Three-dimensional photocatalysts with a network structure

Wenjun Jiang, Yongfa Zhu,* Guoxiang Zhu, Zijiang Zhang, Xianjie Chen and Wenqing Yao

Three-dimensional (3D) photocatalysts with a network structure are presently attracting enormous research interests due to their excellent properties, such as a high specific surface area, high adsorptive capacity, high structure stability, low gas resistance and a large number of exposed active sites, which suggest it could act as a promising candidate for solar energy conversion or environmental pollution elimination. This review first introduces the limiting factors for the photocatalytic efficiency of such photocatalysts and the corresponding solutions. Then, the superiorities of 3D network photocatalysts are highlighted. Importantly, we summarize the most common 3D photocatalysts and their synthetic strategies. Furthermore, the most important applications, including solar energy storage and conversion and photocatalytic pollutant degradation, are also discussed. Finally, this review presents some perspectives concerning the challenges and new directions of 3D photocatalysts with a network structure.

1. Introduction

Nowadays, the energy crisis and environmental pollution are causing global concern. Consequently, growing attention has been paid to efficient energy conversion and environmental protection. Photocatalytic technology is regarded as one of the most promising solutions to solve these problems, since photocatalytic processes can generally be grouped into green and sustainable reactions. Photocatalysis has been widely used in water splitting,1–3 CO2 reduction,4 N2 fixation,5 organic synthesis6,7 and pollutant degradation8–9 since 1972.10

Generally, the photocatalytic reaction consists of the following five fundamental processes (shown in Fig. 1):11 (1) light harvesting: photons are absorbed by semiconductors; (2–3) excitation and charge separation: the photoinduced electrons are excited and transferred from the filled valence band (VB) to the empty conduction band (CB) when the energy of the absorbed photons is equal to or larger than the forbidden band energy \( E_g \); (4) charge migration: the separated charges then migrate to the surface of the photocatalysts; (5) surface reaction: the photoinduced electrons take part in a surface reduction reaction.

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reaction, while the photoinduced holes take part in surface oxidation, respectively. Meanwhile, recombination of the separated electrons and holes also occurs both in the bulk and on the surface of the photocatalysts, with the release of light or heat. The recombination of photoinduced carriers is a competitive process to the surface reactions, which is a disadvantage in the photocatalytic process.

Currently, there are some serious drawbacks limiting the practical application of photocatalytic technology. In particular, the poor efficiency is far from satisfactory. The current activity improvement strategies can be ascribed to the following several measures (Fig. 1): (1) methods promoting light harvesting, including dye sensitization\textsuperscript{12–14} and surface plasma resonance (SPR);\textsuperscript{15–17} (2) the use of cocatalysts,\textsuperscript{18–21} heterojunctions\textsuperscript{22–29} and surface hybridization,\textsuperscript{30–38} which are the most widely used techniques to increase separation and migration efficiency; (3) doping (metal or non-metal),\textsuperscript{39–44} solid solution,\textsuperscript{45–49} surface defect\textsuperscript{5,32,50–55} and conjugation of π-bonds,\textsuperscript{56,57} which are typically adopted to modify the band; (4) crystalline phase/crystal face\textsuperscript{58–61} or size/morphology control,\textsuperscript{62–66} which are the most commonly used methods for regulating the structure or morphology.

Different photochemical reactions require meeting different thermodynamic constraints. Fig. 2 shows the thermodynamic constraints for photocatalytic water splitting,\textsuperscript{67} CO\textsubscript{2} reduction\textsuperscript{68,69} and N\textsubscript{2} fixation\textsuperscript{5,70} and degradation.\textsuperscript{71} As for overall water splitting, the potential of the CB should be more negative than \(-0.41\) V, while the potential of the VB should be more positive than \(0.82\) V, respectively. For H\textsubscript{2} generation, the

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potential of the CB only needs to be more negative than $-0.41$ V, while the potential of the VB only needs to be more positive than $0.82$ V for O$_2$ evolution. Generally, the materials adopted in water splitting could also be applied to CO$_2$ reduction. However, the activity and selectivity of photocatalytic CO$_2$ reduction are usually low, since the liquid H$_2$O may compete with CO$_2$ to capture the photoinduced electrons to form H$_2$. A variety of products, such as HCOOH, CO, HCHO, CH$_3$OH and CH$_4$, may be possible products. Fig. 2 displays the redox potentials of different products from CO$_2$. Photocatalytic N$_2$ fixation is much more challenging than water splitting and CO$_2$ reduction since the redox potential of N$_2$(aq) and N$_2$H are $-4.2$ V and $-3.2$ V, respectively. As for photocatalytic pollutant degradation, on the hand, the holes on the VB of the semiconductor could oxidize the pollutant directly, whereas on the other hand, the holes could oxidize OH$^-$ to generate 'OH if the VB of the semiconductor is more positive than 2.29 V, where this is a kind of non-selective, powerful, oxidizing radical. Meanwhile, the electrons could reduce O$_2$ to generate 'O$_2$ when the CB of the semiconductor is more negative than $-0.33$ V. Both 'OH and 'O$_2$ could take part in the oxidation of environmental pollutants into CO$_2$, H$_2$O or other smaller molecules.

2. Superiorities of 3D network photocatalysts

As is known, whether a reaction takes place efficiently is not only determined by the thermodynamic constraints but also depends on the kinetics restrictions. Among the five fundamental processes of the photocatalytic reaction, the charge separation-migration and surface reaction processes are considered as the rate determining steps, and which can lead to a low quantum efficiency. The use of 3D photocatalysts may be an appealing and effective strategy to address these two issues. 3D photocatalysts usually refer to those photocatalysts with a 3D network structure. Generally, the 3D network photocatalysts can be divided into two types: loaded type photocatalysts and unloaded type photocatalysts. For the former, supporting materials are used as framework and the photocatalysts are then loaded onto the framework. For the latter, the photocatalysts already possess a 3D network structure. The 3D network structure can hold plenty of photocatalysts on account of the huge specific surface area, which can promote adsorption and photocatalytic reactions, which are then able to expose more reactive sites, thereby accelerating the surface photocatalytic reactions. This process is greatly effective in eliminating environmental pollutants in the liquid phase owing to the cooperation of adsorptive enrichment and photocatalysis. First, pollutants are adsorbed and enriched into the 3D network structure. Then, the target environmental pollutants are in situ oxidized through photocatalysis. Furthermore, the photocatalyst has a more effective light harvesting ability on account of the multirefection within the interconnected framework. Furthermore, the 3D network structure is able to prevent the aggregation or stacking of subunits, which indicates that the structural stability is high. In addition, photocatalysts with a network structure usually possess large pore sizes and low gas resistance, which is beneficial for pollutant degradation in the gaseous phase (Fig. 3).

Hydrogel- and aerogel-based photocatalysts are two of the most popular 3D network photocatalysts, and are used as adsorption and supporting materials by providing convenient mass transfer channels. Typically, 3D network structured composite hydrogels and aerogels have high photocactivity in nano-sized materials and possess a separation-free superiority over bulk materials, meaning that the composite hydrogel is easy to recycle. Although there have been lots of preeminent reviews with respect to photocatalysis$^{72-78}$ or the fabrication of porous...
materials, a review concerning 3D photocatalysts with a network structure is still needed. Consequently, in this review, we highlight the superiorities of 3D network photocatalysts and summarize their synthetic strategies and potential applications in solar energy storage and conversion and in photocatalytic pollutant degradation. Finally, we highlight the ongoing challenges and perspectives in this field.

3. Synthetic strategies for fabricating 3D network photocatalysts

Generally, different 3D network photocatalysts require different fabrication strategies. The synthetic strategies for the loaded type photocatalysts include: the template method, the self-assembly method and the sol–gel process. The fabrication approaches for unloaded type photocatalysts include: in situ polymerization, the hydrothermal/solvothermal method and so on.

3.1 Template method (hard and soft)

Generally, the template method consists of a hard template or soft template, which depends on the type of adopted template. Silica is one of the most popular hard templates utilized to fabricate 3D network structures, with HF or NH$_4$HF$_2$ adopted to remove the silica template. Liu et al. developed novel 3D sulphur and nitrogen co-doped carbon foams (S–N-CF) with a network structure via a hard template method. Fig. 4 shows a schematic illustration of the synthesis of S–N-CF. First, a mixture of thiourea and sucrose was infiltrated into an SBA-15 template. Then, the obtained sample was calcined under an argon environment at high temperature. Finally, HF was adopted to remove the template to obtain silica-free S–N-CF. Importantly, the mass ratio of thiourea to sucrose is an important factor to control the structures and morphologies of the samples. The morphological transformation procedure is
illustrated in Fig. 4 (CMK-3-1000, 5 : 0; S–N-CF-1000-2, 3 : 2; S–N-CF-1000, 1 : 4; S–N-CF-1000-4, 1 : 8). Structured carbon materials (CMK-3-1000) were fabricated adopting sucrose as the only carbon source. By adding thiourea, carbon foams (S–N-CF-1000-2 and S–N-CF-1000) with a 3D network and plentiful macropores (about 400 nm) were obtained. The form of the 3D network structure may come from the fact that thiourea pyrolysis generates a large pore structure, while structured carbon materials leave a small pore structure. When the mass ratio of sucrose to thiourea reached 1 : 8, the 3D network structure disappeared and wrinkled and graphene-like features were obtained, owing to the extensive thiourea pyrolygenation (S–N-CF-1000-4). The 3D S–N-CF showed excellent ORR performances compared to the commercial Pt/C catalyst, which was arose from a synergistic effect of a high number of catalytic sites contributed to the excellent electron-transfer rate provided by the 3D network structure, outstanding reactant transport, contributed to the 3D pore structure, and the high S–N heteroatom loading. CaCO3 is also an excellent hard template candidate for fabrication of a 3D network, and could be removed easily via dilute acidic solution. Similarly, Meng et al. designed and prepared a freestanding porous graphene film (3D-rGO) via an easy hard template approach. Here, polyaniline (PANI) nanowire arrays (3D-rGO/PANI) were adopted to fabricate a hierarchical composite film to combine the benefits of both materials. CaCl2 was first put into a GO dispersion to generate a homogeneous mixture. Then, CO2 was bubbled into the mixture, and CaCO3 particles were generated and were then in situ wrapped by GO sheets. The composite film of CaCO3 and GO was obtained via vacuum filtration. Hydrazine vapour was adopted to reduce GO, and then CaCO3 was removed via a dilute acid. The flexible 3D-rGO framework was then obtained. Then, PANI nanowire arrays were formed on the skeleton of the 3D-rGO framework via a polymerization method to produce the hierarchical 3D-rGO/PANI composite film. The 3D network film possessed unique characteristics of both an interconnected network structure and excellent flexibility. The generation of interconnected pores promotes access of electrolyte ions into the internal surface of the film, resulting in an excellent charge-discharge rate performance.

Most porous carbon aerogels (CAs) are fabricated via the carbonization of organic precursor aerogels with porous hierarchical structures. However, almost no organic precursor aerogels can withstand the capillary force related to the surface tension of the liquid during drying. Hence, supercritical CO2 drying or freeze-drying are needed to avoid the collapse of the micropores, which limits its large-scale application. Yu et al. provided a facile, sustainable and inexpensive route to fabricate robust phenol-formaldehyde resin-based hard-carbon aerogel, which took advantage of the chelation effect of phenol and Fe3+. The chelation effect of metal ions with polymer monomers can improve the dispersion of metal catalysts into carbon precursor units, yielding a better catalytic effect. The obtained aerogel consisted of a 3D interconnected carbon network embedded with hydrogen-rich, ordered microstructures of expanded nanographites and carbon micropores. Fig. 6 shows the typical synthesis of a modified PFR-derived hard-carbon aerogel (mPFR-HCA). Ferric nitrate nonahydrate, chitosan and acetic acid are added into deionized water to yield a sol. After that, phenol and formaldehyde are added into the as-obtained sol. After hydrothermal treatment (160 °C for 8 h), the as-obtained wet gel is freeze-dried. Next, the gel is heated under flowing nitrogen atmosphere at 800 °C for 4 h. Then, the ferruginous carbon aerogel is reacted with an excessive amount of concentrated nitric acid under 80 °C for 12 h to remove the Fe species, followed by repeatedly washing by deionized water until the pH reaches neutral, and finally drying under vacuum at 60 °C for 24 h to yield the mPFR-HCA.

In addition to the polymer template, the bio-templated synthesis method may also be a good choice. Zhao et al. reported a biomorphic mixed metal oxide (MMO) with a 3D network structure via a bio-templated method. A kind of legume with a specific tubular trichome on the surface was selected as the bio-template. Fig. 7 shows a schematic illustration of the fabrication of a bio-templated layered double
hydroxide (LDH) film and MMO framework from the legume. First, Al₂O₃ is coated uniformly on the surface of the legume via a low temperature atomic layer deposition (ALD) approach. Second, the ZnAl-LDH film, which holds the initial surface structure of the legume, is fabricated via an in situ growth method. Finally, the polycrystalline ZnAl-MMO with a 3D network structure is obtained via a sacrificial template method through calcination of the LDH film precursor, which is regarded as an efficient and recyclable photocatalyst for the degradation of dyes due to its huge specific surface area and 3D network structure.

The Lewis acid catalytic template method is also a good choice to fabricate 3D network structures. Bai et al. reported a facile furfural alcohol (FA)-derived polymerization–carbonization–combustion (FAPCC) method for the fabrication of single-component (such as SnO₂, WO₃, Fe₂O₃, CeO₂, CuO, NiO and Co₃O₄) and multi-component (TiO₂/WO₃) large-scale metal oxides with 3D network structures. The large-scale metal oxide with a 3D network structure holds a huge macromolecular scale and mesoporous nanostructure with a large pore volume and huge surface exposure area. The approach can also be adopted for the fabrication of nanoparticles loaded onto 3D network structures (such as Au/WO₃). The photocatalytic oxidation of azo dyes indicated that the large-scale metal oxides with 3D network structures possess high photocatalytic activity. Fig. 8 shows the schematic procedure for the generation of the SnO₂ with 3D network structure, where Mn⁺ = Sn⁴⁺. Here, SnCl₄, anhydrous ethanol and FA are mixed together forming a transparent solution with a yellow colour. Then, the solution is heated to 90 °C for 8 h. Owing to the Lewis acid catalytic effect of the Sn⁴⁺, the FA monomer increasingly polymerizes into cross-linked FAR. The cross-linked FAR includes plentiful functionalized hydroxyl groups. Hence, Sn⁴⁺ can bind the hydroxyl groups via a synergistic effect in the polymerization reaction, resulting in a uniform hybrid FAR-Sn composite. Finally, the carbon component in the FAR-M composite is eliminated via calcining and Sn⁴⁺ ions are oxidized to generate large-scale 3D network mesoporous SnO₂.

3.2 Self-assembly method

Self-assembly is also one of the most important methods for fabricating photocatalysts with a 3D network structure. Self-assembled biomolecular nanostructures can act as a skeleton for the nanoscale arrangement of chromophores to form lots of Förster-type resonance energy transfer (FRET), which improves the delocalization of excitation energy to catalysts for photocatalytic oxygen evolution. Kim et al. incorporated metalloporphyrins into a transparent and rigid 3D network of Fmoc-FF via an in situ self-assembly method. The self-assembled Fmoc-FF structure could promote the J-aggregation of the metalloporphyrin, which could promote the excitation energy transfer (EET). meso-Tetra(4-pyridyl)porphyrin (TPyP) was adopted since it holds four pyridyl groups in the meso-functional position, which could interact with the carboxylic and hydroxyl groups of the Fmoc-FF nanofibres (Fig. 9c). To fabricate the Fmoc-FF/TPyP composite hydrogel, Fmoc-FF, TPyP and a certain amount of 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) were mixed together and then diluted with DI water for 50-times. Fig. 9a and b indicate that the incorporation of the TPyP molecules could not influence the morphology of the Fmoc-FF nanofibres and the inherent β-sheet structure of the Fmoc-FF hydrogel was not changed. As shown in Fig. 9d, for free

Fig. 6 Schematic plot of the formation of the mPFR-derived hard-carbon aerogel. Reproduced with permission. Copyright 2016, American Chemical Society.

Fig. 7 Schematic plot of the formation of a bio-templated LDH film and MMO framework from the legume. Reproduced with permission. Copyright 2009, American Chemical Society.

Fig. 8 Schematic procedure for the fabrication of 3D mesoporous SnO₂ networks, Mn⁺ = Sn⁴⁺. Reproduced with permission. Copyright 2013, Nature Publishing Group.
SnTPyP, there is only a relaxation pathway. In contrast, an improved proportion of SnTPyP to Fmoc-FF could promote EET on account of the closer distance between the SnTPyP molecules, which prevents the degradation pathway of excited SnTPyP by the generation of a new relaxation style. Therefore, a higher catalytic activity was obtained.

Cong et al. reported a stretchable and self-healing graphene oxide (GO)/poly(acryloyl-6-aminocaproic acid) (PAACA) composite hydrogel.\textsuperscript{170} Fig. 10a illustrates two types of hydrogen bonding in the PAACA 3D network between the polar groups of the polymer side chains. Fig. 10b illustrates the helispherical double networks of the hydrogen-bonds and coordination interactions related to the generation process of the composite hydrogel. First, the powerful hydrogen-bonding networks came from not only the interactions of the PAACA side chains, but also from the polar groups of the PAACA side chains with the oxygen-related groups of GO. Second, the synergistic interactions of Ca\textsuperscript{2+} with both the oxygen-related groups of GO and the polar groups of the PAACA side chains contribute to the Ca\textsuperscript{2+}-induced 3D network. Fig. 10c and d show the SEM images of the GO-PAACA hydrogel. The interconnected 3D network of composite hydrogel consists of a pliable 3D porous structure with the sizes ranging from the sub-micrometre to several micrometres. Interestingly, no GO nanosheets were observed, since the GO nanosheets were almost overspread by polymers because of the hydrogen bond interactions between the polar functional groups of the PAACA side chains and the oxygen-related groups of GO.

Graphite carbon nitride (g-C\textsubscript{3}N\textsubscript{4}) is considered as one of the star materials on account of its adjustable electronic structure and outstanding physico-chemical stability.\textsuperscript{171} The self-assembly method is widely used to construct carbon nitride-based photocatalysts with a 3D network structure. Huang et al. reported a facile precursor pre-treatment method, through forming hydrogen bond-induced supramolecular aggregates, to construct g-C\textsubscript{3}N\textsubscript{4} with a simultaneous 3D network structure and controllable O-doping.\textsuperscript{172} First, melanine was treated by H\textsubscript{2}O\textsubscript{2} to form hydrogen-bond-induced supramolecular aggregates (MHP). Then the mixture was ground into powder and calcined at 550 °C for 2 h in a N\textsubscript{2} atmosphere to obtain g-C\textsubscript{3}N\textsubscript{4} with a simultaneous 3D network structure and O-doping (MCN). Owing to the synergistic interaction of the 3D network structure and O-doping, the light harvesting ability and charge separation efficiency were improved greatly and the solar-energy-driven hydrogen evolution activity was increased remarkably (AQE = 7.8% at 420 nm).

### 3.3 Sol-gel process

The sol-gel process is another commonly used method for constructing 3D network photocatalysts. Melone et al. reported hybrid metal oxide aerogels by a sol–gel process.\textsuperscript{173} Cellulose nanofibres (CNF) hydrogels and TiO\textsubscript{2}/SiO\textsubscript{2} or TiO\textsubscript{2} sols were first prepared. Then, the CNF hydrogels were mixed with TiO\textsubscript{2}/SiO\textsubscript{2} or TiO\textsubscript{2} sols and the mixtures then freeze-dried. Finally, ceramic aerogels were obtained by calcination at the proper temperature. Thermal treatment of the CNF-T and CNF-TS aerogels destructed the CNF structure and led to a pure inorganic matrix. Titanium oxides-based ceramic aerogels couple the physical properties of ceramic aerogels with TiO\textsubscript{2}, thus promoting the performance of pollutant photodegradation, selective organic photosynthesis, and antibacterial activity. Nardecchia et al. also reported the in situ preparation of amorphous calcium phosphate (ACP) and ciprofloxacin crystals (CFX) in the generation of chitosan hydrogels (CHI).\textsuperscript{174} Fig. 11a illustrates the transition from sol to gel with the increase in pH and time. First, the CHI aqueous solution in acetic acid is mixed with the CFX aqueous solution in acetic acid and a urea aqueous solution (including calcium-phosphate salts) through continuous stirring under an ice-cold bath. Then, the obtained solution is mixed with 0.175 mL fresh urease aqueous solution and then stirred for about...
0.5 h. The obtained apparent liquid mixture is then transferred into injection syringes and aged for gelation. Fig. 11b shows the SEM micrographs of the obtained ACP-CFX-CHI. The skeletons show a cellular nest-like structure. It is clear that ACP and CFX were successfully loaded onto the 3D network framework of the CHI hydrogel (Fig. 11c). The unique structure could provide some possibilities as multifunctional biomaterials in bone tissue repair, since it could unite multiple substances in the skeleton structure, which could enhance osteogenesis treatment and prevent bacterial infections after surgical skeleton implantation.

Chen and his co-authors presented a one-pot method to synthesis agar/polyacrylamide double-network (agar/PAM DN) hydrogels with highly recoverable and mechanical properties. The agar biopolymer was a strong gelling polysaccharide with a thermoreversible sol–gel transition. The agar becomes a gel under low temperature, while melting to a sol under high temperature. The sol–gel phase transition of the agar comes from the coil–helix structural transition under high or low temperature, which indicates that the phase transition is thermoreversible. As shown in Fig. 12, AM monomers, agar, a chemical cross-linker and UV-initiators were mixed in a water bath to form DN hydrogels by a heating–cooling–photo-polymerization method. Thanks to the distinct thermoresponsive character of the agar, the agarose was first dissolved at 90–95 ºC to generate linear macromolecules to generate a low-viscosity, transparent solution. Next, the solution was increasingly cooled down to room temperature, and the agar generated the first-network gel that was physically linked via the agar helix bundles. Finally, the loose chemically cross-linked PAM gel was generated as the second network by photo-initiation, and thus the agar/PAM DN gel was resoundingly prepared.

3.4 In situ polymerization
Conjugated polymers with a photoactive π-electron backbone and 3D network structure are widely used as stable heterogeneous photocatalysts. Wang et al. fabricated a conjugated porous polymer with a 3D network structure through the Sonogashira cross-coupling reaction via a high internal phase emulsion polymerization approach. Fig. 13a shows the preparation route of the conjugated porous polymer $B_2$-$FL_2$-$BBT$. $B_2$-$FL_3$ was prepared to test the photocatalytic activity of the dehalogenation reaction without the electron acceptor BBT. Fig. 13b and c show the SEM images of $B_2$-$FL_2$-$BBT$ and $B_2$-$FL_3$. The interconnected 3D network structures had cavities ranging from 10 to 20 mm, whereas the interconnected pores exhibited diameters from 0.5 to 1 mm. It was shown in tests that the obtained conjugated porous polymer $B_2$-$FL_2$-$BBT$ and $B_2$-$FL_3$ had good photocatalytic performance.
monolithic cross-linked polymers were insoluble under almost all of the usual organic solvents. The benzobisthiadiazole-based porous polymer exhibited high activity for the reductive dehalogenation of haloketones under visible light.

Similarly, Liu and his co-authors fabricated photolatently adjustable hydrogels, consisting of a polymer network containing titania nanosheets at all the cross-linking points. TINNs were dispersed in an aqueous solution containing water-soluble vinyl monomers, and the obtained translucent dispersion was exposed to light for 20 min under room temperature. Meanwhile, radical polymerization of the vinyl monomers occurred, resulting in a translucent hydrogel. The probable elementary steps of the photoinduced hydrogelation process were as follows. First, a photoinduced hydroxyl radical was generated by the TINNs from water. Then, in situ polymerization of the vinyl monomers through the photogenerated hydroxyl radical took place. Lastly, physical cross-linking of the polymer chains occurred by TINNs through noncovalent interactions.

### 3.5 Hydrothermal/solvothermal method

The unique physical properties and 2D structure of graphene make it a suitable building block for fabricating graphene hydrogels with a 3D network structure. These 3D network architectures show high specific surface area and quick mass and electron transport kinetics on account of the outstanding 3D network structure and the excellent inherent photoelectronic property. More than that, the 3D network structure is enhanced as the reaction progresses, which promotes a degree of π–π stacking cross-links between the graphene sheets.

#### 3.6 Other methods

Other than the above-mentioned commonly used methods, there are also all kinds of special-interest methods to construct a 3D network structure. For example, the low temperature reduction method is also widely adopted to fabricate 3D network graphene hydrogels. Hou et al. reported graphene hydrogels and functionalized composite hydrogels through the introduction of P25 nanoparticles or multi-walled carbon nanotubes (MWCNTs) via a low temperature reduction method. GO was first prepared through Hummers’ method. Hydrazine hydrate and L-ascorbic acid were then dispersed to GO aqueous solution via ultrasonication. Then, the mixture was left to stand at room temperature for approximately 8 h. Lastly, the rGO hydrogels were doused in water to eliminate by-products. Composite hydrogels were obtained through a similar method, except that a certain amount of P25 or MWCNTs were dispersed in the GO aqueous solution. As shown in Fig. 15, the π-conjugated structures of reduced GO sheets are enhanced as the reaction progresses, which promotes a degree of π–π stacking cross-links between the graphene sheets.

![Image](https://example.com/image.png)

**Fig. 14**  (a) Schematic of the preparation of porous GHAs via a hydrothermal co-assembly method. The photographs of Au-NPs, TiO2-NPs, CNTs, PANI-NFs, MnO2-NWs, InN-NWs and Zn2SnO4-NWs in (b) water and (c) GO aqueous suspension. (d) Photograph and (e) SEM image of rGO/TiO2-NP hybrid architecture. (f) Photograph of the mixed rGO/TiO2-NP/InN-NW suspension. (g) Photograph and (h) SEM image of the rGO/TiO2-NP/InN-NW hybrid architecture. Reproduced with permission. Copyright 2014, Wiley-VCH.

![Image](https://example.com/image.png)

**Fig. 15** The schematic plots of the generation of (1) graphene hydrogels, (2) P25–graphene hydrogels, and (3) P25–MWCNTs–graphene hydrogels. Reproduced with permission. Copyright 2012, Elsevier.
coalescing or partial overlapping of the soft graphene sheets leads to fabrication of the 3D network structure. The residual oxygen-related functional groups on the graphene sheets can hold abundant water in the graphene network to generate graphene-based hydrogels. Ti–O–C bonds are generated between P25 nanoparticles and graphene sheets in P25–graphene hydrogels. However, as for P25–MWCNTs–graphene hydrogels, the P25 are loaded on the MWCNTs, which holds back interactions between P25 and graphene. Therefore, whether or not there were chemical bonds between the nanoparticles and graphene sheets is the key difference between the P25–MWCNTs–graphene and the P25–graphene hydrogels.

The ion-exchange/activation combination approach is also a good choice to generate a 3D hierarchical porous graphene-like (3D HPG) material, and involves adopting a metal ion-exchange resin as a carbon precursor. As shown in Fig. 16a, the synthesis of 3D HPG can be ascribed to the following two necessary steps. First, the graphitization of the resin could be carried out through the ion-exchange resin exchanging catalytic ions, such as Ni²⁺. Second, KOH could be put into the exchange resin and heated to generate a huge surface area and greatly graphitized 3D HPG materials. The obtained 3D HPG possesses plentiful micro- and mesopores, which could offer a large surface area. The large capacitance and sub-micrometre-sized macropores could generate ion-buffering reservoirs and offer a short diffusion distance to the interior surfaces, and the interconnected micro-, meso-, and macropores, which could offer ion channels to promote ion transportation, while the graphene-like structure provides outstanding electronic conductivity and excellent electrochemical stability, leading to the outstanding rate capability and excellent stability.

The anodic oxidation method is also an excellent candidate to fabricate a 3D network structure. Liu et al. presented an electrostatic-assisted method of loading gold nanoclusters (AuNCs) onto the TNA electrodes to fabricate a 3D network structure. First, TiO₂ nanotube arrays (TNAs) were dipped into hydrochloric acid solution for 1 h, leading to a positively charged surface of TNAs. The AuNCs possessed a negatively charged surface since there were lots of deprotonated carboxyl groups in the ligands of the AuNCs. Then, the acid-treated TNAs were dipped into the AuNCs for 48 h. The strong electrostatic effect results in the loading of the AuNCs onto the TNA surface. Fig. 17 shows the FESEM images of: (a and b) AuNC/short-TNA and (c and d) AuNC/long-TNA. The loading of AuNCs could extend the absorption of visible light and promote the photocatalytic oxidation of pollutants. The synergetic effect between the photocatalytic and electrochemical processes could be ascribed to the matching of the energy levels between the TiO₂ and photosensitizers (Fig. 17e).

4. Applications of 3D network photocatalysts

4.1 Applications concerning solar energy storage and conversion

Photocatalysts with a 3D network structure are widely adopted in the area of solar energy conversion and storage thanks to the advantages of a huge specific surface area and an interconnected open-framework, which is able to exhibit more active sites, offer a short diffusion distance to the interior surfaces and accelerate the catalytic surface reactions. Banerjee et al. reported that chalcogels containing FeMoS inorganic clusters are able to photoreduce N₂ to NH₃ under white light irradiation, room temperature and ambient pressure. The chalcogels consisted of [Mo₅Fe₂S₈(SPh)₃]⁴⁻ and [Sn₂S₆]⁴⁻ clusters. The initial N₂ binding point was a FeMoS core cluster, which could be reduced through other nearby iron-sulphur
clusters. These chalcogels possessed multiple immobilized FeMoS active points, which possessed a pretty high spatial density of these sites densely and closely introduced into a 3D matrix. The high density of clusters promotes the performance of multielectron transformations. That is to say, the photoactive chalcogels are a nice mimic of nitrogenases but with the additional character of good light harvesting, which is generally a property of semiconductors and photosynthetic centres. Ammonia was detected by UV-vis spectra (Fig. 18B), and the concentration gradually increased with time (Fig. 18A). Fig. 18C shows the kinetic plot exhibiting the increasing ammonia yield detected by ion chromatography (Fig. 18D). Isotopic labelling experiments were adopted to demonstrate that N₂ was the source of NH₃. 2D ^1H-^15N heteronuclear single quantum coherence (HSQC) NMR spectroscopy was also adopted, where ^15NH₄⁺ was certainly confirmed in solution with the typical ^15N-^1H coupling ^3J_N-H = 72 Hz (Fig. 18E and F).

Liu et al. then presented other nitrogenase-mimic Fe-related chalcogels as photoinduced nitrogen-fixation catalysts. Redox-active bioinspired Fe-related sulphide clusters could generate photoexcited states with a high energy that bind and reduce N₂ to NH₃. Fig. 19a and b show the ^1H NMR of NH₄⁺ for the obtained samples in a typical photocatalytic reaction. Fig. 22c shows NH₄⁺ generation from the photoinduced reduction of N₂. As shown in Fig. 19c, Mo₂Fe₆S₈(SPh)₃ with Fe₄S₄ clusters coexisting in one single chalcogel structure could promote NH₃ formation over Mo₂Fe₆S₈(SPh)₃ alone, while the Fe₄S₄-only chalcogel (FeS-SnS) not only showed activity in photocatalytic N₂ fixation but showed more NH₃ production. DRIFTS was used to detect the binding events or probable intermediates in the early process of the reaction (Fig. 19d).

Two peaks at 1753 and 1746 cm⁻¹ were observed, which were attributed to the N–N stretching mode of the M–N–N moiety (Fig. 19e). When D₂O was adopted instead of H₂O, the peak at 1746 cm⁻¹ shifted to 1724 cm⁻¹, whereas the peak at 1753 cm⁻¹ didn’t change (Fig. 19f), which indicates that H was only related to the stretching mode of M–N–N species at 1753 cm⁻¹. When ^15N₂ was adopted instead of ^14N₂, a new peak at 1687 cm⁻¹ was detected with the time increasing (Fig. 19g). The isotopic peak shift of about 66 cm⁻¹ from 1753 cm⁻¹ to 1687 cm⁻¹ demonstrated that N₂ could bind to the chalcogel through light irradiation. Through original generation of the M–N–N intermediates, proton and electron transfer could take place followed by an additional light-generated electron reduction and protonation until the N≡N bond splits to NH₃. DFT calculations also demonstrated that the generation of the M–N≡N intermediate from N₂ binding to multiply reduced Mo₂Fe₆S₈(SPh)₃ and Fe₄S₄ clusters is viable, which could activate N₂ towards final NH₃ formation.
In addition to photocatalytic N₂ fixation, photocatalysts with a 3D network structure are also widely adopted in hydrogen production. Weingarten et al. fabricated a hydrogel skeleton through the perylene monoimide amphiphilic supramolecular self-assembly for photocatalytic hydrogen production. Fig. 20 shows the chemical constitution of a water-soluble proton-reduction photocatalyst. Fig. 20a shows the chemical constitution of a water-soluble proton-reduction photocatalyst. Fig. 20b shows the chemical constitution of a water-soluble proton-reduction photocatalyst. A photocatalytic gel was also fabricated by adopting PDDA on glass (Fig. 20f). Executing photocatalysis on a support is able to offer merits in the process technology for recycling. When the gels were dried on glass ahead of immersion in the ascorbic acid/catalyst solution, diminished H₂ production was observed, which indicates that gel rehydration is infeasible, which then demonstrates the necessity of the 3D network for H₂ generation. When filling the anodic aluminium oxide (AAO) membrane with CA, lower TON was exhibited compared to the TONs of gels cast on glass slides. Nevertheless, when converting the data according to TON per CA, it was discovered that the AAO samples showed the highest TON per CA value.

Polymer photocatalysts with a 3D network structure also play an important role in photocatalytic hydrogen generation. Schwab et al. reported a 3D conjugated poly(azomethine) network photocatalyst for efficient hydrogen evolution. The calculations on the model segments indicated that the frontier orbitals were centred on the B2 parts of the strut, indicating their possibilities for modification (Fig. 21a and b). As shown in Fig. 21c, all the samples gradually showed steady H₂ generation. The production rate was discovered to highly depend on the core size of the B2 unit of the network and persistently increased to the maximum of 7 μmol h⁻¹ as for ANW 2. In particular, there was no evident decline for ANW 2 when the sample was exposed to sequential photocatalytic tests for 20 h (Fig. 21d), demonstrating that the poly(azomethine) backbone was stable.

4.2 Synergistic removal of adsorption-enrichment and photocatalytic degradation

Water pollution can seriously threaten human health, and is a major type of environmental pollution. The 3D network materials have attracted lots of attentions on account of their excellent performance of adsorption and enrichment of pollutants. However, most of the pollutants were only enriched instead of degraded totally in most instances. Even worse, only when the photocatalysts underwent intricate desorption treatment could they be reused. Hence, photocatalysts with both properties of adsorption and photodegradation are imperative to meet these requirements. Zhang et al. reported that semiconductor nanoparticles could be adopted for triggering the polymerization of monomers under light irradiation and for cross-linking to generate composite hydrogels with the help of clay nanosheets. The nanocomposite (NC) hydrogel could retain the semiconductor nanoparticle character after immobilization, which allowed it to exhibit outstanding mechanical strength and enables the recyclable photodegradation of pollutants. As shown in Fig. 22a, semiconductor DMAA, clay and NS NPs were dispersed as precursors. The semiconductor...
NPs could trigger polymerization in light irradiation to generate inorganic-PDMA brushes and a 3D network NC hydrogel through the further cross-linking of the brushes. As shown in Fig. 22b, the obtained ZnO-NC gel is tough and translucent under light illumination for about 1 h. The SEM images indicate that anomalous pores with different sizes were obtained (Fig. 22c). Bio-cutting TEM analysis demonstrated that agglomerative NPs and individual clay-NS particles were dispersed in the gel (Fig. 22d). As illustrated in Fig. 22e, the TiO2-NC hydrogel could concentrate plenty of MBs to generate a dark blue hydrogel through the electrostatic effect. The maximum adsorbing capacity of MB in the first round was 59.5 mg g\(^{-1}\) for the dried hydrogel (Fig. 22f). The deep blue hydrogel in 5 times excess of water could recover to be pale blue under UV irradiation for 2 h by the loaded TiO2. Furthermore, the photoinduced holes at the VB of TiO2 can be transferred to the HOMO of PANI and then transferred via the immobilized photocatalyst. The adsorbing capacity of MB after 2 runs could still retain 86.3% of the capacity of the fresh hydrogel.

Although the above-mentioned method could realize the recyclable photodegradation of pollutants, the operation is still far too complicated. Jiang and his co-author presented a method of synergistic removal of adsorption–enrichment and photocatalytic degradation through a flow or dynamic system.\(^{73}\) Fig. 23a shows a schematic illustration of the photocatalytic evaluation equipment for the flow system. Liquid flows through Beaker 1 and the reactor and finally flows into Beaker 2. The power is provided by a peristaltic pump. At a certain time, a certain number of samples are taken from the reactor. It is not necessary to centrifuge the samples and the samples can thus be directly analysed. As shown in Fig. 23b, the elimination rate of MB increases with the drop in the flow rate, indicating that a shorter time is needed to reach adsorption–desorption equilibrium as the flow rate increases. Fig. 23c–e demonstrate that the composite exhibits a high removal rate for cationic dye (MB), anionic dye (MO) and phenol. Fig. 23f illustrates the synergistic removal mechanism of the PANI/TiO2 composite hydrogel in UV light. First, pollutants are adsorbed and concentrated onto the surface of the TiO2 nanoparticles via the 3D network structure of the PANI hydrogel. The pollutants are then in situ oxidized in UV light illumination. Therefore, the synergistic elimination of the adsorption and photocatalysis is realized. Furthermore, the photoinduced holes at the VB of TiO2 can be transferred to the HOMO of PANI and then transferred away via the 3D network structure of the PANI hydrogel, which promotes the separation efficiency of the photoinduced carriers and increases the catalytic performance. This work facilitates the potential application of composite hydrogels for the synergistic elimination of all kinds of pollutants in the field of water protection.

After that a series of g-C\(_3\)N\(_4\)-based composite hydrogels were fabricated for the synergistic removal of environmental pollutant by Zhu’s group.\(^{72,74,75}\) Jiang et al. reported the fabrication of a polyaniline (PANI)/carbon nitride nanosheets (CNNS) composite hydrogel with a 3D network structure through a polymerization method.\(^{74}\) The 3D network structure was stable and robust, which meant that the composite hydrogel was separation-free and easy to recycle. It was also efficient in eliminating pollutants for PANI/CNNS composite hydrogel thanks to the synergy of the adsorptive enrichment and photocatalytic degradation. As shown in Fig. 24a, CNNS can be formed through the thermal oxidation etching of bulk carbon nitride (BCN) under an air atmosphere. Then, CNNS, phytic acid and aniline are mixed together. After dropping (NH\(_4\))\(_2\)S\(_2\)O\(_8\), dendritic PANI nanofibres are generated between layers of the CNNS through polymerizing aniline, which fabricates the 3D network structure of the composite hydrogel. As shown in Fig. 24b, the maximum elimination rate of PANI/CNNS-5% was 79.2% at 1 h. When the adsorption–desorption equilibrium was finished, the elimination rate still maintained 56.2%, demonstrating that the composite hydrogel was stable and did not flow away. In contrast, both CNNS and BCN exhibited a gradually reduce removal rate, indicating that CNNS and BCN flowed away.
In addition to the above organic hydrogels, an inorganic hydrogel was also adopted to fabricate the g-C3N4-based composite hydrogel. For example, 3D network separation-free graphitic carbon nitride/SiO2 (C3N4/SiO2) composite hydrogels were constructed through an alkali-solution and acid–gel approach (Fig. 24e). The 3D network structure made certain the C3N4/SiO2 composite hydrogels could be used in succession ruling out the adsorption saturation problem, which could inhibit aggregation and secondary pollution of the photocatalysts. As shown in Fig. 24f, on account of the synergistic effect of adsorption and photocatalytic oxidation, MB could be eliminated by 90%-C3N4/SiO2 composite hydrogel in succession. The elimination rate of MB through the composite hydrogel was 5 times higher than that of the pure g-C3N4. Furthermore, the total organic carbon content (TOC) following the C3N4/SiO2 hybrid hydrogel for the typical coking wastewater was about 33%, which is 4 times higher than that of pure g-C3N4.

Graphene hydrogel is also an excellent candidate for the fabrication of graphene-based composite hydrogels. Li et al. reported the elimination of Cr(vi) via 3D TiO2–graphene hydrogel in a flow system. As shown in Fig. 25a, the TiO2-rGH composite exhibits a 3D network structure, which provides a large accessible surface area and exhibits greatly connected pores. TiO2 nanospheres were evenly dispersed on the rGO sheets. As shown in Fig. 25b, the adsorption rate of Cr(VI) began to decrease at 3 h, while the adsorption sites of TiO2-rGH increasingly reached saturation. After 18 h, the TiO2-rGH composite hydrogel reached total saturation and the adsorption of Cr(vi) was not detected. In comparison, the adsorption–photocatalytic activity stayed the same within 15 h under the same experimental conditions. After 15 h, the Cr(vi)-elimination rate began to drop till a new equilibrium state was obtained (86%). Fig. 25c shows the results of the test for TiO2-rGH in alternating dark–light cycles in flow systems. It was found that no Cr(vi) elimination was observed after stopping the UV light.
demonstrating that the adsorption sites of TiO$_2$-rGH reached saturation after the equilibrium point. When re-introducing the UV light, the Cr$_{(v)}$-elimination rate came to the initial level at the equilibrium point, indicating that Cr$_{(v)}$ was reduced on the TiO$_2$-rGH surface.

Yang et al. reported a visible-light 3D–3D Bi$_2$WO$_6$/graphene hydrogel (BWO/GH) photocatalyst through the synergy of adsorption and photocatalysis via a facile one-step hydrothermal method.$^{28}$ Fig. 25d shows the FE-SEM images of the morphology and microstructure of the BWO/GH composite hydrogel. GH shows a 3D porous network structure with interconnected pores composed of randomly oriented GO nanosheets. The 3D flower-like BWO grew homogeniously into the framework of GH in the composites. Long-time photodegradation tests of 2,4-CDP and MB solutions in dynamic system were conducted to further investigate the synergistic effect of the BWO/GH composite hydrogel (Fig. 25e and f). As shown in Fig. 25e, the pure BWO almost had no ability to eliminate 2,4-CDP in solution, whereas the 78.31%-BWO/GH showed a distinct elimination ability for 2,4-CDP, which was about 4 times as high as that of the pure BWO. Fig. 25f shows the photocatalytic stability test of the BWO and 78.31%-BWO/GH composite. When the illumination time reached 74 h, the elimination rate of MB by the pure BWO was 25.2%, while the elimination rate of MB by the 78.31%-BWO/GH composite was still 36.1%, which demonstrated that the BWO/GH composite was very stable.

5. Conclusions and perspectives

3D photocatalysts with a network structure have been attracting enormous research interests on account of their excellent properties, such as huge specific surface area, high adsorptive capacity and more exposed active sites, which can facilitate adsorption and photoreaction and accelerate catalytic surface reactions. There have been all kinds of methods reported for fabricating 3D network structures; however, different materials require different techniques. There is no universal method that is applicable to all materials. In addition, many of the existing methods are either too complicated or are environmentally unfriendly. Therefore, new techniques are still needed to construct 3D network structures. In addition, as for the loaded type photocatalysts, supporting materials are used as a framework and photocatalysts are then loaded onto the framework, which usually then act as the active sites. However, the loading capacity of photocatalysts in most cases is not high enough. Therefore, the loading capacity of photocatalysts should be improved urgently via novel methods.

The 3D photocatalysts with network structure have been widely used in the field of solar energy conversion and for pollutant elimination, such as water splitting, CO$_2$ reduction, N$_2$ fixation, organic synthesis and pollutant degradation. However, their photocatalytic efficiency is still far from satisfactory due to the high charge recombination probability and severe thermodynamic constraints. In our opinion, photoelectric synergy may be a good choice to solve these problems, since an external electric field could help promote the charge separation and migration efficiency and overcome the severe thermodynamic constraints. In this sense, photoelectric CO$_2$ reduction, N$_2$ fixation or environmental elimination through 3D network photocatalysts may become a new research highlight. Furthermore, haze has been becoming a serious threat to human health recently. Conventional adsorption materials can only adsorb harmful substances. Once adsorption saturation is reached, the adsorption efficiency will be greatly reduced. However, 3D photocatalysts with a network structure may be excellent candidates to solve this problem since the synergistic removal of adsorption–enrichment and photocatalytic degradation could be realized.

In this review, we concluded the superiorities of 3D network photocatalysts and summarized the common 3D photocatalysts and their synthetic strategies. Furthermore, the important applications including solar energy storage and conversion and photocatalytic pollutant degradation, were also discussed. We hope that this review could promote greater scientific interest in the controllable synthesis and potential environmental and energy-related applications of 3D network photocatalysts.

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