Front. Energy 2021, 15(3): 577–595
https://doi.org/10.1007/s11708-021-0756-x

REVIEW ARTICLE

Wenwei LEI, Norihiro SUZUKI, Chiaki TERASHIMA, Akira FUJISHIMA

Hydrogel photocatalysts for efficient energy conversion and environmental treatment

© Higher Education Press 2021

Abstract Photocatalysts have attracted great research interest owing to their excellent properties and potential for simultaneously addressing challenges related to energy needs and environmental pollution. Photocatalytic particles need to be in contact with their respective media to exhibit efficient photocatalytic performances. However, it is difficult to separate nanometer-sized photocatalytic materials from reaction media later, which may lead to secondary pollution and a poor recycling performance. Hydrogel photocatalysts with a three-dimensional (3D) network structures are promising support materials for photocatalysts based on features such as high specific surface areas and adsorption capacities and good environmental compatibility. In this review, hydrogel photocatalysts are classified into two different categories depending on their elemental composition and recent progresses in the methods for preparing hydrogel photocatalysts are summarized. Moreover, current applications of hydrogel photocatalysts in energy conversion and environmental remediation are reviewed. Furthermore, a comprehensive outlook and highlight future challenges in the development of hydrogel photocatalysts are presented.

Keywords hydrogel, photocatalysts, energy conversion, environmental treatment

Received Dec. 28, 2020; accepted Mar. 9, 2021; online Jul. 15, 2021

Wenwei LEI
School of Environmental and Chemical Engineering, Yanshan University, Qinhuangdao 066004, China; Photocatalysis International Research Center, Tokyo University of Science, 2641 Yamazaki, Noda, Chiba 278-8510, Japan

Norihiro SUZUKI, Chiaki TERASHIMA (✉), Akira FUJISHIMA
Photocatalysis International Research Center, Tokyo University of Science, 2641 Yamazaki, Noda, Chiba 278-8510, Japan
E-mail: terashima@rs.tus.ac.jp

Special Issue—Photocatalysis: From Solar Light to Hydrogen Energy (Guest editors: Wenfeng SHANGGUAN, Akihiko KUDO, Zhi JIANG, Yuichi YAMAGUCHI)

1 Introduction

Environmental remediation and sustainable energy are pressing issues that require effective, sustainable, and green solutions [1]. Solar energy offers a plentiful, clean, and sustainable source of energy, which might be harnessed to address these issues [2–8]. Photocatalytic technologies effectively use solar energy for sustainable energy conversion (such as H_2 evolution, CO_2 reduction, and nitrogen fixation) and environmental treatments (such as conversion of NO_x and volatile organic compounds, removal of heavy metal ions removal, and degradation of organic pollutants) [9–16]. Therefore, there is an urgent need for efficient photocatalysts and reliable methods to meet growing development requirements.

The Fujishima-Honda effect, whereby H_2 and O_2 are produced under UV light irradiation of a TiO_2 photoelectrode, was first reported in 1972 [17]. Numerous novel materials, such as black TiO_2 [18–21], ZnO_2 [22–25], g-C_3N_4 [26–30], $SrTiO_3$ [31–35], $BiVO_4$ [36–39], $ZnInS_4$ [39,40] and their hybrid materials have been developed for applications in photocatalytic water splitting and environmental remediation. Many effective strategies have also been examined to further increase the efficiency of photocatalysis, including the use of doping, co-catalysts, defect manipulation, junctions, quantum confinement effects, and Z-scheme configurations [41–45]. However, owing to requirements for the material bandgap, specific surface area, and charge separation, most photocatalytic materials are applied in the form of nanometer-sized particles, which are difficult to separate from the reaction media. Additionally, for materials in this form there is the possibility of secondary pollution to the environment and poor recycling performance, which greatly hinders practical applications. Hence, there is an urgent need to find suitable substrates to avoid these limitations.

To date, there have been many reports on nanometer-sized photocatalytic materials loaded into foamed metals, plastics, hydrogels, and blended with polymers or adhesives to form thin films [46–50]. Hydrogels have

also been recognized as potential 3D network supports for photocatalysis. Hydrogels feature good flexibility, stretchability, ionic conductivity, and environmental compatibility have high surface areas and adsorption capacities [51–56]. The strategy of combining photocatalysts and hydrogels may contribute to more efficient and environmentally friendly energy conversion and environmental management. Here hydrogel photocatalysts of these new materials are denoted (Fig. 1). The physical and chemical properties of hydrogels can also be tuned to enhance the photocatalytic effect by tailoring of cross-linking points, changing basic building blocks, surface structure, and other modifications. Hydrogels provide a suitable platform for photocatalysts to achieve efficient energy conversion and environmental regulation (Fig. 1).

In this review, various kinds of hydrogel photocatalysts and their applications in energy conversion and environmental treatment are focused on. Design and fabrication methods are described for photocatalyst systems. In addition, progresses toward hydrogels with different functionalities constructed based on conventional and emerging strategies are summarized. Moreover, applications of these hydrogel photocatalysts related to water splitting, CO_2 conversion, wastewater treatment, air purification, and their roles in fundamental studies are highlighted. Furthermore, future challenges and outlook of hydrogel photocatalysts are discussed. It is believed that this review will encourage innovation in the field of hydrogel photocatalysts for energy conversion and environmental remediation.

2 Fabrication of hydrogel photocatalysts

In most cases, hydrogel photocatalysts comprise a nanometer-sized photocatalyst supported by a cross-linked hydrogel network. The three-dimensional (3D) hydrogel network provides a porous skeleton structure that limits catalyst leakage into the reaction media (air or water) and facilitates loading of a large amount of catalyst. The photocatalyst provides active sites for the catalytic reaction. Existing methods for preparing hydrogel photocatalytic materials can be divided into three categories: embedding of photocatalysts in hydrogel networks, *in situ* synthesis of photocatalysts in hydrogel networks, and self-assembly of hydrogel photocatalysts. The fabrication processes of hydrogels with photocatalysts are illustrated in Fig. 2. In the process of fabricating hydrogel photocatalysts, photocatalysts materials, such as semiconductors, g-C_3N_4, conjugated organic molecules, and their hybrids have been widely studied. In this section, fabrication methods frequently used to fabricate hydrogel photocatalysts are outlined based on different photocatalyst materials.

2.1 Inorganic semiconductor-based hydrogel photocatalysts

Inorganic semiconductor photocatalysts (ISPCs) are considered excellent photocatalysts for H_2 evolution and decomposition of organic compounds in effluents [57–59]. The photocatalytic efficiencies of these materials may be enhanced by appropriate textural design, doping, and formation of a semiconductor heterojunction by combination with metals and/or other semiconductors [60–62]. Generally, there are two main fabrication methods that have been applied in the development of inorganic semiconductor-based hydrogels photocatalysts.

One approach is to gel a mixture of ISPCs and hydrophilic polymers/monomers by self-assembly or introducing cross-linkable elements, which allow the ISPCs to be embedded in the hydrogel network [63–66]. For example, a nanocomposite hydrogel of alginate/carboxymethyl cellulose with encapsulated TiO_2 was successfully synthesized by barium-ion cross linking. This system exhibited excellent photocatalytic activity toward degradation of Congo red dye under direct solar

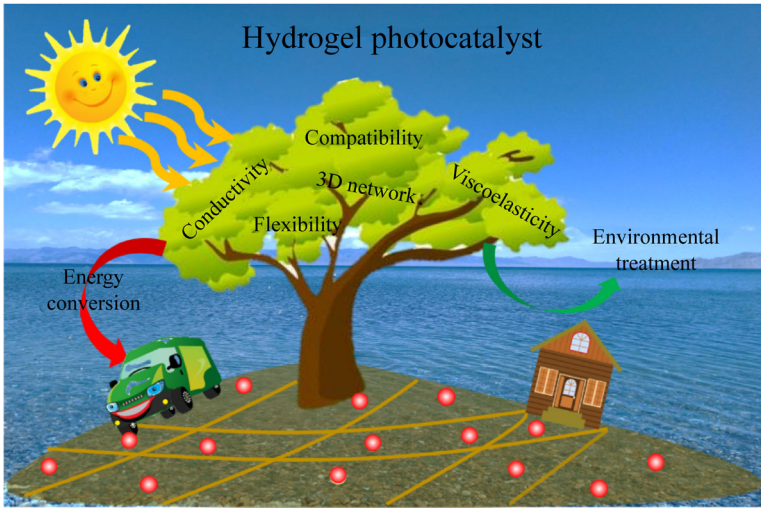

Fig. 1 Hydrogel photocatalysts as an effective strategy for energy conversion and environmental treatment.

light irradiation (Fig. 3(a)) [67]. In the same way, TiO_2 has been added to a polyaniline (PANI)-phytate hydrogel system (Fig. 3(b)). Efficient removal of organic pollutants is achieved through the synergistic effects of absorption of organic pollutants to the hydrogel and *in situ* photocatalytic degradation by TiO_2 [68]. The networks of 3D hydrogel photocatalysts have also been formed through self-assembly of TiO_2 and reduced graphene oxide (rGO) [69,70]. As shown in Fig. 3(c), a PANI/TiO_2 composite graphene hydrogel (GH) was successfully prepared by chemical reduction of graphene oxide (GO) followed by H-bond and π-π self-assembly. The rGO and PANI acted as a transmitter for e^- and H^+ to further enhance the photocatalytic performance [71]. Graphene is the most widely used additive for self-assembly of ISPCs to form hydrogel photocatalysts, whereas other conductive materials, such as carbon nanotubes, polypyrrole, and poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS), have also been used as additives to prepare hydrogel photocatalysts. Figure 3(d) demonstrates hydrogel photocatalytic composites based on TiO_2(P25) and graphene, multi-walled carbon nanotubes formed by a simple room temperature self-assembly [72].

Another method is *in situ* synthesis of photocatalysts in a hydrogel network by oxidation, reduction, and sulfuration. By using this approach, hydrogel photocatalysts with tunable catalytic activities based on different active species can be prepared for a variety of applications [73–77]. Recently, a poly 2-hydroxyethyl acrylate (HEA) -co- N-hydroxymethyl acrylamide (HAM) hydrogel photocatalyst, denoted P(HEA-co-HAM)-CdS hydrogel, was fabricated to adsorb and photocatalytically degrade organic pollutants [76]. A Cd precursor was introduced by swelling a preformed hydrogel network, synthesized by 60Co-γ irradiation-induced radical polymerization. The sulfur precursor was added to enable *in situ* synthesis of CdS photocatalysts (Fig. 4(a)). A Bi_2WO_6 (BWO)/GH photocatalyst is an example of a high performance visible-light-driven photocatalyst with a narrow band gap, which was fabricated by utilizing a simple one-step hydrothermal method. The 3D flower-like structures of BWO were formed *in situ* by addition of Na_2WO_4 to a mixture of $Bi(NO_3)_3$ and GO solution (Fig. 4(b)). The solution was then hydrothermally reduced to self-assemble the hydrogel through hydrogen bonding and π-π stacking interactions. The novel structure of the BWO/GH hydrogel photocatalyst improved the light utilization efficiency and absorption of the organic compounds and provided many effective multidimensional electron transfer channels [77]. This hydrogel photocatalyst effectively decomposed methylene blue (MB) and 2, 4-dichlorophenol (2, 4-CDP) under visible light irradiation ($\lambda \geqslant 420$ nm) in both static and dynamic systems.

TiO_2 is a well-known photocatalytic material in the field of photocatalysis because of its low cost, low-toxicity, chemical stability, and high resistance to photocorrosion

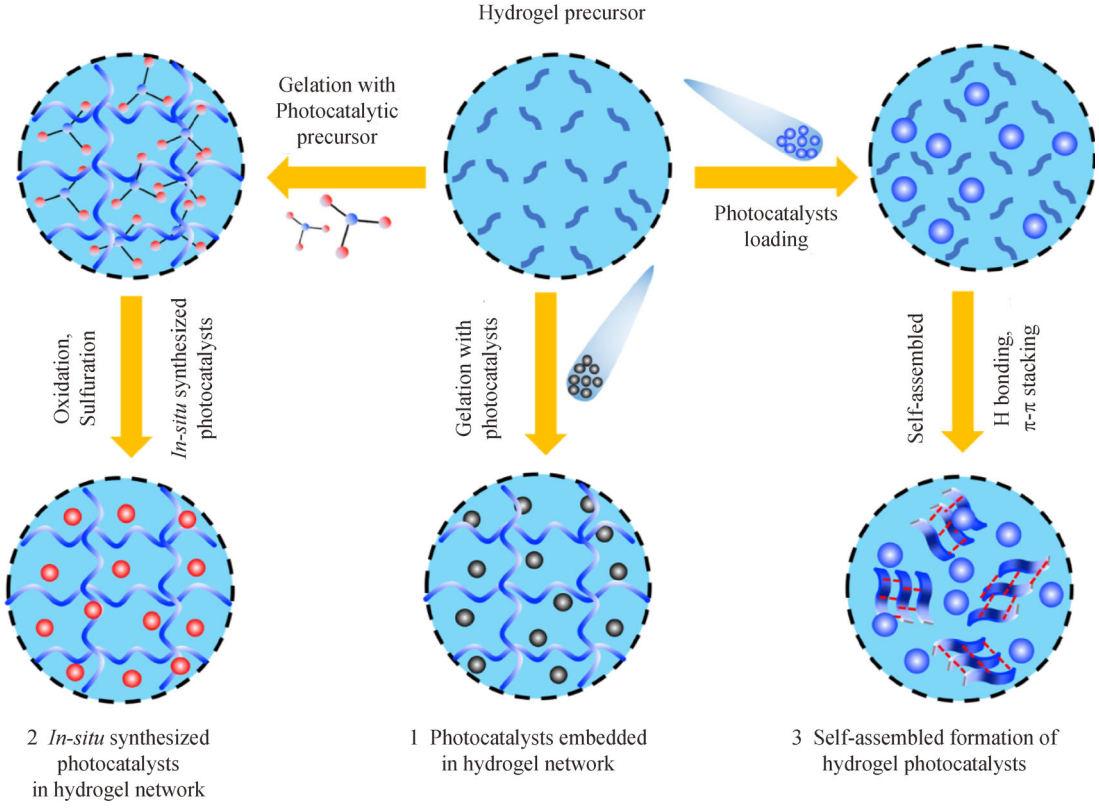

Fig. 2 Schematic illustrations of the fabrication process of hydrogel photocatalysts.

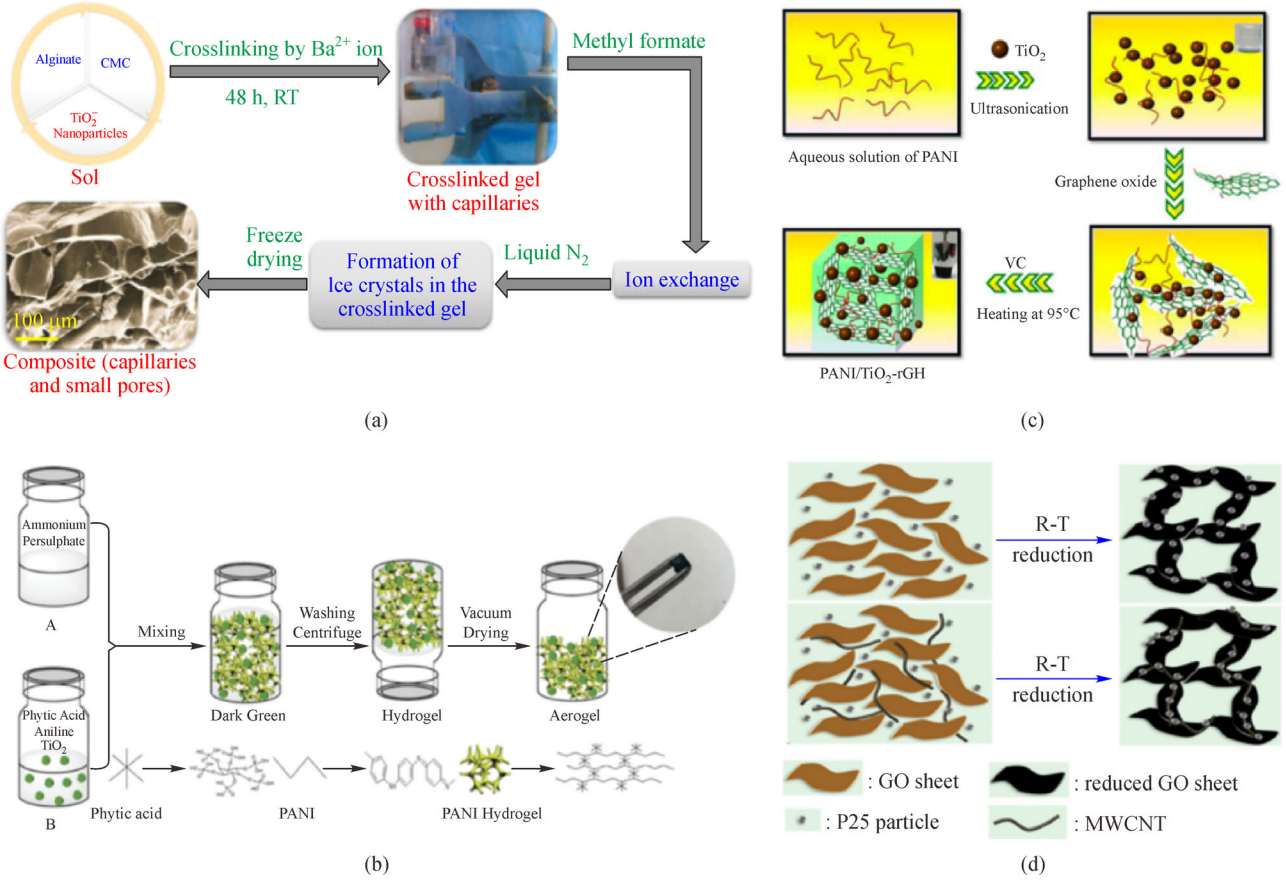

Fig. 3 Inorganic semiconductor photocatalysts embedded in hydrogel network.
(a) and (b) TiO_2 embedded in hydrogel network (adapted with permission from Refs. [67,68]); (c) and (d) TiO_2 hydrogel formation through graphene self-assembly (adapted with permission from Refs. [71,72]).

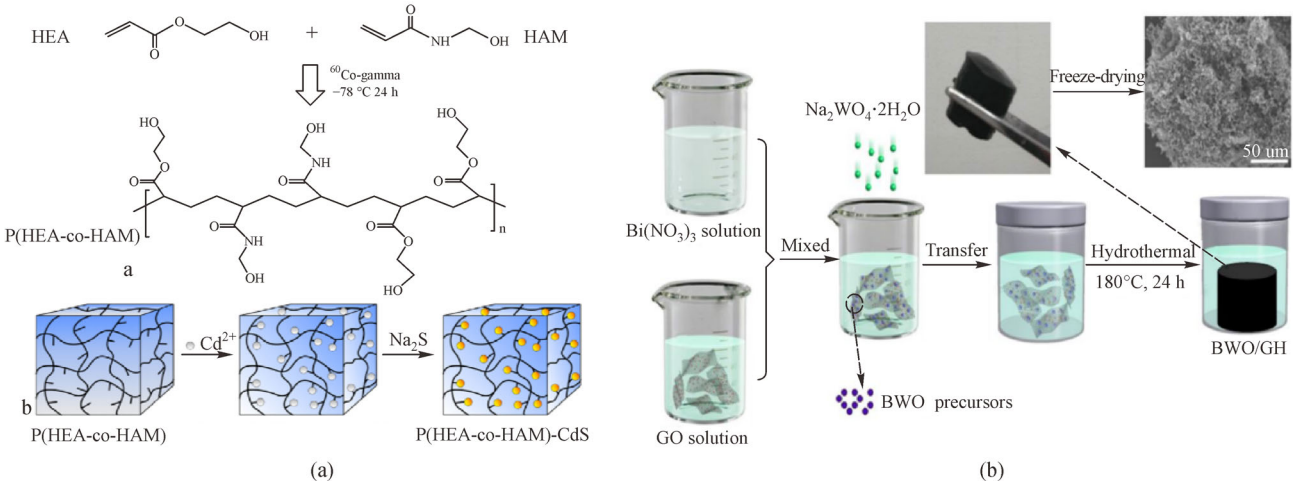

Fig. 4 *In situ* synthesized hydrogel photocatalysts.
(a) P(HEA-co-HAM)-CdS hydrogel (adapted with permission from Ref. [76]); (b) BWO/GH (adapted with permission from Ref. [77]).

[78–87]. Therefore, many hydrogel photocatalytic materials based on TiO_2 have been reported [65,88–91]. In addition to the above-mentioned general preparation strategies, several novel methods have been developed to prepare hydrogel photocatalysts. For example, TiO_2 can be used to induce radical formation under light irradiation to trigger the polymerization reaction. The TiO_2 also acts as a crosslinking site to induce gelling of the solution [92]. In this system, the gelling water provides a source of radicals and the TiO_2 nanosheets act as a stable photocatalysis to

support the formation of the hydrogels. Microfluidics have also been used to prepare hydrogel microspheres for various applications. Very recently, a glass capillary-based microfluidic technique was used for highly efficient encapsulation of photocatalytic nanoparticles in a thin shell of hydrogel microcapsules (Fig. 5). An aqueous dispersion of photocatalytic nanoparticles and methacrylic anhydride formed the core and shell of the double emulsion drops, respectively [93]. The hydrogel microcapsules containing photocatalytic nanoparticles were gelatinized by external photopolymerization. These thin shell hydrogel microcapsules with photocatalytic nanoparticle cores more effectively promoted the photocatalytic reaction, absorption, diffusion, and separation of molecular species when compared with the performance of bulk hydrogels.

However, the inherent wide bandgap (3.0–3.2 eV) and low quantum efficiency of TiO_2 materials owing to rapid recombination of photogenerated electrons and holes, limits their practical applications [94–97]. Considerable efforts have been made to develop alternative photocatalysts to overcome these problems and improve the photocatalytic activities. These efforts have focused on new semiconductor photocatalysts that have a strong absorption of visible light. Hydrogel photocatalysts have also been investigated for applications ins degradation of pollutants driven by solar energy [98–103]. For example, β-FeOOH/cellulose composite hydrogels (TCH-Fe) were fabricated from a cellulose solution by regeneration in ethanol and *in situ* synthesis of β-FeOOH nanoparticles (Fig. 6(a)). The photocatalytic degradation of MB over TCH-Fe was as high as 99.89% within 30 min under visible-light irradiation [99]. The performance remained at about 98% after treatment for 8 h, indicating a highly efficient and stable photodegradation of MB. The layered structure of MoS_2 has a strong absorption in the solar

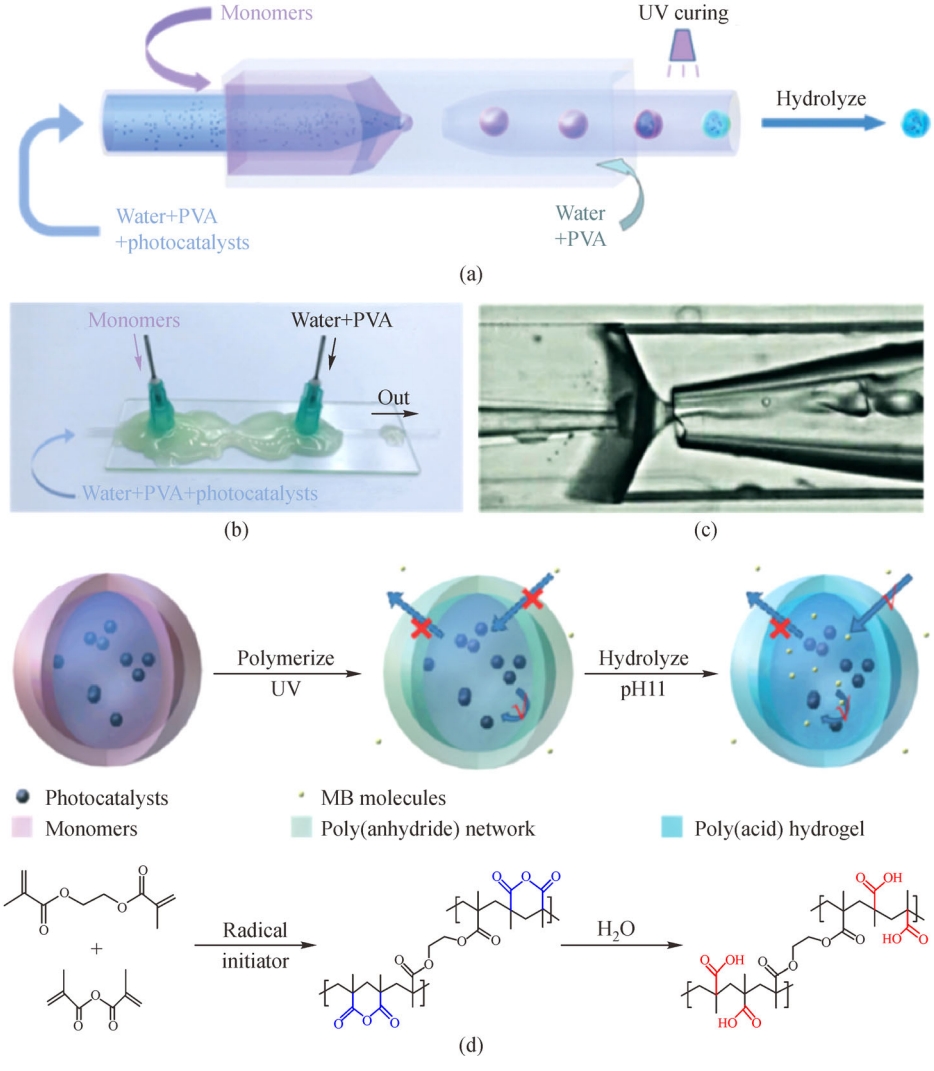

Fig. 5 Preparation of hydrogel photocatalyst microspheres by microfluidic process (adapted with permission from Ref. [93]).
(a) Schematic diagram of preparation of hydrogel photocatalyst; (b) optical picture of the device; (c) glass microfluidic devices producing microcapsules; (d) photopolymeric monomers producing core-shell hydrogel capsules.

spectrum region owing to its narrow band gap of approximately 1.8 eV. Hence, this material has also been embedded into hydrogels to degrade pollutants. As shown in Fig. 6(b), a MoS_2-rGO composite hydrogel was fabricated through a one-step hydrothermal method of mixing a solution of GO and exfoliated MoS_2 nanosheets [100]. Furthermore, Mu and coworkers reported a silver phosphate/Gh (Ag_3PO_4/GH) that efficiently degraded bisphenol A (BPA) through a synergy of adsorption and photocatalysis [101]. Owing to the high quantum yield under visible light of Ag_3PO_4, this composite hydrogel photocatalyst achieved 100% removal of BPA in a continuous flow reaction system. In addition, hydrogels can also be used to prepare composite structures for photocatalytic materials. Core-shell Fe_3O_4-CuO at carbon hollow spheres have been assembled from metal organic framework (MOF) composite hydrogels through a combination of chemical vapor deposition (CVD) and pyrolysis (Fig. 6(d)) [102]. This work also provides a new route to develop highly active and stable bimetallic hydrogel photocatalysts.

2.2 Organic semiconductor-based hydrogel photocatalysts

Compared with the extensive development of ISPCs, the progress related to organic semiconductor photocatalysts (OSPCs) has been more gradual. However, OSPCs have been intensively examined for heterogeneous photocatalysis under visible light illumination and offer advantages in terms of structural designability and stability over conventional molecular photocatalysts [104–109]. Currently, there are two main classes of polymer-semiconductor photocatalysts, graphitic carbon nitride (g-C_3N_4) and chromophore amphiphiles (based on conjugated molecules), that have been studied for water splitting and aqueous pollutant remediation.

As a metal-free polymer n-type semiconductor, C_3N_4 has shown great promise in the field of photocatalysis since Wang and coworkers first reported photocatalytic H_2 and O_2 evolution over C_3N_4 in 2009 [110]. The methods used to prepare C_3N_4-based hydrogel photocatalysts are similar to the aforementioned techniques. The preparation of

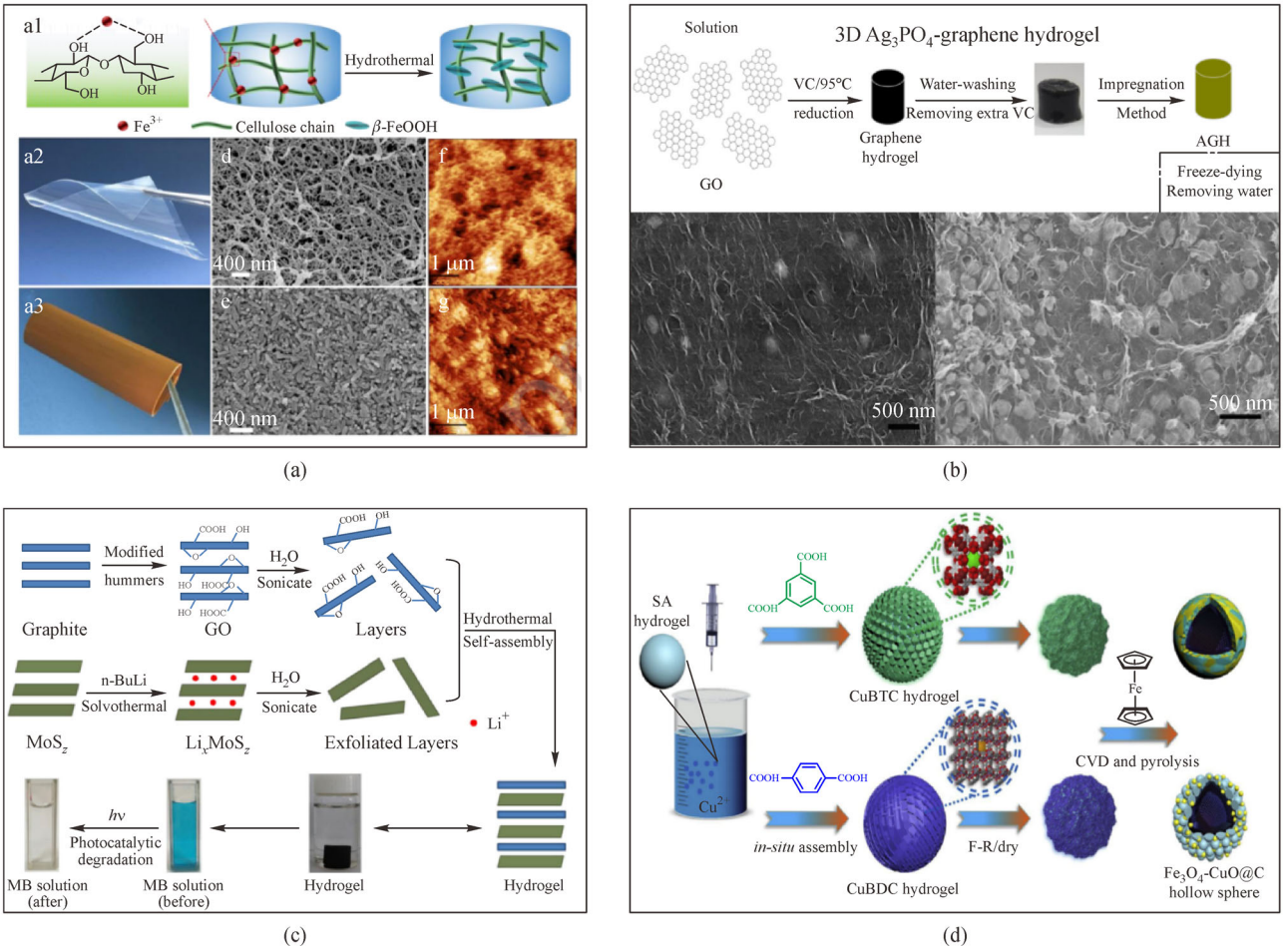

Fig. 6 Narrow bandgap semiconductor-based hydrogel photocatalysts.
(a) TCH-Fe (adapted with permission from Ref. [99]); (b) MoS_2-rGO composite hydrogel (adapted with permission from Ref. [100]); (c) Ag_3PO_4/GH (adapted with permission from Ref. [101]); (d) preparation of hydrogel-assisted composite photocatalytic materials (adapted with permission from Ref. [102]).

graphitic carbon nitride-based hydrogels as photocatalysts has also been reviewed [111,112]. Therefore, detailed synthesis will be omitted. Instead, some of the latest outstanding developments of C_3N_4-based hydrogel photocatalysts are presented. Li and coworkers reported a 3D-2D-3D BiOI/porous g-C_3N_4/GH (BPG) composite photocatalyst based on a two-step hydrothermal method (Fig. 7(a)). The 3D GH had a high absorption capacity. The excellent photocatalytic properties of the heterojunction between the 3D BiOI, which had a flower-like structure, contributed to effective adsorption-photocatalysis and effective degradation of MB and levofloxacin hydrochloride compared with that of BiOI [113]. Co-doping of g-C_3N_4 with non-metal ions can also improve the effectiveness of pure g-C_3N_4. Chu et al. reported the use of P, S, and O co-doped g-C_3N_4 to produce photocatalyst hydrogels. A combination of theoretical calculations and experimental analyses of the P, S, and O doping indicated that rapid charge separation of photo-excited electrons took place across the heptazine rings, which enhanced the photocatalytic activity of doped g-C_3N_4. This doped g-C_3N_4 hydrogel photocatalyst exhibited a high photocatalytic activity for MB removal under simulated solar irradiation and could be easily separated and cleaned for reuse (Fig. 7(b)) [114]. In addition, C_3N_4-based hydrogel photocatalysts, such as g-C_3N_4 at ppy-rGO [115], Fe-g-C_3N4 graphene [116], and N-isopropyl acrylamide/high-substituted hydroxypropyl cellulose/g-C_3N_4 hydrogels [117], were reported for efficient catalytic removal of heavy metal ions and degradation of organic pollutants.

Supramolecular assemblies of chromophore molecules benefit from their good environmental stability, strong visible-light absorption, and tunable redox potentials (molecular orbital energy levels) arising from variable structural functionalization. Hence, these systems have been recognized as promising materials for photocatalytic reactions [118–121]. The n-type organic perylene imides, including perylenediimides (PDIs), perylenemonoimides (PMIs), and their oligomers and analogs, have been proven to have excellent photocatalytic properties [122–124]. Recently, Zhang and coworkers reported a urea-linked PDI polymer photocatalyst (Urea-PDI). Based on the energy band structure, excellent crystallization, and the large molecular dipole of Urea-PDI, the photocatalyst has a highest oxygen evolution rate of 3223.9 μmol/(g·h) with 100 h of stable performance under visible light irradiation without a cocatalyst [125]. Several reports of PMI-based hydrogel photocatalysts from Stupp and coworkers have inspired many related studies [126–128].

A photocatalyst-embedded hydrogel was reported in 2020 (Fig. 8(a)), which featured a PMI photocatalyst embedded in a polyelectrolyte hydrogel network. The catalyst-loaded hybrid PMI/polyelectrolyte hydrogel was used in photocatalytic hydrogen production and could be reused over multiple cycles as a photosensitizer [128]. To further enhance the performance of hydrogel photocatalysts, a conjugated polymer hydrogel photocatalyst which expanded in water to expose more active sites was reported by Byun and coworkers [129]. This system could also be recovered by solvent exchange. The stable polymer ionic complexation between a benzothiadiazole-based polymer containing cationic side chains as the polycation and poly (acrylic acid) as the polyanion, exhibited a good water compatibility, absorbing up to 470 times of its weight in deionized water (Fig. 8(b)). The excellent swelling performance greatly expanded the availability of active sites and enhanced the photocatalytic activity of the hydrogel photocatalyst. The effectiveness of this material was demonstrated by its application to photodegradation of organic dyes and the formation of the enzyme cofactor nicotinamide adenine dinucleotide by photo-oxidation in

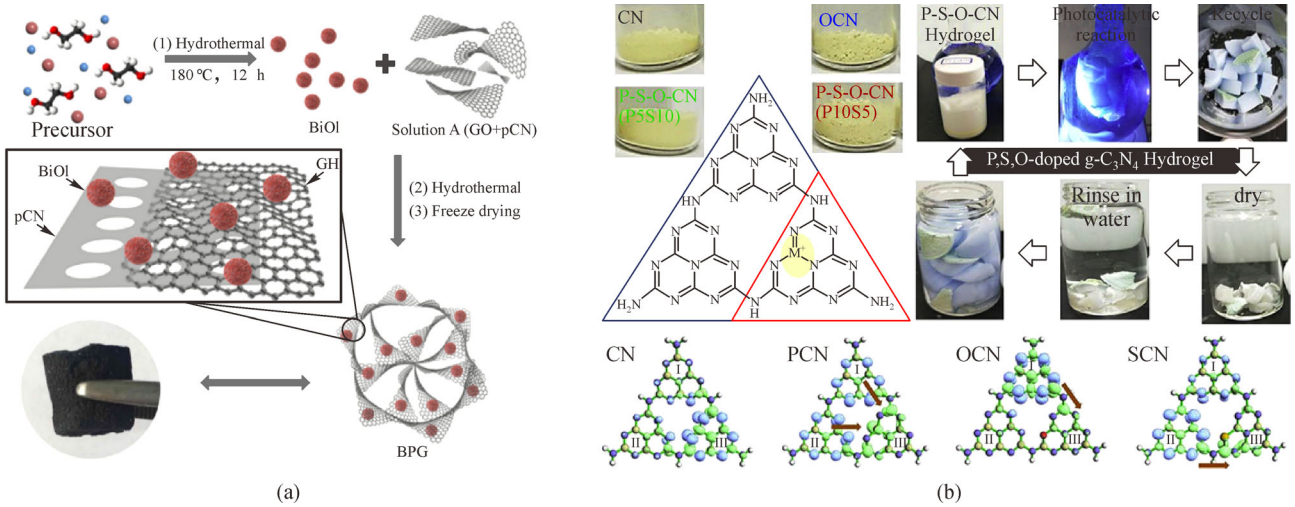

Fig. 7 g-C_3N_4 based hydrogel photocatalysts.
(a) 3D-2D-3D BiOI/porous g-C_3N_4/GH composite photocatalyst (adapted with permission from Ref. [113]); (b) P, S, O-co-doped g-C_3N_4 hydrogel photocatalyst (adapted with permission from Ref. [114]).

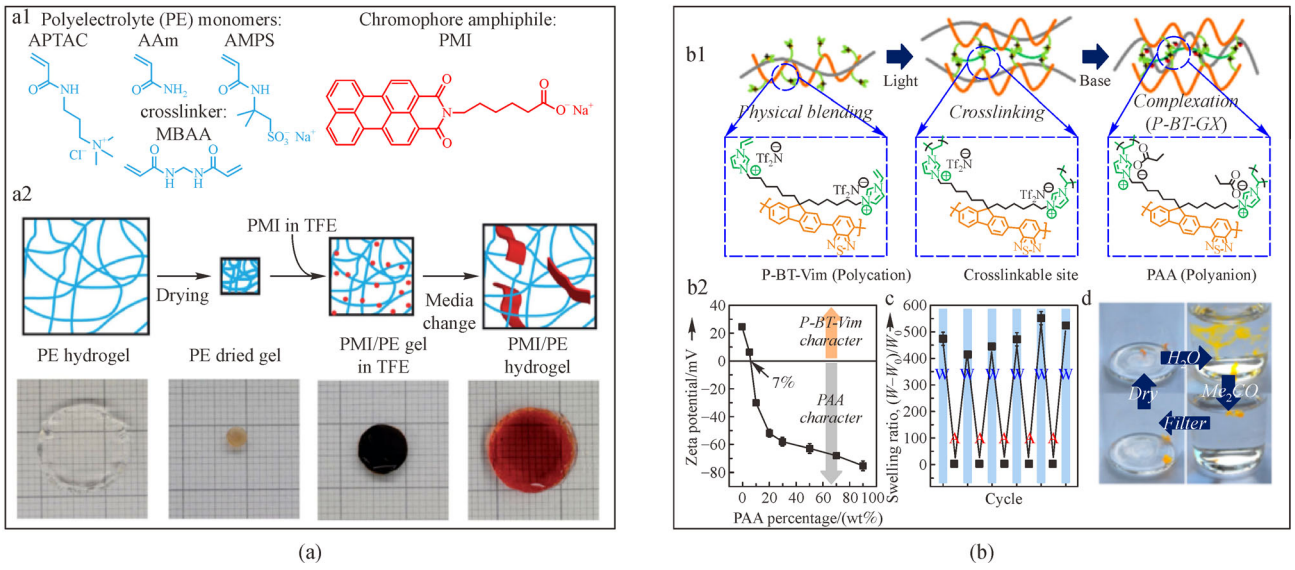

Fig. 8 Chromophore amphiphile conjugated polymer hydrogel photocatalyst.
(a) PMI-based photocatalyst-embedded hydrogel (adapted with permission from Ref. [128]); (b) polymer ionic complexation hydrogel photocatalyst (adapted with permission from Ref. [129]).

water. Furthermore, this hydrogel photocatalyst could be regenerated by a simple solvent exchange with methanol after the reaction.

3 Applications of hydrogel photocatalysts

In this section, current progresses in the application of hydrogel photocatalysts in energy conversion and environmental treatments are highlighted, focusing primarily on hydrogen evolution and CO_2 reduction in Section 3.1, and organic pollutant degradation and removal of metal ions in Section 3.2. In Section 3.3, emerging applications of hydrogel photocatalysts for synergistic water evaporation and energy conversion are introduced.

3.1 Energy conversion

3.1.1 Photocatalytic hydrogen evolution

Hydrogen (H_2) is considered to be an ideal energy storage media due to its high energy capacity and environmental compatibility. The generation of H_2 induced by water splitting over photocatalysts is regarded as a promising strategy for achieving a H_2-based economy. Owing to the inherent water absorption capacity of hydrogels, hydrogel photocatalysts act as reaction centers for hydrogen production by photocatalysis. Li and coworkers reported *in situ* growth of CdS hydrogels (CdS/HGel) for photocatalytic hydrogen generation [130]. Owing to the high dispersibility of CdS nanoparticles in the hydrogels, high hydrophilic and swelling ability of the hydrogel, and high diffusion rate of reactants, $CdS/HGel_{PDMA2}$ had the best photocatalytic hydrogen production rate of 51.75 μmol/h (based on 5 mg catalyst powder) and allowed for easy recovery (Fig. 9(a)). The suppression of charge recombination at the catalyst interface is important for improving photocatalytic efficiency. Cocatalyst deposition is an effective strategy that can improve the activity, stability, and selectivity of primary catalysts in a catalytic reaction. A co-assembled aerogel of spherical Au, Pd, and PdAu with TiO_2 nanoparticles was prepared by light-induced gelation of a hydrogel-precursor (Fig. 9(b1)) [131]. PdAu-TiO_2 aerogels were the most efficient photocatalysts, followed by Pd-TiO_2 and Au-TiO_2, demonstrating that enhanced hot-electron transfer and near-field electromagnetic effects contribute to H_2 formation (Fig. 9(b3)). The efficient reagent mass transport and light-harvesting of the monolithic porous networks also promoted photocatalysis.

As an inspiration for rational design of multicomponent hydrogel photocatalysts for photocatalytic hydrogen evolution, a CdS and ZnS containing hydrogel was obtained by a modified gel crystal growth method [132]. The hydrogel (HR) framework inhibited the agglomeration of the CdS and ZnS nanoparticles. Owing to the synergistic effects of the quantum dots and hydrogel, the composite hydrogel photocatalyst exhibited high rates of H_2 evolution compared with those of non-supported nanoparticles (Fig. 10(a)).

Chromophore-amphiphile conjugated PMI hydrogel photocatalysts also play an important role in photocatalytic hydrogen generation. Weingarten et al. fabricated a hydrogel skeleton based on PMI and a cationic analog with an outer ligand sphere functionalized with primary amines as a supramolecular self-assembly for photocatalytic hydrogen production [127]. The highest catalytic turnover number (TON) of this PMI-based hydrogel photocatalyst was approximately 340 under different charge-screening conditions with poly(diallyldimethylam-

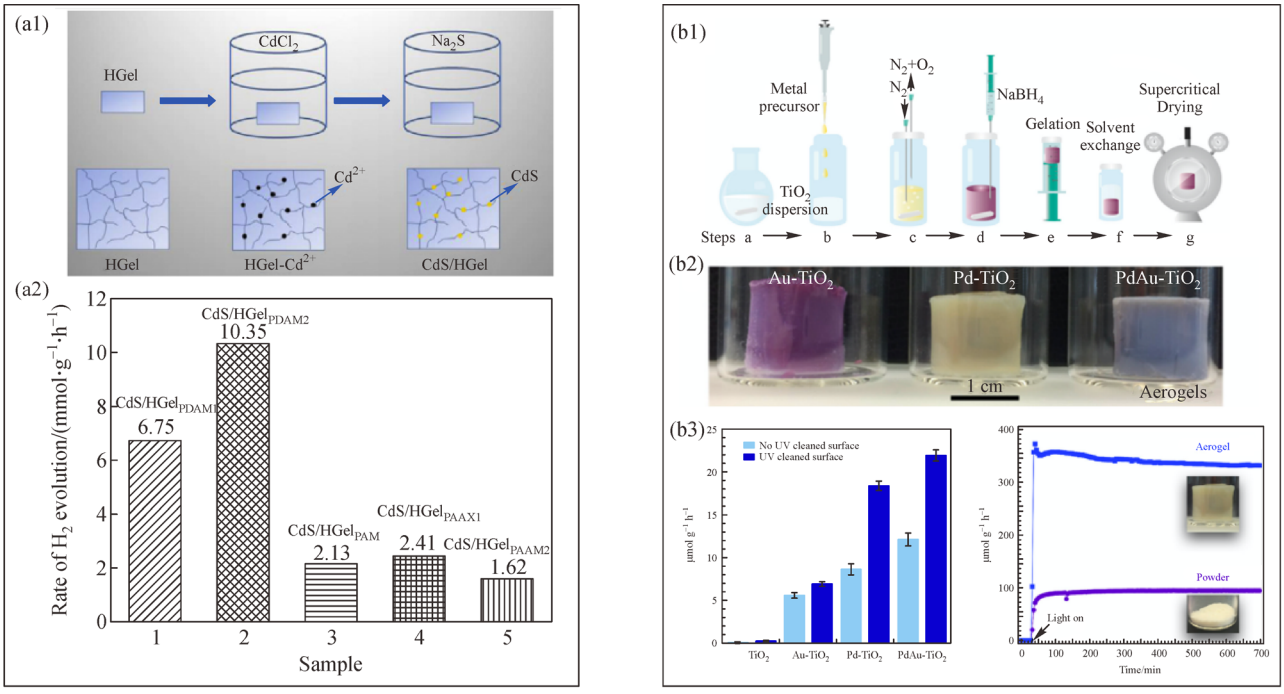

Fig. 9 Hydrogel photocatalysts for hydrogen generation.

(a) *In situ* growth of CdS/HGel for photocatalytic hydrogen generation (adapted with permission from Ref. [130]; (b) co-assembled spherical Au, Pd, and PdAu with TiO_2 nanoparticles aerogels for photocatalytic hydrogen generation (adapted with permission from Ref. [131]).

monium) chloride (PDDA) (Fig. 10). The gel catalyst could also be cast on glass slides for H_2 generation.

3.1.2 Photocatalytic CO_2 conversion

Photocatalytic conversion of CO_2 into renewable fuels driven by sunlight is considered as an ideal scenario for reducing the concentration of carbon dioxide in the atmosphere while also generating energy [133–137]. However, because of the inherent high-water content of hydrogel photocatalysts, there is a possibility that an excess of carbon dioxide may dissolve, reducing the conversion. Therefore, much research on CO_2 conversion is based on aerogels, which are mostly derived from freeze-drying and supercritical drying of hydrogels. Layers of MoS_2 on a hierarchical porous structure of mesoporous TiO_2 and macroporous 3D graphene aerogel (TGM) photocatalysts have been fabricated by freeze-drying gel composites (Fig. 11(a)) [138]. The morphologies of the mesopores and macropores that contribute to the high photocatalytic catalyst performance, can be regulated by adjusting the relative amounts of each component and the configuration of the composite. The TGM photocatalyst has a higher CO photoconversion rate (92.33 μmol CO/(g·h)) and is more stable (i.e., maintains its original conversion rate of over 15 cycles) than other composite combinations. Niederberger's group reported several studies on the preparation of aerogel photocatalysts based on supercritical drying of hydrogel precursors. Figure 11(b1, b2) shows TiO_2-Au composite aerogel samples before and after photocatalytic reduction of CO_2 with water to methanol with high selectivity and reproducibility [139]. Niederberger's group also found that translucent nanoparticle-based aerogel monoliths were promising photocatalysts for gas phase reactions such as CO_2 reduction.

3.2 Environmental treatment

3.2.1 Organic pollutant degradation

Owing to their high degree of swelling and adsorption capacity, hydrogels have drawn research interest for applications to adsorption of dyes, metal cations, and other pollutants. Although great progress has been made, many different materials accumulate in hydrogels, making it difficult to selectively target specific contaminants [140–142]. Hydrogel photocatalysts promote synergistic absorption and *in situ* photocatalytic degradation of pollutants, which is important for environmental treatments, especially wastewater treatments. Zhang et al. prepared dynamic systems for total organic carbon (TOC) removal based on graphitic carbon nitride/SiO_2 (C_3N_4/SiO_2) hybrid hydrogels with 3D network structures (Fig. 12(a)) [143]. The hybrid C_3N_4 /SiO_2 hydrogel photocatalyst had excellent cyclic stability and removal abilities for phenol and MB, with performances 3.1 and 6 times as great as those of pure g-C_3N_4, respectively. The C_3N_4/SiO_2 hybrid

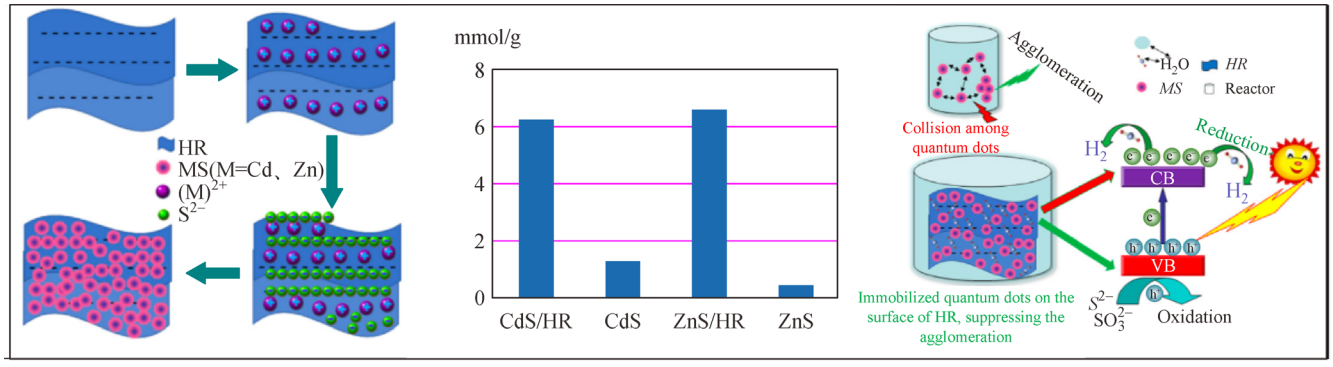

Fig. 10 Multicomponent (individual CdS and ZnS nanocrystals) hydrogel photocatalysts for photocatalytic hydrogen generation (adapted with permission from Ref. [132]).

(a) Mechanism of growth of photocatalysts; (b) hydrogen evolution performance of hydrogel photocatalyst in 16 h; (c) photocatalytic H_2 evolution process of CdS and ZnS hydrogel photocatalyst.

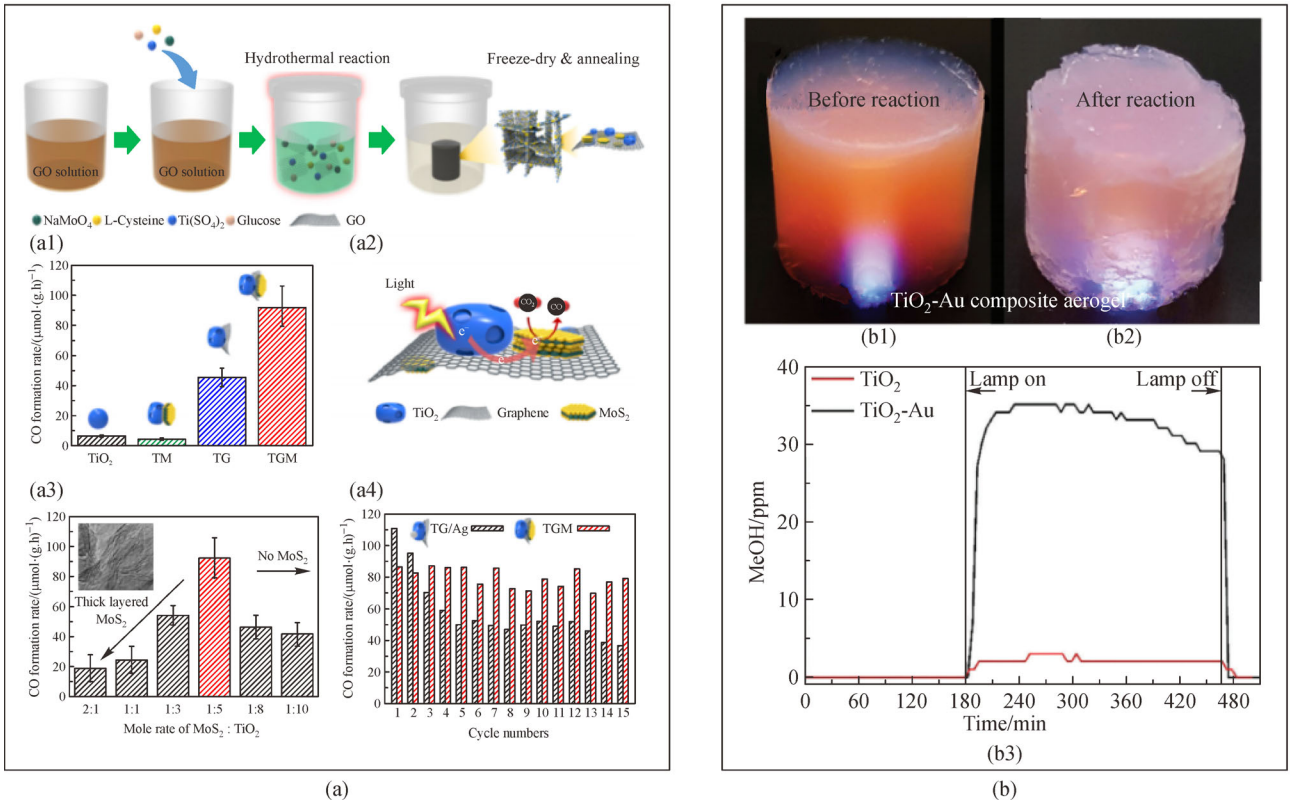

Fig. 11 Gel-based photocatalyst for CO_2 conversion.

(a) TGM photocatalyst for CO_2 conversion to CO (adapted with permission from Ref. [138]); (b) TiO_2-Au composite aerogel for CO_2 reduction (adapted with permission from Ref. [139]).

hydrogel photocatalyst could be used continuously without adsorption saturation or separation from water, avoiding aggregation and secondary pollution of the photocatalysts. Similarly, agar-C_3N_4 hybrid hydrogel photocatalysts have been prepared by a simple heating-cooling polymerization process. These catalysts exhibit excellent performances in photocatalytic degradation of MB and cyclic stability under visible light [144].

In addition to common colored pollutants, some colorless pollutants can also be degraded using hydrogel photocatalysts, e.g., BPA [63,76,101], phenol [116,144], and sulfonamide antibiotics (SAs). Yang et al. used irradiation polymerization and *in situ* precipitation methods to form a novel hydrogel photocatalyst [p(HEA/NMMA)-CuS] for efficient photocatalytic sulfamethoxazole (SMX) degradation [145]. The mechanism is detailed

in Fig. 12(b). First, the [p(HEA/NMMA)-CuS] hydrogel photocatalyst adsorbed SMX through a process similar to Langmuir monolayer adsorption that followed a pseudo second-order rate equation. Thereafter, a photocatalytic decomposition process of SMX, which followed pseudo-first-order kinetics, was promoted by CuS under visible light irradiation. Theoretical calculations of the frontier electron densities and their degradation pathways supported this mechanism.

3.2.2 Removal of metal ions

Toxic metal ions such as copper (Cu^{2+}), arsenic (As), zinc (Zn^{2+}), cobalt (Co^{2+}), nickel (Ni^{2+}), lead (Pb^{2+}), cadmium (Cd^{2+}), and chromium (Cr^{6+}) cause serious damage to human health and the environment [146–148]. Among these, Cr(VI), a common heavy metal contaminate, is a threat to human health because of its carcinogenic and bioaccumulative properties. The photocatalytic removal of cadmium ions has received extensive attention owing to its potential for treatment with high efficiency, low energy consumption, and mild reaction conditions. Li et al. fabricated a novel TiO_2 and rGH by π-π conjugation induced overlapping and coalescence among the graphene sheets (Fig. 12(c)) [149]. The TiO_2-rGH 3D structure had an excellent adsorption-photocatalysis performance for removal of Cr(VI) from aqueous solutions. The synergistically enhanced photo-induced charge separation, nonporous surface, and π-π interactions contributed to a removal rate of Cr (VI) from a solution of 100%. Furthermore, using a continuous flow system, the removal rate of cadmium was maintained at 100% over a long time.

3.3 Synergistic water evaporation and energy conversion

In recent years, there has been a great interest in obtaining clean water through solar evaporation. In particular, some hydrogel-based photothermal evaporation materials have

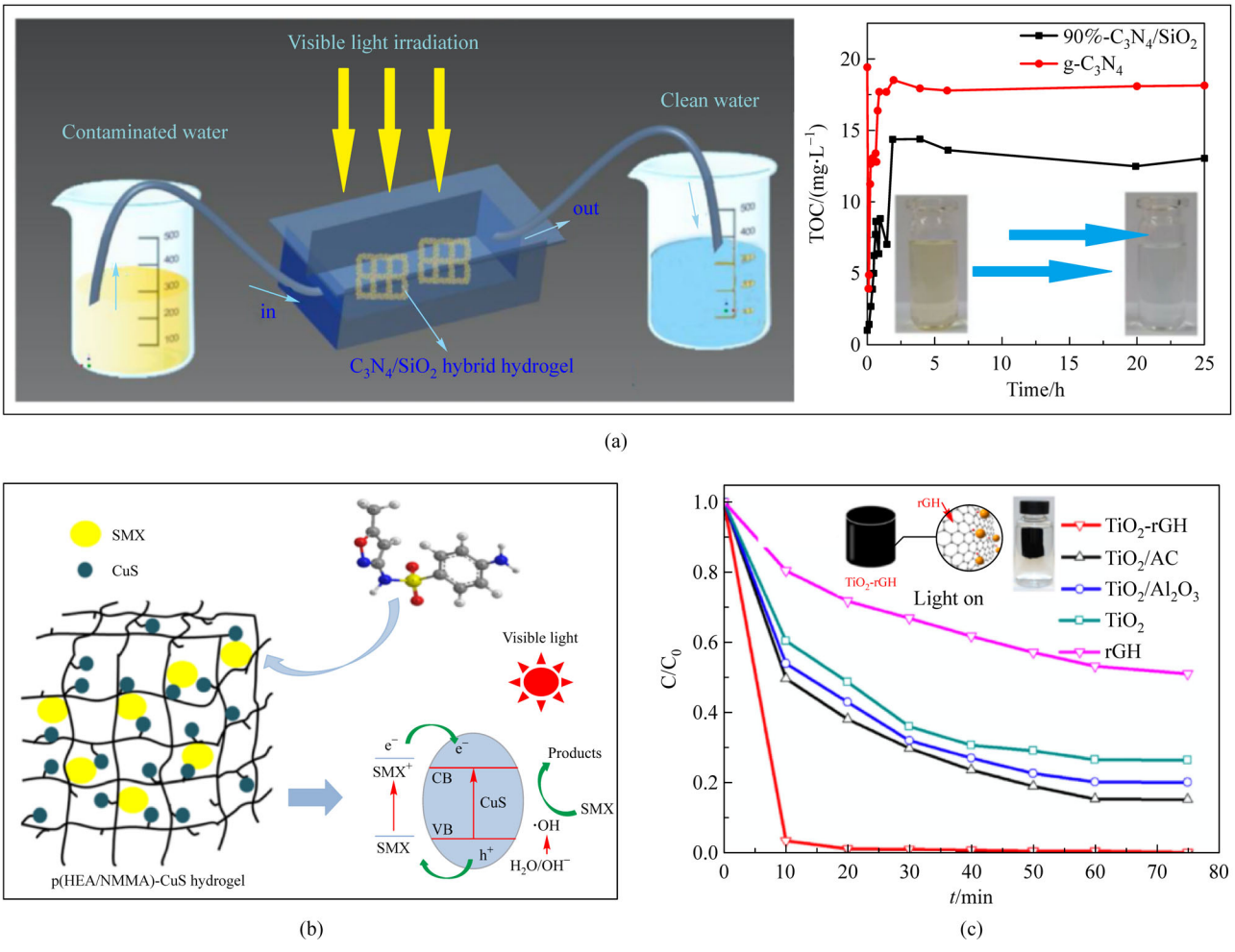

Fig. 12 Removal of metal ions using hydrogel photocatalyst.
(a) Hybrid C_3N_4 /SiO_2 hydrogel photocatalyst for TOC removal based on a continuously dynamic system (adapted with permission from Ref. [143]); (b) [p(HEA/NMMA)-CuS] hydrogel photocatalyst for photocatalytic SMX degradation (adapted with permission from Ref. [145]); (c) adsorption-photocatalysis for removal of Cr (VI) with TiO_2-rGH (adapted with permission from Ref. [149]).

shown great potential for solar evaporation [150–154]. On this basis, many photothermal materials are embedded in hydrogels to efficiently absorb sunlight for photothermal evaporation. Photothermal materials, such as plasmonic absorbers, semiconductors, carbon-based materials, and conductive polymers can be embedded in hydrogels to efficiently absorb sunlight for photothermal evaporation.

Gao et al. structured a photothermal catalytic (PTC) gel with a hydrophobic membrane to realize a H_2O-H_2 cogeneration system (HCS) for concurrent photothermal-enhanced solar desalination and hydrogen generation [155]. The PTC gel comprised photothermal and photocatalytic TiO_2/Ag nanofibers and a strong water-absorbing chitosan polymer (Fig. 13(a)). The photocatalytic hydrogen production was enhanced by efficient light absorption of the gel interface with a 3D structure. Furthermore, the porous structure of the array provided effective confinement, interfacial heating, and thermal conductivity. A

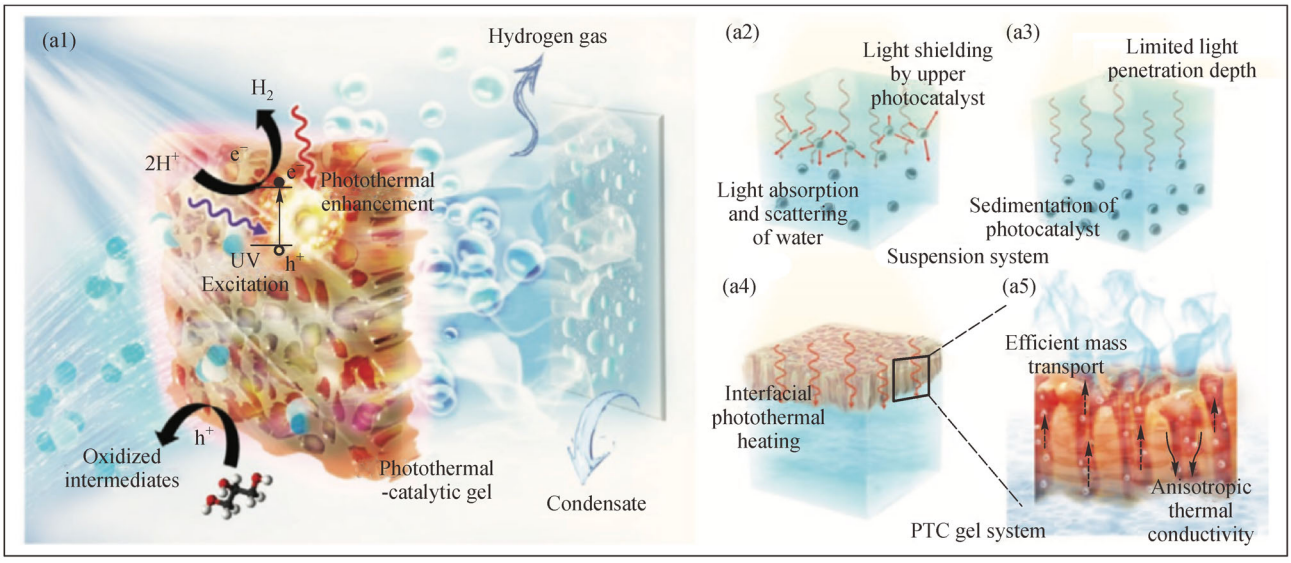

Fig. 13 Synergistic water evaporation and H_2 generation.
(a) H_2O-H_2 co-generation system (HCS) for concurrent photothermal-enhanced solar desalination and hydrogen generation based on PTC gel (adapted with permission from Ref. [155]; (b) photograph of custom-made device used in HCS for parallel freshwater production and hydrogen energy generation (adapted with permission from Ref. [155]).

custom-made device was used in the HCS for parallel freshwater production and hydrogen energy generation. The amount of condensate collected and hydrogen gas generated from the water and seawater sources were both increased (Fig. 13(b3)). Later, the same group developed a defective semiconductor nanosheet aerogel that contained oxygen vacancy defect-rich HNb_3O_8 nanosheets (D-HNb_3O_8) and a polymeric polyacrylamide (PAM) network [156]. The hybrid defective HNb_3O_8 aerogel had a high-performance for photothermal water evaporation and photochemical degradation (photocatalytic degradation of Rhodamine B) driven by light over the entire solar spectrum. These developments have broadened applications of hydrogel photocatalysts and inspired future research into hydrogel photocatalysts.

4 Summary and outlook

Through ongoing efforts, many photocatalytic materials have been developed, including single ISPCs, composite nanostructured hybrid photocatalysts, Z-scheme photocatalytic materials, and organic semiconductor photocatalytic materials. The photocatalytic properties of these systems have contributed to major breakthroughs in energy conversion and environmental treatment. However, the problems of secondary pollution and poor recycling performance are related to the difficulty in separating nanometer-sized photocatalytic materials from their reaction media in practical applications. The emergence of hydrogel photocatalysts offers a good solution to these problems. Many hydrogel photocatalysts have shown an excellent photocatalytic performance and cycling stability.

In this review, different approaches to synthesizing different kinds of hydrogel photocatalyst materials were summarized. Those hydrogel photocatalysts have been developed by incorporating various photocatalysts, such as TiO_2, C_3N_4, CdS, CuS, PMI, and graphene hybrid complexes. In addition, two main applications of hydrogel photocatalysts in energy conversion and environmental treatments were discussed in detail. Recent progresses in hydrogel photocatalysts for various applications were summarized in Table 1. From Table 1, it can be observed that based on the synergistic absorption and catalysis of hydrogel photocatalytic materials, they are found to show great advantages in environmental treatment, especially for water environment. At the same time, the hydrogel contains a large amount of water, which makes it

Table 1 Summary of various types of hydrogel photocatalysts employed for different applications

Applications	Materials	References
H_2 evolution	CdS/HGel	[130]
	PdAu-TiO_2 aerogels	[131]
	CdS and ZnS containing hydrogel	[132]
	PMI-based hydrogel	[119,126–128]
CO_2 conversion	Macroporous 3D TGM	[138]
	TiO_2-Au composite aerogel	[139]
Organic pollutant degradation	GH-AgBr at rGO	[63]
	ZnO/rGO-rGH hydrogel	[64]
	TiO_2 based hydrogel	[65,67–72,88–91,93]
	Fe^0 at Guar gum-crosslinked-soya lecithin nanocomposite hydrogel	[66]
	CdS based hydrogel	[73,75,76]
	Chitosan-Gelatin based hydrogels	[74]
	Bi_2WO_6/GH	[77]
	β-FeOOH at tunicate cellulose nanocomposite hydrogels	[99]
	MoS_2-rGO composite hydrogel	[100]
	Ag_3PO_4/rGH hydrogel	[101]
	AgCl/ZnO nanocomposites hydrogel	[103]
	C_3N_4 based hydrogel	[113–117,143,144]
	polymer ionic complexation hydrogel photocatalyst	[129]
	p(HEA/NMMA)-CuS hydrogel	[145]
Removal of metal ions	TiO_2-rGH 3D structure hydrogel	[149]
Photothermal evaporation	TiO_2/Ag nanofibers gel	[155]
	D-HNb_3O_8 and a PAM network	[156]

unfavorable for pollutant gas treatment. It is anticipated that this review could provide new insights into the design and fabrication of advanced hydrogel photocatalyst materials for highly efficient photocatalysis.

Despite some achievements in terms of component and structural design of hydrogel photocatalysts in recent years, this field is still in its early stage of development and many challenges remain to improve photocatalytic efficiency and stability to satisfy the demands of practical applications. To address these challenges, efforts are needed in the following aspects:

Current research on hydrogel photocatalysts focuses on random co-mingling of photocatalysts and gel networks, which can limit exposure of photocatalytically active sites. Granular dry gels can result, which can complicate the operation and lead to difficult separation and secondary contamination because of photocatalyst leakage, and poor recyclability.

Research has focused mainly on the design and modification of photocatalysts. However, there have been fewer studies of the intrinsic properties of the hydrogel components. Regulation of the gel network structure and swelling properties and adsorption properties of the gel also synergistically contributes to photocatalyst performance and require further investigation.

To further expand the catalytic performance of hydrogel photocatalytic materials, interfacial modification of hydrogel monomers and photocatalysts together with modulation of the gel network will be likely to offer an effective strategy for achieving efficient and sustainable recycling of photocatalytic gels to overcome the drawbacks of existing hydrogel photocatalysts.

Acknowledgements This work was supported by Japan Science and Technology-Strategic International Collaborative Research Program (JSTSI-CORP) Grant JPMJSC18H1 and Japan Science and Technology-Program on Open Innovation Platform with Enterprises, Research Institute and Academia (JST-OPERA) Grant JPMJOP1843. This work was also supported by Natural Science Foundation of Hebei province (No.B2021203028).

References

1. Weaver P, Jansen L, van Grootveld G, et al. Sustainable Technology Development. London: Routledge, 2017
2. Lewis N S. Research opportunities to advance solar energy utilization. Science, 2016, 351(6271): aad1920
3. Tao P, Ni G, Song C, et al. Solar-driven interfacial evaporation. Nature Energy, 2018, 3(12): 1031–1041
4. Chen C, Kuang Y, Hu L. Challenges and opportunities for solar evaporation. Joule, 2019, 3(3): 683–718
5. Hosseini S E, Wahid M A. Hydrogen from solar energy, a clean energy carrier from a sustainable source of energy. International Journal of Energy Research, 2020, 44(6): 4110–4131
6. Zhang Y, Ren J, Pu Y, et al. Solar energy potential assessment: a framework to integrate geographic, technological, and economic indices for a potential analysis. Renewable Energy, 2020, 149: 577–586
7. Gong J, Li C, Wasielewski M R. Advances in solar energy conversion. Chemical Society Reviews, 2019, 48(7): 1862–1864
8. Kannan N, Vakeesan D. Solar energy for future world: a review. Renewable & Sustainable Energy Reviews, 2016, 62: 1092–1105
9. Wang Q, Hisatomi T, Jia Q, et al. Scalable water splitting on particulate photocatalyst sheets with a solar-to-hydrogen energy conversion efficiency exceeding 1%. Nature Materials, 2016, 15 (6): 611–615
10. Ong W J, Tan L L, Ng Y H, et al. Graphitic carbon nitride (g-C_3N_4)-based photocatalysts for artificial photosynthesis and environmental remediation: are we a step closer to achieving sustainability? Chemical Reviews, 2016, 116(12): 7159–7329
11. Luo J, Zhang S, Sun M, et al. A critical review on energy conversion and environmental remediation of photocatalysts with remodeling crystal lattice, surface, and interface. ACS Nano, 2019, 13(9): 9811–9840
12. Tian B, Tian B, Smith B, et al. Supported black phosphorus nanosheets as hydrogen-evolving photocatalyst achieving 5.4% energy conversion efficiency at 353 K. Nature Communications, 2018, 9(1): 1397
13. Zhang P, Lou X W D. Design of heterostructured hollow photocatalysts for solar-to-chemical energy conversion. Advanced Materials, 2019, 31(29): 1900281
14. Dhiman P, Naushad M, Batoo K M, et al. Nano $Fe_xZn_{1-x}O$ as a tuneable and efficient photocatalyst for solar powered degradation of bisphenol A from aqueous environment. Journal of Cleaner Production, 2017, 165: 1542–1556
15. Tang X, Huang Z, Cao Y, et al. Mo promotes interfacial interaction and induces oxygen vacancies in 2D/2D of Mo-g-C_3N_4 and $Bi_2O_2CO_3$ photocatalyst for enhanced NO oxidation. Industrial & Engineering Chemistry Research, 2020, 59(20): 9509–9518
16. Yi J, Liao J, Xia K, et al. Integrating the merits of two-dimensional structure and heteroatom modification into semiconductor photocatalyst to boost NO removal. Chemical Engineering Journal, 2019, 370: 944–951
17. Fujishima A, Honda K. Electrochemical photolysis of water at a semiconductor electrode. Nature, 1972, 238(5358): 37–38
18. Zhou W, Li W, Wang J, et al. Ordered mesoporous black TiO_2 as highly efficient hydrogen evolution photocatalyst. Journal of the American Chemical Society, 2014, 136(26): 9280–9283
19. Hu Y. A highly efficient photocatalyst—hydrogenated black TiO_2 for the photocatalytic splitting of water. Angewandte Chemie International Edition, 2012, 51(50): 12410–12412
20. Naldoni A, Altomare M, Zoppellaro G, et al. Photocatalysis with reduced TiO_2: from black TiO_2 to cocatalyst-free hydrogen production. ACS Catalysis, 2019, 9(1): 345–364
21. Liu N, Häublein V, Zhou X, et al. "Black" TiO_2 nanotubes formed by high-energy proton implantation show noble-metal-co-catalyst free photocatalytic H_2-evolution. Nano Letters, 2015, 15(10): 6815–6820
22. Hsu C C, Wu N L. Synthesis and photocatalytic activity of ZnO/ZnO_2 composite. Journal of Photochemistry and Photobiology A Chemistry, 2005, 172(3): 269–274
23. Elmolla E S, Chaudhuri M. Degradation of amoxicillin, ampicillin

and cloxacillin antibiotics in aqueous solution by the UV/ZnO photocatalytic process. Journal of Hazardous Materials, 2010, 173 (1–3): 445–449
24. Yu W, Zhang J, Peng T. New insight into the enhanced photocatalytic activity of N-, C- and S-doped ZnO photocatalysts. Applied Catalysis B: Environmental, 2016, 181: 220–227
25. Tian C, Zhang Q, Wu A, et al. Cost-effective large-scale synthesis of ZnO photocatalyst with excellent performance for dye photodegradation. Chemical Communications, 2012, 48(23): 2858–2860
26. Fu J, Yu J, Jiang C, et al. g-C_3N_4-based heterostructured photocatalysts. Advanced Energy Materials, 2018, 8(3): 1701503
27. Wen J, Xie J, Chen X, et al. A review on g-C_3N_4-based photocatalysts. Applied Surface Science, 2017, 391: 72–123
28. Ye L, Liu J, Jiang Z, et al. Facets coupling of BiOBr-g-C_3N_4 composite photocatalyst for enhanced visible-light-driven photocatalytic activity. Applied Catalysis B: Environmental, 2013, 142–143: 1–7
29. Li Y, He R, Han P, et al. A new concept: volume photocatalysis for efficient H_2 generation—using low polymeric carbon nitride as an example. Applied Catalysis B: Environmental, 2020, 279: 119379
30. Xu M, Han L, Dong S. Facile fabrication of highly efficient g-C_3N_4/Ag_2O heterostructured photocatalysts with enhanced visible-light photocatalytic activity. ACS Applied Materials & Interfaces, 2013, 5(23): 12533–12540
31. Kato H, Kudo A. Visible-light-response and photocatalytic activities of TiO_2 and $SrTiO_3$ photocatalysts codoped with antimony and chromium. Journal of Physical Chemistry B, 2002, 106(19): 5029–5034
32. Domen K, Kudo A, Onishi T. Mechanism of photocatalytic decomposition of water into H_2 and O_2 over NiOSrTiO$_3$. Journal of Catalysis, 1986, 102(1): 92–98
33. Iwashina K, Kudo A. Rh-doped $SrTiO_3$ photocatalyst electrode showing cathodic photocurrent for water splitting under visible-light irradiation. Journal of the American Chemical Society, 2011, 133(34): 13272–13275
34. Takata T, Jiang J, Sakata Y, et al. Photocatalytic water splitting with a quantum efficiency of almost unity. Nature, 2020, 581 (7809): 411–414
35. Xu C, Ravi Anusuyadevi P, Aymonier C, et al. Nanostructured materials for photocatalysis. Chemical Society Reviews, 2019, 48 (14): 3868–3902
36. Wei Z, Zhu Y, Guo W, et al. Enhanced twisting degree assisted overall water splitting on a novel nano-dodecahedron $BiVO_4$-based heterojunction. Applied Catalysis B: Environmental, 2020, 266: 118664
37. Jiang Z, Huang Z, Guo W, et al. Photocatalytic overall water splitting on isolated semiconductor photocatalyst sites in an ordered mesoporous silica matrix: a multiscale strategy. Journal of Catalysis, 2019, 370: 210–223
38. Fang W, Jiang Z, Yu L, et al. Novel dodecahedron $BiVO_4$:YVO_4 solid solution with enhanced charge separation on adjacent exposed facets for highly efficient overall water splitting. Journal of Catalysis, 2017, 352: 155–159
39. Li Y, Han P, Hou Y, et al. Oriented $Zn_mIn_2S_{m+3}$@In_2S_3 heterojunction with hierarchical structure for efficient photocatalytic hydrogen evolution. Applied Catalysis B: Environmental, 2019, 244: 604–611
40. Li Y, Hou Y, Fu Q, et al. Oriented growth of $ZnIn_2S_4$/$In(OH)_3$ heterojunction by a facile hydrothermal transformation for efficient photocatalytic H_2 production. Applied Catalysis B: Environmental, 2017, 206: 726–733
41. Meng A, Zhang L, Cheng B, et al. Dual cocatalysts in TiO_2 photocatalysis. Advanced Materials, 2019, 31(30): 1807660
42. Ran J, Zhang J, Yu J, et al. Earth-abundant cocatalysts for semiconductor-based photocatalytic water splitting. Chemical Society Reviews, 2014, 43(22): 7787–7812
43. Wang Q, Domen K. Particulate photocatalysts for light-driven water splitting: mechanisms, challenges, and design strategies. Chemical Reviews, 2020, 120(2): 919–985
44. Nakata K, Fujishima A. TiO_2 photocatalysis: design and applications. Journal of Photochemistry and Photobiology C, Photochemistry Reviews, 2012, 13(3): 169–189
45. Chen H, Lee S W, Kim T H, et al. Photocatalytic decomposition of benzene with plasma sprayed TiO_2-based coatings on foamed aluminum. Journal of the European Ceramic Society, 2006, 26(12): 2231–2239
46. Shang J, Li W, Zhu Y. Structure and photocatalytic characteristics of TiO_2 film photocatalyst coated on stainless steel webnet. Journal of Molecular Catalysis A Chemical, 2003, 202(1–2): 187–195
47. Carneiro J O, Teixeira V, Portinha A, et al. Iron-doped photocatalytic TiO_2 sputtered coatings on plastics for self-cleaning applications. Materials Science and Engineering B, 2007, 138(2): 144–150
48. Liu X, Chen Q, Lv L, et al. Preparation of transparent PVA/TiO_2 nanocomposite films with enhanced visible-light photocatalytic activity. Catalysis Communications, 2015, 58: 30–33
49. Zhang R, Ma M, Zhang Q, et al. Multifunctional g-C_3N_4/graphene oxide wrapped sponge monoliths as highly efficient adsorbent and photocatalyst. Applied Catalysis B: Environmental, 2018, 235: 17–25
50. Jiang W, Luo W, Zong R, et al. Polyaniline/carbon nitride nanosheets composite hydrogel: a separation-free and high-efficient photocatalyst with 3D hierarchical structure. Small, 2016, 12(32): 4370–4378
51. Zhang Z, Xiao F, Guo Y, et al. One-pot self-assembled three-dimensional TiO_2-graphene hydrogel with improved adsorption capacities and photocatalytic and electrochemical activities. ACS Applied Materials & Interfaces, 2013, 5(6): 2227–2233
52. Mai N X D, Bae J, Kim I T, et al. A recyclable, recoverable, and reformable hydrogel-based smart photocatalyst. Environmental Science: Nano, 2017, 4(4): 955–966
53. Im J S, Bai B C, In S J, et al. Improved photodegradation properties and kinetic models of a solar-light-responsive photocatalyst when incorporated into electrospun hydrogel fibers. Journal of Colloid and Interface Science, 2010, 346(1): 216–221
54. Lei L, Wang W, Wang C, et al. Hydrogel-supported graphitic carbon nitride nanosheets loaded with Pt atoms as a novel self-water-storage photocatalyst for H_2 evolution. Journal of Materials Chemistry A, Materials for Energy and Sustainability, 2020, 8(45): 23812–23819
55. Lei W, Qi S, Rong Q, et al. Diffusion-freezing-induced microphase

separation for constructing large-area multiscale structures on hydrogel surfaces. Advanced Materials, 2019, 31(32): 1808217
56. Xiang Q, Yu J, Jaroniec M. Graphene-based semiconductor photocatalysts. Chemical Society Reviews, 2012, 41(2): 782–796
57. Mills A, Le Hunte S. An overview of semiconductor photocatalysis. Journal of Photochemistry and Photobiology A Chemistry, 1997, 108(1): 1–35
58. Maeda K. Z-scheme water splitting using two different semiconductor photocatalysts. ACS Catalysis, 2013, 3(7): 1486–1503
59. Wang H, Zhang L, Chen Z, et al. Semiconductor heterojunction photocatalysts: design, construction, and photocatalytic performances. Chemical Society Reviews, 2014, 43(15): 5234–5244
60. Liu G, Yu J C, Lu G Q, et al. Crystal facet engineering of semiconductor photocatalysts: motivations, advances and unique properties. Chemical Communications, 2011, 47(24): 6763–6783
61. Jing L, Qu Y, Wang B, et al. Review of photoluminescence performance of nano-sized semiconductor materials and its relationships with photocatalytic activity. Solar Energy Materials and Solar Cells, 2006, 90(12): 1773–1787
62. Abe R, Sayama K, Sugihara H. Development of new photocatalytic water splitting into H_2 and O_2 using two different semiconductor photocatalysts and a shuttle redox mediator IO_3^-/I^-. Journal of Physical Chemistry B, 2005, 109(33): 16052–16061
63. Chen F, An W, Liu L, et al. Highly efficient removal of bisphenol A by a three-dimensional graphene hydrogel—AgBr@rGO exhibiting adsorption/photocatalysis synergy. Applied Catalysis B: Environmental, 2017, 217: 65–80
64. Liu C, Yue M, Liu L, et al. A separation-free 3D network ZnO/rGO-rGH hydrogel: adsorption enriched photocatalysis for environmental applications. RSC Advances, 2018, 8(40): 22402–22410
65. Yun J, Jin D, Lee Y S, et al. Photocatalytic treatment of acidic waste water by electrospun composite nanofibers of pH-sensitive hydrogel and TiO_2. Materials Letters, 2010, 64(22): 2431–2434
66. Sharma G, Kumar A, Sharma S, et al. Fabrication and characterization of novel Fe^0@Guar gum-crosslinked-soya lecithin nanocomposite hydrogel for photocatalytic degradation of methyl violet dye. Separation and Purification Technology, 2019, 211: 895–908
67. Thomas M, Naikoo G A, Sheikh M U D, et al. Effective photocatalytic degradation of Congo red dye using alginate/carboxymethyl cellulose/TiO_2 nanocomposite hydrogel under direct sunlight irradiation. Journal of Photochemistry and Photobiology A Chemistry, 2016, 327: 33–43
68. Jiang W, Liu Y, Wang J, et al. Separation-free polyaniline/TiO_2 3D hydrogel with high photocatalytic activity. Advanced Materials Interfaces, 2016, 3(3): 1500502
69. Chen Y, Xiang Z, Wang D, et al. Effective photocatalytic degradation and physical adsorption of methylene blue using cellulose/GO/TiO_2 hydrogels. RSC Advances, 2020, 10(40): 23936–23943
70. Chen X, Chen Q, Jiang W, et al. Separation-free TiO_2-graphene hydrogel with 3D network structure for efficient photoelectrocatalytic mineralization. Applied Catalysis B: Environmental, 2017, 211: 106–113
71. Chen F, An W, Li Y, et al. Fabricating 3D porous PANI/TiO_2-graphene hydrogel for the enhanced UV-light photocatalytic degradation of BPA. Applied Surface Science, 2018, 427: 123–132
72. Hou C, Zhang Q, Li Y, et al. P25-graphene hydrogels: room-temperature synthesis and application for removal of methylene blue from aqueous solution. Journal of Hazardous Materials, 2012, 205–206: 229–235
73. Jiang R, Zhu H, Yao J, et al. Chitosan hydrogel films as a template for mild biosynthesis of CdS quantum dots with highly efficient photocatalytic activity. Applied Surface Science, 2012, 258(8): 3513–3518
74. Kaur K, Jindal R. Comparative study on the behaviour of Chitosan-Gelatin based Hydrogel and nanocomposite ion exchanger synthesized under microwave conditions towards photocatalytic removal of cationic dyes. Carbohydrate Polymers, 2019, 207: 398–410
75. Yang J, Gao J, Wang X, et al. Polyacrylamide hydrogel as a template *in situ* synthesis of CdS nanoparticles with high photocatalytic activity and photostability. Journal of Nanoparticle Research, 2017, 19(10): 350
76. Zhu H, Li Z, Yang J. A novel composite hydrogel for adsorption and photocatalytic degradation of bisphenol A by visible light irradiation. Chemical Engineering Journal, 2018, 334: 1679–1690
77. Yang J, Chen D, Zhu Y, et al. 3D–3D porous Bi_2WO_6/graphene hydrogel composite with excellent synergistic effect of adsorption-enrichment and photocatalytic degradation. Applied Catalysis B: Environmental, 2017, 205: 228–237
78. Hashimoto K, Irie H, Fujishima A. TiO_2 photocatalysis: a historical overview and future prospects. Japanese Journal of Applied Physics, Part 1: Regular Papers and Short Notes and Review Papers, 2005, 44(12): 8269–8285
79. Fujishima A, Zhang X, Tryk D A. TiO_2 photocatalysis and related surface phenomena. Surface Science Reports, 2008, 63(12): 515–582
80. Schneider J, Matsuoka M, Takeuchi M, et al. Understanding TiO_2 photocatalysis: mechanisms and materials. Chemical Reviews, 2014, 114(19): 9919–9986
81. Guo Q, Zhou C, Ma Z, et al. Fundamentals of TiO_2 photocatalysis: concepts, mechanisms, and challenges. Advanced Materials: Deerfield Beach, Fla, 2019, 31(50): 1901997
82. Leary R, Westwood A. Carbonaceous nanomaterials for the enhancement of TiO_2 photocatalysis. Carbon, 2011, 49(3): 741–772
83. Jiang Y, Ning H, Tian C, et al. Single-crystal TiO_2 nanorods assembly for efficient and stable cocatalyst-free photocatalytic hydrogen evolution. Applied Catalysis B: Environmental, 2018, 229: 1–7
84. Zhang W, He H, Tian Y, et al. Synthesis of uniform ordered mesoporous TiO_2 microspheres with controllable phase junctions for efficient solar water splitting. Chemical Science (Cambridge), 2019, 10(6): 1664–1670
85. Hu J, Xie J, Jia W, et al. Interesting molecule adsorption strategy induced energy band tuning: boosts 43 times photocatalytic water splitting ability for commercial TiO_2. Applied Catalysis B: Environmental, 2020, 268: 118753
86. Li X, Shi J, Hao H, et al. Visible light-induced selective oxidation of alcohols with air by dye-sensitized TiO_2 photocatalysis. Applied

Catalysis B: Environmental, 2018, 232: 260–267
87. Qian R, Zong H, Schneider J, et al. Charge carrier trapping, recombination and transfer during TiO_2 photocatalysis: an overview. Catalysis Today, 2019, 335: 78–90
88. Yue Y, Wang X, Wu Q, et al. Highly recyclable and super-tough hydrogel mediated by dual-functional TiO_2 nanoparticles toward efficient photodegradation of organic water pollutants. Journal of Colloid and Interface Science, 2020, 564: 99–112
89. Arikal D, Kallingal A. Photocatalytic degradation of azo and anthraquinone dye using TiO_2/MgO nanocomposite immobilized chitosan hydrogels. Environmental Technology, 2019, online, doi:10.1080/09593330.2019.1701094
90. Lučić M, Milosavljević N, Radetić M, et al. The potential application of TiO_2/hydrogel nanocomposite for removal of various textile azo dyes. Separation and Purification Technology, 2014, 122: 206–216
91. Zhao K, Feng L, Lin H, et al. Adsorption and photocatalytic degradation of methyl orange imprinted composite membranes using TiO_2/calcium alginate hydrogel as matrix. Catalysis Today, 2014, 236: 127–134
92. Liu M, Ishida Y, Ebina Y, et al. Photolatently modulable hydrogels using unilamellar titania nanosheets as photocatalytic crosslinkers. Nature Communications, 2013, 4(1): 2029
93. Liu J, Chen H, Shi X, et al. Hydrogel microcapsules with photocatalytic nanoparticles for removal of organic pollutants. Environmental Science: Nano, 2020, 7(2): 656–664
94. Khan S, Kubota Y, Lei W, et al. One-pot synthesis of (anatase/bronze-type)-TiO_2/carbon dot polymorphic structures and their photocatalytic activity for H_2 generation. Applied Surface Science, 2020, 526: 146650
95. Wu Q, Huang F, Zhao M, et al. Ultra-small yellow defective TiO_2 nanoparticles for co-catalyst free photocatalytic hydrogen production. Nano Energy, 2016, 24: 63–71
96. Nowotny M K, Sheppard L R, Bak T, et al. Defect chemistry of titanium dioxide. Application of defect engineering in processing of TiO_2-based photocatalysts. Journal of Physical Chemistry C, 2008, 112(14): 5275–5300
97. Elbanna O, Zhu M, Fujitsuka M, et al. Black phosphorus sensitized TiO_2 mesocrystal photocatalyst for hydrogen evolution with visible and near-infrared light irradiation. ACS Catalysis, 2019, 9 (4): 3618–3626
98. Su R, Ge S, Li H, et al. Synchronous synthesis of Cu_2O/Cu/rGO@carbon nanomaterials photocatalysts via the sodium alginate hydrogel template method for visible light photocatalytic degradation. Science of the Total Environment, 2019, 693: 133657
99. Wang J, Li X, Cheng Q, et al. Construction of β-FeOOH@tunicate cellulose nanocomposite hydrogels and their highly efficient photocatalytic properties. Carbohydrate Polymers, 2020, 229: 115470
100. Ding Y, Zhou Y, Nie W, et al. MoS_2-GO nanocomposites synthesized via a hydrothermal hydrogel method for solar light photocatalytic degradation of methylene blue. Applied Surface Science, 2015, 357: 1606–1612
101. Mu C, Zhang Y, Cui W, et al. Removal of bisphenol A over a separation free 3D Ag_3PO_4-graphene hydrogel via an adsorption-photocatalysis synergy. Applied Catalysis B: Environmental, 2017, 212: 41–49
102. Qin L, Ru R, Mao J, et al. Assembly of MOFs/polymer hydrogel derived Fe_3O_4-CuO@hollow carbon spheres for photochemical oxidation: freezing replacement for structural adjustment. Applied Catalysis B: Environmental, 2020, 269: 118754
103. Taghizadeh M T, de Siyahi V, Ashassi-Sorkhabi H, et al. ZnO, AgCl and AgCl/ZnO nanocomposites incorporated chitosan in the form of hydrogel beads for photocatalytic degradation of MB, E. coli and S. aureus. International Journal of Biological Macromolecules, 2020, 147: 1018–1028
104. Chen S, Jacobs D L, Xu J, et al. 1D nanofiber composites of perylene diimides for visible-light-driven hydrogen evolution from water. RSC Advances, 2014, 4(89): 48486–48491
105. Chen S, Li Y, Wang C. Visible-light-driven photocatalytic H_2 evolution from aqueous suspensions of perylene diimide dye-sensitized Pt/TiO_2 catalysts. RSC Advances, 2015, 5(21): 15880–15885
106. Chen S, Wang C, Bunes B R, et al. Enhancement of visible-light-driven photocatalytic H_2 evolution from water over g-C_3N_4 through combination with perylene diimide aggregates. Applied Catalysis A, General, 2015, 498: 63–68
107. Yang S, Gong Y, Zhang J, et al. Exfoliated graphitic carbon nitride nanosheets as efficient catalysts for hydrogen evolution under visible light. Advanced Materials, 2013, 25(17): 2452–2456
108. Wang Y, Wang X, Antonietti M. Polymeric graphitic carbon nitride as a heterogeneous organocatalyst: from photochemistry to multipurpose catalysis to sustainable chemistry. Angewandte Chemie International Edition, 2012, 51(1): 68–89
109. Wang X, Maeda K, Chen X, et al. Polymer semiconductors for artificial photosynthesis: hydrogen evolution by mesoporous graphitic carbon nitride with visible light. Journal of the American Chemical Society, 2009, 131(5): 1680–1681
110. Wang X, Maeda K, Thomas A, et al. A metal-free polymeric photocatalyst for hydrogen production from water under visible light. Nature Materials, 2009, 8(1): 76–80
111. Hu C, Lin Y, Yang H C. Recent developments in graphitic carbon nitride based hydrogels as photocatalysts. ChemSusChem, 2019, 12(9): 1769–1806
112. Jiang W, Zhu Y, Zhu G, et al. Three-dimensional photocatalysts with a network structure. Journal of Materials Chemistry A, Materials for Energy and Sustainability, 2017, 5(12): 5661–5679
113. Li J, Yu X, Zhu Y, et al. 3D–2D-3D BiOI/porous g-C_3N_4/graphene hydrogel composite photocatalyst with synergy of adsorption-photocatalysis in static and flow systems. Journal of Alloys and Compounds, 2021, 850: 156778
114. Chu Y C, Lin T J, Lin Y, et al. Influence of P, S, O-doping on g-C_3N_4 for hydrogel formation and photocatalysis: an experimental and theoretical study. Carbon, 2020, 169: 338–348
115. Liang Y, Wang X, An W, et al. Ag-C_3N_4@ppy-rGO 3D structure hydrogel for efficient photocatalysis. Applied Surface Science, 2019, 466: 666–672
116. Hu J, Zhang P, Cui J, et al. High-efficiency removal of phenol and coking wastewater via photocatalysis-Fenton synergy over a Fe-g-C_3N_4 graphene hydrogel 3D structure. Journal of Industrial and Engineering Chemistry, 2020, 84: 305–314
117. Liu G, Li T, Song X, et al. Thermally driven characteristic and

highly photocatalytic activity based on *N*-isopropyl acrylamide/high-substituted hydroxypropyl cellulose/g-C_3N_4 hydrogel by electron beam pre-radiation method. Journal of Thermoplastic Composite Materials, 2020, online, doi:10.1177/0892705-720944214

118. Zhang G, Lan Z, Wang X. Conjugated polymers: catalysts for photocatalytic hydrogen evolution. Angewandte Chemie International Edition, 2016, 55(51): 15712–15727
119. Wang X, Chen L, Chong S Y, et al. Sulfone-containing covalent organic frameworks for photocatalytic hydrogen evolution from water. Nature Chemistry, 2018, 10(12): 1180–1189
120. Liu D, Wang J, Bai X, et al. Self-assembled PDINH supramolecular system for photocatalysis under visible light. Advanced Materials: Deerfield Beach, Fla, 2016, 28(33): 7284–7290
121. Cohen E, Weissman H, Pinkas I, et al. Controlled self-assembly of photofunctional supramolecular nanotubes. ACS Nano, 2018, 12 (1): 317–326
122. Chen S, Slattum P, Wang C, et al. Self-assembly of perylene imide molecules into 1D nanostructures: methods, morphologies, and applications. Chemical Reviews, 2015, 115(21): 11967–11998
123. Krieg E, Bastings M M C, Besenius P, et al. Supramolecular polymers in aqueous media. Chemical Reviews, 2016, 116(4): 2414–2477
124. Singh P, Mittal L S, Vanita V, et al. Self-assembled vesicle and rod-like aggregates of functionalized perylene diimide: reaction-based near-IR intracellular fluorescent probe for selective detection of palladium. Journal of Materials Chemistry B, Materials for Biology and Medicine, 2016, 4(21): 3750–3759
125. Zhang Z, Chen X, Zhang H, et al. A highly crystalline perylene imide polymer with the robust built-in electric field for efficient photocatalytic water oxidation. Advanced Materials, 2020, 32(32): 1907746
126. Weingarten A S, Kazantsev R V, Palmer L C, et al. Supramolecular packing controls H_2 photocatalysis in chromophore amphiphile hydrogels. Journal of the American Chemical Society, 2015, 137 (48): 15241–15246
127. Weingarten A S, Kazantsev R V, Palmer L C, et al. Self-assembling hydrogel scaffolds for photocatalytic hydrogen production. Nature Chemistry, 2014, 6(11): 964–970
128. Sai H, Erbas A, Dannenhoffer A, et al. Chromophore amphiphile-polyelectrolyte hybrid hydrogels for photocatalytic hydrogen production. Journal of Materials Chemistry A, Materials for Energy and Sustainability, 2020, 8(1): 158–168
129. Byun J, Landfester K, Zhang K. Conjugated polymer hydrogel photocatalysts with expandable photoactive sites in water. Chemistry of Materials, 2019, 31(9): 3381–3387
130. Li F, Yang J, Gao J, et al. Enhanced photocatalytic hydrogen production of CdS embedded in cationic hydrogel. International Journal of Hydrogen Energy, 2020, 45(3): 1969–1980
131. Luna A L, Matter F, Schreck M, et al. Monolithic metal-containing TiO_2 aerogels assembled from crystalline pre-formed nanoparticles as efficient photocatalysts for H_2 generation. Applied Catalysis B: Environmental, 2020, 267: 118660
132. Jiang Z, Zhang X, Yang G, et al. Hydrogel as a miniature hydrogen production reactor to enhance photocatalytic hydrogen evolution activities of CdS and ZnS quantum dots derived from modified gel crystal growth method. Chemical Engineering Journal, 2019, 373: 814–820
133. Yu J, Low J, Xiao W, et al. Enhanced photocatalytic CO_2-reduction activity of anatase TiO_2 by coexposed {001} and {101} facets. Journal of the American Chemical Society, 2014, 136(25): 8839–8842
134. Habisreutinger S N, Schmidt-Mende L, Stolarczyk J K. Photocatalytic reduction of CO_2 on TiO_2 and other semiconductors. Angewandte Chemie International Edition, 2013, 52(29): 7372–7408
135. Ran J, Jaroniec M, Qiao S. Cocatalysts in semiconductor-based photocatalytic CO_2 reduction: achievements, challenges, and opportunities. Advanced Materials, 2018, 30(7): 1704649
136. Bie C, Zhu B, Xu F, et al. *In situ* grown monolayer N-doped graphene on CdS hollow spheres with seamless contact for photocatalytic CO_2 reduction. Advanced Materials, 2019, 31(42): 1902868
137. Fu J, Jiang K, Qiu X, et al. Product selectivity of photocatalytic CO_2 reduction reactions. Materials Today, 2020, 32: 222–243
138. Jung H, Cho K M, Kim K H, et al. Highly efficient and stable CO_2 reduction photocatalyst with a hierarchical structure of mesoporous TiO_2 on 3D graphene with few-layered MoS_2. ACS Sustainable Chemistry & Engineering, 2018, 6(5): 5718–5724
139. Rechberger F, Niederberger M. Translucent nanoparticle-based aerogel monoliths as 3-dimensional photocatalysts for the selective photoreduction of CO_2 to methanol in a continuous flow reactor. Materials Horizons, 2017, 4(6): 1115–1121
140. Godiya C B, Martins Ruotolo L A, Cai W. Functional biobased hydrogels for the removal of aqueous hazardous pollutants: current status, challenges, and future perspectives. Journal of Materials Chemistry A, Materials for Energy and Sustainability, 2020, 8(41): 21585–21612
141. Jing G, Wang L, Yu H, et al. Recent progress on study of hybrid hydrogels for water treatment. Colloids and Surfaces A, Physicochemical and Engineering Aspects, 2013, 416: 86–94
142. Mohammadzadeh Pakdel P, Peighambardoust S J. A review on acrylic based hydrogels and their applications in wastewater treatment. Journal of Environmental Management, 2018, 217: 123–143
143. Zhang M, Luo W, Wei Z, et al. Separation free C_3N_4/SiO_2 hybrid hydrogels as high active photocatalysts for TOC removal. Applied Catalysis B: Environmental, 2016, 194: 105–110
144. Zhang M, Jiang W, Liu D, et al. Photodegradation of phenol via C_3N_4-agar hybrid hydrogel 3D photocatalysts with free separation. Applied Catalysis B: Environmental, 2016, 183: 263–268
145. Yang J, Li Z, Zhu H. Adsorption and photocatalytic degradation of sulfamethoxazole by a novel composite hydrogel with visible light irradiation. Applied Catalysis B: Environmental, 2017, 217: 603–614
146. Hua M, Zhang S, Pan B, et al. Heavy metal removal from water/wastewater by nanosized metal oxides: a review. Journal of Hazardous Materials, 2012, 211–212: 317–331
147. Fu F, Wang Q. Removal of heavy metal ions from wastewaters: a review. Journal of Environmental Management, 2011, 92(3): 407–418
148. Tahir M B, Kiran H, Iqbal T. The detoxification of heavy metals

from aqueous environment using nano-photocatalysis approach: a review. Environmental Science and Pollution Research International, 2019, 26(11): 10515–10528

149. Li Y, Cui W, Liu L, et al. Removal of Cr(VI) by 3D TiO_2-graphene hydrogel via adsorption enriched with photocatalytic reduction. Applied Catalysis B: Environmental, 2016, 199: 412–423
150. Guo Y, Bae J, Fang Z, et al. Hydrogels and hydrogel-derived materials for energy and water sustainability. Chemical Reviews, 2020, 120(15): 7642–7707
151. Zhou X, Guo Y, Zhao F, et al. Hydrogels as an emerging material platform for solar water purification. Accounts of Chemical Research, 2019, 52(11): 3244–3253
152. Zhou X, Zhao F, Guo Y, et al. Architecting highly hydratable polymer networks to tune the water state for solar water purification. Science Advances, 2019, 5(6): eaaw5484
153. Zhao F, Zhou X, Shi Y, et al. Highly efficient solar vapour generation via hierarchically nanostructured gels. Nature Nanotechnology, 2018, 13(6): 489–495
154. Lei W, Khan S, Chen L, et al. Hierarchical structures hydrogel evaporator and superhydrophilic water collect device for efficient solar steam evaporation. Nano Research, 2021, 14(4): 1135–1140
155. Gao M, Peh C K, Zhu L, et al. Photothermal catalytic gel featuring spectral and thermal management for parallel freshwater and hydrogen production. Advanced Energy Materials, 2020, 10(23): 2000925
156. Yang M, Tan C, Lu W, et al. Spectrum tailored defective 2D semiconductor nanosheets aerogel for full-spectrum-driven photothermal water evaporation and photochemical degradation. Advanced Functional Materials, 2020, 30(43): 2004460