₂ O-G)	Synthesis stable photocatalyst for high production of hydrogen	H ₂ /76559	[74]
N- and Co-doped graphene/TiO ₂	Hydrothermal synthesis for TiO ₂ , sonochemical and calcination methods for composite	–	Photocatalytic generation of H ₂ O ₂ within the visible light range	H ₂ /677.44	[307]
Graphene/Cu ₂ O	Pyrolysis for graphene	–	Photoassisted methanation	CH ₄ /14930	[164]
Graphene/reduced blue titania/Pt NPs	Annealing the mixture of graphene and RBT, Pt photo deposited composite	2.22	Photoconversion of CO ₂ to CH ₄ and C ₂ H ₆	CH ₄ /37 C ₂ H ₆ /11	[231]

(continued)

Table 26.2 (continued)

Catalyst	Synthesize-preparation method	Optical bandgap (eV)	Application	Products/Activity ($\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$)	References
Graphene/chlorophyll Cu	Film preparation method	2.66	Conversion of CO_2 to C_2H_6	$\text{C}_2\text{H}_6/68.23$	[282]
GO/Benzidine	Hummers' method for graphene, hydrothermal synthesis for composite	–		$\text{H}_2/690$	[339]
Multilayer Graphene/Gold nanoplatelets	Pyrolysis for composite	–	Synthesize an efficient photocatalyst for water splitting	$\text{H}_2/1200000$	[166]
Graphene nanoribbon/CdS	Solvothermal method for composite	2.17	H_2 evolution under visible-light illumination	$\text{H}_2/1890$	[285]

evolution for G-doped UIO-66-NH₂, and the evolution decreased for UIO-66-NH₂/3.0GR compared to UIO-66-NH₂/2.0GR [269]. The reason for the reduction is attributed to the excessive graphene which covers the active regions of the MOF structure. It is understood from the results that the optimum amount of G/GO doped materials increase the CH₄/H₂ evolution.

Any other G-doped nanostructure is bismuth oxyhalides, which are materials that may be the candidates for third-generation solar cell, can provide photocatalytic activity with visible light [305]. Recently, PbBiO₂Br/GO composite was produced via hydrothermal method as a new novel material with different grams of GO [141]. The morphology can be seen in Fig. 26.4. The bandgap energy of the composite was to 2.40 eV, which was lower compared to 2.47 eV bandgap energy of PbBiO₂Br. Thus, the composite material increased the photocatalytic conversion rate from CO₂ to CH₄. This change has been attributed to the double-bond resonant structure of GO which transports photo-generated electrons and suppresses the electron-hole recombination of the photocatalyst. Although the conversion of CO₂ to CH₄ is thermodynamically favorite, the requirement of 8 electrons makes this process kinetically complicated this process compared to the CO conversion, which requires 2 electrons transfer. In a study in which CO₂ conversion to CO was carried out by using multi-leg TiO₂ nanotubes wrapped with GO and rGO layer [204].

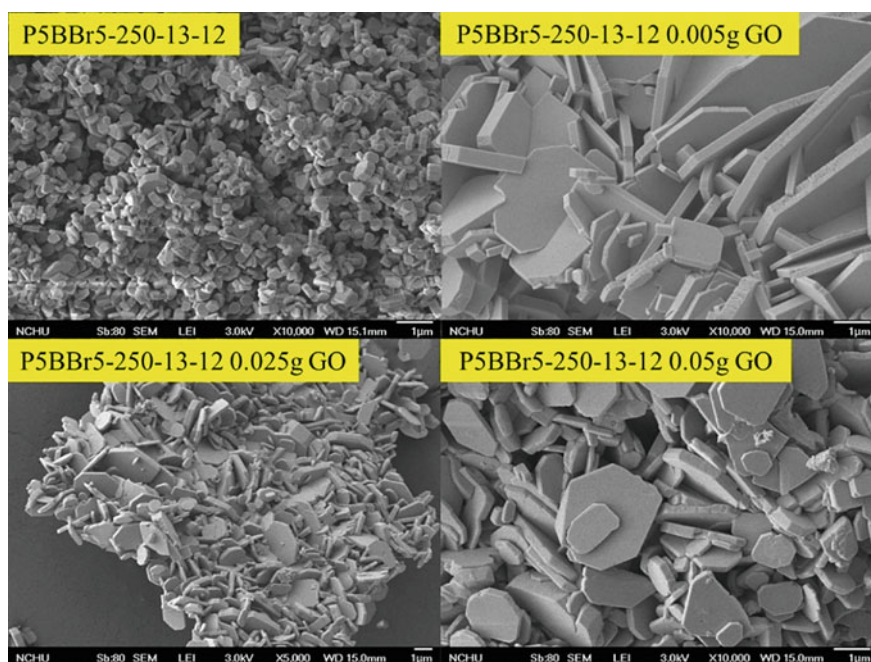


Fig. 26.4 SEM images of as-prepared samples by the hydrothermal autoclave method at different grams of GO (Molar ratio Pb:Br = 5:5, temp = 250 °C, time = 12 h) (Reprinted from Ref. [141] with permission from Elsevier)

Multi-leg TiO_2 nanotubes wrapped with GO and rGO were exposed to CO_2 for different periods. The rate of CO formation was observed to remain at the highest level ($760 \mu\text{mol g}^{-1}$) after 120 min for rGO wrapped nanotubes when compared to GO wrapped and bare multi-leg TiO_2 nanotubes. The high CO formation has been attributed to the electrical conductivity of GO/rGO layers connecting adjacent nanotubes which increased interaction between adsorbed CO_2 and photo-generated electrons.

The most important advantage of using graphene-based nanomaterials is that it increases the energy conversion by enhancing the photoabsorption and electron-hole separation with its high surface area. Moreover, the absorption spectrum of doped graphene and graphene with layer stacking defects extends from UV to NIR, which makes them an important class of material candidates for photocatalysis solar light [6].

26.3.2 Graphitic Carbon-Nitride

Two-dimensional (2-D) graphitic carbon nitride ($\text{g-C}_3\text{N}_4$) has become interested due to its unique properties such as its metal-free structure, easy preparation, high thermal and chemical stability, low cost [146, 161, 181]. The $\text{g-C}_3\text{N}_4$ has the photocatalytic activity under the visible-light with the bandgap of 2.7 eV [334]. However the photocatalytic performance of pure $\text{g-C}_3\text{N}_4$ is low, due to the rapid recombination rate of the photo-generated electron-hole pair and low specific surface area, but a growing number of studies exist about improvement in the lifetime of charge carriers in the literature [62, 325].

In order to enhance the photocatalytic performance, heterostructures are formed by combining with another semiconductor suitable for the band structure of $\text{g-C}_3\text{N}_4$ [62]. Li et al. classified the $\text{g-C}_3\text{N}_4$ heterojunction structures based on the charge transfer routes and the characteristics of $\text{g-C}_3\text{N}_4$ as type-II, Z-scheme, S-scheme, p-n heterojunctions and Schottky heterojunctions [135]. Type II heterojunctions are constructed with metal oxides (TiO_2 [7, 278, 284, 301, 336], CuO [301], ZnO [18, 100, 281] SnO [34, 263], Fe_2O_3 [200, 244, 294], CeO_2 [154, 232], WO_3 [28, 255], metal sulfides (CdS [33, 73, 81, 132, 257, 340]), SnS_2 [324], MoS_2 [131, 260], ZnIn_2S_4 [131, 202, 250]), metal telluride (ZnTe [264]) which have a more positive valence band than $\text{g-C}_3\text{N}_4$. While type II heterojunctions are successful in improvement of the charge carriers separation, the redox activity would be weakened due to the migration of the electrons and holes to the lower level of CB and VB, respectively [209]. For this reason, the charge transfer model inspired from the green plants, $\text{g-C}_3\text{N}_4$ based Z-scheme heterojunctions systems have been developed to ensure efficient separation of the charge carriers and to advance the redox activity of the charges in the liquid phase [123]. The system, called the direct Z-scheme, has been developed to perform electron transfer via solid materials instead of the liquid medium [293]. One of the drawbacks of the Z-scheme heterojunction systems is that the conductor material also absorbs light, and the light-harvesting efficiency of

both photocatalysts is reduced. In another drawback is; if the Fermi level of the solid conductor material which transfers the electron from the higher CB of one photocatalyst to the lower VB of the other photocatalyst is lower than the photocatalysts, a Schottky barrier forms causing the suppression of the electron flow. Besides, if the solid conductor during the synthesis is not precisely embedded between the photocatalysts, it only acts as a co-catalyst instead of charge transfer carrier [209, 292]. In order to eliminate these shortcomings, reduction photocatalyst (RP) and oxidation photocatalyst (OP) is used in g-C₃N₄ based S-scheme heterojunction systems. The internal electric field, band bending, and Coulombic attraction ensure the driving force for the charge transfer [292].

Various methods such as heat treatment, photo deposition, pyrolysis, ion exchange method, solvothermal and hydrothermal method, electrospinning method, deposition–precipitation method have been used in order to synthesize of g-C₃N₄ based materials with controllable morphology. The photocatalytic activities of the structures are summarized in Table 26.3 depending on the specific types of heterojunction with particular application, bandgap, and synthesis method for the composites.

Visible light responsive g-C₃N₄ material, which is an alternative to TiO₂ due to its unique properties, is being studied water splitting application for the efficient H₂ evolution. In order to improve the drawbacks mentioned above, type II, Z-scheme, and S-scheme heterojunction structures were developed to ensure high charges redox ability and efficient charge separation, especially in S-scheme heterojunctions, resulting in higher photocatalytic performance.

26.3.3 Carbon Quantum Dots (CQDs)

CQDs, which are zero-dimensional (0D) nanoparticles with sizes below 10 nm, are attractive because of their many unique and novel properties [295]. Their optical properties, fluorescence emissions, tunable bandgaps, and good chemical stability make it a great candidate for solar fuel applications [149]. Top-down synthesis approach with laser ablation, arc-discharge, and electrochemical oxidation, and bottom-up approach hydrothermal/solvothermal, microwave pyrolysis methods are known for the CQDs [13, 273]. During the synthesis process, the core structure of the CQDs can be functionalized with rich oxygen-containing functional groups such as carboxyl and hydroxyl [13]. That functional groups provide hybridization between CQDs and noble metals (NMs), which are turning up superior properties [65].

In solar fuel applications, CQDs increase the number of electron–hole pairs; thus, the enhancing charge transfer promotes photocatalytic activity. The hydrogen production mechanism has been depicted in four steps by using the carbon dots, as shown in Fig. 26.5. First, light irradiation and photon absorption occur; secondly, the electron is stimulated from the VB to the CB. Thirdly, the photo-produced electrons pass to the semiconductor surface, and finally, the resulting electrons and holes conduct the water-splitting process.

Table 26.3 The photocatalytic activities of the g-C₃N₄ based heterojunction type structures

g-C ₃ N ₄ based heterojunction type	Catalyst	Synthesis method	Application	Products/activity (μmol·g ⁻¹ ·h ⁻¹)	Optical bandgap (eV)	References
Type II	Ag ₂ S/K	Deposition	H ₂ evolution	H ₂ /895	2.65	[323]
	r-TiO ₂	Theoretical study	H ₂ S splitting	-	2.40	[278]
	SiC	Theoretical study	H ₂ production	-	2.0	[290]
	KNbO ₃ (100)	Theoretical study	Enhancing the photocatalytic performance	-	2.11	[155]
	ZnTe	Hydrothermal	CO ₂ reduction	CH ₃ CH ₂ OH/ 17.1 μmol cm ⁻² h ⁻¹	2.22	[264]
	Nb ₂ O ₅	Pulse sonication	PEC water splitting	-	2.82	[103]
	MoS ₂ QDs/ g-C ₃ N ₄	Calcination under Ar/H ₂	Degradation of methyl orange and phenol	-	2.52	[222]
	rGO/Fe ₂ O ₃	Hydrothermal	H ₂ production	H ₂ /6607	1.9	[244]
	Bi ₄ O ₅ Br ₂	Water-induced self-assembled	H ₂ O ₂ production of	H ₂ O ₂ / 300 μmol cm ⁻² h ⁻¹ g ⁻¹	2.39	[331]
	SWCNT	Two-step air etching	H ₂ evolution	H ₂ /1346	-	[275]
	NiMoO ₄	Calcination	CO ₂ conversion	CH ₄ /635, CO/432, O ₂ / 1853, HCOOH/647	2.31	[248]
	Cu ₂ O	Calcination	CO ₂ conversion	CH ₃ OH/2.83	2.1	[330]
	ZnO/ZnWO ₄	Calcination	CO ₂ conversion	-	-	[342]

(continued)

Table 26.3 (continued)

g-C ₃ N ₄ based heterojunction type	Catalyst	Synthesis method	Application	Products/activity (μmol·g ⁻¹ ·h ⁻¹)	Optical bandgap (eV)	References
S-scheme				CO/1.12, CH ₄ /6.24, CH ₃ OH/3.85, CH ₃ CH ₂ OH/1.98		
	SnFe ₂ O ₄	Hydrothermal	CO ₂ conversion	CO/7.56	–	[98]
	Nb-doped TiO ₂	Calcination	CO ₂ reduction	CH ₄ /562 CO/420 O ₂ /1702 HCOOH/698	~2.79	[247]
	WO ₃	Electrostatic self-assembly	H ₂ production	H ₂ /982	WO ₃ /2.68	[61]
	Zn _{0.2} Cd _{0.8} S/diethylenetriamine	Solvothermal	H ₂ production	H ₂ /6.69	Zn _{0.2} Cd _{0.8} S-DETA/ 2.48	[168]
	CdS	Calcination and hydrothermal	H ₂ production	H ₂ /15.3	CdS/2.30	[207]
	CuInS ₂	Hydrothermal	H ₂ production	H ₂ /373	CuInS ₂ /1.20	[150]

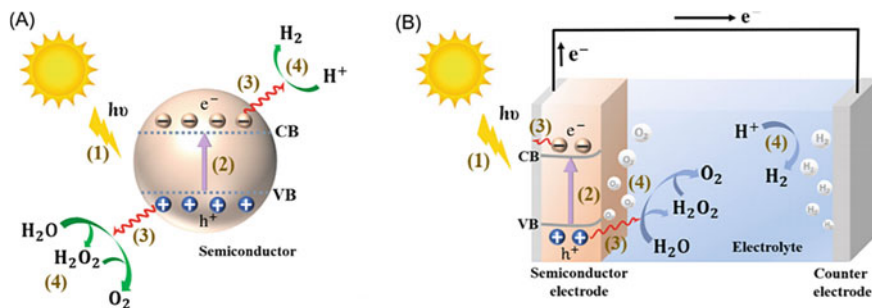


Fig. 26.5 Schematic illustration of the mechanisms for **A** photocatalytic and **B** photoelectrochemical hydrogen evolution (Reprinted from Ref. [71] with permission from Elsevier)

Sun et al. coated the Ag NPs with the CQDs to investigate the photocatalytic activity of the composite in which the highest photocatalytic obtained for AgNPs with 16% CQDs. The methanol (CH_3OH) formed as the main product by reduction of CO_2 in this reaction as $17.82 \mu\text{mol}$ after 10 h of illumination. The produced CH_3OH was three times more than the pure Ag catalyst [238]. Additionally, the dispersion effects of the CQDs prevents the NPs from the aggregation, thus increasing surface area is another crucial reason for the boosted photocatalytic activity [65]. Cobalt monoxide (CoO), which also has an aggregation problem during the synthesis, has high photocatalytic activity with 5% solar—to hydrogen efficiency (STH) [138]. Since the conversion efficiency obtained as a result of CoO/ $g\text{-}C_3N_4$ type II heterojunction systems were not optimal [261], this system was combined with CQDs. The ternary CoO/ $g\text{-}C_3N_4$ /CQDs system showed higher photocatalytic activity with the optimum H_2 conversion rate of $987.4 \mu\text{mol g}^{-1} \text{h}^{-1}$ compare to $BiVO_4$ /CQDs/ CdS with $1.24 \mu\text{mol/h}$ and NiO /CQDs/ $BiVO_4$ with $1.21 \mu\text{mol h}^{-1}$ [223]. The highly efficient photocatalytic activities of the carbon dots can be attributed to their electron-donating and accepting abilities, and possible active surface sites [124].

Some limiting factors to use of CQDs are the low absorption for long-wavelength, rapid decay in the initial excited state, long-term stability problem, and the weak interfacial interaction between carbon dots [149]. It is recommended that the chemical structure of the CQDs should be investigated to enhance charge transfer properties. Moreover, the future composite structures should be formed with biomaterials and copper chalcogenide structures other than metal, oxides, bismuth-based metal compounds, and carbon materials composite structures which already exist in the literature [30].

26.4 Metal Sulfide-Based Nanomaterials

Metal sulfides are one of the class of the semiconductor structures that are widely used in photocatalytic reactions for the conversion of water into hydrogen fuel using solar energy. The outstanding features; low cost, promising photocatalytic activity, long lifetime, high absorption in the visible spectrum with great mobilities of electrons and holes are the main reasons for their popularity [182]. Until today, there are various heterogeneous and hybrid structures produced with metal sulfides with superior properties for energy conversion [80].

The most commonly used structures in PEC applications of metal sulphides are CdS, ZnS, FeS₂, MoS₂, CuS, Bi₂S₃ and Sb₂S₃. Top-down and bottom-up approaches are used to synthesize these nanostructures. While the top-down approaches consist of sputtering, electrospinning, lithography, exfoliation, and milling; the bottom-up approaches have consisted of chemical vapor deposition, atomic layer deposition, pyrolysis, thermal deposition, pulsed laser deposition, micro-emulsion, precipitation, hydrothermal and solvothermal synthesis, electrodeposition, and microwave irradiation techniques [27, 36].

Especially CdS have drawn attention with the narrower direct band gap of 2.42 eV compared to TiO₂ which has 3.2 eV bandgap. Moreover, among the other sulfide structures, CdS have favorable photocatalytic performance due to the absorption wavelength, which is shorter 516 nm. This wavelength corresponds to a broader absorption spectrum, again compared with TiO₂, which absorbs the ultra-violet light with a wavelength of less than 387 nm [36]. However, the main issue that limits the use of CdS as photocatalyst is photocorrosion, lack of active sites, the high photo-generated electron-hole recombination rate [329]. Different types of heterostructures [243], co-catalysts incorporation [148], sacrificial reagents addition [72], metallic/non-metallic catalysts coupling [308] have been utilized to overcome the limitations.

Recently, Ren et al. have synthesized CdS coupled with a 2D Cu₇S₄ co-catalyst nanosheets, which increase the active sites and electron transfer yield, for photocatalytic hydrogen generation application [206]. It will be useful to consider the most striking aspects of this study based on the fundamental mechanism. The electron-hole pair of CdS nanosheets (NSs) easily recombined under irradiation, and H₂ evolution rate is lower. Efficient separation of electron-hole pairs was achieved by the presence of large contact areas, which is also shown by PL measurements between CdS/Cu₇S₄ NSs. The H₂ production for pure CdS increased from 2.6 mmol g⁻¹ h⁻¹ to 27.8 mmol g⁻¹ h⁻¹ for CdS-2% Cu₇S₄ composite. Moreover, the apparent quantum efficiency value of the composite decreased with increasing light wavelength at 420, 450, 500, and 550 nm resulted in 14.7%, 12.3%, 9.6%, and 7.2%, respectively. Light absorption wavelength of the heterostructure has affected the H₂ evolution. As another literature study, the 10 wt % CdS/g-C₃N₄ nanocomposite structure enabled the increase in the surface area and the improvement of charge separation. The H₂ evolution rate was increased to 216.48 μmol h⁻¹ g⁻¹, which is four times higher compared to pure CdS [97].

However, it was found that the photocatalytic activity obtained with 20% CdS/g-C₃N₄ nanocomposite was lower than pure CdS. This situation is attributed to the fact that the number of electrons generated from g-C₃N₄ may be decreased by the shielding effect of CdS. The H₂ production rate, experimental conditions, and bandgap values of the composites which were obtained with high efficiency by using sulphide-based nanostructures including CdS and MoS₂ are shown in Table 26.4.

Zinc sulfide, which belongs to II–VI group semiconductor, has been worked as a photocatalyst due to the remarkable features such as thermal stability, nontoxicity, and lower cost [118]. It has cubic zinc blende and hexagonal wurtzite crystalline forms with the bandgap 3.72 eV and 3.77 eV, respectively [60]. As a result of this wide-bandgap, UV light absorption for electron–hole separation occurs at $\lambda < 340$ nm wavelength. In order to use the advantages of ZnS in accordance with solar fuel applications, efforts have been made to expand the light absorption in the visible wave spectrum [118].

One of the attempts to decrease the bandgap of ZnS is the use of the proper amount of dopant. For this purpose, Pang et al. modulated the electronic band structure of ZnS using Ni dopant, which is a non-toxic metal [188]. They showed that the photocatalytic CO₂ reduction activity decreased as a result of the diminishment in sulfur vacancies with the increasing amount of Ni doping. The obtained H₂ evolution was almost nine times higher with 0.1wt% Ni dopant by using full Xe arc lamp compare to pure ZnS.

The heterostructure formed by ZnS/ZnO, which has common anion, has been synthesized for increased solar fuel production [127]. The lattice mismatch (15%) between these two structures, the proposed Z-scheme system, and different annealing time for in-situ growth of ZnO directly on the ZnS enabled this structure to result in high H₂ evolution compared to pure ZnS. These results show that the particle size, shape, crystal structure, and degree of crystallinity which changes via the thermal treatment, affect the charge separation of the nanostructures alike the using various heterostructure and dopant materials.

MoS₂, a 2D structure of transition-metal dichalcogenides (TMDCs), has been widely used for solar fuel application to enhance hydrogen evolution. Its tunable bandgap within the 1.2–1.9 eV depending on the number of the sheet layers, high surface area, and abundant active sites are the advantages that make it able to be modified to increase photocatalytic activity [280]. Methods such as mechanical and chemical exfoliation, chemical vapor deposition are used in their synthesis [111]. While producing in large quantities is a drawback of mechanical exfoliation; chemical exfoliation may result in a low yield due to the wild control of the intercalation process with liquid and lithium intercalation. Besides, the toxicity of the solvents used for intercalation and long reaction time for chemical exfoliation are the other drawbacks for production of the MoS₂ [280]. CVD is the ideal method for large scale production, and it can provide high-quality MoS₂ production by controlling morphology, crystallinity, and defects [114].

MoS₂ has been used to obtain different heterostructures with other semiconductor materials which resulted in efficient solar energy conversion by changing

Table 26.4 Typical photocatalytic H₂-production systems of metal sulfides

Catalyst	Synthesis method	Products/activity ($\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$)	AQY (%)/ Wavelength (nm)	Light source	Optical bandgap (eV)	References
CdS/TiO ₂	Hydrothermal	CH ₄ /27.85 $\mu\text{mol}\cdot\text{g}^{-1}$	–	350 W Xe lamp	CdS/2.27 TiO ₂ /3.04	[267]
L-Cys/CdS/NiCoP	Self-assembly	H ₂ /218000	76.3/420 nm	300 W Xe lamp	2.65	[92]
CdS/Ru	Deposition/precipitation	CH ₄ /2.585	–	0.71 W cm^{-2}	2.17	[22]
CdS/Nb ₂ O ₅ /SnS ₂	Ultrasonication	H ₂ /43198 $\mu\text{mol}\cdot\text{g}^{-1}$	0.65/425	300 W Xe lamp	1.96	[162]
CdS frame-in-cage	Solution reaction	H ₂ /13.6	3.2/400	300 W Xe lamp	~2.3	[322]
CdS/InP	Wet impregnation	CO/216	0.44 /425	150 W Xe lamp	CdS/2.34 InP/2.20	[50]
CdS/Bi ₂ MoO ₆	Solvothermal	H ₂ /6830	5.9/420	150 W Xe lamp	2.40	[29]
ZnS/CdS/ Cd _{0.5} Zn _{0.5} S/MoS ₂	Template-assisted ion-exchange/ electrostatic assembly	H ₂ /50650	13.7/420	300 W Xe lamp	2.49	[237]
CoOx/N, S-C/CdS	Reflux process	H ₂ /40100	57.6/420	300 W Xe lamp	3.6	[258]
C _{50.33} WO ₃ /CdS	Precipitation	H ₂ /2648	–	300 W Xe lamp	2.78	[126]
CoP QDs/CdS NRs	Ultrasound	H ₂ /104947	32.16/420	300 W Xe lamp	CdS/2.37	[239]
CdS/Cd _{0.5} Zn _{0.5} S/ ZnS-Ni(OH) ₂	Photodeposition	H ₂ /86790	22.8/420	300 W xenon lamp	CdS/2.42 Cd _{0.5} Zn _{0.5} S/ 2.52 ZnS/3.32	[211]

interfacial charge transfer properties [37]. Cho et al. obtained a few layered MoS₂/CdS QD. It was stated that the catalytic activity of the system in the hydrogen formation reaction (HER) would increase due to the enhanced carrier concentrations [37, 119, 329]. According to the results of transient absorption spectroscopy, ultrafast charge separation and long-lasting charge-separated states in heterostructures were obtained compared to bare MoS₂. In the other study, MoS₂ had been used as a co-catalyst in the heterostructure which was produced by in situ sulfidation of CdMoO₄ nanooctahedrons for the production of CdS/MoS₂ nanooctahedrons [329]. The pure CdS exhibited poor HER activity, and lower photocurrent density compares to bare MoS₂. Moreover, the heterostructure of CdS/MoS₂ showed highest HER activity photocurrent density. The results revealed that the heterostructure was promoting the electron transfer across the interface with the longest lifetime of photoinduced electron–hole pairs. The optimum H₂ production rate was in 27.16 mmol h⁻¹ g⁻¹ under visible light.

In an outstanding study in which MoS₂ was used as a co-catalyst, the H₂ production rate was obtained as 275 mmol h⁻¹ g⁻¹ [119]. Co-doped MoS₂/CdS structure is obtained firstly, by producing the Co crystals via pulsed laser ablation in liquid; secondly, Co doped into a few layers of MoS₂ by ultrasonication and lastly, integrated with CdS. The synthesize steps can be seen on Fig. 26.6. The reasons to be achieved the high H₂ evolution rate by the system are; activation of the MoS₂ basal plane with the appropriate size (3.1 nm) and concentration of dopant, enhancement of the optical and electronic properties due to the crystal size of the dopant, and the exfoliation of MoS₂. Moreover, the heterostructure has demonstrated superior stability up to 5 cycles successfully for the long-term stability test.

The H₂ production rate, experimental conditions, and bandgap values of the composites which were obtained with high efficiency by using sulphide-based nanostructures except MoS₂ and CdS are shown in Table 26.5.

A novel structure, Z-scheme WO₃/CdS/WS₂ tandem heterostructure has been synthesized first embedding the WO₃ nanocrystals into WS₂ nanoplate via the in-situ sulfurization of bulk WO₃ [297]. Afterwards the monodispersed CdS nanograins anchored on the ultrathin WO₃/WS₂ nanoplate. WO₃ has higher oxidation potential in the valence band, and CdS has a higher reduction potential in the conduction band. This situation makes the direct Z-scheme heterojunction possible to form between WO₃ and CdS. Additionally, WS₂ has been used as a co-catalyst which has a direct band on 1.9 eV. Its large surface area makes it easier to couple with photo absorber across the entire surface and WS₂ is the origin of the unsaturated sulfur atoms at the edges. This system efficient spatial charge separation resulted in highly efficient H₂ evolution of 14.34 mmol h⁻¹ g⁻¹ with 22.96% quantum efficiency. Figure 26.7a and b shows the H₂ evolution of the pure and heterostructures for WS₂/CdS/WO₃. The pure WO₃ does not have hydrogen production because of the unsuitable conduction band potential. WO₃/WS₂ nanoplate composite, also, does not generate the H₂ due to the rapid recombination of photo-generated electrons and holes. The CW-3 (WS₂/CdS/WO₃) heterostructure

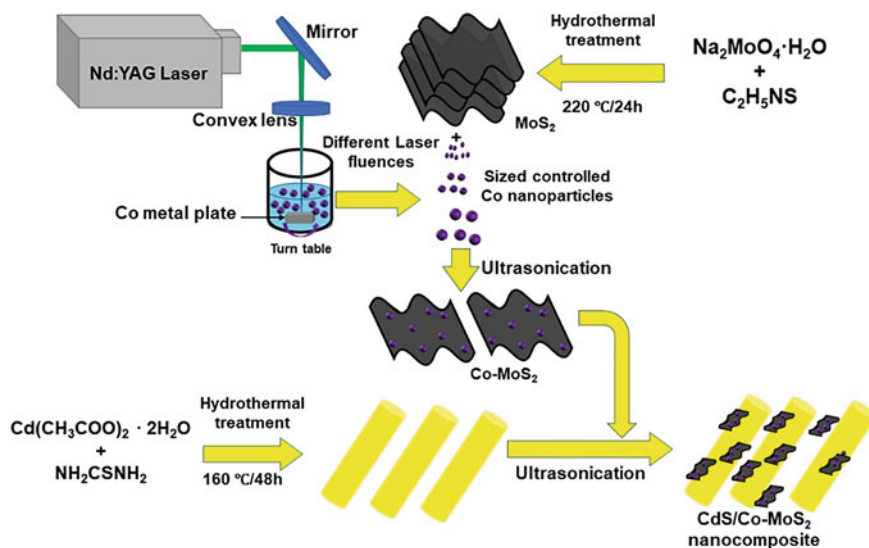


Fig. 26.6 Schematic illustration of the synthesis of CdS/Co–MoS₂ nanocomposites. Step I: Size-controlled cobalt nanocrystal synthesis via PLAL using 532-nm Nd:YAG laser with different laser fluence (0.32, 0.64, 0.96, 1.91, 2.86 and 3.82 J/cm²). Step II: Formation of bulk MoS₂ nanosheets through hydrothermal synthesis. Step III: Formation of few-layer Co–MoS₂ nanocomposites using ultrasonication. Step IV: Integration of ultrathin Co–MoS₂ nanosheets on 1D–CdS nanorods by ultrasonication and long-time magnetic stirring to generate interfacial contact between CdS and Co–MoS₂ nanostructures (Reprinted from Ref. [119] with permission from Elsevier)

has the highest H₂ evolution rate. As well, the dosage of the 2D ultrathin WO₃/WS₂ nanoplate matrix also has a control on the photocatalytic H₂ production. As shown in Fig. 26.7c, the stability of the CW-3 composite did not decrease after six cycles, and AQE was found as 0.88% at 700 nm (Fig. 26.7d).

26.5 Transition Metal Phosphides (TMPs)

Metal transition phosphites are the superior materials that can be an alternative to noble metals with good photocatalytic performance and are even cheaper, abundant, and highly stable [279]. The photocatalytic performance increases due to the electronic structure of the phosphorus in the TMP structure [199], besides the types of different metals and the metal/phosphorus ratio also contribute to the photocatalytic activity. Other types of metal phosphites were produced for solar fuel application such as BP [246], CoP [143], Co₂P [122], Ni₂P [328], MoP [144], Cu₃P [241], FeP [53], RuP₂ [230], WP₂ [195], NbP [70] and NiCoP [92]. The electronegative nature of P atoms limits the electron delocalization of metals, which

Table 26.5 Typical photocatalytic H₂-production systems of metal sulfides

Catalyst	Synthesis method	H ₂ production rate (μmol g ⁻¹ h ⁻¹)	AQY (%) / Wavelength (nm)	Light source	Optical bandgap (eV)	References
NiS/g-C ₃ N ₄	Photodeposition	244	–	LED lamps	g-C ₃ N ₄ / 2.7	[259]
ZnS/Cu	Ion-exchange	1000	17.6/ 410 ± 10	150 W Xe lamp	3.36	[44]
Zn _{1-x} Cu _x S	Hydrothermal	1296	2.48/365	Xe arc lamp	~ 3.5	[153]
WS ₂ /CdS/ WO ₃	Hydrothermal	14,340	22.96/435	300 W Xe lamp	2.32	[297]
SnS ₂ / CdS/ Nb ₂ O ₅	Ultrasonication	55,887 μmol g ⁻¹	0.65/425	300 W Xe lamp	~ 1.96	[162]
CuSbS ₂	Hot-injection	2140	–		1.46	[214]
FeCoS ₂ / CoS ₂	Solvothermal	28.1 μmol h ⁻¹ (per 0.5 mg catalyst)	–	300 W Xe lamp	–	[272]

decreases conductivity. As the P content increases, the structure can be a semiconductor or even insulator. Electronegative P atoms trap protons and stabilize the activation of H₂ atoms attached to the surface [208]. Thus, it is known that the obtained hydrogen evolution activity is greater in CoP than Co₂P and MoP than Mo₃P [23, 286].

TMPs have relatively high photocatalytic conversion rate results in the literature studies. A heterostructure, CoxP/CdS, which has the H₂ evolution of 500 mmol g⁻¹ h⁻¹ was formed by the photochemical method for illumination time up to 50 min [52]. It has been observed that the conversion activity increased by 85 times compared to pure CdS with increasing illumination time. After the 50th minute, the surplus amount of CoxP caused lowering in oxidation reaction sites on the CdS surface, resulting in lower hydrogen evolution. This indicates that composition optimization has a crucial role in modifying photocatalytic activity.

The synthesis methods of TMP nanostructures can be classified according to organic and inorganic phosphorus sources [25, 52]. The organophosphorus, tri-n-octylphosphine (TOP), and triphenylphosphine (TPP), have been used as phosphorus sources by breaking the C–P bond with high-boiling organic solvents at temperatures up to 300 °C. Thus, replacement with a metal precursor can be achieved for TMP synthesis [25]. Hypophosphites are used as inorganic P sources which are decomposed above 250 °C and following by the reaction between metal precursor and PH₃ via CVD method. Alternative methods such as hydrothermal synthesis, a gas–solid response, phosphorization take place under high temperatures. Considering the scope of green synthesis, microwave-assisted and PH₃

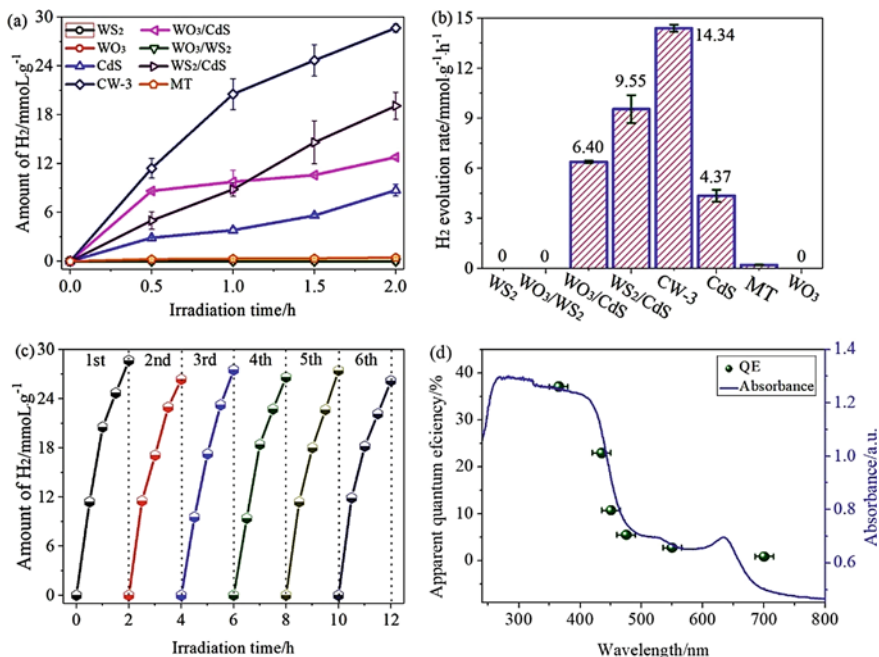


Fig. 26.7 **a** Time-dependent amounts and **b** the rates of H₂ evolution over different samples under visible light irradiation ($\lambda > 420$ nm); **c** Recycling H₂ evolution and **d** wavelength-dependent AQE of H₂ evolution from the CW-3 composite (Reprinted from Ref. [297] with permission from Elsevier)

plasma methods seem more suitable to conduct the synthesis for shorter reaction times by avoiding the high-temperature conditions [25].

The MoP is another TMP structure that draws attention with its similar electronic structure of Pt and its high conductivity [311]. In a study, it was used as a cocatalyst with CdS to construct a heterostructure [302]. The first drawback of the synthesis is the agglomeration which results due to the high-temperature phosphorization process. The second drawback originates from the TOP route due to its toxicity, low yield, and complex operation [271]. These problems were solved by synthesizing freestanding ultra-small MoP quantum dots at low temperatures. The pyrolysis of ammonium molybdate and subsequent calcination steps at different temperatures were used for the synthesis of MoP, and then it has been dispersed with commercial CdS. The photocatalytic H₂ evolution rate of 0.60 mmol h⁻¹ g⁻¹ and 13.88 mmol h⁻¹ g⁻¹ were obtained for the pure CdS and MoP/CdS, respectively. This highly stable photocatalytic performance obtained is 1.44 times higher than Pt cocatalyst with AQY (420 nm) 66.7%.

Table 26.6 shows the synthesis methods of different TMP composite structures with high-performance hydrogen evolution rates, the conditions in which the experiments performed based on the recent literature studies.

Table 26.6 Typical photocatalytic H₂-production systems of transition metal phosphides

Catalyst	Synthesis method	H ₂ production rate ($\mu\text{mol g}^{-1} \text{h}^{-1}$)	AQY (%)/Wavelength (nm)	Light source	Optical bandgap (eV)	Phosphorus source	References
Cu ₃ P-Ni ₂ P/ g-C ₃ N ₄	Hydrothermal	6526.7	18.5/400	300 W Xe lamp	1.66	Red P	[241]
MoP/g-C ₃ N ₄	Self-assembly	327.5	10.2/420	300 W Xe lamp	–	(NH ₄) ₂ HPO ₄	[144]
BP/g-C ₃ N ₄	Calcination	31.5	0.03/400	300 W Xe lamp	1.51/MoP 2.74/ g-C ₃ N ₄	Red P	[246]
Fe _x Co _{1-x} P/CdS	Stirring	18,270	50.6/420	Visible light	1.59/ Fe _{0.4} Co _{0.6} P	NaH ₂ PO ₂ -H ₂ O	[318]
NixP/CuS/CdS	Photochemical deposition	18,160	0.38/420	300 W Xe lamp	–	NaH ₂ PO ₂	[136]
InP/CdS	Wet impregnation	216	0.44 /425	150 W Xe lamp	2.34/CdS 2.20/InP	Tris(diethyl)amino) phosphine	[50]
Ni ₁₂ P ₅ S/ Cd _{0.5} Zn _{0.5} S	Evaporation/deposition/ precipitation	525.5	15/420	300 W Xe lamp	2.31/ Cd _{0.5} Zn _{0.5} S 2.67/S	Red P	[71]
FeP/CdS	Solvothermal	37,920	31.50/420	300 W Xe lamp	2.32/CdS	Red P	[53]
Ni ₂ P/MoP/ g-C ₃ N ₄	Photodeposition	517	5.9/420	300 W Xe lamp	2.75/ g-C ₃ N ₄	NaH ₂ PO ₂ -H ₂ O	[328]
CoP/TiO ₂	Hydrothermal	604	–	300 W Xe lamp	3.11/TiO ₂	NaH ₂ PO ₂ -H ₂ O	[143]
CoP QDs/CdS NRs	Ultrasound	104,947	32.16/420	300 W Xe lamp	2.37/CdS	NaH ₂ PO ₂ -H ₂ O	[239]
Co ₂ P/RB	Hydrothermal	5997.5	–	300 W Xe lamp	1.78/RP	Red P	[122]

26.6 Metal Oxide Frameworks (MOFs)

MOFs are the crystalline hybrid materials consisting of metal ions as inorganic metal centers connected by organic ligands [86]. Metal-organic frameworks (MOFs) materials have attracted photocatalytic H₂ generation application due to high surface area, high porosity, superior visible light absorbance, tunable bandgap, designable structure, good thermal and chemical stability [338]. However, the low conductivity of the MOFs limits their photocatalytic efficiency. The coordinatively unsaturated metal sites and the active groups on the organic linkers in MOF structures provide catalytic activity. The limits of the catalytic activity can be changed by functionalizing the metal sites, organic linkers and confining the pores [99, 142]. As an advantage, the high porosity of MOFs minimizes electron–hole recombination due to their short transport distance. The charge separation and photocatalytic activity will be increased by the addition of the electronegative structures to the MOFs [99].

MOF nanostructures can be synthesized by several methods, including solvothermal [59], layer by layer growth [1], electrochemical deposition [147], chemical vapor deposition [310], atomic/molecular layer deposition methods [172].

The incorporation of noble metals (Au [327], Ag [26], Pd [35], Pt [288], Rh [19], Ru), non-noble metals (Co [140], Cu [67], Fe [235], Ni [32]) has been carried out in previous studies in which the photocatalytic activity increased via the functionalization of the MOFs. The large pores of the MOFs provide an ideal host for nanoparticles (NPs) and single atoms (SAs). Taking advantage of this feature, NPs and/or SAs of Ru³⁺ incorporated NH₂-MIL-125/N-doped TiO₂/C was produced by using NH₂-functionalized MOF, which provides stabilization of metal cations [299]. The highest rate of H₂ evolution reached 100.0 μmol h⁻¹ for NPs/SAs Ru³⁺ incorporated MOF. The evolution rate is higher than 58.3 μmol h⁻¹ for Ru³⁺ composite structure where the only single atom is used, and it is higher than 83.9 μmol h⁻¹, which belongs to Pt/N-doped TiO₂ MOF material. The obtained performance has been attributed to the synergistic coupling between Ru nanoparticles and single atoms.

Nanoparticles (NPs) of noble metals (i.e. Ag, Au, Pt) which are active reaction sites can powerfully harness their surface plasmon resonance (SPR), accordingly, they absorb the visible light [262]. However, due to the high cost of the novel metals, non-noble-metal MOF analogues have been developed for high-performance catalytic activity. Moreover, the mixture of the different species of MOF heterostructures with carbon [128, 245], metal oxides [63], metal sulfides [245] covalent organic frameworks (COF) [84], phosphide [125] based materials have been produced for high photocatalytic performance. The recent studies are summarized in Table 26.7 based on the high photocatalytic performance of MOF systems.

MOFs have tunable porosity, metal centers, and organic ligands which provide advantages in their use. These properties render them the right candidate in catalytic applications such as CO₂ capture and H₂ evolution. In recent years, the studies

Table 26.7 Typical photocatalytic H₂-production systems of MOFs

Catalyst	Synthesis method	H ₂ production rate (mmol g ⁻¹ h ⁻¹)	Light source	Optical bandgap (eV)	References
NH ₂ -UiO-66-MOF/ TpPa-1-COF	One-pot synthesis	23.41	300 W Xe lamp	2.02/ TpPa-1-COF 2.88/ NH ₂ - UiO-66	[314]
MOF-Cu(I)	Solvothermal	4.21	500 W Xe lamp	2.13	[31]
Pt/MIL-125-(SCH ₃)	Solvothermal	3.8	350 W Xe lamp	2.69	[78]
MIL-125/g-C ₃ N ₄ /TiO ₂	Calcination	0.606	300 W Xe lamp	3.04	[277]
UIO-67/Ru/Pt	Solvothermal	1.13	150 W Xe Lamp	–	[303]
NH ₂ -MIL-125 (Ti)/ benzoic acid-functionalized g-C ₃ N ₄	Solvothermal	1.123	300 W Xe lamp	2.60/ NH ₂ - MIL-125	[337]

resulted in high conversion efficiencies by using the MOF structures. While it is an advantage to be produced especially with low cost, MOFs may have stability problems due to factors such as pH and temperature due to organic linkers [253]. Besides, material production on the industrial scale is still another limiting factor.

26.7 Summary

Today, it is known that among the usage of energy resources, renewable energy sources are in demand due to the environmental effects of non-renewable fossil fuels. Solar energy has a greater potential than the total energy of all renewable energy sources. It is quite reasonable to use H₂ as a solar fuel in order to realize the energy generation of fuels obtained from the sun, and photocatalysts are used to achieve this conversion. Nanomaterials have been used in different types and structures to understand its advantages and disadvantages, to provide high H₂ conversion, and to carry out the conversion both efficient and stable. In this chapter of the book, the semiconductor nanomaterials as metal oxides, metal–organic frameworks, carbon-based materials, metal sulfides, and phosphides have been

summarized in view of their usage in photocatalytic conversion. The synthesis and design of the materials and their hybridized structures, doping, heterostructures with each other for the enhanced photocatalytic conversion were discussed in each section. It has been emphasized that each combination performs uniquely depending on both bandgaps and synergetic effects of combination with each other and also the contributions of morphology, crystallinity, composition ratios to this efficiency. The literature studies prove that the different designs of these structures and their stability, performance, and reproducibility can be changed. It can be said that in the near future, for the efficient use of solar fuels, nanomaterial engineering will proceed in the direction of structures that allow industrial production with different interfaces, morphology, and compositions.

References

1. Abbasi AR, Akhbari K, Morsali A (2012) Dense coating of surface mounted CuBTC metal-organic framework nanostructures on silk fibers, prepared by layer-by-layer method under ultrasound irradiation with antibacterial activity. *Ultrason Sonochem* 19(4):846–852
2. Acik M, Chabal YJ (2013) A review on thermal exfoliation of graphene oxide. *J Mater Sci Res* 2(1):101
3. Adegoke KA, Iqbal M, Louis H et al (2019) Synthesis, characterization and application of CdS/ZnO nanorod heterostructure for the photodegradation of Rhodamine B dye. *Mater Sci Energy Technol* 2(2):329–336
4. Al-Shomar SM (2020) Investigation the effect of doping concentration in Ruthenium-doped TiO₂ thin films for solar cells and sensors applications. *Mater Res Express* 7(3):12
5. Al Jitan S, Palmisano G, Garlisi C (2020) Synthesis and surface modification of TiO₂-based photocatalysts for the conversion of CO₂. *Catalysts* 10(2):30
6. Albero J, Mateo D, Garcia H (2019) Graphene-based materials as efficient photocatalysts for water splitting. *Molecules* 24(5):21
7. Alcudia-Ramos MA, Fuentes-Torres MO, Ortiz-Chi F et al (2020) Fabrication of g-C₃N₄/TiO₂ heterojunction composite for enhanced photocatalytic hydrogen production. *Ceram Int* 46(1):38–45
8. Aliaga J, Cifuentes N, Gonzalez G et al (2018) Enhancement photocatalytic activity of the heterojunction of two-dimensional hybrid semiconductors ZnO/V₂O₅. *Catalysts* 8(9):13
9. Ando F, Tanabe T, Gunji T et al (2018) Effect of the d-Band center on the oxygen reduction reaction activity of electrochemically dealloyed ordered intermetallic platinum-lead (PtPb) nanoparticles supported on TiO₂-deposited cup-stacked carbon nanotubes. *ACS Appl Nano Mater* 1(6):2844–2850
10. Ashkarran AA, Fakhari M, Hamidinezhad H et al (2015) TiO₂ nanoparticles immobilized on carbon nanotubes for enhanced visible-light photo-induced activity. *J Mater Res Technol JMRT* 4(2):126–132
11. Bai S, Zhang N, Gao C et al (2018) Defect engineering in photocatalytic materials. *Nano Energy* 53:296–336
12. Bakbolat B, Daulbayev C, Sultanov F et al (2020) Recent developments of TiO₂-based photocatalysis in the hydrogen evolution and photodegradation: a review. *Nanomaterials* 10(9):16
13. Baker SN, Baker GA (2010) Luminescent carbon nanodots: emergent nanolights. *Angew Chem Int Edn* 49(38):6726–6744

14. Bang HJ, Lee H, Park YK et al (2020) Fabrication of Yb-doped TiO₂ using liquid phase plasma process and its photocatalytic degradation activity of naproxen. *J Mater Sci* 55 (23):9665–9675
15. Banin U, Waiskopf N, Hammarstrom L et al (2021) Nanotechnology for catalysis and solar energy conversion. *Nanotechnology* 32(4):28
16. Barreca D, Carraro G, Gasparotto A et al (2015) Fe₂O₃-TiO₂ Nano-heterostructure photoanodes for highly efficient solar water oxidation. *Adv Mater Interfaces* 2(17):11
17. Bayan EM, Lupeiko TG, Kolupaeva EV et al (2017) Fluorine-doped titanium dioxide: synthesis, structure, morphology, size and photocatalytic activity. In: Parinov IA, Chang SH, Jani MA (ed) *Advanced materials: techniques, physics, mechanics and applications*, vol 193. Springer-Verlag Berlin, Berlin, pp 17–24
18. Bayan S, Gogurla N, Midya A et al (2016) White light emission characteristics of two dimensional graphitic carbon nitride and ZnO nanorod hybrid heterojunctions. *Carbon* 108:335–342
19. Benseghir Y, Lemarchand A, Duguet M et al (2020) Co-immobilization of a Rh catalyst and a keggin polyoxometalate in the UiO-67 Zr-based metal-organic framework: in depth structural characterization and photocatalytic properties for CO₂ reduction. *J Am Chem Soc* 142(20):9428–9438
20. Bhuyan MSA, Uddin MN, Islam MM et al (2016) Synthesis of graphene. *Int Nano Lett* 6 (2):65–83
21. Bozkurt H, Diker H, Varlikli C Fabrication and characterization of a solution processed flexible thermal sensor by using chemically synthesized GO and rGO. In: 2019 innovations in intelligent systems and applications conference (ASYU), IEEE
22. Cai SC, Zhang M, Li JJ et al Anchoring single-atom Ru on CdS with enhanced CO₂ capture and charge accumulation for high selectivity of photothermocatalytic CO₂ reduction to solar fuels. *Sol. RRL*: 10
23. Callejas JF, Read CG, Popczun EJ et al (2015) Nanostructured Co₂P electrocatalyst for the hydrogen evolution reaction and direct comparison with morphologically equivalent CoP. *Chem Mater* 27(10):3769–3774
24. Caner N, Bulut A, Yurderi M et al (2017) Atomic layer deposition-SiO₂ layers protected PdCoNi nanoparticles supported on TiO₂ nanopowders: exceptionally stable nanocatalyst for the dehydrogenation of formic acid. *Appl Catal B Environ* 210:470–483
25. Cao S, Wang CJ, Fu WF et al (2017) Metal phosphides as co-catalysts for photocatalytic and photoelectrocatalytic water splitting. *Chemsuschem* 10(22):4306–4323
26. Chandra R, Nath M (2020) Facile synthesis of metal-organic framework (ZIF-11) and Ag NPs encapsulated-ZIF-11 composite as an effective heterogeneous catalyst for photodegradation of methylene blue. *Appl Organomet Chem* 34(11):19
27. Chandrasekaran S, Yao L, Deng LB et al (2019) Recent advances in metal sulfides: from controlled fabrication to electrocatalytic, photocatalytic and photoelectrochemical water splitting and beyond. *Chem Soc Rev* 48(15):4178–4280
28. Chang F, Zheng JJ, Wu FY et al (2019) Binary composites WO₃/g-C₃N₄ in porous morphology: facile construction, characterization, and reinforced visible light photocatalytic activity. *Colloid Surf A-Physicochem Eng Asp* 563:11–21
29. Chava RK, Son N, Kim YS et al (2020) Integration of perovskite type Bi(2)MoO (6)nanosheets onto one dimensional CdS: a type-II heterostructured photocatalytic system for efficient charge separation in the hydrogen evolution reaction. *Inorg Chem Front* 7 (15):2818–2832
30. Chen BB, Liu ML, Huang CZ (2020) Carbon dot-based composites for catalytic applications. *Green Chem* 22(13):4034–4054
31. Chen D-M, Sun C-X, Liu C-S et al (2018) Stable layered semiconductive Cu (I)-organic framework for efficient visible-light-driven Cr (VI) reduction and H₂ evolution. *Inorg Chem* 57(13):7975–7981

32. Chen JX, Xing Z, Han J et al (2020) Enhanced degradation of dyes by Cu-Co-Ni nanoparticles loaded on amino-modified octahedral metal-organic framework. *J Alloy Compd* 834:14
33. Chen L, Xu YM, Chen B (2019) In situ photochemical fabrication of CdS/g-C₃N₄ nanocomposites with high performance for hydrogen evolution under visible light. *Appl Catal B Environ* 256:8
34. Chen YF, Tang D, Wang ZH et al (2020) Sn-bridge type-II PCN/Sn/SnO heterojunction with enhanced photocatalytic activity. *Semicond Sci Technol* 35(11):15
35. Cheng HM, Long XY, Bian FX et al (2020) Efficient photocatalytic one-pot hydrogenation and N-alkylation of nitrobenzenes/benzonitriles with alcohols over Pd/MOFs: effect of the crystal morphology & “quasi-MOF” structure. *J Catal* 389:121–131
36. Cheng L, Xiang QJ, Liao YL et al (2018) CdS-Based photocatalysts. *Energy Environ Sci* 11(6):1362–1391
37. Cho JS, Suwandaratne NS, Razek S et al (2020) Elucidating the mechanistic origins of photocatalytic hydrogen evolution mediated by MoS₂/CdS quantum-dot heterostructures. *ACS Appl Mater Interfaces* 12(39):43728–43740
38. Chowdhury MS, Rahman KS, Selvanathan V et al Current trends and prospects of tidal energy technology. *Environ Dev Sustain* 16
39. Chung YH, Han K, Lin CY et al (2020) Photocatalytic hydrogen production by photo-reforming of methanol with one-pot synthesized Pt-containing TiO₂ photocatalysts. *Catal Today* 356:95–100
40. Cifuentes B, Bustamante F, Cobo M (2019) Single and dual metal oxides as promising supports for carbon monoxide removal from an actual syngas: the crucial role of support on the selectivity of the Au-Cu system. *Catalysts* 9(10):25
41. Clarizia L, Andreozzi R, Apuzzo J et al (2020) Efficient acetaldehyde production and recovery upon selective Cu/TiO₂-photocatalytic oxidation of ethanol in aqueous solution. *Chem Eng J* 393:7
42. Cybula A, Priebe JB, Pohl MM et al (2014) The effect of calcination temperature on structure and photocatalytic properties of Au/Pd nanoparticles supported on TiO₂. *Appl Catal B Environ* 152:202–211
43. Das A, Patra M, Hazarika M et al (2019) ZnO-In(2)O(3)nanocomposite: an efficient solar photocatalyst. In: Kaurav N, Choudhary KK, Dixit RC, Mishra A (eds) Prof. Dinesh Varshney memorial national conference on physics and chemistry of materials, 2100. Amer Inst Physics, Melville
44. Daskalakis I, Vamvasakis I, Papadas IT et al (2020) Surface defect engineering of mesoporous Cu/ZnS nanocrystal-linked networks for improved visible-light photocatalytic hydrogen production. *Inorg Chem Front* 7(23):4687–4700
45. Diao W, He J, Wang Q et al (2020) K, Na and Cl co-doped TiO₂ nanorod arrays on carbon cloth for efficient photocatalytic degradation of formaldehyde under UV/visible LED irradiation. *Catal Sci Technol*
46. Didi A, Gomez-Calcerrada LM, Benhamou A et al (2018) Versatility in the catalytic and photocatalytic reactions of composites based on Zr- and Zr-Pd-doped titania nanoparticles. *Ceram Int* 44(14):17266–17276
47. Diker H, Bozkurt H, Varlikli C (2020) Dispersion stability of amine modified graphene oxides and their utilization in solution processed blue OLED. *Chem Eng J* 381:122716
48. Diker H, Varlikli C, Mizrak K et al (2011) Characterizations and photocatalytic activity comparisons of N-doped nc-TiO₂ depending on synthetic conditions and structural differences of amine sources. *Energy* 36(2):1243–1254
49. Ding L, Yang SR, Liang ZQ et al (2020) TiO₂ nanobelts with anatase/rutile heterophase junctions for highly efficient photocatalytic overall water splitting. *J Colloid Interface Sci* 567:181–189
50. Do KH, Kumar DP, Rangappa AP et al (2020) Indium phosphide quantum dots integrated with cadmium sulfide nanorods for photocatalytic carbon dioxide reduction. *ChemCatChem* 12(18):4550–4557

51. Dong F, Zhao WR, Wu ZB (2008) Characterization and photocatalytic activities of C, N and S co-doped TiO₂ with 1D nanostructure prepared by the nano-confinement effect. *Nanotechnology* 19(36):10
52. Dong Y, Kong L, Wang G et al (2017) Photochemical synthesis of CoxP as cocatalyst for boosting photocatalytic H₂ production via spatial charge separation. *Appl Catal B* 211:245–251
53. Dou M-Y, Han S-R, Du X-X et al (2020) Well-defined FeP/CdS heterostructure construction with the assistance of amine for the efficient H₂ evolution under visible light irradiation. *Int J Hydrog Energy* 45(56):32039–32049
54. Douven S, Mahy JG, Wolfs C et al (2020) Efficient N, Fe Co-Doped TiO₂ active under cost-effective visible LED light: from powders to films. *Catalysts* 10(5):22
55. Du MM, Qiu BC, Zhu QH et al (2019) Fluorine doped TiO₂/mesocellular foams with an efficient photocatalytic activity. *Catal Today* 327:340–346
56. El Roubi WMA, Antuch M, You SM et al (2019) Novel nano-architected water splitting photoanodes based on TiO₂-nanorod mats surface sensitized by ZIF-67 coatings. *Int J Hydrog Energy* 44(59):30949–30964
57. Elhousseini MH, Isik T, Kap O et al (2020) Dual remediation of waste waters from methylene blue and chromium (VI) using thermally induced ZnO nanofibers. *Appl Surf Sci* 514:10
58. Eslami A, Amini MM, Yazdanbakhsh AR et al (2016) N, S co-doped TiO₂ nanoparticles and nanosheets in simulated solar light for photocatalytic degradation of non-steroidal anti-inflammatory drugs in water: a comparative study. *J Chem Technol Biotechnol* 91(10):2693–2704
59. Esrafil L, Tehrani AA, Morsali A et al (2019) Ultrasound and solvothermal synthesis of a new urea-based metal-organic framework as a precursor for fabrication of cadmium (II) oxide nanostructures. *Inorg Chim Acta* 484:386–393
60. Fang XS, Zhai TY, Gautam UK et al (2011) ZnS nanostructures: from synthesis to applications. *Prog Mater Sci* 56(2):175–287
61. Fu JW, Xu QL, Low JX et al (2019) Ultrathin 2D/2D WO₃/g-C₃N₄ step-scheme H₂-production photocatalyst. *Appl Catal B Environ* 243:556–565
62. Fu JW, Yu JG, Jiang CJ et al (2018) g-C₃N₄-based heterostructured photocatalysts. *Adv Energy Mater* 8(3):31
63. Fu N, Ren XC (2020) Synthesis of double-shell hollow TiO₂@ZIF-8 nanoparticles with enhanced photocatalytic activities. *Front Chem* 8:10
64. Fu PF, Luan Y, Dai XG (2004) Preparation of activated carbon fibers supported TiO₂ photocatalyst and evaluation of its photocatalytic reactivity. *J Mol Catal A Chem* 221(1–2):81–88
65. Fu YK, Zeng GM, Lai C et al (2020) Hybrid architectures based on noble metals and carbon-based dots nanomaterials: a review of recent progress in synthesis and applications. *Chem Eng J* 399:22
66. Gao LK, Gan WT, Qiu Z et al (2017) Preparation of heterostructured WO₃/TiO₂ catalysts from wood fibers and its versatile photodegradation abilities. *Sci Rep* 7:13
67. Gao YJ, Zhang L, Gu YM et al (2020) Formation of a mixed-valence Cu(I)/Cu(II) metal-organic framework with the full light spectrum and high selectivity of CO(2) photoreduction into CH₄. *Chem Sci* 11(37):10143–10148
68. Garcia-Lopez E, Marci G, Pomilla FR et al (2018) ZrO₂ Based materials as photocatalysts for 2-propanol oxidation by using UV and solar light irradiation and tests for CO₂ reduction. *Catal Today* 313:100–105
69. Gogoi D, Namdeo A, Golder AK et al (2020) Ag-doped TiO₂ photocatalysts with effective charge transfer for highly efficient hydrogen production through water splitting. *Int J Hydrog Energy* 45(4):2729–2744
70. Gujt J, Zimmer P, Zysk F et al (2020) Water structure near the surface of Weyl semimetals as catalysts in photocatalytic proton reduction. *Struct Dyn US* 7(3):6

71. Guo M, Guo X, Lin H et al (2020) Novel noble-metal free S/Ni₁₂P₅/Cd₀. 5Zn₀. 5S composite with enhanced H₂ evolution activity under visible light. *Int J Hydrog Energy*
72. Guo Q, Liang F, Li XB et al (2019) Efficient and selective CO₂ reduction integrated with organic synthesis by solar energy. *Chem* 5(10):2605–2616
73. Guy N (2020) Directional transfer of photocarriers on CdS/g-C₃N₄ heterojunction modified with Pd as a cocatalyst for synergistically enhanced photocatalytic hydrogen production. *Appl Surf Sci* 522:12
74. Hafeez HY, Lakhera SK, Narayanan N et al (2019) Environmentally sustainable synthesis of a CoFe₂O₄-TiO₂/rGO ternary photocatalyst: a highly efficient and stable photocatalyst for high production of hydrogen (Solar Fuel). *ACS Omega* 4(1):880–891
75. Hajizadeh-Oghaz M (2019) Synthesis and characterization of Nb-La co-doped TiO₂ nanoparticles by sol-gel process for dye-sensitized solar cells. *Ceram Int* 45(6):6994–7000
76. Hamdi A, Ferraria AM, do Rego AMB et al (2013) Bi-Y doped and co-doped TiO₂ nanoparticles: characterization and photocatalytic activity under visible light irradiation. *J Mol Catal A Chem* 380:34–42
77. Han C, Wang YD, Lei YP et al (2015) In situ synthesis of graphitic-C₃N₄ nanosheet hybridized N-doped TiO₂ nanofibers for efficient photocatalytic H₂ production and degradation. *Nano Res* 8(4):1199–1209
78. Han SY, Pan DL, Chen H et al (2018) A Methylthio-Functionalized-MOF Photocatalyst with High Performance for Visible-Light-Driven H₂ Evolution. *Angew Chem Int Ed* 57(31):9864–9869
79. Han WJ, Ren L, Zhang Z et al (2015) Graphene-supported flocculent-like TiO₂ nanostructures for enhanced photoelectrochemical activity and photodegradation performance. *Ceram Int* 41(6):7471–7477
80. Hao HM, Lang XJ (2019) Metal sulfide photocatalysis: visible-light-induced organic transformations. *ChemCatChem* 11(5):1378–1393
81. Hao XQ, Hu Y, Cui ZW et al (2019) Self-constructed facet junctions on hexagonal CdS single crystals with high photoactivity and photostability for water splitting. *Appl Catal B Environ* 244:694–703
82. Hasan M, Hadzifejzovi E, Rohan JF et al (2018) Electrochemical synthesis of nanoporous hematite (α -Fe₂O₃) and their applications towards photocatalytic water oxidation. The Electrochemical Society, Glasgow, Scotland, Meeting Abstracts
83. Hassan SM, Ahmed AI, Mannaa MA (2019) Preparation and characterization of SnO₂ doped TiO₂ nanoparticles: effect of phase changes on the photocatalytic and catalytic activity. *J Sci* 4(3):400–412
84. He SJ, Rong QF, Niu HY et al (2019) Platform for molecular-material dual regulation: a direct Z-scheme MOF/COF heterojunction with enhanced visible-light photocatalytic activity. *Appl Catal B Environ* 247:49–56
85. Hezam A, Namratha K, Drmash QA et al (2020) CeO₂ nanostructures enriched with oxygen vacancies for photocatalytic CO₂ reduction. *ACS Appl Nano Mater* 3(1):138–148
86. Hilal ME, Aboulouard A, Akbar AR et al (2020) Progress of MOF-derived functional materials toward industrialization in solar cells and metal-air batteries. *Catalysts* 10(8):31
87. Horzum N, Hilal ME, Isik T (2018) Enhanced bactericidal and photocatalytic activities of ZnO nanostructures by changing the cooling route. *New J Chem* 42(14):11831–11838
88. Horzum N, Mari M, Wagner M et al (2015) Controlled surface mineralization of metal oxides on nanofibers. *RSC Adv* 5(47):37340–37345
89. Horzum N, Munoz-Espi R, Glasser G et al (2012) Hierarchically structured metal oxide/silica nanofibers by colloid electrospinning. *ACS Appl Mater Interfaces* 4(11):6338–6345
90. Hu BB, Guo Q, Wang K et al (2019) Enhanced photocatalytic activity of porous In₂O₃ for reduction of CO₂ with H₂O. *J Mater Sci Mater Electron* 30(8):7950–7962
91. Hurtado L, Natividad R, Garcia H (2016) Photocatalytic activity of Cu₂O supported on multi layers graphene for CO₂ reduction by water under batch and continuous flow. *Catal Commun* 84:30–35

92. Iqbal S (2020) Spatial charge separation and transfer in L-cysteine capped NiCoP/CdS nano-heterojunction activated with intimate covalent bonding for high-quantum-yield photocatalytic hydrogen evolution. *Appl Catal B Environ* 274:10
93. Isik T, Hilal ME, Horzum N (2019) Green synthesis of zinc oxide nanostructures. In: Zinc oxide based nano materials and devices. IntechOpen
94. Ismael M, Wu Y, Wark M (2019) Photocatalytic activity of ZrO₂ composites with graphitic carbon nitride for hydrogen production under visible light. *New J Chem* 43(11):4455–4462
95. Jayasree P, Remya N (2020) Photocatalytic degradation of paracetamol using aluminosilicate supported TiO₂. *Water Sci Technol* 82(10):2114–2124
96. Jeon JP, Kweon DH, Jang BJ et al Enhancing the photocatalytic activity of TiO₂ catalysts. *Adv Sustain Syst* 19
97. Ji C, Du C, Steinkruger JD et al (2019) In-situ hydrothermal fabrication of CdS/g-C₃N₄ nanocomposites for enhanced photocatalytic water splitting. *Mater Lett* 240:128–131
98. Jia YF, Ma HX, Zhang WB et al (2020) Z-scheme SnFe₂O₄-graphitic carbon nitride: reusable, magnetic catalysts for enhanced photocatalytic CO₂ reduction. *Chem Eng J* 383:11
99. Jiao L, Wang Y, Jiang HL et al (2018) Metal-organic frameworks as platforms for catalytic applications. *Adv Mater* 30(37):23
100. Jin C, Li W, Chen YS et al (2020) Efficient photocatalytic degradation and adsorption of tetracycline over type-II heterojunctions consisting of ZnO nanorods and K-Doped exfoliated g-C₃N₄ nanosheets. *Ind Eng Chem Res* 59(7):2860–2873
101. Karachi N, Hosseini M, Parsaee Z et al (2018) Novel high performance reduced graphene oxide based nanocatalyst decorated with Rh₂O₃/Rh-NPs for CO₂ photoreduction. *J Photochem Photobiol A Chem* 364:344–354
102. Khan H, Jiang ZR, Berk D (2018) Molybdenum doped graphene/TiO₂ hybrid photocatalyst for UV/visible photocatalytic applications. *Sol Energy* 162:420–430
103. Khan I, Baig N, Qurashi A (2019) Graphitic carbon nitride impregnated niobium oxide (g-C₃N₄/Nb₂O₅) type (II) heterojunctions and its synergetic solar-driven hydrogen generation. *ACS Appl Energy Mater* 2(1):607–615
104. Khan MI, Sabir M, Mustafa GM et al (2020) 300 keV cobalt ions irradiations effect on the structural, morphological, optical and photovoltaic properties of Zn doped TiO₂ thin films based dye sensitized solar cells. *Ceram Int* 46(10):16813–16819
105. Khojasteh H, Salavati-Niasari M, Abbasi A et al (2016) Synthesis, characterization and photocatalytic activity of PdO/TiO₂ and Pd/TiO₂ nanocomposites. *J Mater Sci Mater Electron* 27(2):1261–1269
106. Kim SG, Dhandole LK, Seo YS et al (2018) Active composite photocatalyst synthesized from inactive Rh & Sb doped TiO₂ nanorods: enhanced degradation of organic pollutants & antibacterial activity under visible light irradiation. *Appl Catal A Gen* 564:43–55
107. Kim TH, Go GM, Cho HB et al (2018) A novel synthetic method for N doped TiO₂(2) nanoparticles through plasma-assisted electrolysis and photocatalytic activity in the visible region. *Front Chem* 6:10
108. Kiss J, Sapi A, Toth M et al (2020) Rh-induced support transformation and Rh incorporation in titanate structures and their influence on catalytic activity. *Catalysts* 10(2):29
109. Kokorin AI, Sviridova TV, Konstantinova EA et al (2020) Dynamics of photogenerated charge carriers in TiO₂/MoO₃, TiO₂/WO₃ and TiO₂/V₂O₅ photocatalysts with mosaic structure. *Catalysts* 10(9):14
110. Kongsong P, Jantaporn W, Masae M (2020) Enhanced photocatalytic activity of Ni doped TiO₂(2)nanowire-nanoparticle hetero-structured films prepared by hydrothermal and sol-gel methods. *Surf Interface Anal* 52(8):486–492
111. Krishnan U, Kaur M, Singh K et al (2019) A synoptic review of MoS₂: synthesis to applications. *Superlattices Microstruct* 128:274–297
112. Ku Y, Lin CN, Hou WM (2011) Characterization of coupled NiO/TiO₂ photocatalyst for the photocatalytic reduction of Cr(VI) in aqueous solution. *J Mol Catal A Chem* 349(1–2):20–27

113. Kubacka A, Munoz-Batista MJ, Ferrer M et al (2018) Er-W codoping of TiO₂-anatase: structural and electronic characterization and disinfection capability under UV-vis, and near-IR excitation. *Appl Catal B Environ* 228:113–129
114. Kumar R, Sahoo S, Joanni E et al (2019) A review on synthesis of graphene, h-BN and MoS₂ for energy storage applications: recent progress and perspectives. *Nano Res* 12 (11):2655–2694
115. Kumaravel V, Rhatigan S, Mathew S et al (2020) Mo doped TiO₂: impact on oxygen vacancies, anatase phase stability and photocatalytic activity. *J Phys Mater* 3(2):15
116. Kus M, Hakli Ö, Zafer C et al (2008) Optical and electrochemical properties of polyether derivatives of perylenediimides adsorbed on nanocrystalline metal oxide films. *Org Electron* 9(5):757–766
117. Lee C, Wei XD, Kysar JW et al (2008) Measurement of the elastic properties and intrinsic strength of monolayer graphene. *Science* 321(5887):385–388
118. Lee GJ, Wu JJ (2017) Recent developments in ZnS photocatalysts from synthesis to photocatalytic applications—a review. *Powder Technol* 318:8–22
119. Lee H, Reddy DA, Kumar DP et al (2019) Ultra-small cobalt nanocrystals embedded in 2D-MoS₂ nano-sheets as efficient co-catalyst for solar-driven hydrogen production: study of evolution rate dependence on cobalt nanocrystal size. *Appl Surf Sci* 494:239–248
120. Lee MG, Kim DH, Sohn W et al (2016) Conformally coated BiVO₄ nanodots on porosity-controlled WO₃ nanorods as highly efficient type II heterojunction photoanodes for water oxidation. *Nano Energy* 28:250–260
121. Lewandowska-Bernat A, Desideri U (2018) Opportunities of power-to-gas technology in different energy systems architectures. *Appl Energy* 228:57–67
122. Li CY, Fu M, Wang Y et al (2020) In situ synthesis of Co₂P-decorated red phosphorus nanosheets for efficient photocatalytic H₂ evolution. *Catal Sci Technol* 10(7):2221–2230
123. Li HJ, Tu WG, Zhou Y et al (2016) Z-Scheme photocatalytic systems for promoting photocatalytic performance: recent progress and future challenges. *Adv Sci* 3(11):12
124. Li HT, Liu RH, Lian SY et al (2013) Near-infrared light controlled photocatalytic activity of carbon quantum dots for highly selective oxidation reaction. *Nanoscale* 5(8):3289–3297
125. Li K, Zhang Y, Lin YZ et al (2019) Versatile functional porous cobalt-nickel phosphide-carbon cocatalyst derived from a metal-organic framework for boosting the photocatalytic activity of graphitic carbon nitride. *ACS Appl Mater Interfaces* 11 (32):28918–28927
126. Li N, Fan HK, Dai YJ et al (2020) Insight into the solar utilization of a novel Z-scheme Cs_{0.33}WO₃/CdS heterostructure for UV-Vis-NIR driven photocatalytic hydrogen evolution. *Appl Surf Sci* 508:9
127. Li P, He T (2018) Common-cation based Z-scheme ZnS@ZnO core-shell nanostructure for efficient solar-fuel production. *Appl Catal B-Environ* 238:518–524
128. Li S, Ji K, Zhang M et al (2020) Boosting the photocatalytic CO₂ reduction of metal–organic frameworks by encapsulating carbon dots. *Nanoscale* 12(17):9533–9540
129. Li T, Ding DY (2020) Photoelectrochemical water splitting with black Ni/Si-doped TiO₂ nanostructures. *Int J Hydrog Energy* 45(41):20983–20992
130. Li WJ, Liang R, Zhou NY et al (2020) Carbon black-doped anatase TiO₂ nanorods for solar light-induced photocatalytic degradation of methylene blue. *ACS Omega* 5(17):10042–10051
131. Li WJ, Lin ZY, Yang GW (2017) A 2D self-assembled MoS₂/ZnIn₂S₄ heterostructure for efficient photocatalytic hydrogen evolution. *Nanoscale* 9(46):18290–18298
132. Li X, Edelmannova M, Huo PW et al (2020) Fabrication of highly stable CdS/g-C₃N₄ composite for enhanced photocatalytic degradation of RhB and reduction of CO₂. *J Mater Sci* 55(8):3299–3313
133. Li X, Qian JH, Xu JS et al (2018) Synthesis, characterization and electrical properties of TiO₂ modified with SiO₂ and antimony-doped tin oxide. *J Mater Sci Mater Electron* 29 (14):12100–12108

134. Li Y, Zhao HJ, Yang MJ (2017) TiO₂ nanoparticles supported on PMMA nanofibers for photocatalytic degradation of methyl orange. *J Colloid Interface Sci* 508:500–507
135. Li YF, Zhou MH, Cheng B et al (2020) Recent advances in g-C₃N₄-based heterojunction photocatalysts. *J Mater Sci Technol* 56:1–17
136. Li YH, Yi MY, Li JY et al (2019) Noble metal free CdS@CuS-NixP hybrid with modulated charge transfer for enhanced photocatalytic performance. *Appl Catal B Environ* 257:6
137. Li YY, Walsh AG, Li DS et al (2020) W-Doped TiO(2)for photothermocatalytic CO(2) reduction. *Nanoscale* 12(33):17245–17252
138. Liao LB, Zhang QH, Su ZH et al (2014) Efficient solar water-splitting using a nanocrystalline CoO photocatalyst. *Nat Nanotechnol* 9(1):69–73
139. Lin ZY, Du C, Yan B et al (2018) Two-dimensional amorphous NiO as a plasmonic photocatalyst for solar H-2 evolution. *Nat Commun* 9:11
140. Liu F, Cao J, Yang ZH et al (2021) Heterogeneous activation of peroxymonosulfate by cobalt-doped MIL-53 (Al) for efficient tetracycline degradation in water: coexistence of radical and non-radical reactions. *J Colloid Interface Sci* 581:195–204
141. Liu FY, Dai YM, Chen FH et al (2020) Lead bismuth oxybromide/graphene oxide: synthesis, characterization, and photocatalytic activity for removal of carbon dioxide, crystal violet dye, and 2-hydroxybenzoic acid. *J Colloid Interface Sci* 562:112–124
142. Liu M, Wu J, Hou H (2019) Metal–Organic Framework (MOF)-based materials as heterogeneous catalysts for C–H bond activation. *Chem Eur J* 25(12):2935–2948
143. Liu Q, Huang J, Tang H et al (2020) Construction 0D TiO₂ nanoparticles/2D CoP nanosheets heterojunctions for enhanced photocatalytic H₂ evolution activity. *J Mater Sci Technol*
144. Liu W, Shen J, Liu QQ et al (2018) Porous MoP network structure as co-catalyst for H-2 evolution over g-C₃N₄ nanosheets. *Appl Surf Sci* 462:822–830
145. Liu X, Yang J, Hu LQ et al {001}/{101} facets co-exposed TiO(2) microsheet arrays with Lanthanum doping for enhancing photocatalytic CO(2) reduction. *J Mater Sci Mater Electron* 11
146. Liu XL, Ma R, Zhuang L et al Recent developments of doped g-C₃N₄ photocatalysts for the degradation of organic pollutants. *Crit Rev Environ Sci Technol* 40
147. Liu Y, Xu N, Chen W et al (2018) Supercapacitor with high cycling stability through electrochemical deposition of metal–organic frameworks/polypyrrole positive electrode. *Dalton Trans* 47(38):13472–13478
148. Lu XX, Toe CY, Ji F et al (2020) Light-induced formation of MoOxSy clusters on CdS nanorods as cocatalyst for enhanced hydrogen evolution. *ACS Appl Mater Interfaces* 12(7):8324–8332
149. Luo H, Guo Q, Szilagyi PA et al (2020) Carbon dots in solar-to-hydrogen conversion. *Trends Chem* 2(7):623–637
150. Luo JH, Lin ZX, Zhao Y et al (2020) The embedded CuInS₂ into hollow-concave carbon nitride for photocatalytic H₂O splitting into H-2 with S-scheme principle. *Chin J Catal* 41(1):122–130
151. Luo KY, Li J, Hu WY et al (2020) Synthesizing CuO/CeO₂/ZnO ternary nano-photocatalyst with highly effective utilization of photo-excited carriers under sunlight. *Nanomaterials* 10(10):13
152. Luo S, Nguyen-Phan TD, Vovchok D et al (2018) Enhanced, robust light-driven H-2 generation by gallium-doped titania nanoparticles. *Phys Chem Chem Phys* 20(3):2104–2112
153. Lv PW, Xu CS, Huang JJ et al (2020) Reversible photochromism for the enhancement of carrier separation in Zn1-xCuxS. *J Alloy Compd* 844:8
154. Ma R, Zhang S, Li L et al (2019) Enhanced visible-light-induced photoactivity of type-II CeO₂/g-C₃N₄ nanosheet toward organic pollutants degradation. *ACS Sustain Chem Eng* 7(10):9699–9708
155. Ma YY, Shen YQ, Gao X et al (2019) First-principles investigation on hydrogen evolution reaction in KNbO₃ (100)/g-C₃N₄ heterojunction. *Appl Catal A Gen* 582:7

156. Macdonald TJ, Nann T (2011) Quantum dot sensitized photoelectrodes. *Nanomaterials* 1 (1):79–88
157. Mahy JG, Lambert SD, Tilkin RG et al (2019) Ambient temperature ZrO₂-doped TiO₂ crystalline photocatalysts: highly efficient powders and films for water depollution. *Mater Today Energy* 13:312–322
158. Majeed I, Nadeem MA, Badshah A et al (2017) Titania supported MOF-199 derived Cu-Cu₂O nanoparticles: highly efficient non-noble metal photocatalysts for hydrogen production from alcohol-water mixtures. *Catal Sci Technol* 7(3):677–686
159. Malik P, Awasthi M, Sinha S Biomass-based gaseous fuel for hybrid renewable energy systems: an overview and future research opportunities. *Int J Energy Res* 31
160. Malika M, Rao CV, Das RK et al (2016) Evaluation of bimetal doped TiO₂ in dye fragmentation and its comparison to mono-metal doped and bare catalyts. *Appl Surf Sci* 368:316–324
161. Mamba G, Mishra AK (2016) Graphitic carbon nitride (g-C₃N₄) nanocomposites: a new and exciting generation of visible light driven photocatalysts for environmental pollution remediation. *Appl Catal B Environ* 198:347–377
162. Mandari KK, Son N, Pandey S et al (2020) Nb₂O₅-SnS₂-CdS heteronanostructures as efficient visible-light-harvesting materials for production of H₂ under solar light irradiation. *J Alloy Compd* 835:15
163. Margha FH, Radwan EK, Badawy MI et al (2020) Bi₂O₃-BiFeO₃ glass-ceramic: controllable beta/gamma-Bi₂O₃ transformation and application as magnetic solar-driven photocatalyst for water decontamination. *ACS Omega* 5(24):14625–14634
164. Mateo D, Albero J, Garcia H (2017) Photoassisted methanation using Cu₂O nanoparticles supported on graphene as a photocatalyst. *Energy Environ Sci* 10(11):2392–2400
165. Mateo D, Albero J, Garcia H (2018) Graphene supported NiO/Ni nanoparticles as efficient photocatalyst for gas phase CO₂ reduction with hydrogen. *Appl Catal B Environ* 224:563–571
166. Mateo D, Esteve-Adell I, Albero J et al (2016) 111 oriented gold nanoplatelets on multilayer graphene as visible light photocatalyst for overall water splitting. *Nat Commun* 7:8
167. Mateo D, Garcia-Mulero A, Albero J et al (2019) N-doped defective graphene decorated by strontium titanate as efficient photocatalyst for overall water splitting. *Appl Catal B Environ* 252:111–119
168. Mei FF, Li Z, Dai K et al (2020) Step-scheme porous g-C₃N₄/Zn_{0.2}Cd_{0.8}S-DETA composites for efficient and stable photocatalytic H₂ production. *Chin J Catal* 41(1):41–49
169. Memisoglu G, Varlikli C, Diker H (2013) Solution-processed polyfluorene: naphthalenediimide-N-doped TiO₂ hybrids for ultraviolet photodetector applications. *J Electron Mater* 42(12):3502–3511
170. Mendiola-Alvarez SY, Guzman-Mar JL, Turnes-Palomino G et al (2019) Synthesis of Cr₃₊-doped TiO₂ nanoparticles: characterization and evaluation of their visible photocatalytic performance and stability. *Environ Technol* 40(2):144–153
171. Mendiola-Alvarez SY, Hernandez-Ramirez MA, Guzman-Mar JL et al (2019) Phosphorous-doped TiO₂ nanoparticles: synthesis, characterization, and visible photocatalytic evaluation on sulfamethazine degradation. *Environ Sci Pollut Res* 26(5):4180–4191
172. Meng X (2017) An overview of molecular layer deposition for organic and organic-inorganic hybrid materials: mechanisms, growth characteristics, and promising applications. *J Mater Chem A* 5(35):18326–18378
173. Min YX, Yang XY, Wang DW et al (2019) Tuning mixed-phase Nb-doped titania films for high-performance photocatalysts with enhanced whole-spectrum light absorption. *Catal Sci Technol* 9(21):6027–6036
174. Mkhaldid IA, Fierro JLG, Mohamed RM et al (2020) Impact of the PtO loading on mesoporous TiO₂ nanoparticles for enhanced photodegradation of Imazapyr herbicide under simulated solar light. *J Nanopart Res* 22(11):14
175. Mohammed SA, Al Amouri L, Youisif E et al (2018) Synthesis of NiO:V₂O₅ nanocomposite and its photocatalytic efficiency for methyl orange degradation. *Heliyon* 4(3):12

176. Mondal I, Gonuguntla S, Pal U (2019) Photoinduced fabrication of Cu/TiO₂ core-shell heterostructures derived from Cu-MOF for solar hydrogen generation: the size of the Cu nanoparticle matters. *J Phys Chem C* 123(43):26073–26081
177. Moniz SJA, Shevlin SA, An XQ et al (2014) Fe₂O₃-TiO₂ nanocomposites for enhanced charge separation and photocatalytic activity. *Chem Eur J* 20(47):15571–15579
178. Muller A, Kondofersky I, Folger A et al (2017) Dual absorber Fe₂O₃/WO₃ host-guest architectures for improved charge generation and transfer in photoelectrochemical applications. *Mater Res Express* 4(1):9
179. Nair SB, John KA, Joseph JA et al (2020) Role of magnesium doping for ultrafast room temperature crystallization and improved photocatalytic behavior of TiO₂ nanotubes. *Mater Today Proc* 25:203–207
180. Naraginti S, Stephen FB, Radhakrishnan A et al (2015) Zirconium and silver co-doped TiO₂ nanoparticles as visible light catalyst for reduction of 4-nitrophenol, degradation of methyl orange and methylene blue. *Spectrochim Acta Pt A Molec Biomolec Spectrosc* 135:814–819
181. Naseri A, Samadi M, Pourjavadi A et al (2017) Graphitic carbon nitride (g-C₃N₄)-based photocatalysts for solar hydrogen generation: recent advances and future development directions. *J Mater Chem A* 5(45):23406–23433
182. Nasir JA, Rehman ZU, Shah SNA et al (2020) Recent developments and perspectives in CdS-based photocatalysts for water splitting. *J Mater Chem A* 8(40):20752–20780
183. Nematollahi R, Ghotbi C, Khorasheh F et al (2020) Ni-Bi co-doped TiO₂ as highly visible light response nano-photocatalyst for CO₂ photo-reduction in a batch photo-reactor. *J CO₂ Util* 41:101289
184. Nguyen CC, Dinh CT, Do TO (2017) Hollow Sr/Rh-codoped TiO₂ photocatalyst for efficient sunlight-driven organic compound degradation. *RSC Adv* 7(6):3480–3487
185. Nguyen VH, Do HH, Nguyen TV et al (2020) Perovskite oxide-based photocatalysts for solar-driven hydrogen production: progress and perspectives. *Sol Energy* 211:584–599
186. Osuntokun J, Onwudiwe DC, Ebenso EE (2017) Biosynthesis and photocatalytic properties of SnO₂ nanoparticles prepared using aqueous extract of cauliflower. *J Clust Sci* 28(4):1883–1896
187. Panayotov DA, Yates JT (2007) Spectroscopic detection of hydrogen atom spillover from Au nanoparticles supported on TiO₂: use of conduction band electrons. *J Phys Chem C* 111(7):2959–2964
188. Pang H, Meng XG, Song H et al (2019) Probing the role of nickel dopant in aqueous colloidal ZnS nanocrystals for efficient solar-driven CO₂ reduction. *Appl Catal B Environ* 244:1013–1020
189. Pant B, Ojha GP, Kuk YS et al (2020) Synthesis and characterization of ZnO-TiO₂/carbon fiber composite with enhanced photocatalytic properties. *Nanomaterials* 10(10):11
190. Parrino F, Bellardita M, Garcia-Lopez EI et al (2018) Heterogeneous photocatalysis for selective formation of high-value-added molecules: some chemical and engineering aspects. *ACS Catal* 8(12):11191–11225
191. Paulauskas IE, Modeshia DR, Ali TT et al (2013) Photocatalytic activity of doped and undoped titanium dioxide nanoparticles synthesised by flame spray pyrolysis platinum-doped TiO₂ composites show improved activity compared to commercially available product. *Platin Met Rev* 57(1):32–43
192. Peng C, Wei P, Li XY et al (2018) High efficiency photocatalytic hydrogen production over ternary Cu/TiO₂@Ti₃C₂Tx enabled by low-work-function 2D titanium carbide. *Nano Energy* 53:97–107
193. Perez R, Perez M (2009) A fundamental look at energy reserves for the planet. *The IEA SHC solar update* 50(2)
194. Pham TD, Lee BK (2017) Novel photocatalytic activity of Cu@V co-doped TiO₂/PU for CO₂ reduction with H₂O vapor to produce solar fuels under visible light. *J Catal* 345:87–95
195. Pi MY, Wu TL, Zhang DK et al (2016) Facile preparation of semimetallic WP₂ as a novel photocatalyst with high photoactivity. *RSC Adv* 6(19):15724–15730

196. Pierpaoli M, Zheng X, Bondarenko V et al (2019) Paving the way for a sustainable and efficient $\text{SiO}_2/\text{TiO}_2$ photocatalytic composite. *Environments* 6(8):12
197. Pillai VV, Lonkar SP, Alhassan SM (2020) Template-free, solid-state synthesis of hierarchically macroporous S-Doped TiO_2 nano-photocatalysts for efficient water remediation. *ACS Omega* 5(14):7969–7978
198. Pooseekheaw P, Thongpan W, Panthawan A et al (2020) Porous $\text{V}_2\text{O}_5/\text{TiO}_2$ nanoheterostructure films with enhanced visible-light photocatalytic performance prepared by the sparking method. *Molecules* 25(15):11
199. Pu Z, Liu T, Aminu IS et al (2020) Transition-metal phosphides: activity origin, energy-related electrocatalysis applications, and synthetic strategies. *Adv Funct Mater* 2004009
200. Qi YH, Xu JX, Fu YL et al (2019) Metal-organic framework templated synthesis of $\text{g-C}_3\text{N}_4/\text{Fe}_2\text{O}_3@/\text{FeP}$ composites for enhanced hydrogen production. *ChemCatChem* 11(15):3465–3473
201. Qian JC, Chen ZG, Chen F et al (2018) Exploration of $\text{CeO}_2\text{-CuO}$ quantum dots in situ grown on graphene under hypha assistance for highly efficient solar-driven hydrogen production. *Inorg Chem* 57(23):14532–14541
202. Qin YY, Li H, Lu J et al (2020) Synergy between van der waals heterojunction and vacancy in $\text{ZnIn}_2\text{S}_4/\text{g-C}_3\text{N}_4$ 2D/2D photocatalysts for enhanced photocatalytic hydrogen evolution. *Appl Catal B Environ* 277:10
203. Raizada P, Sudhaik A, Patial S et al (2020) Engineering nanostructures of CuO-based photocatalysts for water treatment: current progress and future challenges. *Arab J Chem* 13(11):8424–8457
204. Rambabu Y, Kumar U, Singhal N et al (2019) Photocatalytic reduction of carbon dioxide using graphene oxide wrapped TiO_2 nanotubes. *Appl Surf Sci* 485:48–55
205. Razmyar S, Sheng T, Akter M et al (2019) Low-temperature photocatalytic hydrogen addition to two-dimensional MoO_3 nanoflakes from isopropyl alcohol for enhancing solar energy harvesting and conversion. *ACS Appl Nano Mater* 2(7):4180–4192
206. Ren DD, Shen RC, Jiang ZM et al (2020) Highly efficient visible-light photocatalytic H_2 evolution over 2D–2D $\text{CdS}/\text{Cu}_7\text{S}_4$ layered heterojunctions. *Chin J Catal* 41(1):31–40
207. Ren DD, Zhang WN, Ding YN et al (2020) In situ fabrication of robust cocatalyst-free $\text{CdS}/\text{g-C}_3\text{N}_4$ 2D–2D step-scheme heterojunctions for highly active H_2 evolution. *Sol RRL* 4(8):11
208. Ren XH, Philo D, Li YX et al (2020) Recent advances of low-dimensional phosphorus-based nanomaterials for solar-driven photocatalytic reactions. *Coord Chem Rev* 424:34
209. Rhimi B, Wang CY, Bahnemann DW (2020) Latest progress in $\text{g-C}(3)\text{N}(4)$ based heterojunctions for hydrogen production via photocatalytic water splitting: a mini review. *J Phys Energy* 2(4):16
210. Rodriguez JA, Evans J, Graciani J et al (2009) High water-gas shift activity in $\text{TiO}_2(110)$ supported Cu and Au nanoparticles: role of the oxide and metal particle size. *J Phys Chem C* 113(17):7364–7370
211. Ruan QQ, Ma XW, Li YY et al (2020) One-dimensional $\text{CdS}@/\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}@/\text{ZnS-Ni(OH)}(2)$ nano-hybrids with epitaxial heterointerfaces and spatially separated photo-redox sites enabling highly-efficient visible-light-driven H_2 evolution. *Nanoscale* 12(39):20522–20535
212. Rusinque B, Escobedo S, de Lasa H (2020) Photoreduction of a Pd-doped mesoporous TiO_2 photocatalyst for hydrogen production under visible light. *Catalysts* 10(1):24
213. Sahin C, Dittich T, Varlikli C et al (2010) Role of side groups in pyridine and bipyridine ruthenium dye complexes for modulated surface photovoltage in nanoporous TiO_2 . *Sol Energy Mater Sol Cells* 94(4):686–690
214. Sarilmaz A, Genc E, Aslan E et al (2020) Photocatalytic hydrogen evolution via solar-driven Water splitting by CuSbS_2 with different shapes. *J Photochem Photobiol A Chem* 400:6

215. Saroj S, Singh L, Singh SV (2020) Solution-combustion synthesis of anion (iodine) doped TiO₂ nanoparticles for photocatalytic degradation of Direct Blue 199 dye and regeneration of used photocatalyst. *J Photochem Photobiol A Chem* 396:13
216. Schiper DE, Zhao ZH, Leitner AP et al (2017) A TiO₂/FeMnP Core/Shell nanorod array photoanode for efficient photoelectrochemical oxygen evolution. *ACS Nano* 11(4):4051–4059
217. Shabdan Y, Markhabayeva A, Bakranov N et al (2020) Photoactive Tungsten-Oxide Nanomaterials for Water-Splitting. *Nanomaterials* 10(9):37
218. Shahan M, Ahmed AM, Shehata N et al (2019) Ni-doped and Ni/Cr co-doped TiO₂ nanotubes for enhancement of photocatalytic degradation of methylene blue. *J Colloid Interface Sci* 555:31–41
219. Shakir I, Choi JH, Shahid M et al (2012) MoO₃-MWCNT nanocomposite photocatalyst with control of light-harvesting under visible light and natural sunlight irradiation. *J Mater Chem* 22(38):20549–20553
220. Shehzad N, Tahir M, Johari K et al (2018) Improved interfacial bonding of graphene-TiO₂ with enhanced photocatalytic reduction of CO₂ into solar fuel. *J Environ Chem Eng* 6(6):6947–6957
221. Shi L, Benetti D, Li FY et al (2020) Phase-junction design of MOF-derived TiO₂ photoanodes sensitized with quantum dots for efficient hydrogen generation. *Appl Catal B Environ* 263:10
222. Shi L, He Z, Liu SQ (2018) MoS₂ quantum dots embedded in g-C₃N₄ frameworks: a hybrid 0D–2D heterojunction as an efficient visible-light driven photocatalyst. *Appl Surf Sci* 457:30–40
223. Shi WL, Wang JB, Yang S et al (2020) Fabrication of a ternary carbon dots/CoO/g-C₃N₄ nanocomposite photocatalyst with enhanced visible-light-driven photocatalytic hydrogen production. *J Chem Technol Biotechnol* 95(8):2129–2138
224. Shin HU, Lolla D, Nikolov Z et al (2016) Pd-Au nanoparticles supported by TiO₂ fibers for catalytic NO decomposition by CO. *J Ind Eng Chem* 33:91–98
225. Singh J, Kaur H, Kukkar D et al (2019) Green synthesis of SnO₂ NPs for solar light induced photocatalytic applications. *Mater Res Express* 6(11):8
226. Singh K, Harish S, Kristy AP et al (2018) Erbium doped TiO₂ interconnected mesoporous spheres as an efficient visible light catalyst for photocatalytic applications. *Appl Surf Sci* 449:755–763
227. Smith WA, Sharp ID, Strandwitz NC et al (2015) Interfacial band-edge energetics for solar fuels production. *Energy Environ Sci* 8(10):2851–2862
228. Sohail M, Baig N, Sher M et al (2020) A novel tin-doped titanium oxide nanocomposite for efficient photo-anodic water splitting. *ACS Omega* 5(12):6405–6413
229. Song GX, Chu ZY, Jin WQ et al (2015) Enhanced performance of g-C₃N₄/TiO₂ photocatalysts for degradation of organic pollutants under visible light. *Chin J Chem Eng* 23(8):1326–1334
230. Song LM, Zhang SJ (2018) RuP2/CdS photocatalysts for enhanced hydrogen evolution in water spitting and mechanism of enhancement. *Powder Technol* 339:479–486
231. Sorcar S, Thompson J, Hwang Y et al (2018) High-rate solar-light photoconversion of CO₂ to fuel: controllable transformation from C-1 to C-2 products. *Energy Environ Sci* 11(11):3183–3193
232. Sreekanth TVM, Nagajyothi PC, Dillip GR et al (2017) Determination of band alignment in the synergistic catalyst of electronic structure-modified graphitic carbon nitride-integrated ceria quantum-dot heterojunctions for rapid degradation of organic pollutants. *J Phys Chem C* 121(45):25229–25242
233. Stolarczyk JK, Bhattacharyya S, Polavarapu L et al (2018) Challenges and prospects in solar water splitting and CO₂ reduction with inorganic and hybrid nanostructures. *ACS Catal* 8(4):3602–3635
234. Su N, Hu XL, Zhang JB et al (2017) Plasma-induced synthesis of Pt nanoparticles supported on TiO₂ nanotubes for enhanced methanol electro-oxidation. *Appl Surf Sci* 399:403–410

235. Su SY, Xing ZP, Zhang SY et al (2021) Ultrathin mesoporous g-C₃N₄/NH₂-MIL-101(Fe) octahedron heterojunctions as efficient photo-Fenton-like system for enhanced photo-thermal effect and promoted visible-light-driven photocatalytic performance. *Appl Surf Sci* 537:11
236. Sudrajat H, Babel S, Ta AT et al (2020) Mn-doped TiO₂ photocatalysts: Role, chemical identity, and local structure of dopant. *J Phys Chem Solids* 144:9
237. Sun BW, Wang H, Wu JK et al (2020) Designed synthesis of unique ZnS@CdS@Cd_{0.5}Zn_{0.5}S-MoS₂ hollow nanospheres for efficient visible-light-driven H₂ evolution. *Crystengcomm* 22(16):2743–2755
238. Sun FC, Maimaiti H, Liu YE et al (2018) Preparation and photocatalytic CO₂ reduction performance of silver nanoparticles coated with coal-based carbon dots. *Int J Energy Res* 42 (14):4458–4469
239. Sun QQ, Yu ZB, Jiang RH et al (2020) CoP QD anchored carbon skeleton modified CdS nanorods as a co-catalyst for photocatalytic hydrogen production. *Nanoscale* 12(37):19203–19212
240. Sun T, Fan J, Liu EZ et al (2012) Fe and Ni co-doped TiO₂ nanoparticles prepared by alcohol-thermal method: application in hydrogen evolution by water splitting under visible light irradiation. *Powder Technol* 228:210–218
241. Sun WJ, Fu ZY, Shi HX et al (2020) Cu(3)P and Ni(2)P co-modified g-C(3)N(4) nanosheet with excellent photocatalytic H(2) evolution activities. *J Chem Technol Biotechnol* 95 (12):3117–3125
242. Suppuraja P, Parthiban S, Swaminathan M et al (2019) Hydrothermal fabrication of ternary NrGO-TiO₂/ZnFe₂O₄ nanocomposites for effective photocatalytic and fuel cell applications. *Mater Today Proc* 15:429–437
243. Teixeira IF, Quiroz J, Homsí MS et al (2020) An overview of the photocatalytic H₂ evolution by semiconductor-based materials for nonspecialists. *J Braz Chem Soc* 31(2):211–229
244. Thangavel N, Bellamkonda S, Arulraj AD et al (2018) Visible light induced efficient hydrogen production through semiconductor-conductor-semiconductor (S-C-S) interfaces formed between g-C₃N₄ and rGO/Fe₂O₃ core-shell composites. *Catal Sci Technol* 8 (19):5081–5090
245. Thi QV, Tamboli MS, Ta QTH et al (2020) A nanostructured MOF/reduced graphene oxide hybrid for enhanced photocatalytic efficiency under solar light. *Mater Sci Eng B* 261:114678
246. Tian B, Wu YQ, Lu GX (2021) Metal-free plasmonic boron phosphide/graphitic carbon nitride with core-shell structure photocatalysts for overall water splitting. *Appl Catal B Environ* 280:9
247. Truc NTT, Bach LG, Hanh NT et al (2019) The superior photocatalytic activity of Nb doped TiO₂/g-C₃N₄ direct Z-scheme system for efficient conversion of CO₂ into valuable fuels. *J Colloid Interface Sci* 540:1–8
248. Truc NTT, Pham TD, Nguyen MV et al (2020) Advanced NiMoO₄/g-C₃N₄ Z-scheme heterojunction photocatalyst for efficient conversion of CO₂ to valuable products. *J Alloy Compd* 842:8
249. Tseng IH, Sung YM, Chang PY et al (2017) Photocatalytic performance of titania nanosheets templated by graphene oxide. *J Photochem Photobiol A Chem* 339:1–11
250. Uddin A, Muhmood T, Guo ZC et al (2020) Hydrothermal synthesis of 3D/2D heterojunctions of ZnIn₂S₄/oxygen doped g-C₃N₄ nanosheet for visible light driven photocatalysis of 2,4-dichlorophenoxyacetic acid degradation. *J Alloy Compd* 845:11
251. Uma K, Muniranthinam E, Chong SH et al (2020) Fabrication of hybrid catalyst ZnO nanorod/alpha-Fe₂O₃ composites for hydrogen evolution reaction. *Curr Comput Aided Drug Des* 10(5):12
252. Van CN, Hai NT, Olejnicek J et al (2018) Preparation and photoelectrochemical performance of porous TiO₂/graphene nanocomposite films. *Mater Lett* 213:109–113
253. Verma P, Stewart DJ, Raja R (2020) Recent advances in photocatalytic CO₂ utilisation over multifunctional metal-organic frameworks. *Catalysts* 10(10):1176

254. Walter MG, Warren EL, McKone JR et al (2010) Solar water splitting cells. *Chem Rev* 110 (11):6446–6473
255. Wang CH, Qin DD, Shan DL et al (2017) Assembly of g-C₃N₄-based type II and Z-scheme heterojunction anodes with improved charge separation for photoelectrojunction water oxidation. *Phys Chem Chem Phys* 19(6):4507–4515
256. Wang CH, Shao CL, Zhang XT et al (2009) SnO₂ nanostructures-TiO₂ nanofibers heterostructures: controlled fabrication and high photocatalytic properties. *Inorg Chem* 48 (15):7261–7268
257. Wang GZ, Zhou F, Yuan BF et al (2019) Strain-tunable visible-light-responsive photocatalytic properties of two-dimensional CdS/g-C₃N₄: a hybrid density functional study. *Nanomaterials* 9(2):10
258. Wang JM, Xu QC, Liu ML et al (2020) The synergetic effect of N, S-codoped carbon and CoOx nanodots derived from ZIF-67 as a highly efficient cocatalyst over CdS nanorods. *Sustain Energy Fuels* 4(4):1954–1962
259. Wang M, Cheng JJ, Wang XF et al (2021) Sulfur-mediated photodeposition synthesis of NiS cocatalyst for boosting H₂-evolution performance of g-C₃N₄ photocatalyst. *Chin J Catal* 42 (1):37–45
260. Wang M, Ju P, Li JJ et al (2017) Facile synthesis of MoS₂/g-C₃N₄/GO ternary heterojunction with enhanced photocatalytic activity for water splitting. *ACS Sustain Chem Eng* 5(9):7878–7886
261. Wang N, Li XJ (2018) Facile synthesis of CoO nanorod/C₃N₄ heterostructure photocatalyst for an enhanced pure water splitting activity. *Inorg Chem Commun* 92:14–17
262. Wang P, Huang BB, Dai Y et al (2012) Plasmonic photocatalysts: harvesting visible light with noble metal nanoparticles. *Phys Chem Chem Phys* 14(28):9813–9825
263. Wang Q, Chen X, Tian J et al The preparation of S-SnO₂/g-C(3)N(4)heterojunction and its photocatalytic degradation of phenol and trichlorophenol. *J Mater Sci Mater Electron* 12
264. Wang QL, Wang XK, Yu ZH et al (2019) Artificial photosynthesis of ethanol using type-II g-C₃N₄/ZnTe heterojunction in photoelectrochemical CO₂ reduction system. *Nano Energy* 60:827–835
265. Wang QQ, Zhu SL, Liang YQ et al (2017) One-step synthesis of size-controlled Br-doped TiO₂ nanoparticles with enhanced visible-light photocatalytic activity. *Mater Res Bull* 86:248–256
266. Wang S, Wang L, Huang W (2020) Bismuth-based photocatalysts for solar energy conversion. *J Mater Chem A*
267. Wang SJ, Chen L, Zhao XL et al (2020) Efficient photocatalytic overall water splitting on metal-free 1D SWCNT/2D ultrathin C₃N₄ heterojunctions via novel non-resonant plasmonic effect. *Appl Catal B-Environ* 278:8
268. Wang XF, Li SF, Yu HG et al (2011) Ag₂O as a new visible-light photocatalyst: self-stability and high photocatalytic activity. *Chem Eur J* 17(28):7777–7780
269. Wang XJ, Zhao XL, Zhang DQ et al (2018) Microwave irradiation induced UIO-66-NH₂ anchored on graphene with high activity for photocatalytic reduction of CO₂. *Appl Catal B-Environ* 228:47–53
270. Wang XK, Wang C, Jiang WQ et al (2012) Sonochemical synthesis and characterization of Cl-doped TiO₂ and its application in the photodegradation of phthalate ester under visible light irradiation. *Chem Eng J* 189:288–294
271. Wang Y, Kong B, Zhao D et al (2017) Strategies for developing transition metal phosphides as heterogeneous electrocatalysts for water splitting. *Nano Today* 15:26–55
272. Wang Y, Wang S, Zhang SL et al (2020) Formation of hierarchical FeCoS₂-CoS₂ double-shelled nanotubes with enhanced performance for photocatalytic reduction of CO₂. *Angew Chem*
273. Wang YF, Hu AG (2014) Carbon quantum dots: synthesis, properties and applications. *J Mater Chem C* 2(34):6921–6939

274. Wang ZC, Song YC, Cai XF et al (2019) Rapid preparation of terbium-doped titanium dioxide nanoparticles and their enhanced photocatalytic performance. *R Soc Open Sci* 6 (10):14
275. Wang ZL, Chen YF, Zhang LY et al (2020) Step-scheme CdS/TiO₂ nanocomposite hollow microsphere with enhanced photocatalytic CO₂ reduction activity. *J Mater Sci Technol* 56:143–150
276. Wattanawikkam C, Pecharapa W (2020) Structural studies and photocatalytic properties of Mn and Zn co-doping on TiO₂ prepared by single step sonochemical method. *Radiat Phys Chem* 171:8
277. Wei C, Zhang W, Wang X et al (2020) MOF-derived mesoporous gC₃N₄/TiO₂ heterojunction with enhanced photocatalytic activity. *Catal Lett* 1–15
278. Wei SQ, Wang F, Yan P et al (2019) Interfacial coupling promoting hydrogen sulfide splitting on the staggered type II g-C₃N₄/r-TiO₂ heterojunction. *J Catal* 377:122–132
279. Weng C-C, Ren J-T and Yuan Z-Y (2020) Transition metal phosphide-based materials for efficient electrochemical hydrogen evolution: a critical review. *ChemSusChem*
280. Wu C, Zhang J, Tong X et al (2019) A critical review on enhancement of photocatalytic hydrogen production by molybdenum disulfide: from growth to interfacial activities. *Small* 15(35):25
281. Wu SJ, Zhao HJ, Li CF et al (2019) Type II heterojunction in hierarchically porous zinc oxide/graphitic carbon nitride microspheres promoting photocatalytic activity. *J Colloid Interface Sci* 538:99–107
282. Wu TS, Zhu C, Han DX et al (2019) Highly selective conversion of CO₂ to C₂H₆ on graphene modified chlorophyll Cu through multi-electron process for artificial photosynthesis. *Nanoscale* 11(47):22980–22988
283. Wu YA, McNulty I, Liu C et al (2019) Facet-dependent active sites of a single Cu₂O particle photocatalyst for CO₂ reduction to methanol. *Nat Energy* 4(11):957–968
284. Wu YX, Liu LM, An XQ et al (2019) New insights into interfacial photocharge transfer in TiO₂/C₃N₄ heterostructures: effects of facets and defects. *New J Chem* 43(11):4511–4517
285. Xia Y, Cheng B, Fan JJ et al (2019) Unraveling photoexcited charge transfer pathway and process of CdS/graphene nanoribbon composites toward visible-light photocatalytic hydrogen evolution. *Small* 15(34):9
286. Xiao Z, Bi C, Shao Y et al (2014) Efficient, high yield perovskite photovoltaic devices grown by interdiffusion of solution-processed precursor stacking layers. *Energy Environ Sci* 7(8):2619–2623
287. Xie W, Li R, Xu QY (2018) Enhanced photocatalytic activity of Se-doped TiO₂ under visible light irradiation. *Sci Rep* 8:10
288. Xing HM, Teng SY, Xing ZH et al (2020) Effect of Pt cocatalyst on visible light driven hydrogen evolution of anthracene-based zirconium metal-organic framework. *Appl Surf Sci* 532:7
289. Xing M, Zhang J, Qiu B et al (2015) A brown mesoporous TiO₂-x/MCF composite with an extremely high quantum yield of solar energy photocatalysis for H₂ evolution. *Small* 11 (16):1920–1929
290. Xu L, Li Q, Li XF et al (2019) Rationally designed 2D/2DSiC/g-C₃N₄ photocatalysts for hydrogen production. *Catal Sci Technol* 9(15):3896–3906
291. Xu M, Wu H, Tang YW et al (2020) One-step in-situ synthesis of porous Fe³⁺-doped TiO₂ octahedra toward visible-light photocatalytic conversion of CO₂ into solar fuel. *Microporous Mesoporous Mat* 309:7
292. Xu QL, Zhang LY, Cheng B et al (2020) S-Scheme Heterojunction Photocatalyst. *Chem* 6 (7):1543–1559
293. Xu QL, Zhang LY, Yu JG et al (2018) Direct Z-scheme photocatalysts: principles, synthesis, and applications. *Mater Today* 21(10):1042–1063
294. Xu QL, Zhu BC, Jiang CJ et al (2018) Constructing 2D/2D Fe₂O₃/g-C₃N₄ direct Z-scheme photocatalysts with enhanced H₂ generation performance. *Sol RRL* 2(3):10

295. Xu XY, Ray R, Gu YL et al (2004) Electrophoretic analysis and purification of fluorescent single-walled carbon nanotube fragments. *J Am Chem Soc* 126(40):12736–12737
296. Xu YH, Liang DH, Liu ML et al (2008) Preparation and characterization of $\text{Cu}_2\text{O-TiO}_2$: Efficient photocatalytic degradation of methylene blue. *Mater Res Bull* 43(12):3474–3482
297. Xue C, Zhang P, Shao GS et al (2020) Effective promotion of spacial charge separation in direct Z-scheme $\text{WO}_3/\text{CdS}/\text{WS}_2$ tandem heterojunction with enhanced visible-light-driven photocatalytic H₂ evolution. *Chem Eng J* 398:10
298. Yadav V, Verma P, Sharma H et al (2020) Photodegradation of 4-nitrophenol over B-doped TiO_2 nanostructure: effect of dopant concentration, kinetics, and mechanism. *Environ Sci Pollut Res* 27(10):10966–10980
299. Yan BL, Liu DP, Feng XL et al (2020) Ru species supported on MOF-derived N-doped TiO_2/C hybrids as efficient electrocatalytic/photocatalytic hydrogen evolution reaction catalysts. *Adv Func Mater* 30(31):9
300. Yan BL, Zhang LJ, Tang ZY et al (2017) Palladium-decorated hierarchical titania constructed from the metal-organic frameworks $\text{NH}_2\text{-MIL-125(Ti)}$ as a robust photocatalyst for hydrogen evolution. *Appl Catal B-Environ* 218:743–750
301. Yan MY, Jiang ZY, Zheng JM et al (2020) Theoretical study on transport-scheme conversion of g- $\text{C}_3\text{N}_4/\text{TiO}_2$ heterojunctions by oxygen vacancies. *Appl Surf Sci* 531:7
302. Yang F, Liu D, Li Y, et al Solid-state synthesis of ultra-small freestanding amorphous MoP quantum dots for highly efficient photocatalytic H₂ production. *Chem Eng J* 406:126838
303. Yang S, Fan D, Hu W et al (2018) Elucidating charge separation dynamics in a hybrid metal-organic framework photocatalyst for light-driven H₂ evolution. *J Phys Chem C* 122(6):3305–3311
304. Yang XH, Wang Y, Zhang LT et al (2020) The use of tunable optical absorption plasmonic Au and Ag decorated TiO_2 structures as efficient visible light photocatalysts. *Catalysts* 10(1):14
305. Yang Y, Zhang C, Lai C et al (2018) BiOX (X = Cl, Br, I) photocatalytic nanomaterials: applications for fuels and environmental management. *Adv Colloid Interface Sci* 254:76–93
306. Yang YJ, Yu YL, Wang JS et al (2017) Doping and transformation mechanisms of Fe_3^+ ions in Fe-doped TiO_2 . *CrystEngComm* 19(7):1100–1105
307. Yi LH, Lan FJ, Li JE et al (2018) Efficient noble-metal-free Co-NG/ TiO_2 photocatalyst for H₂ evolution: synergistic effect between single-atom Co and N-doped graphene for enhanced photocatalytic activity. *ACS Sustain Chem Eng* 6(10):12766–12775
308. Yi SS, Zhang XB, Wulan BR et al (2018) Non-noble metals applied to solar water splitting. *Energy Environ Sci* 11(11):3128–3156
309. Yoon JW, Kim DH, Kim JH et al (2019) $\text{NH}_2\text{-MIL-125(Ti)/TiO}_2$ nanorod heterojunction photoanodes for efficient photoelectrochemical water splitting. *Appl Catal B-Environ* 244:511–518
310. Young C, Wang J, Kim J et al (2018) Controlled chemical vapor deposition for synthesis of nanowire arrays of metal-organic frameworks and their thermal conversion to carbon/metal oxide hybrid materials. *Chem Mater* 30(10):3379–3386
311. Yu P, Wang F, Shifa TA et al (2019) Earth abundant materials beyond transition metal dichalcogenides: a focus on electrocatalyzing hydrogen evolution reaction. *Nano Energy* 58:244–276
312. Yuan J, Zhang JJ, Yang MP et al (2018) CuO nanoparticles supported on TiO_2 with high efficiency for CO_2 electrochemical reduction to ethanol. *Catalysts* 8(4):11
313. Zang YP, Li LP, Xu YS et al (2014) Hybridization of brookite TiO_2 with g- C_3N_4 : a visible-light-driven photocatalyst for As_3^+ oxidation, MO degradation and water splitting for hydrogen evolution. *J Mater Chem A* 2(38):15774–15780
314. Zhang FM, Sheng JL, Yang ZD et al (2018) Rational design of MOF/COF hybrid materials for photocatalytic H₂ evolution in the presence of sacrificial electron donors. *Angew Chem Int Edn* 57(37):12106–12110

315. Zhang GX, Song AK, Duan YW et al (2018) Enhanced photocatalytic activity of TiO₂/zeolite composite for abatement of pollutants. *Microporous Mesoporous Mat* 255:61–68
316. Zhang H, Tang Q, Li QS et al (2020) Enhanced photocatalytic properties of PET filaments coated with Ag-N Co-doped TiO₂ nanoparticles sensitized with disperse blue dyes. *Nanomaterials* 10(5):24
317. Zhang HY, Wang ZW, Li RN et al (2017) TiO₂ supported on reed straw biochar as an adsorptive and photocatalytic composite for the efficient degradation of sulfamethoxazole in aqueous matrices. *Chemosphere* 185:351–360
318. Zhang J, Zhao Q, Zhang JX et al (2020) Highly active Fe_xCo_{1-x}P cocatalysts modified CdS for photocatalytic hydrogen production. *Int J Hydrog Energy* 45(43):22722–22731
319. Zhang JF, Zhou P, Liu JJ et al (2014) New understanding of the difference of photocatalytic activity among anatase, rutile and brookite TiO₂. *Phys Chem Chem Phys* 16(38):20382–20386
320. Zhang L, Wang WZ, Sun SM et al (2013) Solar light photocatalysis using Bi₂O₃/Bi₂SiO₅ nanoheterostructures formed in mesoporous SiO₂ microspheres. *CrystEngComm* 15(46):10043–10048
321. Zhang P, Lu XF, Luan D et al (2020) Fabrication of heterostructured Fe₂TiO₅-TiO₂ nanocages with enhanced photoelectrochemical performance for solar energy conversion. *Angew Chem* 132(21):8205–8209
322. Zhang P, Luan DY, Lou XW (2020) Fabrication of CdS frame-in-cage particles for efficient photocatalytic hydrogen generation under visible-light irradiation. *Adv Mater* 32(39):6
323. Zhang QL, Chen PF, Chen L et al (2020) Facile fabrication of novel Ag₂S/K-g-C₃N₄ composite and its enhanced performance in photocatalytic H₂ evolution. *J Colloid Interface Sci* 568:117–129
324. Zhang R, Bi LL, Wang DJ et al (2020) Investigation on various photo-generated carrier transfer processes of SnS₂/g-C₃N₄ heterojunction photocatalysts for hydrogen evolution. *J Colloid Interface Sci* 578:431–440
325. Zhang S, Gu PC, Ma R et al (2019) Recent developments in fabrication and structure regulation of visible-light-driven g-C₃N₄-based photocatalysts towards water purification: a critical review. *Catal Today* 335:65–77
326. Zhang XY, Li L, Zhou QL et al (2019) Facile synthesis of novel gully-like double-sized mesoporous structural Sr-doped ZrO₂-TiO₂ composites with improved photocatalytic efficiency. *J Solid State Chem* 269:375–385
327. Zhang YM, Song J, Shao WH et al (2021) Au@NH₂-MIL-125(Ti) heterostructure as light-responsive oxidase-like mimic for colorimetric sensing of cysteine. *Microporous Mesoporous Mat* 310:9
328. Zhao J, Fu B, Li X et al (2020) Construction of the Ni₂P/MoP heterostructure as a high-performance cocatalyst for visible-light-driven hydrogen production. *ACS Appl Energy Mater*
329. Zhao L, Dong T, Du J et al (2020) Synthesis of CdS/MoS₂ nanooctahedrons heterostructure with a tight interface for enhanced photocatalytic H₂ evolution and biomass upgrading. *Sol. RRL*: 2000415
330. Zhao X, Fan YY, Zhang WS et al (2020) Nanoengineering construction of Cu₂O nanowire arrays encapsulated with g-C₃N₄ as 3D spatial reticulation all-solid-state direct Z-Scheme photocatalysts for photocatalytic reduction of carbon dioxide. *ACS Catal* 10(11):6367–6376
331. Zhao XS, You YY, Huang SB et al (2020) Z-scheme photocatalytic production of hydrogen peroxide over Bi₄O₅Br₂/g-C₃N₄ heterostructure under visible light. *Appl Catal B-Environ* 278:11
332. Zhao YX, Yang BF, Xu J et al (2012) Facile synthesis of Ag nanoparticles supported on TiO₂ inverse opal with enhanced visible-light photocatalytic activity. *Thin Solid Films* 520(9):3515–3522
333. Zhao ZW, Zhang WD, Lv XS et al (2016) Noble metal-free Bi nanoparticles supported on TiO₂ with plasmon-enhanced visible light photocatalytic air purification. *Environ Sci Nano* 3(6):1306–1317

334. Zheng Y, Liu J, Liang J et al (2012) Graphitic carbon nitride materials: controllable synthesis and applications in fuel cells and photocatalysis. *Energy Environ Sci* 5(5):6717–6731
335. Zhong YM, Yang SY, Cai X et al (2020) Bio-inspired multilayered graphene-directed assembly of monolithic photo-membrane for full-visible light response and efficient charge separation. *Appl Catal B-Environ* 263:13
336. 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-C₃N₄ quantum dots/a-TiO₂/r-TiO₂ for highly efficient photocatalytic hydrogen and oxygen evolution. *Nanoscale* 12(10):6037–6046
337. Zhou G, Wu M-F, Xing Q-J et al (2018) Synthesis and characterizations of metal-free semiconductor/MOFs with good stability and high photocatalytic activity for H₂ evolution: a novel Z-scheme heterostructured photocatalyst formed by covalent bonds. *Appl Catal B* 220:607–614
338. Zhou H-C, Long JR, Yaghi OM (2012) Introduction to metal–organic frameworks, ACS Publications
339. Zhou X, Cui SC, Liu JG (2020) Three-dimensional graphene oxide cross-linked by benzidine as an efficient metal-free photocatalyst for hydrogen evolution. *RSC Adv* 10 (25):14725–14732
340. Zhou XF, Fang YX, Cai X et al (2020) In situ photodeposited construction of Pt-CdS/g-C₃N₄-MnOx composite photocatalyst for efficient visible-light-driven overall water splitting. *ACS Appl Mater Interfaces* 12(18):20579–20588
341. Zhu LL, Hong MH, Ho GW (2015) Hierarchical assembly of SnO₂/ZnO nanostructures for enhanced photocatalytic performance. *Sci Rep* 5:11
342. Zhu LY, Li H, Xu QL et al (2020) High-efficient separation of photoinduced carriers on double Z-scheme heterojunction for superior photocatalytic CO₂ reduction. *J Colloid Interface Sci* 564:303–312
343. Zhu XD, Pei LX, Zhu RR et al (2018) Preparation and characterization of Sn/La co-doped TiO₂ nanomaterials and their phase transformation and photocatalytic activity. *Sci Rep* 8:14
344. Zhu YH, Yao Y, Luo Z et al (2020) Nanostructured MoO₃ for efficient energy and environmental catalysis. *Molecules* 25(1):26
345. Zhu ZZ, Han Y, Chen CP et al (2018) Reduced graphene oxide-cadmium sulfide nanorods decorated with silver nanoparticles for efficient photocatalytic reduction carbon dioxide under visible light. *ChemCatChem* 10(7):1627–1634