available at www.sciencedirect.com

journal homepage: www.elsevier.com/locate/chnjc

Review

Interfacial engineering of graphitic carbon nitride (g-C₃N₄)-based metal sulfide heterojunction photocatalysts for energy conversion: A review

Yijie Ren ^a, Deqian Zeng ^{b,#}, Wee-Jun Ong ^{a,c,*}^a School of Energy and Chemical Engineering, Xiamen University Malaysia, Selangor Darul Ehsan 43900, Malaysia^b School of Resources, Environment and Materials, Guangxi University, Nanning 530004, Guangxi, China^c College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, Fujian, China

ARTICLE INFO

Article history:

Received 18 November 2018

Accepted 28 December 2018

Published 5 March 2019

Keywords:

Graphitic carbon nitride

Metal sulfide

Photocatalysis

Energy transformation

Water splitting

Reduction of carbon dioxide

Pollutant degradation

Nitrogen fixation

ABSTRACT

As one of the most appealing and attractive technologies, photocatalysis is widely used as a promising method to circumvent the environmental and energy problems. Due to its chemical stability and unique physicochemical, graphitic carbon nitride (g-C₃N₄) has become research hotspots in the community. However, g-C₃N₄ photocatalyst still suffers from many problems, resulting in unsatisfactory photocatalytic activity such as low specific surface area, high charge recombination and insufficient visible light utilization. Since 2009, g-C₃N₄-based heterostructures have attracted the attention of scientists worldwide for their greatly enhanced photocatalytic performance. Overall, this review summarizes the recent advances of g-C₃N₄-based nanocomposites modified with transition metal sulfide (TMS), including (1) preparation of pristine g-C₃N₄, (2) modification strategies of g-C₃N₄, (3) design principles of TMS-modified g-C₃N₄ heterostructured photocatalysts, and (4) applications in energy conversion. What is more, the characteristics and transfer mechanisms of each classification of the metal sulfide heterojunction system will be critically reviewed, spanning from the following categories: (1) Type I heterojunction, (2) Type II heterojunction, (3) p-n heterojunction, (4) Schottky junction and (5) Z-scheme heterojunction. Apart from that, the application of g-C₃N₄-based heterostructured photocatalysts in H₂ evolution, CO₂ reduction, N₂ fixation and pollutant degradation will also be systematically presented. Last but not least, this review will conclude with invigorating perspectives, limitations and prospects for further advancing g-C₃N₄-based heterostructured photocatalysts toward practical benefits for a sustainable future.

© 2019, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

Published by Elsevier B.V. All rights reserved.

1. Introduction

With the gradual improvement of people's living standards and the arrival of industrialization, the energy shortage and serious environmental pollution caused by the massive use of fossil fuels have become two major problems that human beings have to face in the 21st century. It is reported that the con-

sumption of global primary energy in 2013 was ca. 17 TW. Based on an investigation, it is anticipated that global energy demand will require two times its current energy supply by 2050 [1]. To date, almost 90% of the global energy supply is supplied by the carbon-based fuels, namely natural gas, coal and oil [2]. Thus, solar energy acting as one of the main energy sources for sustainable development is considered as a good

* Corresponding author. Tel: +603-87055149; E-mail: weejun.ong@xmu.edu.my, ongweejun@gmail.com

Corresponding author. E-mail: dqzeng@gxu.edu.cn

DOI: S1872-2067(19)63293-6 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 40, No. 3, March 2019

remedy to address this global issue. It is interesting to know that the energy provided by sunlight hitting the earth's surface every hour can in fact meet the world's energy needs for one year [3]. Photovoltaic-assisted electrolysis (PVE), photoelectrochemical (PEC) cells and photocatalysis are the three major types of solar energy conversion systems at present [4–20]. Amid all technologies, photocatalysis has become the most appealing approach to utilize solar energy as an inexhaustible energy resource [21–32].

By and large, photocatalysis is the reaction of semiconductor photocatalyst to catalyze redox reaction of reactants under light condition [33–37]. Generally, the photocatalytic reactions can be divided into three basic steps. First, light absorption: upon sunlight irradiation, the semiconductor photocatalysts absorb effective photons whose energy ($h\nu$) is equal to or exceed the optical bandgap (E_g), which will result in the generation of electrons in the conduction band (CB) and holes in the valance band (VB), denoted as charge carriers or electron-hole pairs. Second, charge separation and transfer: the charge carriers generated in the first step will be transferred to the surface of photocatalysts. Third, surface reactions: the photogenerated electrons and holes participate in the reduction and oxidation (redox) reactions of substances adsorbed on the surface of the photocatalysts [38–41].

Although the photocatalytic technology made a lot of progress in the last decade, the photocatalytic performance of the currently known photocatalysts is still below par for the commercial application. It is a well-known fact that in order to compete with the present fossil-fuel technology, the solar-to-hydrogen (STH) conversion efficiency should reach around 10% of hydrogen production to endow a competitive advantage [42]. Therefore, it is of utmost importance to seek for robust and stable solar-light-driven photocatalysts as the core to ameliorate the catalytic efficiency.

Since the pioneering work by Fujishima et al. [43] in 1972 which has spanned for the past 46 years, a plethora of potential ultraviolet (UV)-active and visible-light-active photocatalysts have been extensively employed such as TiO_2 , ZnO , SrTiO_3 , CdS , In_2S_3 , BiOBr , Bi_2MoO_6 , Ag_3PO_4 and so forth [44–53]. Despite the research has made countless progress, there is still no robust and commercially available photocatalyst that could meet all requirements up to now, including toxic-free, high efficiency, high chemical stability, cost-effective and robust performance. As the most widely used “golden” material, TiO_2 almost accounts for three-fifths of all photocatalytic research [54–60]. Although it is the most popular photocatalyst material due to its high chemical inertness, safety and robust reactivity, the large band gap of TiO_2 restricts the utilization of visible light [61,62]. In other words, it can only use the UV light in the sunlight, accounting for only 4% of the solar spectrum [63]. Apart from the conventional TiO_2 , most metal oxides have a very wide band gap [64,65]. Precious metals (e.g. Pt and Pd) though superior in performance, are limited for potential applications owing to their high price and scarcity. Phosphating materials (e.g. Ni_2P , CoP) suffer from the difficulty of synthesizing because of the complex preparation methods [66–69]. Not only that, the metal sulfide semiconductor is also hindered by photocorro-

sion, whereby the hydroxyl radicals generated by electron-hole pairs will oxidize the sulfur ions on the metal sulfide [70–72]. As a result, this leads to weak stability, which is the main “bottleneck” of photocatalysts in order to satisfy the requirement for commercial applications. From the viewpoint of chemical kinetics, the time of these redox reactions from the generation of electron-hole pairs to produce fuels are always in the time span of 10^{-6} – 10^{-12} [73]. Such a long time span is a big challenge to control the reaction kinetics.

In 2009, Wang et al. [74] first reported the use of two-dimensional (2D) metal-free $\text{g-C}_3\text{N}_4$ semiconductor photocatalyst, which was active under visible light for the H_2 evolution. Since then, $\text{g-C}_3\text{N}_4$ has gained considerable interdisciplinary attention with ample advances and breakthrough [75,76]. This fascinating conjugated polymer endow a magnificent prospect in the arena of energy and environmental science thanks to its appealing electronic band structure, medium band gap (~ 2.7 eV), and excellent chemical and thermal stability [77,78]. In addition, the earth-abundant carbon and nitrogen elements in $\text{g-C}_3\text{N}_4$ can be facily prepared by nitrogen-rich precursors, namely urea, thiourea, melamine and dicyandiamide. In the course of the $\text{g-C}_3\text{N}_4$ research, the triazine (C_3N_3) and tri-s-triazine/heptazine (C_6N_7) rings were found to be the basic tectonic units to form allotropes of $\text{g-C}_3\text{N}_4$ [79,80]. It is generally recognized the tri-s-triazine as the building block for the formation of $\text{g-C}_3\text{N}_4$. Compared with the widely used photocatalyst TiO_2 , $\text{g-C}_3\text{N}_4$ has a lower band gap attributed to the presence of sp^2 -hybridized carbon and nitrogen, which establishes the π -conjugated electronic structures. In addition, the aromatic C-N heterocycles of the $\text{g-C}_3\text{N}_4$ make it excellent thermal stability, which can be stable up to ca. 600 °C in air. To date, $\text{g-C}_3\text{N}_4$ has been widely employed in the breadth of nanoscience research for multifunctional applications, including remediation of environmental pollutants, water splitting, reduction of carbon dioxide, nitrogen fixation, hydrogen peroxide production and organic synthesis and bacteria disinfection [81–93]. Nevertheless, the activity of bare $\text{g-C}_3\text{N}_4$ is still hampered for large scale applications [94]. The quantum efficiency of photocatalytic reaction using bare $\text{g-C}_3\text{N}_4$ is merely 0.1% at 420–460 nm [95], which is unable to meet the requirement for practical benefits. This is ascribed to the inadequate optical absorption in the range of visible light, low specific surface area, poor electric conductivity as well as rapid recombination rate of charge carriers [1,75,96]. To circumvent the above burgeoning challenges, a broad range of modifications have been employed to improve the performance of bare $\text{g-C}_3\text{N}_4$ such as doping [97,98], surface sensitization [99], introducing defects [100–104] or amorphous disorder layers [105,106], and combining $\text{g-C}_3\text{N}_4$ with metals, carbonaceous materials, metal chalcogenides, metal phosphides, metal carbides or other semiconductors [107–122] to form intact heterojunction interfaces.

The terms “ $\text{g-C}_3\text{N}_4$ ”, “graphitic carbon nitride” and “photocatal*” have become the frequent topic keywords in the Web of Science database (Fig. 1). This is an undoubted evidence to elucidate the great interest of research in $\text{g-C}_3\text{N}_4$ -based photocatalysts field. Among these typical strategies, the construction of a semiconductor heterojunction interface between two dis-

Fig. 1. (a) Annual collections of published items and (b) total number of citations using “g-C₃N₄”, “graphitic carbon nitride” and “photocatal*” as the topic keywords since 2009. Adapted from the Web of Science, dated 8th November 2018.

similar semiconductors has become a hot research area attributed to the intimate contact interface formed by the heterojunction. The formed interface can make up for the shortcomings of g-C₃N₄ such as low charge separation and visible-light absorption. Besides that, the well-defined electronic structure and band gap configuration due to the construction of heterojunction interfaces can efficiently boost the photocatalytic activity [63,123–125]. Since the seminal report on g-C₃N₄ photocatalysts in the H₂ evolution was published, there is a significant growth with respect to g-C₃N₄-based heterojunction nanocomposites. So far, there are seven categories of heterojunction photocatalysts: (1) metal-free g-C₃N₄-based heterojunction, (2) g-C₃N₄/metal oxide heterojunction, (3) g-C₃N₄/metal sulfide heterojunction, (4) g-C₃N₄/halide heterojunction, (5) g-C₃N₄/transition metal heterostructures, (6) g-C₃N₄/noble metal heterostructures, and (7) g-C₃N₄-based complex system. Among all types of heterojunction systems, the modification of g-C₃N₄ with metal sulfide has been regarded as an appealing pursuit, which warrants further review along this topic. In addition to constructing heterojunction between g-C₃N₄ and metal sulfide semiconductor [126–130], metal sulfides can play the role of co-catalysts to significantly increase the photocatalytic efficiency [130–134]. Compared with other materials, metal sulfides possess suitable band structures that can meet the thermodynamic requirement for water splitting and improved sunlight responses than many oxides ascribed to the higher valence band (less negative) formed by S3p orbitals. These excellent properties of sulfides make g-C₃N₄/metal sulfide heterojunction systems better photocatalytic performance [135]. Thus, the incorporation with metal sulfide serves as a tangible benefit for the desired photocatalytic reactions by forming tunable band structures [136], which will be auspicious in prolonging the lifetime of charge carriers and enhancing the charge separation efficiency.

A number of fascinating reviews pertaining to g-C₃N₄ have been largely published especially in the past 3 years, focusing on preparation techniques, characteristics, charge mechanism and promising applications [137–149]. With such increasing number of published works in g-C₃N₄ photocatalysis up to now, herein we will provide an updated review article on the

state-of-the-art advancement of g-C₃N₄ hybridized with transition metal sulfide for photocatalytic energy applications. This encompasses water splitting for hydrogen evolution, CO₂ reduction to energy fuels and N₂ fixation. Specifically, this review article puts an emphasis on the recent progress in metal sulfide-modified g-C₃N₄ photocatalysts over the past 4 years from the aspects of design, fabrication, charge separation and energy applications. This review is then concluded with a summary of outlooks, opportunities and perspectives on this pacy field. As such, we strongly believe that this work will stimulate new horizons and insights into the potential development of next-generation g-C₃N₄-based photocatalysts in the realm of energy and environmental sciences.

2. Pristine g-C₃N₄ and modified g-C₃N₄

2.1. Preparation of pristine g-C₃N₄

g-C₃N₄ as a semiconductor with superior performance consists of carbon and nitrogen elements, which are highly abundant in the earth. By direct condensation of nitrogen-rich organic precursors such as melamine, urea, dicyandiamide and thiourea, this results in the development of g-C₃N₄. Thus far, various synthesis techniques have been employed to prepare g-C₃N₄, including plasma sputtering reaction deposition [150,151], solvothermal [152], thermal polycondensation [153,154], and chemical vapor deposition [155]. Owing to its low cost and facile synthesis process, thermal polycondensation is largely applied for synthesizing g-C₃N₄ as reported in myriads of publications [153,154]. The choice of precursor, reaction temperature and reaction environment all exhibit significant effects on the surface chemical properties and electronic band structures of the as-prepared g-C₃N₄, leading to a different practical application [153,156]. A case in point, g-C₃N₄ synthesized at 650 °C could be used as a photoelectrochemical sensor to detect the existence of dye and estimate its concentration [157]. The detailed preparation of g-C₃N₄ from the aspects of precursor selections and reaction conditions has been comprehensively reviewed in our previous review article [1].

2.2. Modification strategy of pristine $g\text{-C}_3\text{N}_4$

How to make full use of sunlight, especially the visible-light region which accounts for more than 40% of the solar energy, extensive efforts have been done to enhance the photocatalytic performance of $g\text{-C}_3\text{N}_4$. Typically, for an artificial photosynthesis system, the solar energy-to-chemical energy conversion efficiency ($\eta_{\text{SE-CE}}$) is influenced by the three main processes: (1) light harvesting (LH), (2) charge separation and transfer (CST) and (3) final catalytic reactions (CR) [73]. These three processes account for the efficiency: $\eta_{\text{SE-CE}} = \eta_{\text{LH}} \times \eta_{\text{CST}} \times \eta_{\text{CR}}$. Among the three crucial steps, CST is considered as the primary influencing factor of reaction rate that governs the main catalytic reactions. It is commonly accepted that several pivotal requirements must be considered for potential applications: (1) the photocatalyst must have a narrow band gap to enhance the efficiency of solar light absorption. (2) The photogenerated electron-hole pairs can be efficiently separated and transferred. (3) High activity and stability of photocatalyst are of paramount importance. To date, scientists have made tremendous efforts to improve the efficiency of $g\text{-C}_3\text{N}_4$ through various design strategies [81,82,158–167]. As one of the major routes to enhance $g\text{-C}_3\text{N}_4$ through defect engineering, vacancy and elemental doping play essential roles to enhance the activity of $g\text{-C}_3\text{N}_4$ [168–173]. In view of the extremely large theoretical specific surface area of monolayer $g\text{-C}_3\text{N}_4$ ($2500 \text{ m}^2 \text{ g}^{-1}$) [83], exfoliation into nanosheets is one of the effective strategies to augment the specific surface [174–176]. The hard and soft templates have been vastly pursued by researchers to construct nanostructured $g\text{-C}_3\text{N}_4$ with different structures such as hollow $g\text{-C}_3\text{N}_4$ nanosphere and mesoporous $g\text{-C}_3\text{N}_4$ to provide ample active sites and large surface area [26,177–179]. In addition to the methods mentioned above, other modifications routes including nanocarbon loading [126], supramolecular preorganization [180,181], co-catalyst heterojunction construction [124,182] and band gap engineering [183–185] have also been widely used.

The modification of semiconductor's morphology has attracted growing interest for the significant enhancement of photocatalytic efficiency attributed to the increased specific surface area and abundant active sites. For example, by delaminating layer materials into 2D single-atom sheets to form mesoporous nanomesh can efficiently render exceptional physico-chemical properties (Fig. 2(a)), including ultrahigh intrinsic carrier mobility, large surface area and pronounced changes in the band gap structure [186]. In addition, the wrinkled ultrathin nanosheets promises a bright future in remarkably increasing the photocatalytic efficiency (Fig. 2(b)) [187]. The enhancement can be ascribed to the larger specific surface area and ameliorated separation of charge carries, and improved lifetime of the photoinduced charges. Among the recent modification strategies discussed above, the 3D hydrogels (Fig. 2(c)) have gained much attention owing to their remarkable ability of pollutants removal by synergistic effect of photocatalytic degradation and adsorption [188–193]. The bulk structure can efficiently avoid the materials dispersing in water. On the other hand, the adsorption materials with the 3D network

Fig. 2. (a) TEM image of mesoporous $g\text{-C}_3\text{N}_4$ nanomesh. Reprinted with permission from Ref. [186]. Copyright 2016 American Chemical Society. (b) TEM image of the ultrathin $g\text{-C}_3\text{N}_4$. Reprinted with permission from Ref. [187]. Copyright 2018 American Chemical Society. (c) SEM image of $g\text{-C}_3\text{N}_4$ 3D hydrogels. Reprinted with permission from Ref. [188]. Copyright 2017 Wiley-VCH. (d) SEM image of 3D $g\text{-C}_3\text{N}_4$ -agar hybrid aerogels. Reprinted with permission from Ref. [194]. Copyright 2018 Elsevier.

structure can provide the high-speed channels of mass transfer and prevent aggregation. What is more, the pollution can be degraded continuously via $g\text{-C}_3\text{N}_4$ -based hybrid hydrogels photocatalysts without separation. Similarly, the $g\text{-C}_3\text{N}_4$ -agar hybrid aerogel (Fig. 2(d)) also exhibits excellent performances and intriguing features (e.g. ultra-light-weighted characteristic) [194–197]. Its unique 3D porous structure can not only increase the adsorption efficiency, but also provide ample active sites for surface reaction, which can significantly enhance the photocatalytic performance in the removal of wastewater pollutants and water splitting.

Among various modification solutions as discussed above, the construction of an appropriate semiconductor heterojunction interface is one of the most important prerequisite conditions to enhance charge separation efficiency for ameliorated performance of $g\text{-C}_3\text{N}_4$ [182,198,199]. In short, heterostructured photocatalysts could have several potential merits: (a) the formation of coupling hybridization is a feasible approach to enhance efficient spatial separation of photogenerated electron-hole pairs on different sides of the heterojunction, (b) strengthen light absorption by coupling with a lower band gap semiconductor, (c) co-catalyst effect – it can lower the redox overpotential to increase the photocatalytic reaction, and (d) robust stability. Due to diverse superior properties of heterojunction interfaces, various semiconductors have been coupled with $g\text{-C}_3\text{N}_4$ to form heterojunctions, including metal oxides (e.g. TiO_2 , Cu_2O , In_2O_3 , ZnO) [200–204], metal-free nanomaterials (e.g. graphene, carbon nanotubes, carbon nanodots) [99,205–208] and so forth. Among different semiconductors, $g\text{-C}_3\text{N}_4$ -based metal sulfide has elicited ripples of excitement

because of its appealing properties [209–213]. This review will comprehensively discuss five different categories of g-C₃N₄-based metal sulfide heterostructured photocatalysts in Section 3.

3. Categories of g-C₃N₄-based metal sulfide heterostructured photocatalysts

The g-C₃N₄-based metal sulfide heterostructured photocatalysts, which consist of a blend of g-C₃N₄ and metal sulfide phase, have much better photocatalytic efficiency than bare g-C₃N₄. Generally, constructing a suitable heterojunction between g-C₃N₄ and metal sulfide is considered as a useful strategy to promote the spatial separation of photo-generated electron-hole pairs and achieve the enhanced photocatalytic activity. According to the different charge carriers separation mechanisms in various hybrid heterostructures between g-C₃N₄ and the coupled metal sulfides, the g-C₃N₄-based metal sulfide photocatalysts can be classified into the following five types of heterojunctions: (1) Type I heterojunction, Type II heterojunction, (3) p-n heterojunction, (4) Schottky junction and (5) Z-scheme heterojunction. The latest developments of these five heterojunction systems are summarized and discussed in the following section.

3.1. Type I heterojunction

A heterojunction is generally defined as the interface between two regions of different semiconductors with unequal band structure, and create interfacial band alignments. Based on the different energy levels of the CB and VB of the two semiconductors, the formed heterojunction can be classified into several types: Type I (those with a straddling alignment) and Type II (those with a staggered alignment) (Fig. 3). For the Type I heterojunction (Fig. 3(a)), the VB and CB of semiconductor 1 are respectively lower and higher than those of semiconductor 2. Therefore, when the holes and electrons gain energy under light irradiation, photogenerated holes can migrate from the VB of semiconductor 1 to the VB of semiconductor 2, while photoinduced electrons can transfer from the CB of semiconductor 1 to the CB of semiconductor 2.

Lately, tin sulfide (SnS₂) as a visible-light-active photocatalyst has gained considerable attention owing to its narrow band gap (2.5 eV), unique electronic structure and tunable optical properties [214,215]. However, poor photocatalytic activity of SnS₂ can be attributed to the fast recombination rate of photo-generated electron-holes pairs. In order to achieve the enhanced photocatalytic performance of SnS₂, hybridizing SnS₂ with g-C₃N₄ to form the heterojunction interfaces has become a

Fig. 3. Band structure of various types of heterojunctions in a photocatalytic hybrid nanocomposite: (a) Type I heterojunction, (b) Type II heterojunction, (c) p-n junction, (d) Schottky junction, (e) Z-scheme heterojunction (without an electron mediator) and (f) indirect Z-scheme (with an electron mediator). A, D and E_F represent electron acceptor and electron donor and fermi level, respectively.

hot research area. In 2018, $\text{SnS}_2/\text{g-C}_3\text{N}_4$ hybrid heterojunctions were synthesized by combining with different morphologies of SnS_2 , including nanosheets, nanoparticles and 3D flower-like nanostructures [215]. Fig. 4(a) shows that SnS_2 nanoparticles were immobilized on the $\text{g-C}_3\text{N}_4$ surface uniformly. The SnS_2 nanosheets/3D flower-like was homogeneously dispersed on the $\text{g-C}_3\text{N}_4$ layer (Fig. 4(b) and (c)). Based on the optical performances of the different morphologies of SnS_2 (Fig. 4(d)), in comparison with pure $\text{g-C}_3\text{N}_4$, the $\text{SnS}_2/\text{g-C}_3\text{N}_4$ composites displayed the ability of increasing visible light absorption, which was ascribed to the interaction between $\text{g-C}_3\text{N}_4$ and SnS_2 in the composites.

Furthermore, Hou et al. [216] constructed a 2D $\text{MoS}_2/\text{g-C}_3\text{N}_4$ heterojunction for photocatalytic H_2 evolution. MoS_2 and $\text{g-C}_3\text{N}_4$ have analogous layered structures, and such geometric similarity would facilitate the planar growth of MoS_2 over the surface of $\text{g-C}_3\text{N}_4$. The resultant 0.5 wt% $\text{MoS}_2/\text{g-C}_3\text{N}_4$ composites exhibited better photocatalytic activity than the 0.5 wt% $\text{Pt/g-C}_3\text{N}_4$. The enhanced photocatalytic H_2 performance of $\text{MoS}_2/\text{g-C}_3\text{N}_4$ hybrid heterojunctions was ascribed to the modification of MoS_2 cocatalyst, which shortened the electron migration time and distance, thus gaining high efficiency in the utilization of free charge carriers for the H_2 evolution.

As the matter of fact, upon light absorption, all of the charge carriers are accumulated on the semiconductor 2 in the Type I heterojunction (Fig. 3(a)), which yields no improvement to charge carrier separation. Efficient spatial separation plays an important role for the significant enhancement of photocatalytic performance, which can be achieved by the Type II heterojunction (see the following section for more details).

3.2. Type II heterojunction

Among the five types of heterojunction systems, Type II

Fig. 4. TEM images of the as-synthesized (a) SnS_2 nanoparticles/ $\text{g-C}_3\text{N}_4$ composites, (b) SnS_2 nanosheets/ $\text{g-C}_3\text{N}_4$ composites and (c) 3D flower-like $\text{SnS}_2/\text{g-C}_3\text{N}_4$ composites. (d) UV-vis diffuse-reflectance spectra of different morphologies of SnS_2 , $\text{g-C}_3\text{N}_4$ and $\text{SnS}_2/\text{g-C}_3\text{N}_4$ composites. Reprinted with permission from Ref. [215]. Copyright 2018 American Chemical Society.

heterojunctions have unique staggered band structures between the two semiconductors, in which may significantly promote the spatial separation of electrons and holes to retard their recombination. In the Type II heterojunctions, the semiconductors 1 and 2 with similar band potentials are tightly bonded to construct the stable heterostructure. As displayed in Fig. 3(b), photogenerated holes in the VB of semiconductor 2 can be transferred to that of semiconductor 1 if the VB level of semiconductor 2 is lower than that of semiconductor 1 upon light irradiation. Contrarily, when the CB level of semiconductor 1 is higher than that of semiconductor 2, photogenerated electrons in the CB of semiconductor 1 can be migrated to that of semiconductor 2, resulting in a spatial separation of charge carriers. Finally, the internal field can promote the separation and migration of charge carriers. As a result, the probability of electron-hole pairs' recombination can be significantly reduced and the lifetime of electron can be increased, which can be unraveled by transient spectroscopic techniques. In another case, when the energy is only able to excite one semiconductor, the other semiconductor can serve as an electron/hole acceptor. It is commonly accepted that in both cases, the spatial accumulation of charge carriers can be achieved. Type II heterojunction provides the optimum band positions to gain the efficient separation of photogenerated electron-hole pairs. Notably, the construction of Type II alignment is highly desired for photocatalysis. Therefore, most of the examples of heterojunction photocatalysts discussed in the literature are Type II heterojunctions [217–223].

In recent years, the construction of Type II heterojunctions between metal sulfide photocatalyst (e.g. CdS) and $\text{g-C}_3\text{N}_4$ has gained much importance. Zhang et al. [220] reported a solvothermal and chemisorption method to prepare $\text{CdS/g-C}_3\text{N}_4$ core/shell nanowires. During the preparation process, $\text{g-C}_3\text{N}_4$ was exfoliated into thin sheets via a simple ultrasonic method, and then this formed a core/shell configuration by assembling coated on CdS nanowires. In a typical core-shell structure, one semiconductor is loaded by another which not only alters the charge, reactivity and functionality of the surface of photocatalyst, but also significantly improves charge separation efficiency due to its highly interactive interfaces [224]. It exhibits remarkable stability attributed to the stronger protection provided by shell (Fig. 5(a)–(c)). As illustrated in Fig. 5(d), the photocatalytic efficiency nanowires were tremendously improved after the coating of CdS compared with pure CdS . Liu's group [225] reported the synthesis of 0D/2D $\text{CdS/g-C}_3\text{N}_4$ heterojunctions via a facile solvothermal method. It demonstrated that the $\text{CdS/g-C}_3\text{N}_4$ hybrid structure exhibited significantly enhanced photocatalytic activity than the pure CdS and $\text{g-C}_3\text{N}_4$, which can attributed to dramatically promoted charge separation and more binding sites via the interfacial connection. Similar to CdS as discussed above, ZnS nanocage also shows fascinating performance in photocatalysis due to its unique 3D morphology. Wang and colleagues presented a $\text{g-C}_3\text{N}_4/\text{ZnS}$ nanocage hybrid system fabricated through a facile anion exchange route by using ZIF-8 as a self-sacrificing template [221]. Based on the photocatalytic results, the enhancement of photocatalytic activity can be achieved. The photoex-

Fig. 5. Photoactivity of (a) a CdS nanowire with a thin and unclosed g-C₃N₄ shell and (b) a CdS nanowire with a dense and closed g-C₃N₄ shell. (c) Time-dependent photocatalytic H₂ production for the optimal CN2. (d) Comparison of photocatalytic H₂ production activities of pristine CdS nanowires (CN0) and g-C₃N₄ coated CdS nanowires (CN0.5, CN1, CN2, CN3, and CN4) from the 0.35 mol/L of Na₂S and 0.25 mol/L of Na₂SO₃ aqueous solutions. Reprinted with permission from Ref. [220]. Copyright 2013 American Chemical Society.

cited electrons of g-C₃N₄ could be directly injected into the CB of ZnS through the well-developed interfaces between CdS and ZnS, thus inhibiting the recombination of photogenerated electron-hole pairs and promoting the photoactivity.

To date, coupling 2D g-C₃N₄ with other semiconductors to engineer 2D/2D photocatalysts has elicited much research fascination [226–231]. Based on the contact types between two components with different dimensions (Fig. 6), it is evident that the unique 2D/2D structure possesses a larger contact interface between the two adjacent sheets compared with other forms of heterojunctions [232–234]. As a result, this can essentially decrease the charge transfer time and efficiently, thus reducing the possibility of the charge carriers' recombination. Collectively, these remarkable features of 2D/2D endow a fascinating route to construct high efficiency photocatalysts.

Furthermore, layered MoS₂ structure can also be hybridized with g-C₃N₄ to construct 2D/2D nanocomposites. Qi's group [235] presented the successful fabrication of MoS₂/g-C₃N₄ hybrid system via a facile and scalable one-step method. The resultant layered MoS₂ structure was loaded onto the g-C₃N₄ framework. The modification of MoS₂ greatly suppressed the recombination of electron-hole pair. In addition to the binary composites, ternary compounds with multifunctional properties have been vastly pursued by scientists. Chen et al. [222] developed a simple method that could directly synthesize MgIn₂S₄ nanoplates on the surface of mesoporous g-C₃N₄ nanosheets via a one-pot hydrothermal reaction. From the Mott-Schottky plots and microstructure observation, the MgIn₂S₄ nanoplates and g-C₃N₄ nanosheets displayed appropriate band structure and tight heterojunction interface after

hybridization. The current research demonstrated that the resulting MgIn₂S₄ nanocomposites could serve as highly efficient visible-light-driven catalysts for diverse applications.

The photocatalytic efficiency was also related to the morphology of catalysts. Chen and his colleague [219] have fabricated mesoporous g-C₃N₄ to reduce interior defects, and further induced doping by incorporating phosphorus to construct the P-doped g-C₃N₄ nanosheets (P-C₃N₄)/ZnIn₂S₄ nanosheets. In essence, doping can promote the separation of photoinduced hole-electron pairs, which is beneficial to the photoactivity activity. As depicted in HAADF-STEM (Fig. 7(a)), elemental mapping (Fig. 7(b)) and TEM images (Fig. 7(c)), the combination of P-C₃N₄ and ZnIn₂S₄ was confirmed in the hybrid system. No significant decrease in photocatalytic activity was found after four successive recycling runs, indicating that the hybrid structure of ZnIn₂S₄ and P-C₃N₄ could overcome the disadvantage of the photocorrosion that pure sulfide will typically suffer from in photocatalysis. A possible charge transfer path

Fig. 6. Diagram of the heterojunction interfaces between nanomaterials with dissimilar dimensions. Reprinted with permission from Ref. [230]. Copyright 2014, Royal Society of Chemistry.

Fig. 7. (a) HAADF-STEM image of 20 wt% P-C₃N₄/ZnIn₂S₄ nanocomposites. (b) EDX mapping images of P-C₃N₄/ZnIn₂S₄ nanocomposites. (c) TEM image of 20 wt% P-C₃N₄/ZnIn₂S₄ nanocomposites. (d) Illustration of photocatalytic reaction and charge transfer of the P-C₃N₄/ZnIn₂S₄ nanocomposites under visible light irradiation. Reprinted with permission from Ref. [219]. Copyright 2016 Royal Society of Chemistry.

was shown in Fig. 7(d), whereby both ZnIn₂S₄ and P-C₃N₄ would have ability to absorb the energy to generate photoinduced holes and electrons when irradiated by visible light. Due to the more positive Fermi energy level of ZnIn₂S₄ than P-C₃N₄ and well-matched band structure between the ZnIn₂S₄ and P-C₃N₄, the photoinduced electrons in the CB of ZnIn₂S₄ could directly migrate to CB of P-C₃N₄ by following the Type II heterojunction. Simultaneously, the photogenerated holes would jump from the VB of P-C₃N₄ to that of ZnIn₂S₄. The charge pairs could be effectively separated, thus decreasing the recombination rate of charge carrier pairs. As a result, the photocatalytic activity of the nanocomposite was remarkably improved by the Type II heterojunction.

3.3. *p-n heterojunction*

Although the Type II heterojunction can ideally separate charge pairs in space, the achieved improvement in the electron-hole separation across the Type II heterojunction is not sufficient to overcome the ultrafast electron-hole recombination on the semiconductor. In regard of this, the concept of constructing a *p-n* heterojunction photocatalyst is put forward, which is able to provide an additional electric field to accelerate the electron-hole pairs transfer for enhancing the photocatalytic performance. The separation efficiency of the electron-hole pairs in the *p-n* heterojunction is faster than that of the Type II, which can tremendously enhance the photocatalytic activity. By combining *p*-type and *n*-type semiconductor materials, the appealing *p-n* heterojunction photocatalyst can be obtained [213,236–240]. For the *p*-type semiconductor, its Fermi level is near to the VB, while the Fermi level of *n*-type is located near to the CB. Before light irradiation, the holes will

transfer from the *p*-type semiconductor to the *n*-type semiconductor, leaving a negative charge species. The diffusion of electron-hole pairs will stop until the Fermi level system reaches equilibrium [241]. In the end, an electric field is created at the interface between two type semiconductors. Under the influence of the electric field, the photoinduced electron-hole pairs will be separated (Fig. 3(c)). By and large, g-C₃N₄ is an *n*-type semiconductor material because the NH/NH₂ groups present in its structure as electron donors. Therefore, constructing a *p-n* heterojunction can normally enhance the photocatalytic performance of g-C₃N₄.

Copper sulfide (CuS) is a typical *p*-type semiconductor for photocatalysis, which has appealing properties such as suitable band gap, excellent stability [242]. *p-n* heterojunctions could be synthesized by hybridizing CuS with g-C₃N₄, which not only created more interfaces for the efficiently transfer of photo-generated electron-hole pairs to restrict the recombination, but also extended the range of optical absorption with CuS acting as an effective photosensitizer to enlarge the light response range of the composite. A g-C₃N₄/CuS *p-n* heterostructured composite was prepared by Cai's group [242] through an in situ synthesis method (Fig. 8(a)). The enhanced photocatalysis performance could be attributed to the interface formed in the g-C₃N₄/CuS heterojunctions. Under the visible light irradiation, charge carriers could be excited from both CuS and g-C₃N₄. The photogenerated holes on the VB of CuS could easily migrate to the VB of g-C₃N₄ due to the fact that the VB energy of g-C₃N₄ was less positive than that of CuS. Meanwhile, the photoinduced electrons on the CB of g-C₃N₄ could rapidly transfer toward the CB of CuS since the CB energy of CuS was more negative than that of g-C₃N₄ (Fig. 8(b)). In this phenomenon, the photoinduced electron-hole pairs could be effectively separated by the *p-n* heterojunction between CuS and g-C₃N₄. By changing the stoichiometric factor of Cu_{2-x}S, the Cu_{1.96}S/g-C₃N₄ *p-n* heterojunctions were prepared by Ma's group [243]. 3–10 nm nanoparticles were strongly coupled with the surface of g-C₃N₄ wrinkled layers (Fig. 8(c) and (d)), forming the 0D/2D *p-n* heterojunctions, which can supply more photocatalytic reaction centers and promote the separation of the charge carriers efficiently. The much lower PL intensity was observed for the Cu_{1.96}S/g-C₃N₄ nanocomposites, further demonstrating that the recombination of charge pairs was significantly inhibited by the *p-n* heterojunction.

3.4. *Schottky junction*

The Schottky junction consists of a semiconductor and metal-like material, which is beneficial in constructing a space-charge separation region (Fig. 3(d)). Attributed to its exceptional features, the electrons rapidly transfer from one component to the other at the interface of the two components. Therefore, the Fermi energy levels can be aligned and the recombination of the charge carriers is enormously restrained to improve the photocatalytic performance. In a large number of metal-like materials, metal sulfide has attracted wide attention because of its special synergism with g-C₃N₄ [133,134,244–246]. The latest research results of g-C₃N₄-based

Fig. 8. (a) Schematic representation of the synthesis procedure of g-C₃N₄/CuS heterojunctions. (b) Illustration of proposed mechanism for the g-C₃N₄/CuS heterojunction under visible light irradiation. Reprinted with permission from Ref. [242]. Copyright 2017 Elsevier. (c, d) TEM images of the Cu_{1.96}S/g-C₃N₄ 0D/2D p-n heterojunctions, and inset of (d) is the corresponding HRTEM of Cu_{1.96}S/g-C₃N₄. Reprinted with permission from Ref. [243]. Copyright 2017 Elsevier.

metal sulfide Schottky junction will be briefly described in the following part.

For better understanding the role of Schottky junction toward the improvement of photocatalytic activity, Shen et al. designed acetylene black (AB) as the electron bridge, which linked the g-C₃N₄ (CN) and CuS co-catalysts to synthesize the CN-AB-CuS Schottky junction ternary photocatalysts with exceptional stability (Fig. 9) [131]. As illustrated in Fig. 9(a), the elements of C, N, Cu, and S were well-dispersed in the CN-0.5AB-2CuS ternary composites. The CuS and AB were successfully loaded on the surface of g-C₃N₄ nanosheets. The improved photoactivity was mainly attributed to the efficient separation of charge carriers (Fig. 9(b) and (c)). Firstly, the electron-hole pairs were generated by g-C₃N₄ under visible light radiation. After adding AB nanoparticles, the electrons in the CB of g-C₃N₄ transferred to AB owing to the construction of Schottky junctions between CN and AB. The remarkable electronic conductivity of AB led to a significant decrease of photoinduced electron-hole pairs' recombination in g-C₃N₄, thus demonstrating superior photocatalytic performance.

For practical applications, the composite photocatalyst built from NiS and g-C₃N₄ exhibits an obvious advantage compared with bare g-C₃N₄, in which NiS could serve as a co-catalyst to efficiently impede the recombination of electron-hole pairs to boost the photocatalytic activity. Furthermore, the increased near-infrared absorption of NiS could extend the region of

photoresponse remarkably. However, the present bottleneck is the overgrowth and aggregation of NiS. To tackle this draw-

Fig. 9. (a) STEM image of CN-0.5AB-2CuS (left) and the elemental mapping of C, N, Cu and S elements (right). (b) Repeated cycles of photocatalytic H₂ evolution over CN-0.5AB-2CuS. (c) Charge transfer process of CN-0.5AB-2CuS for H₂ evolution. Reprinted with permission from Ref. [131]. Copyright 2018 American Chemical Society.

back, a highly effective NiS@g-C₃N₄ photocatalyst was prepared via employing Ni²⁺ based coordination polymer (NCP) as a precursor and sulfur vacancies rich NiS as a co-catalyst (Fig. 10(a)) [132]. The photothermal conversion efficiency of NiS@g-C₃N₄(A) achieved as high as 58.2% in 1000 s (Fig. 10(b)), which was higher than other photothermal agents (e.g. Cu_{2-x}Se and Cu₉S₅). The excellent photothermal conversion efficiency of NiS@g-C₃N₄(A) was originated from its high sulfur vacancy concentration compared with the other two analogues, which explained the intensive absorption in the near-infrared region of the NiS/g-C₃N₄. From the charge transfer mechanism (Fig. 10(c)), the NiS/g-C₃N₄ nanocomposite was assigned to the typical Schottky junction, giving rise to the remarkable H₂ production rate of NiS@g-C₃N₄(A) after five recycles (Fig. 10(d) and (e)).

3.5. Z-scheme heterojunction

Although all the above-mentioned heterojunction photocatalysts can achieve the improvement of the electron-hole separation efficiency, the redox ability of the composite is compromised due to the fact that the oxidation and reduction processes occur on the semiconductor with the lower oxidation and reduction potentials, respectively [247]. In order to mitigate these problems, the pioneering work of constructing a Z-scheme photocatalytic system was proposed by Bard et al. [248] in 1979. Inspired by the photosynthesis process of green

plants in nature, this desirable charge transfer can not only achieve the efficient separation of photogenerated charge carriers, but also maintain strong and high redox abilities simultaneously. However, by using the redox mediators, the applications of these Z-scheme systems are limited to the liquid phase [249]. Therefore, it is expected to develop all-solid-state Z-scheme photocatalytic systems [250], using a conductive solid material as an electron mediator or even without a mediator (Fig. 3(e) and (f)). In regard of this, a promising type of mediator-free concept was put forward by Yu et al. [251] in 2013. As shown in Fig. 3(e), the photogenerated electrons on the lower level CB of semiconductor 2 can directly migrate to the VB of semiconductor 1 to recombine with the photoinduced holes. This type of charge transfer is called a direct Z-scheme transfer mechanism. The special structure of Z-scheme has been paid considerable attention in recent years [228,252–264]. Ascribed to the superior photocatalytic Z-scheme system, the g-C₃N₄-based metal sulfide nanohybrids have gained interdisciplinary fascination for their diverse potential in energy applications. We will introduce several Z-scheme systems starting from the use of an electron mediator to the direct Z-scheme in the absence of the electron mediator.

Compared with the liquid-phase Z-scheme, the all-solid-state Z-scheme photocatalytic systems can be more widely used in both liquid-solid and gas-solid systems [250]. Due to the good electrical conductivity, nanoscale metals have been commonly used as the electron mediators for designing the Z-scheme systems [265–268]. Considering these advantages, a Z-scheme CdS/Au/g-C₃N₄ ternary photocatalytic system based on hollow carbon nitride nanospheres (HCNS) was successfully fabricated by Zheng et al. [262]. From the elemental mappings of CdS/Au/HCNS photocatalysts (Fig. 11(a)), the C, N, S, Cd and Au were demonstrated homogeneously distributed in the spheres. From the PL spectra of the HCNS (Fig. 11(b)), a strong emission peak was illustrated. Upon incorporating with CdS and Au, the strong PL quenched quickly, manifesting that the charge recombination was greatly suppressed in the CdS-Au-HCNS photocatalyst. This phenomenon stemmed from the effective indirect Z-scheme heterojunction, which greatly enhanced the separation efficiency of charge pairs. The significant enhancement of photocurrent for 2CdS-Au-HCNS was observed (Fig. 11(c)), which was almost 3 times higher than that of the bare HCNS. This supported well with the remarkable mobility of the charge carriers. The Au nanoparticles acted as the electron mediator to accelerate the interparticle transfer of photogenerated electron-hole pairs between CdS and HCNS due to its good electrical conductivity (Fig. 11(d)). Since both CdS and HCNS could be excited by visible light, the photoinduced electrons on the CB of CdS rapidly transferred to Au. Then the electrons subsequently recombined with the photogenerated holes in HCNS. As a result, the photoinduced electrons in the CB of HCNS and holes in the VB of CdS elucidated strong reducing power and oxidizing power, respectively. Apart from Au [269], Ag has also been utilized as an effective electron mediator in the g-C₃N₄/Ag/MoS₂ ternary hybrid photocatalysts [253].

As discussed above, the introduction of an electron media-

Fig. 10. (a) Synthesis of NiS@g-C₃N₄ nanocomposites with NCP as a precursor. (b) Temperature change of NiS@g-C₃N₄ aqueous solution with respect to time. (c) Mechanism and charge transfer process of NiS@g-C₃N₄. (d) Stability of NiS@g-C₃N₄(A) for the photocatalytic H₂ production. (e) XRD patterns of NiS@g-C₃N₄(A) before and after photocatalysis. Reprinted with permission from Ref. [132]. Copyright 2018 American Chemical Society.

Fig. 11. (a) Elemental mapping images of 2CdS-Au-HCNS nanocomposites. (b) PL spectra and (c) transient photocurrent response of 2CdS-Au-HCNS photocatalysts. (d) Illustration of Z-scheme electron transfer in the CdS-Au-HCNS system. Reprinted with permission from Ref. [262]. Copyright 2015 Royal Society of Chemistry.

tor between two semiconductors to construct the indirect Z-scheme systems can significantly accelerate the charge transfer. Apart from the indirect Z-scheme, designing the direct Z-scheme system to form the intimate interface between the two components can also play a pivotal role in boosting the photocatalytic activity [270–277]. In this regard, Li's group [278] synthesized the g-C₃N₄ nanosheets (g-C₃N₄ NS)/CuInS₂ (GsC) direct Z-scheme system composite photocatalysts. Interestingly, the photoelectric current density of GsC was far outperforming than those of the pristine CuInS₂ (CIS) and g-C₃N₄ NS (Fig. 12(a)), denoting its superb charge separation efficiency. The dependence of R_{ct} on the light intensity (Fig. 12(b)) further confirmed that the GsC possessed the lowest R_{ct} at any light intensity, inferring that electrons in the GsC were more easily migrated to protons in the electrolyte to take part in the H₂ evolution relative with the pure CIS and g-C₃N₄. Surprisingly, the 6-fold increase in the PL lifetime of GsC was noted (Fig. 12(c)), signifying a superior performance in the separation of photoinduced electron-hole pairs thanks to the direct Z-scheme system (Fig. 12(d)). After constructing the direct Z-scheme

system, the GsC featured the system to involve the capture of photogenerated electrons in the CB of g-C₃N₄ NS by the VB of CIS. Benefitted from the Z-scheme process, more electrons in the CIS were survived, thus evolving more H₂ over the same time period. As such, this research lays a good foundation and casts new insights into engineering highly efficient g-C₃N₄-based metal sulfide heterojunction photocatalysts via a Z-scheme pathway.

From the above discussion, it can be seen that Type II and Z-scheme possess almost similar in energy band structure with varying charge transfer pathways. As such, how to distinguish a heterojunction type between the two types has become the hot spot for the scientific research. When there is a mediator in the heterojunction, we can postulate that the hybrid photocatalysts follow a Z-scheme, but if there is absence of mediator, then a direct Z-scheme and Type II heterojunctions are both possible. Therefore, more deeply strategies are needed to support the mechanism of charge transfer. A double-beam photoacoustic (DB-PA) spectroscopy can be employed to probe the mechanism of electron-hole transfer. For instance, Z-scheme pathway of WO₃/g-C₃N₄ was confirmed by Ohno's group [279] using the DB-PA analysis as compared to the traditional Type II heterojunction. Apart from that, the Z-scheme mechanism can be postulated by verifying the existence of •O₂⁻ and •OH radicals with respect to the redox potentials in the reaction medium by using a systematic chemical probe.

4. Photocatalytic energy applications of metal sulfide/g-C₃N₄ nanocomposites

The g-C₃N₄-based heterojunctions have exhibited great potential in a broad range of energy conversion applications in recent years. Nevertheless, for bare g-C₃N₄, it is still restricted by the low efficiency attributed to the rapid recombination rate

Fig. 12. (a) Transient photocurrent of GsC, bare CIS and g-C₃N₄ nanosheets under visible light illumination ($\lambda > 420$ nm). (b) Dependence of R_{ct} on light intensities from the EIS experiments. (c) PL spectra of the GsC, g-C₃N₄ nanosheets and bare CIS. (d) Band potentials of bare CIS and g-C₃N₄ NS to design a Z-scheme hybrid photocatalyst. Reprinted with permission from Ref. [278]. Copyright 2018 American Chemical Society.

of charge carries, which impedes their widely use in practical applications. Sulfide semiconductors are vastly pursued by researchers to engineer hybrid structures with g-C₃N₄ for their appealing attributes [130,280–283]. In line with the focus of this review for artificial photosynthesis, we will present the photocatalytic water splitting for H₂ evolution (Section 4.1) [91,216,284–287], photocatalytic CO₂ reduction (Section 4.2) [254,288–292] and photocatalytic N₂ fixation (Section 4.3) [293–295] in this section.

4.1. Water splitting for H₂ evolution

Photocatalytic H₂ production through water splitting is considered to be an ideal pathway for future energy consumption due to its economic and environmental superiority [42,83,137,296–305]. Exploration and development of the suitable photocatalysts with excellent performance is essential to transform this technology into industrial application. Therefore, countless semiconductors have been investigated as photocatalysts over the past four decades. In the process of the research, g-C₃N₄ is found to have excellent performance. To make it an economically feasible photocatalyst for practical application, incessant efforts have been done to render the photocatalyst more efficient. Yet, in most of the methods reported to date, noble metal Pt is the essentially required co-catalyst for H₂ evolution, hence precluding the niche application of g-C₃N₄ due to an exorbitant cost and its scarcity. Recently, transition metal sulfides have been recognized as promising substitutions of noble metals due to their unprecedented optical and electrical properties. So far, numerous metal sulfides have proven efficient to modify g-C₃N₄ in enhancing the photocatalytic H₂ generation, including MoS₂ [245,306–313], WS₂ [280], NiS [129,132,283,314], etc. Herein, the photocatalytic H₂ generation activity of multifarious g-C₃N₄-based metal sulfide systems is summarized in Table 1.

As known to all, vacancy defects have advantageous proper-

ties in altering the electronic structure and modifying the characteristics of charge carriers by introducing additional energy levels [322,323]. Therefore, defect engineering is one of the most prudent strategies for boosting the activity for H₂ production. In 2018, Hao et al. [318] reported the ZnS/g-C₃N₄ heterostructures with abundant zinc vacancy (V_{Zn}) defects. As illustrated in Fig. 13(a), the photoluminescence (PL) emission intensity significantly decreased after coupling with ZnS. Remarkably, the V_{Zn}-rich CZV20 (g-C₃N₄/ZnS-20wt%) heterojunction showed the weakest PL intensity among all the samples, attesting the effective charge transfer between ZnS and g-C₃N₄. CZV20 heterojunction presented the maximum photocatalytic H₂ evolution rate (Fig. 13(b)), which was about 30 times greater than that of the pure g-C₃N₄ (24.09 μmol h⁻¹ g⁻¹). This superior photocatalytic H₂ evolution rate was arisen from the excellent charge separation efficiency and light-absorbing capacity caused by the abundant Zn vacancies. From the linear sweep voltammetry (LSV) analysis (Fig. 13(c)–(d)), the CZV20 electrode demonstrated the highest current density, which clearly manifested the synergistic promotion of charge carriers' separation capability of ZnS/g-C₃N₄ heterojunction. More interestingly, the H₂ production activity of ZnS was originated from the two-photon excitation by the two steps of absorption mechanism (Fig. 13(e)–(f)) due to the existence of Zn vacancy defects in the band gap of ZnS. As such, these results substantiate that appropriate Zn vacancy defect is a propitious approach to ameliorate the H₂ production activity and regulate the behavior of light absorption in photocatalysis, which can be a game-changing breakthrough in energy conversion.

It is universally accepted that one of the fundamental ways to increase the activity of hydrogen production is to increase the number of active centers [324]. According to the extensive studies, the active sites are mainly located at the surface or edges of co-catalysts [325]. Therefore, constructing a polyhedral structure with additional exposed edges can be a viable prospect to modify the morphology feature of co-catalysts to

Table 1

Summary of the photocatalytic activity of g-C₃N₄-based metal sulfide photocatalysts toward H₂ evolution reaction.*

Composite type	Sacrificial reagent	Light source (wavelength)	H ₂ evolution rate (μmol h ⁻¹ g ⁻¹)	AQY (%)	Stability (h)	Type of heterojunction	Ref. (Year)
SnS ₂ /g-C ₃ N ₄	Na ₂ S, Na ₂ SO ₃	300 W Xenon lamp (λ > 400 nm)	6305.18	NA	>9	Type I	[215] (2018)
g-C ₃ N ₄ /ZnIn ₂ S ₄	TEOA	300 W Xenon lamp (λ > 420 nm)	2780	7.05 (420 nm)	>16	Type I	[315] (2018)
Cd _{0.5} Zn _{0.5} S/g-C ₃ N ₄	Na ₂ S, Na ₂ SO ₃	300 W Xenon lamp (λ > 420 nm)	33410	46.65 (425 nm)	>25	Type II	[316] (2016)
Cu ₂ MoS ₄ /g-C ₃ N ₄	TEOA	300 W Xenon lamp (λ > 420 nm)	2170.5	0.41 (400 nm)	>16	Type II	[317] (2018)
Zn vacancy ZnS/g-C ₃ N ₄	Na ₂ S, Na ₂ SO ₃	300 W Xenon lamp (λ > 420 nm)	713.68	NA	>20	Type II	[318] (2018)
Cd _{0.5} Zn _{0.5} S/g-C ₃ N ₄ /MoS ₂	Na ₂ S, Na ₂ SO ₃	500 W Tungsten halogen lamp	4550	38 (420 nm)	>2	Type II	[212] (2018)
CdS/Cu ₇ S ₄ /g-C ₃ N ₄	Na ₂ S, Na ₂ SO ₃	300 W Xenon lamp (λ > 420 nm)	3570	4.4 (420 nm)	>15	Type II, p-n junction	[213] (2018)
Mn _{0.8} Cd _{0.2} S/g-C ₃ N ₄	Na ₂ S, Na ₂ SO ₃	300 W Xenon lamp (λ > 420 nm)	4000	4.1 (420 nm)	>24	Type II	[319] (2016)
g-C ₃ N ₄ /NiS ₂	TEOA	300 W Xenon lamp (λ > 420 nm)	968.2	2 (425 nm)	>15	Schottky	[320] (2018)
g-C ₃ N ₄ /CB/NiS	TEOA	300 W Xenon lamp (λ > 420 nm)	366.4	NA	>12	Schottky	[126] (2017)
CoS _x /g-C ₃ N ₄	TEOA	350 W Xenon lamp (λ > 400 nm)	629	NA	>12	Schottky	[127] (2018)
MoS ₂ /g-C ₃ N ₄	methanol	350 W xenon lamp (λ > 400 nm)	191.2	NA	NA	Schottky	[321] (2018)
CuInS ₂ /g-C ₃ N ₄	Na ₂ S, Na ₂ SO ₃	300 W Xenon lamp (λ > 420 nm)	1290	NA	>25	Z-scheme	[278] (2017)
g-C ₃ N ₄ /Ag/MoS ₂	TEOA	300 W Xenon lamp (λ > 420 nm)	104	NA	>20	Z-scheme	[253] (2017)
MoS ₂ /g-C ₃ N ₄	methanol	300 W Xenon lamp (solar simulator)	577	NA	>12	Z-scheme	[255] (2018)

*TEOA, triethanolamine; AQY, apparent quantum yield; NA, not available; CB, carbon black.

Fig. 13. (a) PL spectra of the ZnS/g-C₃N₄ nanocomposite. (b) Photocatalytic H₂ production rates of g-C₃N₄, ZnS and ZnS/g-C₃N₄ photocatalysts in 0.35 M Na₂S and 0.25 M Na₂SO₃ solution under visible light ($\lambda \geq 420$ nm) irradiation. (c) LSV curves and (d) Tafel slopes for g-C₃N₄, ZnS and CZV20 samples. (e) Diagram of band structures for g-C₃N₄ and ZnS. (f) Visible-light photocatalytic mechanism for H₂ production over CZV20 nanocomposites. Reprinted with permission from Ref. [318]. Copyright 2018 Elsevier.

enhance the photocatalytic activity. In particular, hollow structure can aid in light utilization efficiency by multiple light reflections. g-C₃N₄ hybridized with hollow cobalt sulfide (CoS_x) polyhedrons was put forward by Fu and co-workers [127]. The catalytic sites of CoS_x adsorbed protons from the water and then the photoinduced electrons of g-C₃N₄ migrated to the surface of CoS_x. After undergoing the two protons reaction process, a H₂ molecule was evolved on the catalytic sites of CoS_x. The optimal ratio was 2 wt% of CoS_x loaded on g-C₃N₄ and the rate of H₂ production was enhanced by about 52 times (629 $\mu\text{mol h}^{-1} \text{g}^{-1}$) under visible light compared with the parent C₃N₄. As a whole, these features demonstrate that hollow CoS_x polyhedrons can be widely used for noble-metal-free co-catalysts toward pronounced enhancement in the photocatalytic H₂ generation.

In recent years, much attention has been drawn to the construction of ternary chalcogenide AB₂X₄ (A = Zn, Cd, Ca, Cu, Mg; B = In, Ga, Al; X = S, Se, Te) semiconductors as photocatalysts due to their tunable optical properties, unique electronic structure and suitable band gaps for various applications [222,326–331]. Among these ternary metal sulfide materials, cubic CaIn₂S₄ has been widely employed to construct a heterojunction with g-C₃N₄ due to its excellent stability, well-matched band gap, and robust activity [218]. The CaIn₂S₄/g-C₃N₄ het-

erojunction nanocomposites have demonstrated a tremendous enhancement of H₂ evolution activity under visible light irradiation. Specifically, the 30% CaIn₂S₄/g-C₃N₄ composites revealed the maximum H₂ evolution rate of 102 $\mu\text{mol g}^{-1} \text{h}^{-1}$ (Fig. 14(a)). The stability of the catalysts was maintained without a significant decrease in H₂ evolution rate even after three and five repeated cycling measurements (Fig. 14(b)). The photocatalytic improvement stemmed from the larger specific surface area of the 30% CaIn₂S₄/g-C₃N₄ by a factor of three compared with pristine CaIn₂S₄ and the existence of tight 2D heterojunction interfaces between g-C₃N₄ and CaIn₂S₄ as corroborated by the transient photocurrent responses. Thus, charge carriers can be efficiently separated in space and the probability of photogenerated electron-hole pair's recombination will be dramatically reduced (Fig. 14(c)).

As an important ternary chalcogenide semiconductor of hexagonal phase ZnIn₂S₄ with narrow band gap [209,315,332,333], this 2D layered structure with remarkable chemical stability has been extensively investigated in photocatalysis, especially serving as the synergistic components with g-C₃N₄ to form heterointerfaces for enhancing the photocatalytic H₂ production efficiency. In the recent work, a composite structure comprising of ZnIn₂S₄ and g-C₃N₄ was fabricated by Liu et al. [334] and Jin et al. [335] with high photocatalytic hydrogen evolution using the hydrothermal method. Liu's group have synthesized ZnIn₂S₄ nanoparticles/g-C₃N₄ nanosheet using a one-step hydrothermal strategy. However, the as-developed ZnIn₂S₄/g-C₃N₄ binary composites exemplified a typical 0D/2D type of heterojunction. The composite suffered from the micron-sized bulk aggregate structure of the 0D/2D heterojunction and the limited contacted interface between ZnIn₂S₄ and g-C₃N₄ as a result of the point-to-face contact relative to the larger 2D/2D face-to-face contact.

Fig. 14. (a) Photocatalytic H₂ production activity over CaIn₂S₄/g-C₃N₄ with different contents of CaIn₂S₄ under 12 W UV-LEDs light. (b) Stability test of the CaIn₂S₄/g-C₃N₄ photocatalysts. (c) Charge transfer mechanism for H₂ production. Reprinted with permission from Ref. [253]. Copyright 2015 American Chemical Society.

Enlightened by this phenomenon, the design of intimate 2D/2D interface in the binary heterojunction system of $\text{ZnIn}_2\text{S}_4/\text{g-C}_3\text{N}_4$ renders a promising technique to accelerate the charge separation and migration. According to the aforementioned motivation, Lin and colleagues designed a novel 2D/2D ZnIn_2S_4 nanoleaf@ $\text{g-C}_3\text{N}_4$ nanosheet via a one-step surfactant-assisted solvothermal method strategy with the unique high-speed nanochannels of charge transfer (Fig. 15(a)) [315]. Surprisingly, the 2D/2D ZnIn_2S_4 nanoleaf@ $\text{g-C}_3\text{N}_4$ nanosheet exhibited remarkable photocatalytic H_2 production activity ($2.78 \text{ mmol h}^{-1} \text{ g}^{-1}$), which was nearly 69.5, 8.2 and 1.9 times higher than the bare $\text{g-C}_3\text{N}_4$ nanosheet, ZnIn_2S_4 microsphere@ $\text{g-C}_3\text{N}_4$ nanosheet and pure ZnIn_2S_4 nanoleaf (Fig. 15(b)), respectively. More incredibly, the hydrogen evolution rate, result of 2D/2D ZnIn_2S_4 nanoleaf@ $\text{g-C}_3\text{N}_4$ nanosheet also far exceeded than that of the majority of modified $\text{g-C}_3\text{N}_4$ composites in previous reports, even including the Pt co-catalyst (Fig. 15(c)) [218,336–340]. Furthermore, the 2D/2D ZnIn_2S_4 nanoleaf@ $\text{g-C}_3\text{N}_4$ nanosheet unveiled remarkable apparent quantum yield (AQY) value of 7.05% at 420 nm, which surpassed the ZnIn_2S_4 microsphere@ $\text{g-C}_3\text{N}_4$ nanosheet (1.01%). Hence, this study highlights the crucial advantages of the distinctive 2D/2D heterojunction with high-speed charge transfer nanochannels in the nanocomposite, which can be extended for other 2D/2D nanoarchitectures [341].

By using the same semiconductors, but different from the nanoleaf-nanosheet morphology, Zhang and co-workers presented a “sheet-on-sheet” hierarchical 2D/2D heterostructure [342]. The unique hierarchical structures, which created by mimicking the marvelous fractal and hierarchical structures such as trees, possess interconnected and readily accessible porous networks and large specific surface areas [343]. These

appealing features can not only accelerate the transport of reactant molecules to the active sites, but also increase the efficiency of light harvesting and absorption of visible light [141,342,344–347]. Therefore, the superior improvement of the hierarchical photocatalytic performance can be achieved owing to the synergetic effects of multi-modal pore structures and various dimensional levels. Similar as the above work by Lin et al. [315], the 2D/2D ZnIn_2S_4 nanosheet@ $\text{g-C}_3\text{N}_4$ nanosheet revealed excellent enhancement on the photocatalytic H_2 production activity. Under the illumination of visible light, the rate of H_2 production of the optimized composite ($953.5 \text{ mol h}^{-1} \text{ g}^{-1}$) increased about 1.91 times compared with the bare ZnIn_2S_4 ($500 \text{ mol h}^{-1} \text{ g}^{-1}$). Owing to the ease of transporting the photogenerated charges over the face-to-face contact of the 2D/2D junctions, this contributes to an increase in the charge separation and migration efficiency of ZnIn_2S_4 nanosheet@ $\text{g-C}_3\text{N}_4$. Apart from high activity, a highly stable production of H_2 was attained over $\text{ZnIn}_2\text{S}_4/\text{g-C}_3\text{N}_4$ under visible light irradiation. Through the above discussion, the geometry engineering of 2D/2D heterojunction plays a predominant role in influencing the photocatalytic activity.

As compared with the binary system reviewed above, multitudinous studies have shown that constructing a ternary system by adding another suitable material to the binary system can considerably improve the efficiency of photocatalytic H_2 production. A ternary nanocomposite of amorphous NiS, carbon black co-catalyst and $\text{g-C}_3\text{N}_4$ was synthesized by Wen et al. (Fig. 16(a)) [348]. The optimized ternary photocatalyst system achieved the H_2 production rate of $992 \mu\text{mol g}^{-1} \text{ h}^{-1}$, which recorded ca. 2.51 times higher than the corresponding binary 1.5% NiS/ $\text{g-C}_3\text{N}_4$ photocatalyst ($395 \mu\text{mol g}^{-1} \text{ h}^{-1}$) (Fig. 16(b)). The significant enhancement of photocatalytic H_2 evolution

Fig. 15. (a) Synthesis route of 2D/2D $\text{g-C}_3\text{N}_4$ nanosheet@ ZnIn_2S_4 nanoleaf. (b) Time-dependent noble-metal-free photocatalytic H_2 production over various nanocomposites under visible light irradiation. (c) Stability and durability test of the optimal sample for the H_2 evolution. Reprinted with permission from Ref. [315]. Copyright 2018 Elsevier.

Fig. 16. (a) Formation process of g-C₃N₄-CB-NiS composite photocatalysts. (b) Amount of H₂ production over A) g-C₃N₄, B) g-C₃N₄-0.5% CB, C) g-C₃N₄-1.5% NiS, D) g-C₃N₄-0.5% CB-1.5% NiS, E) g-C₃N₄-1.0% CB-1.5% NiS, F) g-C₃N₄-1.5% CB-1.5% NiS, G) g-C₃N₄-1.5% NiS-0.5% CB. (c) Illustration of visible-light H₂ generation over g-C₃N₄-CdS-NiS ternary photocatalysts. Reprinted with permission from Ref. [348]. Copyright 2015 Elsevier.

performance was emerged from the excellent synergetic combination between NiS and carbon black as co-catalysts, leading to the enhanced H₂ evolution kinetics and improved charge migration (Fig. 16(c)). The incorporation of g-C₃N₄ with 0.5% carbon black and 1.5% NiS displayed the highest photocurrent density in the PEC analysis as compared to binary samples and bare g-C₃N₄. These PEC results demonstrated that the ternary hybrids could remarkably facilitate the separation and migration efficiency of charge carriers, giving rise to substantial enhancements of the photocatalytic H₂ production.

It is envisioned that adding the conductive Ni metallic interface layers as co-catalysts between NiS and g-C₃N₄ can play a prominent role in accelerating the oxidation of triethanolamine (TEOA) and H₂ production reaction kinetics over the single NiS co-catalysts. By inserting Ni into the interfaces between NiS and g-C₃N₄, the optimal g-C₃N₄-0.5%Ni-1.0%NiS nanostructure achieved high H₂ evolution activity of 515 μmol g⁻¹ h⁻¹, which was 4.6 and 2.8 times larger than g-C₃N₄-0.5%Ni and g-C₃N₄-1.0%NiS, respectively. To synergistically maximize the H₂ evolution activity, Yuan's group [314] loaded precious-metal-free NiS onto the heterojunction of g-C₃N₄ nanosheets and CdS nanorods by means of the in situ hydrothermal method. The maximum rate of H₂ production reached ca. 2563 mol g⁻¹ h⁻¹ when the NiS loading amount was 9 wt%, which recorded a whopping 1582 times enhancement relative to pristine g-C₃N₄. From these ternary systems, it is anticipated that high-efficiency g-C₃N₄-based photocatalysts loaded with

co-catalysts to engineer multi-dimensional hybrids can be accomplished for a cornucopia of applications in the future.

Artificial Z-scheme photocatalytic systems provide a budding strategy in boosting the performance of photocatalytic H₂ generation by mimicking the natural photosynthesis in a typical green leaf [250,349,350]. The Z-scheme has been constructed by employing nanocarbon as a solid-state electron mediator to form g-C₃N₄/nanocarbon/ZnIn₂S₄ (CN/C/ZIS) nanocomposite (Fig. 17) [351]. Under visible light irradiation, the photoinduced electrons transferred from the CB of ZnIn₂S₄ to the nanocarbon and then moved to the VB of g-C₃N₄ to combine with the holes (Fig. 17(c)–(d)). As a result, a larger amount of free photoexcited electrons in g-C₃N₄ are available to join in the reduction of protons to H₂. Therefore, this contributed to the enhancement of the H₂ evolution activity by 3.4 and 3.2 times higher than those of pristine ZnIn₂S₄ and ZnIn₂S₄/g-C₃N₄, respectively (Fig. 17(b)).

Different preparation methods will have a profound influence on the stability and associated charge transfer ability of the product materials. Typically, the incorporation of g-C₃N₄ with metal sulfides is performed via a solution-deposition method under mechanical stirring [130,283,314]. The insufficient interface contact between the co-catalyst and g-C₃N₄ obtained by this method will lead to the significant decrease of electron-hole transfer efficiency. Compared with the mechanical deposition strategy, hydrothermal approach has been demonstrated to be versatile to synthesize metal sulfide nano-

Fig. 17. (a) Illustration of the preparation process of the g-C₃N₄/nanocarbon/ZnIn₂S₄ (CN/C/ZIS) nanocomposite. (b) Comparison of the visible-light photocatalytic H₂ production activity of CN, ZIS, CN/ZIS, C/ZIS, C/CN and CN/C/ZIS samples under 12 W UV-LED (λ = 420 nm) in the absence of Pt co-catalysts. Electron transfer mechanisms of (c) ZnIn₂S₄/g-C₃N₄ (Type II) and (d) g-C₃N₄/nanocarbon/ZnIn₂S₄ (Z-scheme). Reprinted with permission from Ref. [351]. Copyright 2015 Royal Society of Chemistry.

particles with high-quality for the decoration on g-C₃N₄. Based on the above idea, a series of g-C₃N₄/NiS₂ hybrid photocatalysts have been fabricated by the hydrothermal method to enhance the physicochemical property [320]. From Fig. 18(a)–(e), the distribution of C, N, Ni and S certified the deposition of quantum-sized NiS₂ nanoclusters on the surface of g-C₃N₄ nanosheet. The maximum activity was achieved when the loading of NiS was 25.3 wt% with a H₂ production rate of 4.841 μmol h⁻¹ and an AQY of 2% at 425 nm (Fig. 18(f)). It is noteworthy that the reported efficiency was higher than that of pure g-C₃N₄ and even larger than that of many Pt/g-C₃N₄. The photoinduced carrier recombination was enormously restrained (Fig. 18(g)–(i)), thus enhancing the photocatalytic reaction.

4.2. CO₂ reduction

Nowadays, the ever-increasing CO₂ emission has riveted worldwide attentions due to rising temperature that causes climate change [352–355]. “Negative carbon economy” is regarded as a way to absorb CO₂-based sustainable model and this phenomenon is gradually recognized by the society. Inspired by the natural photosynthesis in green plants, the solar light-driven photocatalytic conversion of CO₂ into energy-bearing products is considered to be a promising technique

to avert the environment and energy challenges in a sustainable manner [288,289,356–365]. Due to the different choices of the photoactive components in the g-C₃N₄-based composites and various design structures, CO₂ can be converted to different carbon-based fuels according to the following equations [366,367]:

The metal sulfide-modified g-C₃N₄ has been successfully employed as an effective photocatalyst to facilitate the photocatalytic CO₂ reduction. The recent significant progresses of g-C₃N₄-based metal sulfide in the photocatalytic CO₂ reduction will be briefly summarized in this section and Table 2.

Hitherto, Z-scheme heterostructures have been vastly pursued by researchers in the application of photocatalytic CO₂ reduction due to its superior photocatalytic performance compared with the traditional Type II heterojunction [371]. In view

Fig. 18. (a–e) STEM-EDX elemental mapping images of g-C₃N₄/25.3%-NiS₂ nanodots photocatalysts (Scale bar: 20 nm). (f) Rate of H₂ generation rate over pristine g-C₃N₄ (A), g-C₃N₄/56.5%-NiS₂ (B), g-C₃N₄/39.2%-NiS₂ (C), g-C₃N₄/25.3%-NiS₂ (D), g-C₃N₄/12.2%-NiS₂ (E), g-C₃N₄/5.6%-NiS₂ (F), g-C₃N₄/2.5%-NiS₂ (G), g-C₃N₄/0.0%-NiS₂ (H), mechanical mixing of 25.3 wt%-NiS₂ and g-C₃N₄ (I), g-C₃N₄/1%-Pt (J) and g-C₃N₄/3%-Pt photocatalysts (K). (g) PL spectra of g-C₃N₄ and g-C₃N₄/25.3%-NiS₂. (h–i) Diagram of charge transfer and separation over pristine g-C₃N₄ and g-C₃N₄/25.3%-NiS₂. Reprinted with permission from Ref. [320]. Copyright 2018 Wiley-VCH.

Table 2

Summary of the photocatalytic activity of g-C₃N₄-based metal sulfide photocatalysts toward CO₂ reduction reaction.*

Composite type	Sacrificial reagent	Light source (wavelength)	Product evolution rate (μmol h ⁻¹ g ⁻¹)	AQY (%)	Stability (h)	Type of heterojunction	Ref. (Year)
ZnIn ₂ S ₄ /g-C ₃ N ₄	TEOA	300 W Xenon lamp (λ > 420 nm)	CO: 892	2.4 (420 nm)	>8	Type I	[339] (2018)
CdIn ₂ S ₄ /g-C ₃ N ₄	NA	300 W Xenon lamp (λ > 420 nm)	CH ₃ OH: 42.7	14 (420 nm)	>16	Type II	[368] (2017)
SnS/g-C ₃ N ₄	NA	300 W Xenon lamp (λ > 420 nm)	CO: 5.7 CH ₃ OH: 1.9 CH ₄ : 1.3	17.2 (450 nm) 15.3 (525 nm)	>15	Z-scheme	[369] (2018)
Sn ₂ S ₃ -DETA/g-C ₃ N ₄	NA	300 W Xenon lamp (λ > 420 nm)	CH ₃ OH: 1.35 CH ₄ : 4.84	NA	>12	Z-scheme	[370] (2019)
MoS ₂ /g-C ₃ N ₄	NA	300 W Xenon lamp (λ > 420 nm)	CO: 8.37	25.5	>18	Z-scheme	[254] (2018)

* TEOA, triethanolamine; DETA, diethylenetriamine; AQY, apparent quantum yield; NA, not available.

of that, most recently, Huo's group fabricated the porous g-C₃N₄/Sn₂S₃-diethylenetriamine (Pg-C₃N₄/Sn₂S₃-DETA) Z-scheme heterojunction photocatalysts by controlling as-prepared organic-inorganic Sn₂S₃-DETA nanorods on the g-C₃N₄ nanosheets surface via a small-molecule-amine-assisted hydrothermal method (Fig. 19(a)) [290]. As illustrated in Fig. 19(b), Pg-C₃N₄/Sn₂S₃-DETA nanocomposites performed better activity for CH₃OH and CH₄ production than pristine Sn₂S₃-DETA and individual g-C₃N₄. With the increase of Pg-C₃N₄ contents, the CH₃OH and CH₄ production rates grew gradually. When the content of Pg-C₃N₄ was 5%, the sample indicated the highest production rates of CH₃OH (1.35 μmol h⁻¹ g⁻¹) and CH₄ (4.84 μmol h⁻¹ g⁻¹) with a corresponding quantum efficiency of 2.8%. The results showed that only carbonate species was

identified prior to visible light irradiation with flowing the H₂O vapor and CO₂ (Fig. 19(c)). Fascinatingly, the conversion CO₂ to CH₃OH and CH₄ on 5%Pg-C₃N₄/Sn₂S₃-DETA denoted a multi-step reduction process due to the detection of formaldehyde, methoxyl groups and formate species upon the irradiation. From the transfer mechanism of charge carriers over the Pg-C₃N₄/Sn₂S₃-DETA system (Fig. 19(d)), the lifetime of photoinduced electron-hole pairs were enlarged and the redox potential was improved by the all-solid-state direct Z-scheme process.

As a very special type of Z-scheme, the direct Z-scheme heterojunction [349], which can efficiently maintain the high redox power of the charge carrier pairs, has been regarded as one of the green sustainable avenues to tackle the environmental cri-

Fig. 19. (a) Diagram of the synthesis of Pg-C₃N₄/Sn₂S₃-DETA nanocomposites. (b) Rate of CO₂ photoreduction over different studied nanocomposites under visible light. (c) In situ FTIR spectra of 5% Pg-C₃N₄/Sn₂S₃-DETA under various situations: (i) in the absence of CO₂ gas and light illumination; (ii) flowing CO₂ gas for 0.5 h in the absence of light; (iii) flowing CO₂ gas for 1 h in the absence of light, light illumination for (iv) 0.5 h and (v) 1 h. (d) Z-scheme reaction mechanism of Pg-C₃N₄/Sn₂S₃-DETA. Reprinted with permission from Ref. [290]. Copyright 2019 Elsevier.

sis caused by excessive CO₂. To further unravel the function of Z-scheme heterojunction in the CO₂ reduction, a direct Z-scheme g-C₃N₄/SnS₂ heterojunction was fabricated by Di et

al. [372] (Fig. 20). SnS₂ was uniformly immobilized on g-C₃N₄ without obvious aggregation and an intimate interfacial contact between g-C₃N₄ and SnS₂ was observed (Fig. 20(a)). The

Fig. 20. TEM (a), HRTEM (b) and elemental mapping images (c) of C, N, Sn, and S of g-C₃N₄/SnS₂. (d) Hydrocarbon generation rate in comparison with g-C₃N₄, g-C₃N₄/SnS₂ and SnS₂ under the illumination for 1 h. (e) Transient photocurrent responses for SnS₂ (i), g-C₃N₄ (ii) and g-C₃N₄/SnS₂ (iii) under LED light irradiation ($\lambda = 420$ nm) in 0.5 M Na₂SO₄ aqueous solution. (f) IEF-induced direct Z-scheme charge transfer process for g-C₃N₄/SnS₂ in the photocatalytic reduction of CO₂. Reprinted with permission from Ref. [372]. Copyright 2017 Elsevier.

HRTEM image illustrated that SnS₂ was present as quantum dots with a size of 2–3 nm (Fig. 20(b)) and the quantum dots were deposited uniformly on the surface of g-C₃N₄ (Fig. 20(c)). Furthermore, g-C₃N₄/SnS₂ significantly increased the photocurrent compared with SnS₂ and unmodified g-C₃N₄ (Fig. 20(e)). The XPS analysis indicated the interfacial internal electric field (IEF) was formed after depositing SnS₂ on g-C₃N₄. Under visible light irradiation, both g-C₃N₄ and SnS₂ were excited to generate charge pairs, and then electrons in the CB of SnS₂ combined with holes in the VB of g-C₃N₄ driven by this IEF, hence following the Z-scheme pathway (Fig. 20(f)). The Z-scheme configuration improved the electron extraction for g-C₃N₄/SnS₂, which led to robust photocatalytic CO₂ reduction to CH₄ and CH₃OH. Benefitting from the merits of Z-scheme, the optimal sample exhibited the CH₄ and CH₃OH production yields of 0.64 $\mu\text{mol g}^{-1}$ and 2.3 $\mu\text{mol g}^{-1}$, respectively (Fig. 20(d)). Remarkably, the obtained hydrocarbon yields are higher than g-C₃N₄ hybridized with or other semiconductors relative to the

previous reports [272,373,374]. As such, this research casts a favorable prospect in constructing a direct Z-scheme heterojunction without the presence of electron mediator to bolster the efficiency of CO₂ reduction compared with the conventional heterogeneous or single-component photocatalyst.

It is worth mentioning that layered semiconductors with ultrathin 2D nanosheets structure have enthralled a blossoming interest in recent years due to the spectacular structure-dictated virtues [215,218,222]. In line of this consideration, Wang's group synthesized the visible-light photoconversion of CO₂ to CO over polymeric carbon nitride (PCN)/ZnIn₂S₄ nanocomposites in 2018 [375]. The layered PCN/ZnIn₂S₄ heterojunction photocatalyst endowed an extraordinary catalytic activity for deoxygenative CO₂ reduction with a CO evolution rate of 44.6 $\mu\text{mol h}^{-1}$, which recorded around 223 and 3.6 times higher than those of pristine PCN nanosheets (0.2 $\mu\text{mol h}^{-1}$) and nanosheet-assembled ZnIn₂S₄ particles (12.4 $\mu\text{mol h}^{-1}$), respectively. Based on the CO₂ adsorption isotherms of the sample, the maximum CO₂ adsorption of PCN/ZnIn₂S₄ was approximately 17 $\text{cm}^3 \text{g}^{-1}$, which displayed higher CO₂ affinity than those of pure PCN and ZnIn₂S₄. The excellent CO₂ affinity of the optimal composite demonstrated that the activation of CO₂ molecules by the active sites was vital to promote redox catalysis of interfacial CO₂. Notable, the optimal PCN/ZnIn₂S₄ sample presented noticeably enhanced performance, affording a high rate of CO generation of 44.6 $\mu\text{mol h}^{-1}$, which was nearly 223 times higher than that of the pure PCN nanosheets.

Recently, hollow core-shell structures with large surface areas, copious active sites and well-defined internal cavities have become a cutting-edge research area compared to their solid counterparts [376]. The unique yolk-shell structure is able to realize the light reflection in the cavity, thus enhancing the availability ratio of light significantly. With these rationales as the guideline, Liang's group prepared Z-scheme Au@g-C₃N₄/SnS yolk-shell heterostructures by employing Au as an electron mediator to ameliorate the photocatalytic CO₂ conversion (Fig. 21(a)) [369]. The maximum CO₂ adsorption abilities of Au@g-C₃N₄, Au@SnS and Au@g-C₃N₄/SnS (SnS 41.2 wt%) were 0.15, 0.17 and 0.32 mmol g^{-1} , which ascertained that Au@g-C₃N₄/SnS showed better performance than Au@g-C₃N₄ and Au@SnS to operate interfacial CO₂ redox catalysis with high stability even after 5 reaction cycles (Fig. 21(b)). The maximum yields of CH₄ (3.8 $\mu\text{mol g}^{-1}$), CO (17.1 $\mu\text{mol g}^{-1}$) and CH₃OH (5.3 $\mu\text{mol g}^{-1}$) were acquired in the presence of optimal SnS content of 41.5% (Fig. 21(c)). The outstanding improvement of the charge separation efficiency due to the unique structure was the primary factor for the photocatalytic enhancement. In short, the above research has shown boundless frontiers and promises of reducing CO₂ to energy fuels using g-C₃N₄-based metal sulfide nanocomposites. Nevertheless, it should be emphasized that the generation of carbon-based fuels from the reduction of CO₂ requires more confirmation to eliminate the likelihood of the decomposition of organic impurities or carbon-containing samples. Therefore, isotopic ¹³CO₂ analysis is imperative to substantiate that the hydrocarbon products are originated from the CO₂ fixation [377].

Fig. 21. (a) Schematic of the Au@void@g-C₃N₄/SnS yolk-shell heterostructures. (b) Rate of CH₄ production from the CO₂ photoreduction with respect to cycling runs of Au@g-C₃N₄/SnS yolk-shell photocatalysts (with 41.2 wt% SnS). (c) Hydrocarbon generation rates for Au@SnS, Au@g-C₃N₄ and Au@g-C₃N₄/SnS under 4 h irradiation. Reprinted with permission from Ref. [369]. Copyright 2018 American Chemical Society.

4.3. Degradation of organic pollutants

With rapid growth of population and significant industrialization, the toxic and hazardous pollutants emitted into the environment have become a major threat to human health and life all over the world [36,378]. Photocatalysis has proven to be an appealing strategy for environmental decontamination [379–389]. Under visible light illumination, the highly reactive electrons can reduce O₂ to produce •O₂⁻. Simultaneously, the photogenerated holes can initiate reduction reaction to oxidize OH⁻ to produce •OH [390]. The active species can degrade certain organic pollutants [391]. In this section, we will mainly present some g-C₃N₄-based metal sulfide photocatalyst systems in the degradation of organic pollutants.

Recently, incessant efforts have been made to construct Z-scheme heterojunction photocatalysts to degrade the organic pollutants due to its unique charge transfer mechanism, which can significantly improve the photocatalytic efficiency. By anchoring Ag nanoparticles on the g-C₃N₄ and MoS₂ microspheres, a g-C₃N₄/Ag/MoS₂ ternary composite was successfully prepared (Fig. 22(a)) [253]. It can be observed in Fig. 22(b), the g-C₃N₄/Ag/MoS₂ exhibited a higher degradation efficiency than the bare g-C₃N₄ and MoS₂ owing to stronger absorption of visible light, a better separation efficiency of photogenerated charge carriers and a higher photocurrent density. The heterojunction-transfer mechanism in the g-C₃N₄/Ag/MoS₂ photocatalyst elucidated the RhB degradation phenomenon (Fig. 22(c)): the holes in MoS₂ would transfer into the VB of g-C₃N₄, and the photoinduced electrons on the g-C₃N₄ shifted into ei-

Fig. 22. (a) The structure image of MoS₂, Ag@MoS₂ and g-C₃N₄/Ag/MoS₂. (b) Photocatalytic degradation of RhB for different samples. (c) Proposed transfer mechanism of photogenerated charge carriers in the g-C₃N₄/Ag/MoS₂ photocatalyst. Reprinted with permission from Ref. [253]. Copyright 2016 American Chemical Society.

ther the CB of MoS₂ or inject into Ag. As the holes in the VB of Ag or g-C₃N₄ had strong powers of oxidation to degrade RhB molecules, the photodegradation efficiency was remarkably improved in the g-C₃N₄/Ag/MoS₂ system, which recorded 9.43- and 3.56-folds compared with the Ag/MoS₂ and g-C₃N₄/MoS₂ systems, respectively.

It is well known that loading precious metals, such as Pt and Au, can effectively increase the efficiency of photocatalysts. However, these metals are expensive for the commercial application. In view of this, MoS₂ as an economical alternative co-catalyst has been widely used. By using a low temperature hydrothermal method, a MoS₂ and g-C₃N₄ photocatalyst was prepared [392]. Under simulated solar light, the nanocomposite exhibited superior performance and stability in the MO photodegradation. In the same period, a composite structure comprising of MoS₂ nanosheets and g-C₃N₄ was fabricated by Li's group via a facile ultrasonic chemical method [133]. In this architecture, MoS₂ improved light harvesting and served as electron trap to extend the lifetime charge carriers separation, which led to the overall photocatalytic enhancement. Meanwhile, the accumulated holes on the g-C₃N₄ surface directly oxidized the organic dye, which was the main process in the photodegradation of organic pollutants in water treatment. The optimized MoS₂/g-C₃N₄ heterostructures exhibited a high reaction rate constant of 0.301 min⁻¹, which was 3.6 times greater than pure carbon nitride and much superior than many previous reports [393–395].

In order to further improve the photocatalytic performance in the degradation, Zhang's group successfully synthesized

2D/2D ultrathin hexagonal SnS₂ nanosheets/g-C₃N₄ nanosheets heterojunction photocatalysts through a facile ultrasonic dispersion method [396]. From the photocatalytic degradation curves (Fig. 23(A)), the photocatalytic activity was significantly influenced by SnS₂ content. The optimized 5 wt% SnS₂/g-C₃N₄ (SCHN5) photocatalyst removed ~99.8% of RhB under visible light irradiation for only 20 min, which was better than the pure SnS₂ (~80.2%), suggesting that the synergistic effect of the g-C₃N₄/SnS₂ heterojunction can effectively increase the photocatalytic activity through the photoinduced interfacial charge transfer. They have investigated the wavelength dependence of the photocatalysis (Fig. 23(B)), signifying that all the photocatalysts showed distinct photocatalytic activities. Because MO and 4-nitrophenol (4-NP) had poor self-sensitization and relatively more stable structures, the photocatalytic activities of SCHN5 of the target pollutants were also studied. The degradation ratios of MO (~95.0%) and 4-NP (~31.3%) for the SCHN5 were much higher than those of bare SnS₂ (MO: ~35.4%; 4-NP: ~15.6%) and g-C₃N₄ (MO: ~45.5%; 4-NP: ~20.1%) (Fig. 23(C) and 23(D)). As such, this work provides new inroads into constructing 2D/2D photocatalysts with effective charge separation for boosting photodegradation efficiency of organic pollutants from wastewater.

Moreover, Zn_{0.8}Cd_{0.2}S, a visible-light-active catalyst, was also selected to combine with g-C₃N₄. By using a simple precipitation method, the in situ decoration of Zn_{0.8}Cd_{0.2}S on P-doped g-C₃N₄ was successfully performed to construct the P-doped g-C₃N₄/Zn_{0.8}Cd_{0.2}S heterostructures [397]. The photocatalytic degradation of methylene blue (MB) was investigated under simulated sunlight. The nanocomposite recorded 91.3% deg-

Fig. 23. Photocatalytic degradation curves of RhB (A), MO (C), and 4-NP (D) over the as-prepared samples under visible light irradiation. (B) Wavelength-dependence for photocatalytic degradation of RhB over the as-prepared samples: (a) g-C₃N₄ nanosheets; (b) 0.5 wt% SnS₂/g-C₃N₄; (c) 1.0 wt% SnS₂/g-C₃N₄; (d) 3.0 wt% SnS₂/g-C₃N₄; (e) 5.0 wt% SnS₂/g-C₃N₄; (f) 10.0 wt% SnS₂/g-C₃N₄; (g) SnS₂ nanosheets, and UV-vis absorption spectra of 5 wt% SnS₂/g-C₃N₄ (h) and RhB aqueous solution (i). Reprinted with permission from Ref. [396]. Copyright 2015 Elsevier.

radiation efficiency, which was higher than bare P-doped g-C₃N₄ and Zn_{0.8}Cd_{0.2}S. Similarly, g-C₃N₄/Zn_{1-x}Cd_xS nanocomposites with adjustment of band gap were synthesized by Cui et al. [398]. Based on the experiment results, the optimal g-C₃N₄/Zn_{0.8}Cd_{0.2}S nanocomposites showed the highest photocatalytic activities with the degradation efficiency of RhB increasing to 97.9% within 90 min. The improvement of the photoactivity was originated from the effective separation and transposition of the photoinduced electron-hole pairs and the appealing band structures. The work demonstrates that the g-C₃N₄/Zn_{0.8}Cd_{0.2}S composite would not only provide a promising photocatalyst candidate for applications in organic pollutants degradation, but also cast a new insight into the design of highly efficient nanomaterials for diverse photocatalytic applications.

4.4. Nitrogen fixation

N₂ is the necessary element for the growth of animals and plants [399,400]. In nature, N₂ fixation is the second most important chemical process next to photosynthesis. The Haber-Bosch process is the main artificial process for ammonia (NH₃) synthesis industrially [401]. However, the amount of

energy required from this high temperature and pressure process method is around 1%–2% of the world's annual energy consumption [402]. Therefore, developing green and sustainable strategies for NH₃ synthesis using renewable energy is strongly desired. In 1977, Schrauzer et al. [403] first reported that N₂ could be reduced to NH₃ over Fe-doped TiO₂ under from the following reaction:

Since then, many g-C₃N₄-based photocatalysts have been reported for N₂ photofixation [293,404–407]. Among them, g-C₃N₄-based metal sulfide photocatalysts have attracted growing interest for the appealing band gap, excellent electrical and optical properties.

Recent years have witnessed ever-increasing interest in the metal sulfides with sulfur vacancies for the application in N₂ fixation because it not only can adsorb and activate the N₂ molecules serving as the active site, but also can significantly improve the N₂ photofixation ability [72,89]. The ZnMoCdS/g-C₃N₄ heterojunction photocatalysts prepared by Zhang et al. [408] exhibited outstanding N₂ photofixation ability under visible light. As illustrated in Fig. 24(a), g-C₃N₄ showed a typical sheet-like morphology, which was decorated

Fig. 24. (a) TEM image of the 20% ZnMoCdS loaded on g-C₃N₄. (b) Visible-light N₂ fixation performance of as-synthesised catalysts. Reprinted with permission from Ref. [408]. Copyright 2016 Royal Society of Chemistry. (c) TEM image of the 20% ZnSnCdS loaded on g-C₃N₄. (d) N₂ fixation performance of as-synthesised catalysts and the stability of ZnSnCdS-CN(20%). Reprinted with permission from Ref. [406]. Copyright 2016 American Chemical Society.

with plenty of irregular ZnMoCdS particles. When the loading content of ZnMoCdS was 20%, the sample exhibited the maximum rate of generation of NH_4^+ ($3.5 \text{ mg L}^{-1} \text{ h}^{-1}$), which was 1.75- and 13.5-folds greater than those of bare ZnMoCdS and $\text{g-C}_3\text{N}_4$, respectively (Fig. 24(b)). The excellent N_2 fixation ability was attributed to the synergy effect of the sulfur vacancies and heterojunctions. In another research on the artificial photofixation of N_2 , Hu's group [406] fabricated a composite structure comprising of ZnSnCdS and $\text{g-C}_3\text{N}_4$ by hydrothermal method. A size of 30–50 nm of ZnSnCdS was strongly coupled with the surface of the $\text{g-C}_3\text{N}_4$ (Fig. 24(c)). A remarkable separation of charge carriers in the coupled heterojunction was evidenced, giving rise to improved N_2 fixation. In comparison with the earlier work using ZnMoCdS/ $\text{g-C}_3\text{N}_4$, the optimal ZnSnCdS/ $\text{g-C}_3\text{N}_4$ manifested an overwhelmingly better performance in the NH_4^+ generation ($7.543 \text{ mg L}^{-1} \text{ h}^{-1}$) with more than 50 h of reaction stability (Fig. 24(d)), evincing that the Sn-based metal sulfide was propitious to the reduction of N_2 . To sum up, despite very few works on the investigation of N_2 fixation using $\text{g-C}_3\text{N}_4$ -based metal sulfide photocatalysts at present, we envisage that more booming researches are underway to further advance this pacey field in order to fully uncover the prospects for practical benefits.

5. Conclusions, perspective and outlook

Since Wang et al. [74] first discovered $\text{g-C}_3\text{N}_4$ for the use in the photocatalytic H_2 evolution in 2009, various types of $\text{g-C}_3\text{N}_4$ -based nanocomposite systems have been extensively constructed. Particularly, coveted efforts have been undertaken to design the $\text{g-C}_3\text{N}_4$ -based metal sulfide heterojunctions due to their unique properties, such as the extended light absorption range, the remarkable adsorption capacity and the excellent efficiency of charge separation and migration, thus significantly boosting the photocatalytic performance. Taking the merits of the superior characteristics, they are broadly used for the applications in photocatalytic H_2 evolution, reduction of CO_2 and N_2 fixation. Overall, this review depicts an overview of $\text{g-C}_3\text{N}_4$ -based metal sulfide heterostructured photocatalysts, focusing on the charge transfer mechanisms via various types of heterojunctions in the heterostructured photocatalysts for practical applications in energy conversion (Fig. 25).

Despite the significant progress has been accomplished in the $\text{g-C}_3\text{N}_4$ -based metal sulfide heterostructured photocatalysts, the photocatalytic efficiency is still below par and not able to meet the practical benefits for commercialization. Notably, they also suffer from the relatively low stability of the hybrid nanocomposites, relatively narrow absorption range of the spectrum and the ultrafast electron-hole recombination on the semiconductor, which are far from the requirements of technological readiness. In regard of this, there are a plethora of issues, which need to be overcome for remarkable solar-to-chemical energy conversion efficiency before the commercial applications are possible in the future.

Recently, the Z-scheme $\text{g-C}_3\text{N}_4$ -based metal sulfide photocatalytic system has invigorated immense attention as the appealing heterojunction compared with the traditional Type II

Fig. 25. Summary diagram of the hybridization of $\text{g-C}_3\text{N}_4$ with transition metal sulfide (TMS) to form heterojunction interfaces for photocatalytic H_2 evolution, CO_2 reduction and N_2 fixation.

process. To understand the transport directions of charge carriers in the Z-scheme system, the current method is validated by electron paramagnetic resonance (EPR), reactive species scavenging experiments, terephthalic acid assisted PL spectroscopy, and also by the first-principles computational approach. However, advanced characterization such as double-beam photoacoustic (DB-PA) spectroscopy can be employed to systematically probe the electron-hole transfer in the hybrid nanocomposites.

Morphology variation plays a prevailing role in designing highly efficient heterojunction nanostructures [409,410]. Compared with other types of morphologies in constructing nanohybrids such as 1D substrate (0D/1D and 1D/1D) or 2D substrate (0D/2D and 1D/2D), the intriguing 2D/2D structure possesses the highest degree of face-to-face contact, thus endowing higher charge mobility across the interfaces in alleviating the charge recombination to result in significant enhancement of photocatalytic performance. Lately, the unique 2D/2D heterojunction has raised the wave of interests among the community. Strenuous efforts should be further devoted to designing innovative synthesis strategy to aim for mass production of the 2D/2D nanohybrids for practicality.

In addition to that, a more comprehensive understanding of the charge transport process is of vital importance for further boosting the photoactivity of $\text{g-C}_3\text{N}_4$ -based metal sulfide heterostructured composites. It is necessary to understand the migration pathway of the charge pairs in a binary component heterostructure. Additionally, it will become more complex to control the charge transfer in multicomponent heterostructures. Thus, systematic investigations from the experimental and theoretical aspects are necessary for uncovering the underlying photocatalytic enhancement. Therefore, an in-depth study of the charge transport process in the photocatalysts integrated with three or more components is pressingly required to advance this emerging research.

Furthermore, insights into understanding the optical absorption, band potentials, electrical conductivity and charge transport mechanism in the g-C₃N₄-based heterojunction photocatalysts for the energy applications require further systematic exploration by means of the density functional theory (DFT) calculations other than experimental analysis. As such, this will provide a rational context to comprehend the true picture of the properties of the photocatalysts. In addition to the charge transport mechanism, the thermodynamics and kinetics of surface reactions also require more comprehensive investigations. This research should be put more emphasis in the future, which can be explored by the in situ surface-sensitive characterization techniques and theoretical calculations. Hence, our understanding of the relationship between the type of heterojunction and structure activity can be remarkably deepened.

Looking at the future, there is no doubt that the explosive growth of g-C₃N₄-based metal sulfide photocatalysts will significantly accelerate in years to come. With the joint efforts and synergy cooperation from diverse research fields, advanced photocatalysts with unique traits can be designed. In the long run, the energy-related global and the environmental issues could be rationally addressed. Last but not least, we hope that this review can serve as a good guiding star to all researchers for the exploration of next-generation g-C₃N₄-based metal sulfide photocatalysts with the target of achieving renewable en-

ergy technologies to reduce the over dependence on fossil fuel in future.

Acknowledgments

W. J. Ong acknowledges financial assistance and faculty start-up grants/supports from Xiamen University. This work is supported by Xiamen University Malaysia Research Fund (XMUMRF/2019-C3/IENG/0013). W. J. Ong would also like to thank Petronas, ExxonMobil and Shell Malaysia for granting him the '2018 Merdeka Award Grant'.

References

- [1] W. J. Ong, L. L. Tan, Y.H. Ng, S. T. Yong, S. P. Chai, *Chem. Rev.*, **2016**, 116, 7159–7329.
- [2] P. Li, W. Chen, *Chin. J. Catal.*, **2019**, 40, 4–22.
- [3] E. Kabir, P. Kumar, S. Kumar, A. A. Adelodun, K. H. Kim, *Renew. Sustain. Energy Rev.*, **2018**, 82, 894–900.
- [4] T. H. Jeon, M. S. Koo, H. Kim, W. Choi, *ACS Catal.*, **2018**, 8, 11542–11563.
- [5] A. Landman, H. Dotan, G. E. Shter, M. Wullenkord, A. Houaijia, A. Maljusch, G. S. Grader, A. Rothschild, *Nat. Mater.*, **2017**, 16, 646.
- [6] R. Li, *Chin. J. Catal.*, **2017**, 38, 5–12.
- [7] I. Roger, M. A. Shipman, M. D. Symes, *Nat. Rev. Chem.*, **2017**, 1, 0003.
- [8] J. Peng, X. Chen, W. J. Ong, X. Zhao, N. Li, *Chem*, **2019**, 5, 18–50.

Graphical Abstract

Chin. J. Catal., 2019, 40: 289–319 doi: S1872-2067(19)63293-6

Interfacial engineering of graphitic carbon nitride (g-C₃N₄)-based metal sulfide heterojunction photocatalysts for energy conversion: A review

Yijie Ren, Deqian Zeng *, Wee-Jun Ong *

Xiamen University Malaysia, Malaysia; Guangxi University, China; Xiamen University, China

This review presents recent developments of g-C₃N₄-based metal sulfide heterojunction photocatalysts for the energy conversion. The state-of-the-art advancement of this emerging g-C₃N₄ field from the aspects of fabrication and charge separation will be elucidated.

- [9] W. J. Ong, Z. Lin, K. Domen, *Part. Part. Syst. Charact.*, **2018**, 35, 1700451.
- [10] Q. Xu, W. Cai, W. Li, T.S. Sreeprasad, Z. He, W. J. Ong, N. Li, *Mater. Today Energy*, **2018**, 10, 222–240.
- [11] Y. W. Phuan, W. J. Ong, M. N. Chong, J. D. Ocon, *J. Photochem. Photobiol. C*, **2017**, 33, 54–82.
- [12] L. Zhu, M. Gao, C. K. N. Peh, G. W. Ho, *Mater. Horiz.*, **2018**, 5, 323–343.
- [13] J. Jian, G. Jiang, R. van de Krol, B. Wei, H. Wang, *Nano Energy*, **2018**, 51, 457–480.
- [14] T. Yao, X. An, H. Han, J. Q. Chen, C. Li, *Adv. Energy Mater.*, **2018**, 8, 1800210.
- [15] K. Fan, J. Yu, W. Ho, *Mater. Horiz.*, **2017**, 4, 319–344.
- [16] L. Zhang, C. Y. Lin, D. Zhang, L. Gong, Y. Zhu, Z. Zhao, Q. Xu, H. Li, Z. Xia, *Adv. Mater.*, **2018**, doi: 10.1002/adma.201805252.
- [17] S. Y. Bae, I. Y. Jeon, J. Mahmood, J. B. Baek, *Chem. Eur. J.*, **2018**, 24, 18158–18179.
- [18] H. Li, X. Jia, Q. Zhang, X. Wang, *Chem*, **2018**, 4, 1510–1537.
- [19] H. Wang, Q. L. Zhu, R. Zou, Q. Xu, *Chem*, **2017**, 2, 52–80.
- [20] N. Zhang, C. Han, X. Fu, Y. J. Xu, *Chem*, **2018**, 4, 1832–1861.
- [21] Z. Li, X. Meng, Z. Zhang, *J. Photochem. Photobiol. C*, **2018**, 35, 39–55.
- [22] W. Wang, M. O. Tadé, Z. Shao, *Prog. Mater. Sci.*, **2018**, 92, 33–63.
- [23] J. Twilton, C. Le, P. Zhang, M. H. Shaw, R. W. Evans, D. W. C. MacMillan, *Nat. Rev. Chem.*, **2017**, 1, 0052.
- [24] M. R. Hoffmann, S. T. Martin, W. Y. Choi, D. W. Bahnemann, *Chem. Rev.*, **1995**, 95, 69–96.
- [25] S. N. Habisreutinger, L. Schmidt-Mende, J. K. Stolarczyk, *Angew. Chem. Int. Ed.*, **2013**, 52, 7372–7408.
- [26] Y. Chen, X. Wang, *J. Phys. Chem. C*, **2018**, 122, 3786–3793.
- [27] Z. Zheng, W. Xie, B. Huang, Y. Dai, *Chem. Eur. J.*, **2018**, 24, 18322–18333.
- [28] S. Chen, Y. Qi, C. Li, K. Domen, F. Zhang, *Joule*, **2018**, 2, 2260–2288.
- [29] Y. K. Jo, J. M. Lee, S. Son, S. J. Hwang, *J. Photochem. Photobiol. C*, **2018**, doi: 10.1016/j.jphotochemrev.2018.03.002.
- [30] J. Yan, P. Verma, Y. Kuwahara, K. Mori, H. Yamashita, *Small Methods*, **2018**, 2, 1800212.
- [31] B. M. Jun, S. Kim, J. Heo, C. M. Park, N. Her, M. Jang, Y. Huang, J. Han, Y. Yoon, *Nano Res.*, **2018**, doi: 10.1007/s12274-018-2225-3.
- [32] Y. Chen, X. Xin, N. Zhang, Y. J. Xu, *Part. Part. Syst. Charact.*, **2017**, 34, 1600357.
- [33] J. Di, J. Xia, H. Li, Z. Liu, *Nano Energy*, **2017**, 35, 79–91.
- [34] X. Chen, S. Shen, L. Guo, S. S. Mao, *Chem. Rev.*, **2010**, 110, 6503–6570.
- [35] X. Li, R. Shen, S. Ma, X. Chen, J. Xie, *Appl. Surf. Sci.*, **2018**, 430, 53–107.
- [36] C. Regmi, B. Joshi, S. K. Ray, G. Gyawali, R. P. Pandey, *Front. Chem.*, **2018**, 6, 33/1–33/6.
- [37] Q. Xu, W. Li, L. Ding, W. Yang, H. Xiao, W. J. Ong, *Nanoscale*, **2019**, 11, 1475–1504.
- [38] D. Kong, Y. Zheng, M. Kobielusz, Y. Wang, Z. Bai, W. Macyk, X. Wang, J. Tang, *Mater. Today*, **2018**, 21, 897–924.
- [39] W. Han, Z. Li, Y. Li, X. Fan, F. Zhang, G. Zhang, W. Peng, *Front. Chem.*, **2017**, 5, 84/1–84/6.
- [40] A. Li, W. Zhu, C. Li, T. Wang, J. Gong, *Chem. Soc. Rev.*, **2019**, doi: 10.1039/c8cs00711j.
- [41] P. Moroz, A. Boddy, M. Zamkov, *Front. Chem.*, **2018**, 6, 353/1–353/7.
- [42] S. Chen, T. Takata, K. Domen, *Nat. Rev. Mater.*, **2017**, 2, 17050.
- [43] A. Fujishima, K. Honda, *Nature*, **1972**, 238, 37–38.
- [44] R. He, S. Cao, P. Zhou, J. Yu, *Chin. J. Catal.*, **2014**, 35, 989–1007.
- [45] R. He, D. Xu, B. Cheng, J. Yu, W. Ho, *Nanoscale Horiz.*, **2018**, 3, 464–504.
- [46] X. Wu, J. Zhao, L. Wang, M. Han, M. Zhang, H. Wang, H. Huang, Y. Liu, Z. Kang, *Appl. Catal. B*, **2017**, 206, 501–509.
- [47] O. Bechambi, M. Chalbi, W. Najjar, S. Sayadi, *Appl. Surf. Sci.*, **2015**, 347, 414–420.
- [48] X. Chen, Z. Wu, D. Liu, Z. Gao, *Nanoscale Res. Lett.*, **2017**, 12, 143.
- [49] H. Li, W. Li, F. Wang, X. Liu, C. Ren, *Appl. Catal. B*, **2017**, 217, 378–387.
- [50] J. Xu, C. Sun, Z. Wang, Y. Hou, Z. Ding, S. Wang, *Chem. Eur. J.*, **2018**, 24, 18512–18517.
- [51] J. Zhang, H. Wang, X. Yuan, G. Zeng, W. Tu, S. Wang, *J. Photochem. Photobiol. C*, **2019**, 38, 1–26.
- [52] S. Ma, Y. Deng, J. Xie, K. He, W. Liu, X. Chen, X. Li, *Appl. Catal. B*, **2018**, 227, 218–228.
- [53] K. Zhang, Y. Lin, Z. Muhammad, C. Wu, S. Yang, Q. He, X. Zheng, S. Chen, B. Ge, L. Song, *Nano Res.*, **2017**, 10, 3817–3825.
- [54] C. Luo, X. Ren, Z. Dai, Y. Zhang, X. Qi, C. Pan, *ACS Appl. Mater. Interfaces*, **2017**, 9, 23265–23286.
- [55] A. L. Linsebigler, G. Lu, J. T. Yates, *Chem. Rev.*, **1995**, 95, 735–758.
- [56] Y. Ma, X. Wang, Y. Jia, X. Chen, H. Han, C. Li, *Chem. Rev.*, **2014**, 114, 9987–10043.
- [57] M. Ni, M. K. H. Leung, D. Y. C. Leung, K. Sumathy, *Renew. Sust. Energy Rev.*, **2007**, 11, 401–425.
- [58] A. Miyoshi, S. Nishioka, K. Maeda, *Chem. Eur. J.*, **2018**, 24, 18204–18219.
- [59] C. P. Sajan, S. Wageh, A. A. Al-Ghamdi, J. Yu, S. Cao, *Nano Res.*, **2016**, 9, 3–27.
- [60] W. J. Ong, M. M. Gui, S. P. Chai, A. R. Mohamed, *RSC Adv.*, **2013**, 3, 4505–4509.
- [61] W. J. Ong, L. L. Tan, S. P. Chai, S. T. Yong, A. R. Mohamed, *ChemSusChem*, **2014**, 7, 690–719.
- [62] K. Lan, R. Wang, W. Zhang, Z. Zhao, A. Elzatahry, X. Zhang, Y. Liu, D. Al-Dhayan, Y. Xia, D. Zhao, *Chem*, **2018**, 4, 2436–2450.
- [63] W. J. Ong, L. L. Tan, S. P. Chai, S. T. Yong, A. R. Mohamed, *Nanoscale*, **2014**, 6, 1946–2008.
- [64] R. K. Upadhyay, N. Soin, S. S. Roy, *RSC Adv.*, **2014**, 4, 3823–3851.
- [65] K. M. Lee, C. W. Lai, K. S. Ngai, J. C. Juan, *Water Res.*, **2016**, 88, 428–448.
- [66] Z. Sun, H. Zheng, J. Li, P. Du, *Energy Environ. Sci.*, **2015**, 8, 2668–2676.
- [67] D. Zeng, W. Xu, W. J. Ong, J. Xu, H. Ren, Y. Chen, H. Zheng, D. L. Peng, *Appl. Catal. B*, **2018**, 221, 47–55.
- [68] W. Zhen, X. Ning, B. Yang, Y. Wu, Z. Li, G. Lu, *Appl. Catal. B*, **2018**, 221, 243–257.
- [69] Z. Pan, Y. Zheng, F. Guo, P. Niu, X. Wang, *ChemSusChem*, **2017**, 10, 87–90.
- [70] Q. Lu, Y. Yu, Q. Ma, B. Chen, H. Zhang, *Adv. Mater.*, **2016**, 28, 1917–1933.
- [71] C. H. Lai, M. Y. Lu, L. J. Chen, *J. Mater. Chem.*, **2012**, 22, 19–30.
- [72] S. Hu, X. Chen, Q. Li, Y. Zhao, W. Mao, *Catal. Sci. Technol.*, **2016**, 6, 5884–5890.
- [73] Y. Xu, A. Li, T. Yao, C. Ma, X. Zhang, J. H. Shah, H. Han, *ChemSusChem*, **2017**, 10, 4277–4305.
- [74] X. Wang, K. Maeda, A. Thomas, K. Takanabe, G. Xin, J. M. Carlsson, K. Domen, M. Antonietti, *Nat. Mater.*, **2009**, 8, 76–80.
- [75] J. Wen, J. Xie, X. Chen, X. Li, *Appl. Surf. Sci.*, **2017**, 391, 72–123.
- [76] J. Liu, H. Wang, M. Antonietti, *Chem. Soc. Rev.*, **2016**, 45, 2308–2326.
- [77] B. Long, Y. Zheng, L. Lin, K. A. Alamry, A. M. Asiri, X. Wang, *J. Mater. Chem. A*, **2017**, 5, 16179–16188.
- [78] A. Naseri, M. Samadi, A. Pourjavadi, A. Z. Moshfegh, S. Ramakrishna, *J. Mater. Chem. A*, **2017**, 5, 23406–23433.

- [79] Y. Zhao, J. Zhang, L. Qu, *ChemNanoMat*, **2015**, 1, 298–318.
- [80] A. Zambon, J. M. Mouesca, C. Gheorghiu, P. A. Bayle, J. Pécaut, M. Claeys-Bruno, S. Gambarelli, L. Dubois, *Chem. Sci.*, **2016**, 7, 945–950.
- [81] G. Mamba, A. K. Mishra, *Appl. Catal. B*, **2016**, 198, 347–377.
- [82] S. Cao, J. Low, J. Yu, M. Jaroniec, *Adv. Mater.*, **2015**, 27, 2150–2176.
- [83] S. Cao, J. Yu, *J. Phys. Chem. Lett.*, **2014**, 5, 2101–2107.
- [84] S. C. Yan, Z. S. Li, Z. G. Zou, *Langmuir*, **2010**, 26, 3894–3901.
- [85] F. Dong, Z. Zhao, Y. Sun, Y. Zhang, S. Yan, Z. Wu, *Environ. Sci. Technol.*, **2015**, 49, 12432–12440.
- [86] L. Yang, G. Dong, D. L. Jacobs, Y. Wang, L. Zang, C. Wang, *J. Catal.*, **2017**, 352, 274–281.
- [87] Z. Wei, M. Liu, Z. Zhang, W. Yao, H. Tan, Y. Zhu, *Energy Environ. Sci.*, **2018**, 11, 2581–2589.
- [88] Y. Yang, Q. Zhang, R. Zhang, T. Ran, W. Wan, Y. Zhou, *Front. Chem.*, **2018**, 6, 156/1–156/10.
- [89] A. Nikokavouira, C. Trapalis, *Appl. Surf. Sci.*, **2018**, 430, 18–52.
- [90] L. Zhang, N. Ding, M. Hashimoto, K. Iwasaki, N. Chikamori, K. Nakata, Y. Xu, J. Shi, H. Wu, Y. Luo, D. Li, A. Fujishima, Q. Meng, *Nano Res.*, **2018**, 11, 2295–2309.
- [91] W. Niu, Y. Yang, *ACS Energy Lett.*, **2018**, 3, 2796–2815.
- [92] J. Jiang, S. Cao, C. Hu, C. Chen, *Chin. J. Catal.*, **2017**, 38, 1981–1989.
- [93] S. Zhang, P. Gu, R. Ma, C. Luo, T. Wen, G. Zhao, W. Cheng, X. Wang, *Catal. Today*, **2018**, doi: 10.1016/j.cattod.2018.09.013.
- [94] F. Ding, D. Yang, Z. Tong, Y. Nan, Y. Wang, X. Zou, Z. Jiang, *Environ. Sci.: Nano*, **2017**, 4, 1455–1469.
- [95] Y. Zheng, L. Lin, B. Wang, X. Wang, *Angew. Chem. Int. Ed.*, **2015**, 54, 12868–12884.
- [96] Z. Zhao, Y. Sun, F. Dong, *Nanoscale*, **2015**, 7, 15–37.
- [97] L. Jiang, X. Yuan, Y. Pan, J. Liang, G. Zeng, Z. Wu, H. Wang, *Appl. Catal. B*, **2017**, 217, 388–406.
- [98] X. Li, J. Zhang, F. Zhou, H. Zhang, J. Bai, Y. Wang, H. Wang, *Chin. J. Catal.*, **2018**, 39, 1090–1098.
- [99] Q. Liu, T. Chen, Y. Guo, Z. Zhang, X. Fang, *Appl. Catal. B*, **2016**, 193, 248–258.
- [100] X. Chen, X. Zhao, Z. Kong, W. J. Ong, N. Li, *J. Mater. Chem. A*, **2018**, 6, 21941–21948.
- [101] P. Niu, M. Qiao, Y. Li, L. Huang, T. Zhai, *Nano Energy*, **2018**, 44, 73–81.
- [102] H. Yu, R. Shi, Y. Zhao, T. Bian, Y. Zhao, C. Zhou, G. I. N. Waterhouse, L. Z. Wu, C. H. Tung, T. Zhang, *Adv. Mater.*, **2017**, 29, 1605148.
- [103] M. Zhang, Y. Duan, H. Jia, F. Wang, L. Wang, Z. Su, C. Wang, *Catal. Sci. Technol.*, **2017**, 7, 452–458.
- [104] J. Di, J. Xia, X. Li, M. Ji, H. Xu, Z. Chen, H. Li, *Carbon*, **2016**, 107, 1–10.
- [105] Y. Kang, Y. Yang, L. C. Yin, X. Kang, G. Liu, H. M. Cheng, *Adv. Mater.*, **2015**, 27, 4572–4577.
- [106] F. Liu, X. Yan, X. Chen, L. Tian, Q. Xia, X. Chen, *Catal. Today*, **2016**, 264, 243–249.
- [107] Z. Kong, X. Chen, W. J. Ong, X. Zhao, N. Li, *Appl. Surf. Sci.*, **2019**, 463, 1148–1153.
- [108] W. J. Ong, L. K. Putri, Y. C. Tan, L. L. Tan, N. Li, Y. H. Ng, X. Wen, S. P. Chai, *Nano Res.*, **2017**, 10, 1673–1696.
- [109] W. J. Ong, L. L. Tan, S. P. Chai, S. T. Yong, *Dalton Trans.*, **2015**, 44, 1249–1257.
- [110] D. Zeng, P. Wu, W. J. Ong, B. Tang, M. Wu, H. Zheng, Y. Chen, D. L. Peng, *Appl. Catal. B*, **2018**, 233, 26–34.
- [111] D. Zeng, W. J. Ong, H. Zheng, M. Wu, Y. Chen, D. L. Peng, M. Y. Han, *J. Mater. Chem. A*, **2017**, 5, 16171–16178.
- [112] D. Zeng, W. J. Ong, Y. Chen, S. Y. Tee, C. S. Chua, D. L. Peng, M. Y. Han, *Part. Part. Syst. Charact.*, **2018**, 35, 1700251.
- [113] D. Zeng, W. Xu, W. J. Ong, J. Xu, H. Ren, Y. Chen, H. Zheng, D. L. Peng, *Appl. Catal. B*, **2018**, 221, 47–55.
- [114] W. J. Ong, L. K. Putri, L. L. Tan, S. P. Chai, S. T. Yong, *Appl. Catal. B*, **2016**, 180, 530–543.
- [115] L. K. Putri, W. J. Ong, W. S. Chang, S. P. Chai, *Catal. Sci. Technol.*, **2016**, 6, 744–754.
- [116] L. Jing, W. J. Ong, R. Zhang, E. Pickwell-MacPherson, J. C. Yu, *Catal. Today*, **2018**, 315, 103–109.
- [117] Q. Xu, L. Ding, Y. Wen, W. Yang, H. Zhou, X. Chen, J. Street, A. Zhou, W. J. Ong, N. Li, *J. Mater. Chem. C*, **2018**, 6, 6360–6369.
- [118] L. Sun, C. Liu, J. Li, Y. Zhou, H. Wang, P. Huo, C. Ma, Y. Yan, *Chin. J. Catal.*, **2019**, 40, 80–94.
- [119] X. Du, X. Yi, P. Wang, J. Deng, C. C. Wang, *Chin. J. Catal.*, **2019**, 40, 70–79.
- [120] J. Zhang, X. Mao, W. Xiao, Y. Zhuang, *Chin. J. Catal.*, **2017**, 38, 2009–2020.
- [121] B. Xue, Y. Chen, Y. Hong, D. Y. Ma, J. Xu, Y. X. Li, *Chin. J. Catal.*, **2018**, 39, 1263–1271.
- [122] H. Han, M. Fu, Y. Li, W. Guan, P. Lu, X. Hu, *Chin. J. Catal.*, **2018**, 39, 831–840.
- [123] Y. Wang, Q. Wang, X. Zhan, F. Wang, M. Safdar, J. He, *Nanoscale*, **2013**, 5, 8326–8339.
- [124] H. Wang, L. Zhang, Z. Chen, J. Hu, S. Li, Z. Wang, J. Liu, X. Wang, *Chem. Soc. Rev.*, **2014**, 43, 5234–5244.
- [125] J. S. Jang, H. G. Kim, J. S. Lee, *Catal. Today*, **2012**, 185, 270–277.
- [126] J. Wen, J. Xie, Z. Yang, R. Shen, H. Li, X. Luo, X. Chen, X. Li, *ACS Sustainable Chem. Eng.*, **2017**, 5, 2224–2236.
- [127] J. Fu, C. Bie, B. Cheng, C. Jiang, J. Yu, *ACS Sustainable Chem. Eng.*, **2018**, 6, 2767–2779.
- [128] S. Bellamkonda, G. Ranga Rao, *Catal. Today*, **2019**, 321–322, 18–25.
- [129] F. Chen, H. Yang, X. Wang, H. Yu, *Chin. J. Catal.*, **2017**, 38, 296–304.
- [130] J. Wen, J. Xie, H. Zhang, A. Zhang, Y. Liu, X. Chen, X. Li, *ACS Appl. Mater. Interfaces*, **2017**, 9, 14031–14042.
- [131] R. Shen, J. Xie, P. Guo, L. Chen, X. Chen, X. Li, *ACS Appl. Energy Mater.*, **2018**, 1, 2232–2241.
- [132] L. Lu, X. Xu, K. An, Y. Wang, F. N. Shi, *ACS Sustainable Chem. Eng.*, **2018**, 6, 11869–11876.
- [133] Q. Li, N. Zhang, Y. Yang, G. Wang, D. H. L. Ng, *Langmuir*, **2014**, 30, 8965–8972.
- [134] Z. Chen, P. Sun, B. Fan, Z. Zhang, X. Fang, *J. Phys. Chem. C*, **2014**, 118, 7801–7807.
- [135] K. Zhang, L. Guo, *Catal. Sci. Technol.*, **2013**, 3, 1672–1690.
- [136] E. Rahmamanian, R. Malekfar, M. Pumera, *Chem. Eur. J.*, **2018**, 24, 18–31.
- [137] L. Lin, Z. Yu, X. Wang, *Angew. Chem. Int. Ed.*, **2018**, doi: 10.1002/anie.201809897.
- [138] F. K. Kessler, Y. Zheng, D. Schwarz, C. Merschjann, W. Schnick, X. Wang, M. J. Bojdys, *Nat. Rev. Mater.*, **2017**, 2, 17030.
- [139] J. Safaei, N. A. Mohamed, M. F. Mohamad Noh, M. F. Soh, N. A. Ludin, M. A. Ibrahim, W. N. Roslam Wan Isahak, M. A. Mat Teridi, *J. Mater. Chem. A*, **2018**, 6, 22346–22380.
- [140] L. Jiang, X. Yuan, G. Zeng, X. Chen, Z. Wu, J. Liang, J. Zhang, H. Wang, H. Wang, *ACS Sustainable Chem. Eng.*, **2017**, 5, 5831–5841.
- [141] J. Fu, B. Zhu, C. Jiang, B. Cheng, W. You, J. Yu, *Small*, **2017**, 13, 1603938.
- [142] L. Zhou, H. Zhang, H. Sun, S. Liu, M. O. Tade, S. Wang, W. Jin, *Catal. Sci. Technol.*, **2016**, 6, 7002–7023.
- [143] B. Zhu, L. Zhang, B. Cheng, J. Yu, *Appl. Catal. B*, **2018**, 224, 983–999.

- [144] Q. Han, N. Chen, J. Zhang, L. Qu, *Mater. Horiz.*, **2017**, 4, 832–850.
- [145] W. Iqbal, B. Yang, X. Zhao, M. Rauf, M. Waqas, Y. Gong, J. Zhang, Y. Mao, *Catal. Sci. Technol.*, **2018**, 8, 4576–4599.
- [146] D. Huang, Z. Li, G. Zeng, C. Zhou, W. Xue, X. Gong, X. Yan, S. Chen, W. Wang, M. Cheng, *Appl. Catal. B*, **2019**, 240, 153–173.
- [147] J. Fu, Q. Xu, J. Low, C. Jiang, J. Yu, *Appl. Catal. B*, **2019**, 243, 556–565.
- [148] H. An, B. Lin, C. Xue, X. Yan, Y. Dai, J. Wei, G. Yang, *Chin. J. Catal.*, **2018**, 39, 654–663.
- [149] Y. Feng, Y. Wang, M. Li, S. Lv, W. Li, Z. Li, *Appl. Surf. Sci.*, **2018**, 462, 896–903.
- [150] Z. Xu, L. Guan, H. Li, J. Sun, Z. Ying, J. Wu, N. Xu, *J. Phys. Chem. C*, **2015**, 119, 29062–29070.
- [151] L. Guan, N. Xu, X. Liu, Y. Zhao, H. Li, J. Sun, J. Wu, Z. Ying, *Carbon*, **2014**, 79, 578–589.
- [152] Y. Cui, Y. Tang, X. Wang, *Mater. Lett.*, **2015**, 161, 197–200.
- [153] B. Zhu, P. Xia, W. Ho, J. Yu, *Appl. Surf. Sci.*, **2015**, 344, 188–195.
- [154] C. Yang, B. Wang, L. Zhang, L. Yin, X. Wang, *Angew. Chem. Int. Ed.*, **2017**, 56, 6627–6631.
- [155] Y. Wang, F. Wang, Y. Zuo, X. Zhang, L. F. Cui, *Mater. Lett.*, **2014**, 136, 271–273.
- [156] K. Wang, Q. Li, B. Liu, B. Cheng, W. Ho, J. Yu, *Appl. Catal. B*, **2015**, 176–177, 44–52.
- [157] Z. Mo, X. She, Y. Li, L. Liu, L. Huang, Z. Chen, Q. Zhang, H. Xu, H. Li, *RSC Adv.*, **2015**, 5, 101552–101562.
- [158] G. Zhang, M. Zhang, X. Ye, X. Qiu, S. Lin, X. Wang, *Adv. Mater.*, **2014**, 26, 805–809.
- [159] S. Fang, Y. Xia, K. Lv, Q. Li, J. Sun, M. Li, *Appl. Catal. B*, **2016**, 185, 225–232.
- [160] X. Ma, Y. Lv, J. Xu, Y. Liu, R. Zhang, Y. Zhu, *J. Phys. Chem. C*, **2012**, 116, 23485–23493.
- [161] X. Bai, L. Wang, R. Zong, Y. Zhu, *J. Phys. Chem. C*, **2013**, 117, 9952–9961.
- [162] P. Niu, G. Liu, H. M. Cheng, *J. Phys. Chem. C*, **2012**, 116, 11013–11018.
- [163] J. Ran, T. Y. Ma, G. Gao, X. W. Du, S. Z. Qiao, *Energy Environ. Sci.*, **2015**, 8, 3708–3717.
- [164] Y. P. Zhu, T. Z. Ren, Z. Y. Yuan, *ACS Appl. Mater. Interfaces*, **2015**, 7, 16850–16856.
- [165] T. Xiong, W. Cen, Y. Zhang, F. Dong, *ACS Catal.*, **2016**, 6, 2462–2472.
- [166] Y. Gao, F. Hou, S. Hu, B. Wu, Y. Wang, H. Zhang, B. Jiang, H. Fu, *ChemCatChem*, **2018**, 10, 1330–1335.
- [167] M. Li, H. Wang, X. Li, S. Zhang, J. Han, A. F. Masters, T. Maschmeyer, X. Liu, *ChemCatChem*, **2018**, 10, 581–589.
- [168] G. Dong, K. Zhao, L. Zhang, *Chem. Commun.*, **2012**, 48, 6178–6180.
- [169] J. Chen, Z. Hong, Y. Chen, B. Lin, B. Gao, *Mater. Lett.*, **2015**, 145, 129–132.
- [170] Y. Zhou, L. Zhang, W. Huang, Q. Kong, X. Fan, M. Wang, J. Shi, *Carbon*, **2016**, 99, 111–117.
- [171] L. J. Fang, X. L. Wang, J. J. Zhao, Y. H. Li, Y. L. Wang, X. L. Du, Z. F. He, H. D. Zeng, H. G. Yang, *Chem. Commun.*, **2016**, 52, 14408–14411.
- [172] Y. Zhou, L. Zhang, J. Liu, X. Fan, B. Wang, M. Wang, W. Ren, J. Wang, M. Li, J. Shi, *J. Mater. Chem. A*, **2015**, 3, 3862–3867.
- [173] S. Guo, Y. Tang, Y. Xie, C. Tian, Q. Feng, W. Zhou, B. Jiang, *Appl. Catal. B*, **2017**, 218, 664–671.
- [174] J. Xu, L. Zhang, R. Shi, Y. Zhu, *J. Mater. Chem. A*, **2013**, 1, 14766–14772.
- [175] P. Niu, L. Zhang, G. Liu, H. M. Cheng, *Adv. Funct. Mater.*, **2012**, 22, 4763–4770.
- [176] P. Xia, B. Zhu, J. Yu, S. Cao, M. Jaroniec, *J. Mater. Chem. A*, **2017**, 5, 3230–3238.
- [177] D. Zheng, C. Pang, Y. Liu, X. Wang, *Chem. Commun.*, **2015**, 51, 9706–9709.
- [178] S. Zhao, Y. Zhang, Y. Zhou, Y. Wang, K. Qiu, C. Zhang, J. Fang, X. Sheng, *Carbon*, **2018**, 126, 247–256.
- [179] X. Liu, F. Pang, M. He, J. Ge, *Nano Res.*, **2017**, 10, 3638–3647.
- [180] M. Shalom, S. Inal, C. Fettkenhauer, D. Neher, M. Antonietti, *J. Am. Chem. Soc.*, **2013**, 135, 7118–7121.
- [181] Y. Ishida, L. Chabanne, M. Antonietti, M. Shalom, *Langmuir*, **2014**, 30, 447–451.
- [182] J. Low, J. Yu, M. Jaroniec, S. Wageh, A. A. Al-Ghamdi, *Adv. Mater.*, **2017**, 29, 1601694.
- [183] J. Zhang, J. Sun, K. Maeda, K. Domen, P. Liu, M. Antonietti, X. Fu, X. Wang, *Energy Environ. Sci.*, **2011**, 4, 675–678.
- [184] S. Chu, Y. Wang, Y. Guo, J. Feng, C. Wang, W. Luo, X. Fan, Z. Zou, *ACS Catal.*, **2013**, 3, 912–919.
- [185] L. Lu, Z. Lv, Y. Si, M. Liu, S. Zhang, *Appl. Surf. Sci.*, **2018**, 462, 693–712.
- [186] Q. Han, B. Wang, J. Gao, Z. Cheng, Y. Zhao, Z. Zhang, L. Qu, *ACS Nano*, **2016**, 10, 2745–2751.
- [187] M. Gao, J. Feng, Z. Zhang, M. Gu, J. Wang, W. Zeng, Y. Lv, Y. Ren, T. Wei, Z. Fan, *ACS Appl. Nano Mater.*, **2018**, 1, 6733–6741.
- [188] J. Yan, M. T. F. Rodrigues, Z. Song, H. Li, H. Xu, H. Liu, J. Wu, Y. Xu, Y. Song, Y. Liu, P. Yu, W. Yang, R. Vajtai, H. Li, S. Yuan, P. M. Ajayan, *Adv. Funct. Mater.*, **2017**, 27, 1700653.
- [189] X. Liu, J. Iocozzia, Y. Wang, X. Cui, Y. Chen, S. Zhao, Z. Li, Z. Lin, *Energy Environ. Sci.*, **2017**, 10, 402–434.
- [190] B. Kumru, V. Molinari, M. Shalom, M. Antonietti, B. V. K. J. Schmidt, *Soft Matter*, **2018**, 14, 2655–2664.
- [191] J. Sun, B. V. K. J. Schmidt, X. Wang, M. Shalom, *ACS Appl. Mater. Interfaces*, **2017**, 9, 2029–2034.
- [192] M. Zhang, W. Jiang, D. Liu, J. Wang, Y. Liu, Y. Zhu, Y. Zhu, *Appl. Catal. B*, **2016**, 183, 263–268.
- [193] Z. Liu, K. Guo, J. Han, Y. Li, T. Cui, B. Wang, J. Ya, C. Zhou, *Small*, **2014**, 10, 3153–3161.
- [194] L. Tan, C. Yu, M. Wang, S. Zhang, J. Sun, S. Dong, J. Sun, *Appl. Surf. Sci.*, **2019**, 467–468, 286–292.
- [195] Z. Tong, D. Yang, J. Shi, Y. Nan, Y. Sun, Z. Jiang, *ACS Appl. Mater. Interfaces*, **2015**, 7, 25693–25701.
- [196] L. Tang, C. T. Jia, Y. C. Xue, L. Li, A. Q. Wang, G. Xu, N. Liu, M. H. Wu, *Appl. Catal. B*, **2017**, 219, 241–248.
- [197] Y. Hou, Z. Wen, S. Cui, X. Feng, J. Chen, *Nano Lett.*, **2016**, 16, 2268–2277.
- [198] S. J. A. Moniz, S.A. Shevlin, D.J. Martin, Z. X. Guo, J. Tang, *Energy Environ. Sci.*, **2015**, 8, 731–759.
- [199] J. Fu, J. Yu, C. Jiang, B. Cheng, *Adv. Energy Mater.*, **2018**, 8, 1701503.
- [200] Z. Min, X. Wang, Y. Li, J. Jiang, J. Li, D. Qian, J. Li, *Mater. Lett.*, **2017**, 193, 18–21.
- [201] X. Yan, R. Xu, J. Guo, X. Cai, D. Chen, L. Huang, Y. Xiong, S. Tan, *Mater. Res. Bull.*, **2017**, 96, 18–27.
- [202] X. J. Wang, W. Y. Yang, F. T. Li, Y. B. Xue, R. H. Liu, Y. J. Hao, *Ind. Eng. Chem. Res.*, **2013**, 52, 17140–17150.
- [203] S. W. Cao, X. F. Liu, Y. P. Yuan, Z. Y. Zhang, Y. S. Liao, J. Fang, S. C. J. Loo, T. C. Sum, C. Xue, *Appl. Catal. B*, **2014**, 147, 940–946.
- [204] Y. He, Y. Wang, L. Zhang, B. Teng, M. Fan, *Appl. Catal. B*, **2015**, 168–169, 1–8.
- [205] Y. Gong, J. Wang, Z. Wei, P. Zhang, H. Li, Y. Wang, *ChemSusChem*, **2014**, 7, 2303–2309.
- [206] K. Li, F. Y. Su, W. D. Zhang, *Appl. Surf. Sci.*, **2016**, 375, 110–117.
- [207] F. Wang, P. Chen, Y. Feng, Z. Xie, Y. Liu, Y. Su, Q. Zhang, Y. Wang,

- K. Yao, W. Lv, G. Liu, *Appl. Catal. B*, **2017**, 207, 103–113.
- [208] Q. Liu, T. Chen, Y. Guo, Z. Zhang, X. Fang, *Appl. Catal. B*, **2017**, 205, 173–181.
- [209] M. Zhou, S. Wang, P. Yang, Z. Luo, R. Yuan, A. M. Asiri, M. Wakeel, X. Wang, *Chem. Eur. J.*, **2018**, 24, 18529–18534.
- [210] Y. J. Yuan, Y. Yang, Z. Li, D. Chen, S. Wu, G. Fang, W. Bai, M. Ding, L. X. Yang, D. P. Cao, Z. T. Yu, Z. G. Zou, *ACS Appl. Energy Mater.*, **2018**, 1, 1400–1407.
- [211] M. H. Wu, L. Li, Y. C. Xue, G. Xu, L. Tang, N. Liu, W. Y. Huang, *Appl. Catal. B*, **2018**, 228, 103–112.
- [212] G. Gogoi, S. Keene, A. S. Patra, T. K. Sahu, S. Ardo, M. Qureshi, *ACS Sustainable Chem. Eng.*, **2018**, 6, 6718–6729.
- [213] J. Chu, X. Han, Z. Yu, Y. Du, B. Song, P. Xu, *ACS Appl. Mater. Interfaces*, **2018**, 10, 20404–20411.
- [214] Y. C. Zhang, J. Li, M. Zhang, D. D. Dionysiou, *Environ. Sci. Technol.*, **2011**, 45, 9324–9331.
- [215] L. Jing, Y. Xu, Z. Chen, M. He, M. Xie, J. Liu, H. Xu, S. Huang, H. Li, *ACS Sustainable Chem. Eng.*, **2018**, 6, 5132–5141.
- [216] Y. Hou, A. B. Laursen, J. Zhang, G. Zhang, Y. Zhu, X. Wang, S. Dahl, I. Chorkendorff, *Angew. Chem. Int. Ed.*, **2013**, 52, 3621–3625.
- [217] H. Wang, X. Yuan, B. Wang, X. Chen, Z. Wu, L. Jiang, W. Xiong, G. Zeng, *Appl. Catal. B*, **2016**, 193, 36–46.
- [218] D. Jiang, J. Li, C. Xing, Z. Zhang, S. Meng, M. Chen, *ACS Appl. Mater. Interfaces*, **2015**, 7, 19234–19242.
- [219] W. Chen, T. Y. Liu, T. Huang, X. H. Liu, X. J. Yang, *Nanoscale*, **2016**, 8, 3711–3719.
- [220] J. Zhang, Y. Wang, J. Jin, J. Zhang, Z. Lin, F. Huang, J. Yu, *ACS Appl. Mater. Interfaces*, **2013**, 5, 10317–10324.
- [221] J. Wang, P. Guo, Q. Guo, P. G. Jönsson, Z. Zhao, *CrystEngComm*, **2014**, 16, 4485–4492.
- [222] W. Chen, Y. X. Hua, Y. Wang, T. Huang, T. Y. Liu, X. H. Liu, *J. Catal.*, **2017**, 349, 8–18.
- [223] W. J. Kim, E. Jang, T. J. Park, *Appl. Surf. Sci.*, **2017**, 419, 159–164.
- [224] C. Yin, L. Cui, T. Pu, X. Fang, H. Shi, S. Kang, X. Zhang, *Appl. Surf. Sci.*, **2018**, 456, 464–472.
- [225] M. Lu, Z. Pei, S. Weng, W. Feng, Z. Fang, Z. Zheng, M. Huang, P. Liu, *Phys. Chem. Chem. Phys.*, **2014**, 16, 21280–21288.
- [226] W. J. Ong, L. L. Tan, S. P. Chai, S. T. Yong, A. R. Mohamed, *Nano Energy*, **2015**, 13, 757–770.
- [227] Z. Zhang, Y. Huang, K. Liu, L. Guo, Q. Yuan, B. Dong, *Adv. Mater.*, **2015**, 27, 5906–5914.
- [228] P. Xia, B. Zhu, B. Cheng, J. Yu, J. Xu, *ACS Sustainable Chem. Eng.*, **2018**, 6, 965–973.
- [229] B. Luo, G. Liu, L. Wang, *Nanoscale*, **2016**, 8, 6904–6920.
- [230] J. Low, S. Cao, J. Yu, S. Wageh, *Chem. Commun.*, **2014**, 50, 10768–10777.
- [231] P. Chen, N. Li, X. Chen, W. J. Ong, X. Zhao, *2D Mater.*, **2018**, 5, 014002.
- [232] T. Su, Q. Shao, Z. Qin, Z. Guo, Z. Wu, *ACS Catal.*, **2018**, 8, 2253–2276.
- [233] M. Q. Yang, J. Dan, S. J. Pennycook, X. Lu, H. Zhu, Q. H. Xu, H. J. Fan, G. W. Ho, *Mater. Horiz.*, **2017**, 4, 885–894.
- [234] Y. Wu, Z. Liu, Y. Li, J. Chen, X. Zhu, P. Na, *Chin. J. Catal.*, **2019**, 40, 60–69.
- [235] Y. Qi, Q. Liang, R. Lv, W. Shen, F. Kang, Z. H. Huang, *Royal Soc. Open Sci.*, **2018**, 5, 180187.
- [236] G. Liu, G. Zhao, W. Zhou, Y. Liu, H. Pang, H. Zhang, D. Hao, X. Meng, P. Li, T. Kako, J. Ye, *Adv. Funct. Mater.*, **2016**, 26, 6822–6829.
- [237] D. Jiang, L. Chen, J. Zhu, M. Chen, W. Shi, J. Xie, *Dalton Trans.*, **2013**, 42, 15726–15734.
- [238] F. Dong, Z. Zhao, T. Xiong, Z. Ni, W. Zhang, Y. Sun, W. K. Ho, *ACS Appl. Mater. Interfaces*, **2013**, 5, 11392–11401.
- [239] Z. X. Qin, M. L. Wang, R. Li, Y. B. Chen, *Sci. China Mater.*, **2018**, 61, 861–868.
- [240] F. Guo, W. Shi, H. Wang, M. Han, H. Li, H. Huang, Y. Liu, Z. Kang, *Catal. Sci. Technol.*, **2017**, 7, 3325–3331.
- [241] L. K. Putri, B. J. Ng, W. J. Ong, H. W. Lee, W. S. Chang, S. P. Chai, *J. Mater. Chem. A*, **2018**, 6, 3181–3194.
- [242] Z. Cai, Y. Zhou, S. Ma, S. Li, H. Yang, S. Zhao, X. Zhong, W. Wu, *J. Photochem. Photobiol. A*, **2017**, 348, 168–178.
- [243] S. Ma, Y. Song, P. Xu, X. Fu, Z. Ye, J. Xue, *Mater. Lett.*, **2018**, 213, 370–373.
- [244] M. Jourshabani, Z. Shariatnia, G. Achari, C. H. Langford, A. Badii, *J. Mater. Chem. A*, **2018**, 6, 13448–13466.
- [245] L. Ge, C. Han, X. Xiao, L. Guo, *Int. J. Hydrogen Energy*, **2013**, 38, 6960–6969.
- [246] K. He, J. Xie, M. Li, X. Li, *Appl. Surf. Sci.*, **2018**, 430, 208–217.
- [247] K. Qi, B. Cheng, J. Yu, W. Ho, *Chin. J. Catal.*, **2017**, 38, 1936–1955.
- [248] A. J. Bard, M. A. Fox, *Acc. Chem. Res.*, **1995**, 28, 141–145.
- [249] H. Li, W. Tu, Y. Zhou, Z. Zou, *Adv. Sci.*, **2016**, 3, 1500389.
- [250] P. Zhou, J. Yu, M. Jaroniec, *Adv. Mater.*, **2014**, 26, 4920–4935.
- [251] J. Yu, S. Wang, J. Low, W. Xiao, *Phys. Chem. Chem. Phys.*, **2013**, 15, 16883–16890.
- [252] W. K. Jo, T. S. Natarajan, *J. Colloid Interface Sci.*, **2016**, 482, 58–72.
- [253] D. Lu, H. Wang, X. Zhao, K. K. Kondamareddy, J. Ding, C. Li, P. Fang, *ACS Sustainable Chem. Eng.*, **2017**, 5, 1436–1445.
- [254] H. Qin, R. T. Guo, X. Y. Liu, W. G. Pan, Z. Y. Wang, X. Shi, J. Y. Tang, C. Y. Huang, *Dalton Trans.*, **2018**, 47, 15155–15163.
- [255] Y. Liu, H. Zhang, J. Ke, J. Zhang, W. Tian, X. Xu, X. Duan, H. Sun, M. O Tade, S. Wang, *Appl. Catal. B*, **2018**, 228, 64–74.
- [256] Z. Chen, W. Wang, Z. Zhang, X. Fang, *J. Phys. Chem. C*, **2013**, 117, 19346–19352.
- [257] Q. Wang, T. Hisatomi, Y. Suzuki, Z. Pan, J. Seo, M. Katayama, T. Minegishi, H. Nishiyama, T. Takata, K. Seki, A. Kudo, T. Yamada, K. Domen, *J. Am. Chem. Soc.*, **2017**, 139, 1675–1683.
- [258] Z. Wan, G. Zhang, X. Wu, S. Yin, *Appl. Catal. B*, **2017**, 207, 17–26.
- [259] B. Zhu, P. Xia, Y. Li, W. Ho, J. Yu, *Appl. Surf. Sci.*, **2017**, 391, 175–183.
- [260] F. Chen, Q. Yang, X. Li, G. Zeng, D. Wang, C. Niu, J. Zhao, H. An, T. Xie, Y. Deng, *Appl. Catal. B*, **2017**, 200, 330–342.
- [261] X. She, J. Wu, H. Xu, J. Zhong, Y. Wang, Y. Song, K. Nie, Y. Liu, Y. Yang, M. T. F. Rodrigues, R. Vajtai, J. Lou, D. Du, H. Li, P. M. Ajayan, *Adv. Energy Mater.*, **2017**, 7, 1700025.
- [262] D. Zheng, C. Pang, X. Wang, *Chem. Commun.*, **2015**, 51, 17467–17470.
- [263] R. Bala Chandran, S. Breen, Y. Shao, S. Ardo, A. Z. Weber, *Energy Environ. Sci.*, **2018**, 11, 115–135.
- [264] K. He, J. Xie, X. Luo, J. Wen, S. Ma, X. Li, Y. Fang, X. Zhang, *Chin. J. Catal.*, **2017**, 38, 240–252.
- [265] Y. Bu, Z. Chen, C. Sun, *Appl. Catal. B*, **2015**, 179, 363–371.
- [266] N. Zhang, S. Xie, B. Weng, Y. J. Xu, *J. Mater. Chem. A*, **2016**, 4, 18804–18814.
- [267] W. Zhao, L. Xie, M. Zhang, Z. Ai, H. Xi, Y. Li, Q. Shi, J. Chen, *Int. J. Hydrogen Energy*, **2016**, 41, 6277–6287.
- [268] W. Meng, Q. Han, L. Li, L. Tang, H. Li, Y. Zhou, Z. Zou, *Nanotechnology*, **2017**, 28, 274002.
- [269] H. Zhao, X. Ding, B. Zhang, Y. Li, C. Wang, *Sci. Bull.*, **2017**, 62, 602–609.
- [270] Q. Xu, L. Zhang, J. Yu, S. Wageh, A. A. Al-Ghamdi, M. Jaroniec, *Mater. Today*, **2018**, 21, 1042–1063.
- [271] S. Wang, B. Zhu, M. Liu, L. Zhang, J. Yu, M. Zhou, *Appl. Catal. B*, **2019**, 243, 19–26.
- [272] W. Yu, D. Xu, T. Peng, *J. Mater. Chem. A*, **2015**, 3, 19936–19947.
- [273] N. Tian, H. Huang, Y. He, Y. Guo, T. Zhang, Y. Zhang, *Dalton Trans.*,

- 2015**, 44, 4297–4307.
- [274] X. She, J. Wu, J. Zhong, H. Xu, Y. Yang, R. Vajtai, J. Lou, Y. Liu, D. Du, H. Li, P. M. Ajayan, *Nano Energy*, **2016**, 27, 138–146.
- [275] W. Yu, J. Chen, T. Shang, L. Chen, L. Gu, T. Peng, *Appl. Catal. B*, **2017**, 219, 693–704.
- [276] Q. Xu, B. Zhu, C. Jiang, B. Cheng, J. Yu, *Solar RRL*, **2018**, 2, 1800006.
- [277] J. Zhang, Y. Hu, X. Jiang, S. Chen, S. Meng, X. Fu, *J. Hazard. Mater.*, **2014**, 280, 713–722.
- [278] X. Li, K. Xie, L. Song, M. Zhao, Z. Zhang, *ACS Appl. Mater. Interfaces*, **2017**, 9, 24577–24583.
- [279] T. Ohno, N. Murakami, T. Koyanagi, Y. Yang, *J. CO₂ Utiliz.*, **2014**, 6, 17–25.
- [280] M. S. Akple, J. Low, S. Wageh, A. A. Al-Ghamdi, J. Yu, J. Zhang, *Appl. Surf. Sci.*, **2015**, 358, 196–203.
- [281] P. Suyana, S. K. R. B. N. Nair, V. Karunakaran, A. P. Mohamed, K. G. K. Warriar, U. S. Hareesh, *RSC Adv.*, **2016**, 6, 17800–17809.
- [282] X. L. Zhai, J. Liu, L. Y. Hu, J. C. Bao, Y. Q. Lan, *Chem. Eur. J.*, **2018**, 24, 15930–15936.
- [283] Y. Lu, D. Chu, M. Zhu, Y. Du, P. Yang, *Phys. Chem. Chem. Phys.*, **2015**, 17, 17355–17361.
- [284] Y. Zhong, J. Yuan, J. Wen, X. Li, Y. Xu, W. Liu, S. Zhang, Y. Fang, *Dalton Trans.*, **2015**, 44, 18260–18269.
- [285] J. Hong, Y. Wang, Y. Wang, W. Zhang, R. Xu, *ChemSusChem*, **2013**, 6, 2263–2268.
- [286] Q. Li, B. Guo, J. Yu, J. Ran, B. Zhang, H. Yan, J. R. Gong, *J. Am. Chem. Soc.*, **2011**, 133, 10878–10884.
- [287] K. Takanebe, *ACS Catal.*, **2017**, 7, 8006–8022.
- [288] J. Ran, M. Jaroniec, S. Z. Qiao, *Adv. Mater.*, **2018**, 30, 1704649.
- [289] R. Shi, G. I. N. Waterhouse, T. Zhang, *Solar RRL*, **2017**, 1, 1700126.
- [290] Y. Huo, J. Zhang, K. Dai, Q. Li, J. Lv, G. Zhu, C. Liang, *Appl. Catal. B*, **2019**, 241, 528–538.
- [291] J. L. White, M. F. Baruch, J. E. Pander, Y. Hu, I. C. Fortmeyer, J. E. Park, T. Zhang, K. Liao, J. Gu, Y. Yan, T. W. Shaw, E. Abelev, A. B. Bocarsly, *Chem. Rev.*, **2015**, 115, 12888–12935.
- [292] H. Lin, W. Deng, T. Zhou, S. Ning, J. Long, X. Wang, *Appl. Catal. B*, **2015**, 176–177, 36–43.
- [293] R. Li, *Chin. J. Catal.*, **2018**, 39, 1180–1188.
- [294] X. Feng, H. Chen, F. Jiang, X. Wang, *J. Colloid Interface Sci.*, **2018**, 509, 298–306.
- [295] A. J. Medford, M. C. Hatzell, *ACS Catal.*, **2017**, 7, 2624–2643.
- [296] F. Cheng, H. Yin, Q. Xiang, *Appl. Surf. Sci.*, **2017**, 391, 432–439.
- [297] M. Faraji, M. Yousefi, S. Yousefzadeh, M. Zirak, N. Naseri, T. H. Jeon, W. Choi, A. Z. Moshfegh, *Energy Environ. Sci.*, **2019**, doi: 10.1039/c8ee00886h.
- [298] C. Xu, W. Zhang, J. Tang, C. Pan, G. Yu, *Front. Chem.*, **2018**, 6, 592.
- [299] D. W. Wakerley, K. H. Ly, N. Kornienko, K. L. Orchard, M. F. Kuehnle, E. Reisner, *Chem. Eur. J.*, **2018**, 24, 18385–18388.
- [300] Y. Pan, D. Li, H. L. Jiang, *Chem. Eur. J.*, **2018**, 24, 18403–18407.
- [301] M. M. Ayyub, M. Chhetri, U. Gupta, A. Roy, C. N. R. Rao, *Chem. Eur. J.*, **2018**, 24, 18455–18462.
- [302] Z. Liu, J. Liu, Y. Huang, J. Li, Y. Yuan, H. Ye, D. Zhu, Z. Wang, A. Tang, *Nanoscale*, **2019**, 11, 158–169.
- [303] G. D. Gesesse, T. Le Neel, Z. Cui, G. Bachelier, H. Remita, C. Colbeau-Justin, M. N. Ghazzal, *Nanoscale*, **2018**, 10, 20140–20146.
- [304] S. Y. Moon, H. C. Song, E. H. Gwag, I. I. Nedrygailov, C. Lee, J. J. Kim, W. H. Doh, J. Y. Park, *Nanoscale*, **2018**, 10, 22180–22188.
- [305] P. Zhang, T. Wang, J. Gong, *Chem*, **2018**, 4, 223–245.
- [306] D. Zheng, G. Zhang, Y. Hou, X. Wang, *Appl. Catal. A*, **2016**, 521, 2–8.
- [307] G. Zhao, X. Huang, F. Fina, G. Zhang, J. T. S. Irvine, *Catal. Sci. Technol.*, **2015**, 5, 3416–3422.
- [308] H. Yu, P. Xiao, P. Wang, J. Yu, *Appl. Catal. B*, **2016**, 193, 217–225.
- [309] M. Li, L. Zhang, X. Fan, M. Wu, Y. Du, M. Wang, Q. Kong, L. Zhang, J. Shi, *Appl. Catal. B*, **2016**, 190, 36–43.
- [310] H. Zhao, Y. Dong, P. Jiang, H. Miao, G. Wang, J. Zhang, *J. Mater. Chem. A*, **2015**, 3, 7375–7381.
- [311] H. Hou, F. Gao, L. Wang, M. Shang, Z. Yang, J. Zheng, W. Yang, *J. Mater. Chem. A*, **2016**, 4, 6276–6281.
- [312] Q. Gu, H. Sun, Z. Xie, Z. Gao, C. Xue, *Appl. Surf. Sci.*, **2017**, 396, 1808–1815.
- [313] Y. Fu, Z. Li, Q. Liu, X. Yang, H. Tang, *Chin. J. Catal.*, **2017**, 38, 2160–2170.
- [314] J. Yuan, J. Wen, Y. Zhong, X. Li, Y. Fang, S. Zhang, W. Liu, *J. Mater. Chem. A*, **2015**, 3, 18244–18255.
- [315] B. Lin, H. Li, H. An, W. Hao, J. Wei, Y. Dai, C. Ma, G. Yang, *Appl. Catal. B*, **2018**, 220, 542–552.
- [316] L. Yao, D. Wei, Y. Ni, D. Yan, C. Hu, *Nano Energy*, **2016**, 26, 248–256.
- [317] Y. Zou, J. W. Shi, D. Ma, Z. Fan, C. He, L. Cheng, D. Sun, J. Li, Z. Wang, C. Niu, *Catal. Sci. Technol.*, **2018**, 8, 3883–3893.
- [318] X. Hao, J. Zhou, Z. Cui, Y. Wang, Y. Wang, Z. Zou, *Appl. Catal. B*, **2018**, 229, 41–51.
- [319] H. Liu, Z. Xu, Z. Zhang, D. Ao, *Appl. Catal. A*, **2016**, 518, 150–157.
- [320] F. Xue, M. Liu, C. Cheng, J. Deng, J. Shi, *ChemCatChem*, **2018**, 10, 5441–5448.
- [321] N. Li, J. Zhou, Z. Sheng, W. Xiao, *Appl. Surf. Sci.*, **2018**, 430, 218–224.
- [322] M. Long, L. Zheng, *Chin. J. Catal.*, **2017**, 38, 617–624.
- [323] S. Zhang, X. Liu, C. Liu, S. Luo, L. Wang, T. Cai, Y. Zeng, J. Yuan, W. Dong, Y. Pei, Y. Liu, *ACS Nano*, **2018**, 12, 751–758.
- [324] C. Gao, J. Wang, H. Xu, Y. Xiong, *Chem. Soc. Rev.*, **2017**, 46, 2799–2823.
- [325] L. Yin, X. Hai, K. Chang, F. Ichihara, J. Ye, *Small*, **2018**, 14, 1704153.
- [326] W. Chen, T. Huang, T. Y. Liu, G. R. Duan, X. J. Yang, X. H. Liu, *J. Alloys Compd.*, **2017**, 690, 503–511.
- [327] W. Jiang, X. Yin, F. Xin, Y. Bi, Y. Liu, X. Li, *Appl. Surf. Sci.*, **2014**, 288, 138–142.
- [328] M. A. Mahadadalkar, S. B. Kale, R. S. Kalubarme, A. P. Bhirud, J. D. Ambekar, S. W. Gosavi, M. V. Kulkarni, C. J. Park, B. B. Kale, *RSC Adv.*, **2016**, 6, 34724–34736.
- [329] W. K. Jo, T. Sivakumar Natarajan, *ACS Appl. Mater. Interfaces*, **2015**, 7, 17138–17154.
- [330] S. K. Batabyal, S. E. Lu, J. J. Vittal, *Cryst. Growth Des.*, **2016**, 16, 2231–2238.
- [331] M. M. Chen, H. G. Xue, S. P. Guo, *Coord. Chem. Rev.*, **2018**, 368, 115–133.
- [332] D. Zeng, L. Xiao, W. J. Ong, P. Wu, H. Zheng, Y. Chen, D. L. Peng, *ChemSusChem*, **2017**, 10, 4624–4631.
- [333] J. Yan, Z. Chen, H. Ji, Z. Liu, X. Wang, Y. Xu, X. She, L. Huang, L. Xu, H. Xu, H. Li, *Chem. Eur. J.*, **2016**, 22, 4764–4773.
- [334] W. Chen, T. Y. Liu, T. Huang, X. H. Liu, J. W. Zhu, G. R. Duan, X. J. Yang, *J. Mater. Sci.*, **2015**, 50, 8142–8152.
- [335] H. Liu, Z. Jin, Z. Xu, Z. Zhang, D. Ao, *RSC Adv.*, **2015**, 5, 97951–97961.
- [336] Y. Liu, P. Chen, Y. Chen, H. Lu, J. Wang, Z. Yang, Z. Lu, M. Li, L. Fang, *RSC Adv.*, **2016**, 6, 10802–10809.
- [337] M. Yan, Y. Hua, F. Zhu, L. Sun, W. Gu, W. Shi, *Appl. Catal. B*, **2017**, 206, 531–537.
- [338] B. Lin, H. An, X. Yan, T. Zhang, J. Wei, G. Yang, *Appl. Catal. B*, **2017**, 210, 173–183.
- [339] S. Thaweesak, M. Lyu, P. Peerakiatkhajohn, T. Butburee, B. Luo,

- H. Chen, L. Wang, *Appl. Catal. B*, **2017**, 202, 184–190.
- [340] A. Zada, M. Humayun, F. Raziq, X. Zhang, Y. Qu, L. Bai, C. Qin, L. Jing, H. Fu, *Adv. Energy Mater.*, **2016**, 6, 1601190.
- [341] W. J. Ong, *Front. Mater.*, **2017**, 4, 11, doi: 10.3389/fmats.2017.00011.
- [342] Z. Zhang, K. Liu, Z. Feng, Y. Bao, B. Dong, *Sci. Rep.*, **2016**, 6, 19221.
- [343] X. Li, J. Yu, M. Jaroniec, *Chem. Soc. Rev.*, **2016**, 45, 2603–2636.
- [344] Z. Jiang, W. Wan, H. Li, S. Yuan, H. Zhao, P. K. Wong, *Adv. Mater.*, **2018**, 30, 1706108.
- [345] J. Ma, X. Tan, T. Yu, X. Li, *Int. J. Hydrogen Energy*, **2016**, 41, 3877–3887.
- [346] B. Shen, Z. Hong, Y. Chen, B. Lin, B. Gao, *Mater. Lett.*, **2014**, 118, 208–211.
- [347] D. A. Giannakoudakis, N. A. Travlou, J. Secor, T. J. Bandosz, *Small*, **2017**, 13, 1601758.
- [348] J. Wen, X. Li, H. Li, S. Ma, K. He, Y. Xu, Y. Fang, W. Liu, Q. Gao, *Appl. Surf. Sci.*, **2015**, 358, Part A, 204–212.
- [349] J. Low, C. Jiang, B. Cheng, S. Wageh, A. A. Al-Ghamdi, J. Yu, *Small Methods*, **2017**, 1, 1700080/1–1700080/21.
- [350] Z. Qin, W. Fang, J. Liu, Z. Wei, Z. Jiang, W. Shangguan, *Chin. J. Catal.*, **2018**, 39, 472–478.
- [351] F. Shi, L. Chen, M. Chen, D. Jiang, *Chem. Commun.*, **2015**, 51, 17144–17147.
- [352] N. Li, X. Chen, W. J. Ong, D. R. MacFarlane, X. Zhao, A. K. Cheetham, C. Sun, *ACS Nano*, **2017**, 11, 10825–10833.
- [353] Z. Sun, T. Ma, H. Tao, Q. Fan, B. Han, *Chem*, **2017**, 3, 560–587.
- [354] C. Chen, J. F. Khosrowabadi Kotyk, S. W. Sheehan, *Chem*, **2018**, 4, 2571–2586.
- [355] A. Vasileff, C. Xu, Y. Jiao, Y. Zheng, S. Z. Qiao, *Chem*, **2018**, 4, 1809–1831.
- [356] Y. Ma, Z. Wang, X. Xu, J. Wang, *Chin. J. Catal.*, **2017**, 38, 1956–1969.
- [357] Y. Fang, X. Wang, *Chem. Commun.*, **2018**, 54, 5674–5687.
- [358] P. Wang, S. Wang, H. Wang, Z. Wu, L. Wang, *Part. Part. Syst. Charact.*, **2018**, 35, 1700371.
- [359] J. W. Maina, C. Pozo-Gonzalo, L. Kong, J. Schutz, M. Hill, L. F. Dumeé, *Mater. Horiz.*, **2017**, 4, 345–361.
- [360] Z. Sheng, P. Ka, U. K. Tao, K. Shankar, *Nanotechnology*, **2018**, 29, 052001.
- [361] Z. Sun, N. Talreja, H. Tao, J. Texter, M. Muhler, J. Strunk, J. Chen, *Angew. Chem. Int. Ed.*, **2018**, 57, 7610–7627.
- [362] Z. Xiong, Z. Lei, Y. Li, L. Dong, Y. Zhao, J. Zhang, *J. Photochem. Photobiol. C*, **2018**, 36, 24–47.
- [363] Y. Liang, W. Wu, P. Wang, S. C. Liou, D. Liu, S.H. Ehrman, *Nano Res.*, **2018**, 11, 4049–4061.
- [364] X. Chang, T. Wang, P. Yang, G. Zhang, J. Gong, *Adv. Mater.*, **2018**, doi: 10.1002/adma.201804710.
- [365] C. Wang, Z. Sun, Y. Zheng, Y. H. Hu, *J. Mater. Chem. A*, **2018**, doi: 10.1039/c8ta09865d.
- [366] H. Zhang, J. Li, Q. Tan, L. Lu, Z. Wang, G. Wu, *Chem. Eur. J.*, **2018**, 24, 18137–18157.
- [367] J. Low, B. Cheng, J. Yu, *Appl. Surf. Sci.*, **2017**, 392, 658–686.
- [368] H. Liu, Z. Zhang, J. Meng, J. Zhang, *Mol. Catal.*, **2017**, 430, 9–19.
- [369] M. Liang, T. Borjigin, Y. Zhang, H. Liu, B. Liu, H. Guo, *ACS Appl. Mater. Interfaces*, **2018**, 10, 34123–34131.
- [370] Y. Huo, J. Zhang, K. Dai, Q. Li, J. Lv, G. Zhu, C. Liang, *Appl. Catal. B*, **2018**, 241, 528–538.
- [371] Y. L. Wang, Y. Tian, Z. L. Lang, W. Guan, L. K. Yan, *J. Mater. Chem. A*, **2018**, 6, 21056–21063.
- [372] T. Di, B. Zhu, B. Cheng, J. Yu, J. Xu, *J. Catal.*, **2017**, 352, 532–541.
- [373] J. Yu, K. Wang, W. Xiao, B. Cheng, *Phys. Chem. Chem. Phys.*, **2014**, 16, 11492–11501.
- [374] W. J. Ong, L. L. Tan, S. P. Chai, S. T. Yong, *Chem. Commun.*, **2015**, 51, 858–861.
- [375] X. Wang, G. Chen, C. Zhou, Y. Yu, G. Wang, *Eur. J. Inorg. Chem.*, **2012**, 2012, 1742–1749.
- [376] H. Li, Z. Peng, J. Qian, M. Wang, C. Wang, X. Fu, *ACS Appl. Mater. Interfaces*, **2017**, 9, 28704–28715.
- [377] P. Zhang, S. Wang, B. Guan, X. W. D. Lou, *Energy Environ. Sci.*, **2019**, 12, 164–168.
- [378] C. Su, X. Ran, J. Hu, C. Shao, *Environ. Sci. Technol.*, **2013**, 47, 11562–11568.
- [379] M. R. Hoffmann, S. T. Martin, W. Choi, D. W. Bahnemann, *Chem. Rev.*, **1995**, 95, 69–96.
- [380] M. Humayun, Y. Qu, F. Raziq, R. Yan, Z. Li, X. Zhang, L. Jing, *Environ. Sci. Technol.*, **2016**, 50, 13600–13610.
- [381] Q. Zheng, D. P. Durkin, J. E. Elenewski, Y. Sun, N. A. Banek, L. Hua, H. Chen, M. J. Wagner, W. Zhang, D. Shuai, *Environ. Sci. Technol.*, **2016**, 50, 12938–12948.
- [382] U. I. Gaya, A. H. Abdullah, *J. Photochem. Photobiol. C*, **2008**, 9, 1–12.
- [383] D. Chatterjee, S. Dasgupta, *J. Photochem. Photobiol. C*, **2005**, 6, 186–205.
- [384] D. S. Bhatkhande, V. G. Pangarkar, A. A. C. M. Beenackers, *J. Chem. Technol. Biotechnol.*, **2002**, 77, 102–116.
- [385] U.G. Akpan, B.H. Hameed, *J. Hazard. Mater.*, **2009**, 170, 520–529.
- [386] W. J. Ong, S. Y. Voon, L. L. Tan, B.T. Goh, S. T. Yong, S. P. Chai, *Ind. Eng. Chem. Res.*, **2014**, 53, 17333–17344.
- [387] S. N. Ahmed, W. Haider, *Nanotechnology*, **2018**, 29, 342001.
- [388] X. Gu, C. Li, S. Yuan, M. Ma, Y. Qiang, J. Zhu, *Nanotechnology*, **2016**, 27, 402001.
- [389] L. Jin, H. Y. Zeng, S. Xu, C. R. Chen, H. Z. Duan, J. Z. Du, G. Hu, Y. X. Sun, *Chin. J. Catal.*, **2018**, 39, 1832–1841.
- [390] W. J. Ong, J. J. Yeong, L. L. Tan, B.T. Goh, S. T. Yong, S. P. Chai, *RSC Adv.*, **2014**, 4, 59676–59685.
- [391] W. J. Ong, L. L. Tan, S. P. Chai, S. T. Yong, A. R. Mohamed, *ChemSusChem*, **2014**, 7, 690–719.
- [392] W. C. Peng, X. Y. Li, *Catal. Commun.*, **2014**, 49, 63–67.
- [393] Y. Hou, Z. Wen, S. Cui, X. Guo, J. Chen, *Adv. Mater.*, **2013**, 25, 6291–6297.
- [394] S. C. Yan, Z. S. Li, Z. G. Zou, *Langmuir*, **2009**, 25, 10397–10401.
- [395] W. Zhou, Z. Yin, Y. Du, X. Huang, Z. Zeng, Z. Fan, H. Liu, J. Wang, H. Zhang, *Small*, **2013**, 9, 140–147.
- [396] Z. Zhang, J. Huang, M. Zhang, Q. Yuan, B. Dong, *Appl. Catal. B*, **2015**, 163, 298–305.
- [397] W. Tian, N. Li, J. Zhou, *Appl. Surf. Sci.*, **2016**, 361, 251–258.
- [398] X. Cui, Y.F. Zheng, H.Y. Yin, X.C. Song, *Phys. Chem. Chem. Phys.*, **2015**, 17, 29354–29362.
- [399] V. Rosca, M. Duca, M. T. de Groot, M. T. M. Koper, *Chem. Rev.*, **2009**, 109, 2209–2244.
- [400] D. E. Canfield, A. N. Glazer, P. G. Falkowski, *Science*, **2010**, 330, 192.
- [401] A. J. Martín, T. Shinagawa, J. Pérez-Ramírez, *Chem*, **2018**, doi: 10.1016/j.chempr.2018.10.010.
- [402] X. Chen, N. Li, Z. Kong, W. J. Ong, X. Zhao, *Mater. Horiz.*, **2018**, 5, 9–27.
- [403] G. N. Schrauzer, T. D. Guth, *J. Am. Chem. Soc.*, **1977**, 99, 7189–7193.
- [404] H. Liang, H. Zou, S. Hu, *New J. Chem.*, **2017**, 41, 8920–8926.
- [405] Q. Guo, C. Zhou, Z. Ma, Z. Ren, H. Fan, X. Yang, *Chem. Soc. Rev.*, **2016**, 45, 3701–3730.
- [406] S. Hu, Y. Li, F. Li, Z. Fan, H. Ma, W. Li, X. Kang, *ACS Sustainable Chem. Eng.*, **2016**, 4, 2269–2278.
- [407] H. Li, C. Mao, H. Shang, Z. Yang, Z. Ai, L. Zhang, *Nanoscale*, **2018**,

10, 15429–15435.

[408] Q. Zhang, S. Hu, Z. Fan, D. Liu, Y. Zhao, H. Ma, F. Li, *Dalton Trans.*, **2016**, 45, 3497–3505.

[409] B. Huang, N. Zhou, X. Chen, W. J. Ong, N. Li, *Chem. Eur. J.*, **2018**,

24, 18479–18486.

[410] D. Zeng, T. Zhou, W. J. Ong, M. Wu, X. Duan, W. Xu, Y. Chen, Y. A. Zhu, D. L. Peng, *ACS Appl. Mater. Interfaces*, **2019**, doi: 10.1021/acsami.8b20958.

g-C₃N₄界面改性：掺杂金属硫化物构建新型异质结光催化剂的能量转换展望

任亦杰^a, 曾德乾^{b, #}, Wee-Jun Ong^{a, c, *}

^a厦门大学马来西亚分校能源与化学工程学院, 雪兰莪 43900, 马来西亚

^b广西大学资源环境与材料学院, 广西南宁530004, 中国

^c厦门大学化学化工学院, 福建厦门361005, 中国

摘要: 光催化技术不仅可以将太阳能转化为化学能, 还可以直接降解和矿化有机污染物的特性, 因而成为最具吸引力和前景的技术之一, 被广泛应用于解决环境和能源问题。但是目前, 太阳能燃料的最高转化效率为5%, 无法满足商业化要求(≥10%)。各种光催化材料被探索研究以进一步提高光催化效率。但目前广泛使用的材料都有不同的缺点。比如最常用的金属氧化物(TiO₂)由于禁带较宽, 仅能利用太阳光中的紫外光, 限制了其对光的使用效率; 贵金属化合物虽性能优异但成本较高, 不宜规模化应用; 硫化物或非金属单质一般容易发生光腐蚀, 稳定性较差; 非金属化合物或聚合物中光生电子和空穴复合率高, 活性较低。最近几年, 类石墨相氮化碳(g-C₃N₄)以其优异的热稳定性以及化学稳定性, 能带结构易调控和前驱体价格低廉等特点而成为目前研究的热点, 在光解水制氢产氧、污染物降解、光催化CO₂还原、抗菌和有机官能团选择性转换等领域受到广泛的应用。然而, 传统热缩聚法合成的g-C₃N₄光催化剂比表面积小、电荷复合率高、禁带宽度稍微大、光生载流子传输慢, 抑制了其光催化活性。为了进一步提高g-C₃N₄的光催化活性, 出现了多种改性方法。纳米异质结由于能展现出单组分纳米材料或体相异质结所不具备的独特性质, 更能促进光生电子和空穴快速转移, 提供更多的光生电子或使光生电子具有更强的还原性而成为研究的热点。从2009年以来, 基于g-C₃N₄的异质结结构以其优异的光催化性能吸引了世界各国科学家的关注。本文综述了过渡金属硫化物(TMS)/g-C₃N₄纳米复合材料的最近研究进展, 包括: (1) 纯g-C₃N₄的制备, (2) g-C₃N₄的改性方法, (3) TMS/g-C₃N₄异质结光催化剂的设计原则, 以及(4) 能量转换方面的应用。并从以下几个方面对金属硫化物异质结体系的特性和转移机理进行了介绍: (1) I-型异质结, (2) II-型异质结, (3) p-n型异质结, (4) 肖特基异质结和 (5) Z-型异质结。此外, 还系统地介绍了g-C₃N₄基异质结光催化剂在光解水、CO₂还原、固氮和污染物降解等方面的应用。最后, 本文分析了目前g-C₃N₄光催化剂异质结领域面临的问题和挑战, 展望了未来的发展趋势。

关键词: 类石墨相氮化碳; 金属硫化物; 光催化; 能量转换; 光解水; 还原二氧化碳; 污染物降解; 固氮

收稿日期: 2018-11-18. 接受日期: 2018-12-28. 出版日期: 2019-03-05.

*通讯联系人. 电话: (+603) 8705 5149; 电子信箱: weejun.ong@xmu.edu.my, ongweejun@gmail.com

#通讯联系人. 电子信箱: dqzeng@gxu.edu.cn

基金来源: 厦门大学的启动资助(XMUMRF/2019-C3/IENG/0013); 马来西亚国家石油公司, 埃克森美孚公司和壳牌公司赞助独立奖。

本文的电子版全文由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/science/journal/18722067>).