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FEATURE ARTICLE



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Two-dimensional layered composite photocatalysts

Two-dimensional (2D) layered nanostructure composites are promising candidates for conducting highperformance energy conversion and environmental remediation. The construction of 2D layered composite

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photocatalysts can generate many unique properties that do not exist in other kinds of semiconductor composite photocatalyst, which are beneficial for photocatalytic performance enhancement, band gap tuning, heterojunction formation, *etc.* Recently, these advantages have greatly stimulated the study of 2D layered composite photocatalysts in the field of photocatalysis. This feature article summarizes the recent developments of 2D layered composite photocatalysts for photocatalytic applications, such as photocatalytic hydrogen production, bacterial disinfection, and pollutant degradation. Finally, perspectives on the challenges and opportunities for the future exploration of 2D layered composite photocatalysts are put forward.

1. Introduction

Rapid industrial development and population growth have sparked a global crisis concerning energy shortage and environmental pollution. It is now an urgent task to develop green and sustainable technologies for clean energy production and environmental remediation, for the purpose of the long-term development of human society. Among several promising

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co-catalysts onto the surface of photocatalysts, which can not only suppress electron-hole recombination but can also reduce the activation energy for the surface reaction. As a famous candidate, the noble metal Pt has been widely used as a co-catalyst and can greatly enhance the photocatalytic performance. However, Pt is rare and expensive, thus its use is restricted for practical applications. Therefore, it is highly desirable to find efficient but abundant, low-cost and environmentally friendly substitutes for Pt.

Recently, the utilization of 2D layered materials in the field of photocatalysis has attracted particular interest, and has promptly become one of the hottest research topics.^{6,14,15} In comparison with zero-dimensional (0D) and one-dimensional (1D) materials, 2D layered materials possess several extraordinary advantages (see Fig. 1),¹⁶ endowing them with promising potential for photocatalytic applications. Firstly, 2D layered materials have larger specific surface areas as compared to their bulk structures.^{17,18} Thus, it is easy to understand that there are a great number of active sites on the surface of 2D layered materials, which can significantly enhance the

photocatalytic activity.¹ Secondly, some 2D layered materials (such as graphene) have good conductivity and superior electron mobility due to the presence of the 2D π -conjugated structure in graphene, which can provide an ultrafast electron transfer platform to facilitate the transfer and separation of photogenerated electrons and holes in the photocatalyst.^{1,19,20} Thirdly, nano-sized 2D layered materials are excellent catalyst supports, which is beneficial for catalyst dispersion. More importantly, coupling different 2D layered materials will greatly enhance the photocatalytic performance of the 2D composite materials due to an increased contact surface and charge transfer rate (see Fig. 2).²¹ In comparison with other 2D material based composites (*i.e.* 0D-2D and 1D-2D composites), a solid construction can be achieved by the 2D-2D layered composites due to the large contact surface between the sheets, and thus a 2D layered composite exhibits greater stability than 0D-2D and 1D-2D composites. Moreover, the large contact area of the 2D layered composite should lead to more efficient interfacial charge transfer. As a result, high photocatalytic activity of the 2D layered composite can be expected.



Fig. 1 Schematic illustration of the advantages of 2D layered materials in comparison with 0D and 1D materials. The 2D layered materials possess large surface areas, more surface active sites and superior electron mobility, and can serve as good electron transfer platforms and excellent photocatalyst supports.



Fig. 2 Schematic illustration of 2D layered composites in comparison with other kinds of composites.



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2. 2D layered materials

2.1 Graphene

Graphene is the basic structural element of all graphitic-form materials, including fullerenes, carbon nanotubes and graphite (see Fig. 3). It exhibits a 2D nanostructure comprised of a single layer of sp²-bonded carbon atoms with honeycomb rings.¹⁷ Recently, graphene has attracted much attention due to its unique properties, including high electronic conductivity and superior thermal conductivity, a large theoretical specific surface area, quantum hall effects at room temperature, and robustness.^{22,23} As such, graphene is expected to be an ideal material for various applications, such as optical electronics, photosensors, photocatalysis, and energy storage. In particular, much effort has been made to couple graphene with photocatalytic materials to efficiently improve the photocatalytic activity.^{24–26}

Li and coworkers first introduced the use of graphene for the enhancement of photocatalytic activity by coupling with P25.27 They found that the photocatalytic degradation efficiency of P25 over methyl blue was significantly promoted by loading graphene onto P25, which could be mainly attributed to the efficient charge separation between P25 and graphene nanosheets. Moreover, the large specific surface area and π - π conjugation structure of graphene were favorable for the adsorption of dye molecules. Recently, our group has studied the effect of graphene on the photocatalytic activity of CdS.⁷ Notably, the CdS-graphene composite could achieve a 5-fold increased photocatalytic hydrogen production rate compared with pure CdS. It was found that the graphene nanosheets in the composite could help to improve the crystallinity and specific surface area of CdS, which were two important factors for the photocatalytic reaction. Furthermore, graphene nanosheets could act as an excellent supporting material and electron collector for CdS, and consequently inhibited the recombination of photoinduced electron-hole pairs. These studies highlight the benefits of and suggest promising potential for the use of graphene to improve the photocatalytic performance of semiconductor photocatalysts.



Fig. 3 Schematic illustration of the 0D (fullerene), 1D (carbon nanotube) and 2D (graphene) nanostructure of carbon based materials.

2.2 C₃N₄

Covalent C₃N₄ was first found by Berzelius, and the thusformed yellow "pharaohs serpent" was named "melon" by Liebig in 1834.²⁸ Several phases of C₃N₄ can be found naturally with diverse properties, including alpha, beta, pseudocubic and graphitic allotropes.²⁹ Among them, polymeric graphitic carbon nitride $(g-C_3N_4)$ has been recognized as the most stable allotrope with high photoreactivity under ambient conditions.^{30,31} g-C₃N₄ has high thermal stability against high temperatures and chemical stability against acid, base and organic solvents, and has been widely studied in the field of photocatalysis in recent years.³²⁻³⁴ It exhibits a stacking 2D layered structure, similar to that of graphite. Interestingly, g-C₃N₄ possesses a band gap of 2.7 eV, making it active in the visible-light region. In comparison with graphite, the stacking layers of g-C₃N₄ are comprised of C-N instead of C-C bonds, and have shorter interlayer distances and amino functional groups with larger periodic vacancies.³⁵ Moreover, g-C₃N₄ is only composed of carbon and nitrogen, which provides a simple way to tune the reactivity of g-C₃N₄ without changing the overall composition too much.¹⁵

Wang et al. first introduced g-C₃N₄ into the field of photocatalysis for water splitting under visible-light irradiation.³⁶ They investigated the valence band (VB) and conduction band (CB) of g-C₃N₄ based on density functional theory (DFT) simulations, and found that g-C₃N₄ had an appropriate electronic structure for both photocatalytic water reduction and oxidation. This simulation result was further confirmed by using g-C₃N₄ as a photocatalyst to activate the water splitting cycle under visible light, although the quantum efficiency of the g-C₃N₄ photocatalyst was still low. Recently, Liu et al. prepared thinlayer g-C₃N₄ nanosheets with a thickness of ~ 2 nm by a simple thermal oxidation etching process for photocatalytic hydrogen production.¹⁸ As compared to bulk g-C₃N₄, the obtained g-C₃N₄ nanosheets possessed not only a larger surface area to improve the electron transport ability along the in-plane direction, but also a larger band gap to enhance the oxidation and reduction of charge carriers. Consequently, the g-C₃N₄ nanosheets exhibited much higher photocatalytic activity than bulk g-C₃N₄ under visible light. The above studies demonstrated the successful utilization of low-cost g-C3N4 as a novel visible-light photocatalyst.

2.3 MoS₂

The rapid progress in the study of graphene and the methodology developed in preparing ultrathin nanolayers have stimulated the exploration of other 2D materials.³⁷ As one of the most stable layered metal dichalcogenides, molybdenum disulphide (MoS₂) has received increasing attention as a promising visible-light active photocatalyst.³⁸ Bulk MoS₂ is built up of layers constituting an atomic plane of Mo sandwiched between two atomic planes of S in a trigonal prismatic arrangement.³⁹ The stacking 2D layers of bulk MoS₂ have a thickness of ~0.65 nm. These layers are weakly connected by van der Waals interactions, providing the possibility of exfoliating bulk MoS₂ into thin nanosheets for further exploration of the potential of MoS₂. Furthermore, it was found



Fig. 4 Schematic illustration of the band gap sizes and positions of TiO_{27} bulk MoS₂ and quantum sized MoS₂.

that the optical and physicochemical properties of MoS_2 could be readily tuned by adjusting the number of layers. Particularly, bulk MoS_2 has an indirect band gap of 1.2 eV, which is not suitable for photocatalytic applications due to the insufficient reduction and oxidation ability for the activation of the photocatalytic reaction (see Fig. 4).³⁹ However, in the 2D nanosheet structure, MoS_2 exhibits a direct band gap of 1.96 eV resulting from quantum confinement.³⁹ This provides MoS_2 nanosheets with appropriate band positions whilst retaining good visible-light absorption ability, thus it is believed to be a promising material for photocatalytic applications.

Based on first-principle calculations, Li et al. found that the pristine monolayer MoS₂ with an appropriate band gap is a potential photocatalyst and co-catalyst candidate for hydrogen production.⁴⁰ In order to further investigate the unique properties of monolayer MoS₂, Wang et al. studied the photoluminescence of chemically exfoliated MoS₂ monolayers.⁴¹ Different from graphene, the exfoliated monolayer MoS₂ remained chemically unmodified and thus its fundamental electronic properties were preserved. Moreover, the band gap of MoS₂ could be tuned by adjusting its layer thickness due to the quantum size effect. In another study, Li and co-workers reported that the coupling of MoS₂ onto CdS could significantly enhance the photocatalytic hydrogen production activity under visible light by creating a heterojunction between CdS and MoS₂.⁴² At a loading amount of 0.2 wt% MoS₂, a 36-fold enhancement of the photocatalytic activity compared with CdS was achieved, which was attributed to the efficient electron-hole separation between the MoS₂ and CdS heterojunction.

2D layered composite photocatalysts

3.1 Photocatalytic hydrogen production

Due to the overuse of fossil fuels and growing environmental issues, hydrogen energy has received much attention because it is renewable and environmentally friendly. Photocatalytic hydrogen production from water splitting is considered a low-cost and sustainable solution to both energy shortage and environmental problems.⁴³ Since the pioneering study of photocatalytic water splitting using TiO₂ as photocatalyst in

1972,² a variety of semiconductors has been determined to have the ability to photocatalyze hydrogen production from water reduction. However, the maximum hydrogen production efficiency of photocatalytic water splitting is still far from the levels required for practical applications due to the rapid recombination of the photoinduced electron-hole pairs within photocatalysts. Owning to the excellent electron conductivity and large surface area, 2D layered materials can serve as new types of photocatalysts and/or electron acceptors to efficiently suppress the recombination of photoinduced electron-hole pairs and separate the reduction sites of hydrogen and the oxidation sites of oxygen.

Our group has reported the synergetic effect of low-cost MoS₂ (M) and graphene (G) as co-catalysts on TiO₂ for the enhancement of photocatalytic H₂ production.⁴⁴ Particularly, a MoS₂-graphene (MG) hybrid was first prepared via a hydrothermal reaction in a graphene oxide (GO) solution in the presence of Na₂MoO₄ and H₂CSNH₂. Subsequently, the MG hybrid was mixed with $Ti(OC_4H_9)$ and hydrothermally treated in a solvent of ethanol and water to form a TiO₂-MG composite. It was found that the layered MG hybrid could act as a novel support for TiO_2 (see Fig. 5a and b). Note that the TiO_2 nanoparticles were uniformly decorated on the MG hybrid, indicating that a close contact was formed between the MG hybrid and TiO₂, which could promote the charge transfer between MG and TiO₂. The photocatalytic hydrogen production activities of TiO2 alone and the TiO2-MG composites with different contents of MoS2 and graphene were evaluated under xenon arc lamp irradiation using ethanol as a scavenger (see Fig. 5c). The results indicated that TiO_2 nanoparticles



Fig. 5 Transmission electron microscopy (TEM) (a) and high-resolution TEM (HRTEM) (b) images of TiO_2-MoS_2 -graphene. (c) Comparison of photocatalytic H₂ evolution rates of different MoS_2 -graphene- TiO_2 composites. Reprinted with permission from ref. 44. Copyright 2012, American Chemical Society.



Fig. 6 Schematic illustration of the photocatalytic $H_2\mbox{-}production$ mechanism of $MoS_2\mbox{-}graphene\mbox{-}TiO_2$ composites.





exhibited a very low photocatalytic activity due to fast electronhole recombination. After loading of MoS₂, the sample showed a decent enhancement of photocatalytic activity in comparison with pure TiO₂. On the other hand, with the loading of graphene, a remarkable improvement of the photocatalytic activity could be also observed. Notably, when the TiO₂ nanoparticles were coupled with the MG hybrid, the resulting composite showed much higher photocatalytic activity than all the abovementioned samples, in which the amount of graphene and MoS₂ in the MG-TiO₂ composite played a dominant role in enhancing the photocatalytic activity. As shown in Fig. 6, under xenon arc lamp irradiation, electrons in the VB of TiO₂ were excited to the CB, leaving holes in the VB. Owing to the high conductivity of graphene nanosheets, the photoexcited electrons tended to migrate to the graphene nanosheets, and thus reduce the electron-hole recombination. Furthermore, the MoS₂ nanosheets in the MG nanosheets could accept the electrons from both graphene and TiO₂. These accumulated electrons would further engage the water reduction process on the edge of the MoS₂. As a result, a significant improvement of the photocatalytic activity could be achieved for the TiO2-MG composite due to the efficient interfacial charge transfer and abundance of active sites.

In another study, Meng *et al.* deposited the p-type MoS_2 (p- MoS_2) on the n-type nitrogen-doped reduced graphene oxide (n-rGO) to form a multilayer structure and a nanoscale p-n junction.⁴⁵ As shown in Fig. 7, the pure MoS_2 showed a "nanoball" structure composed of aggregated p- MoS_2 nanoplatelets. In the presence of rGO, the aggregation of the MoS_2 nanoplatelets was effectively inhibited and they were uniformly distributed on the n-rGO surface (Fig. 8). Moreover, it could be observed that



Fig. 7 Scanning electron microscopy (SEM) image of single $p-MoS_2$ (a) and TEM image of $p-MoS_2-n-rGO$ composite photocatalyst (b). Reprinted with permission from ref. 45. Copyright 2013, American Chemical Society.

p-MoS₂ and n-rGO had a large contact area, which could promote the charge transfer at the p-MoS₂/n-rGO interface. The obtained p-MoS₂/n-rGO showed higher photocatalytic activity than both p-MoS₂ and p-MoS₂/rGO. It was worth noting that the photocatalytic activity of p-MoS₂/n-rGO was significantly higher than that of p-MoS₂/rGO. This was attributed to the formation of the p–n heterojunction between p-MoS₂ and n-rGO. This work demonstrated that the 2D layered composite of p-MoS₂ and n-rGO had several extraordinary merits, including a large contact area, an efficient p–n heterojunction and fast electron–hole pair separation, indicating that surface engineering is an effective strategy to tune the properties of 2D layered composites.

Ge et al. have prepared a MoS2-g-C3N4 composite by a hydrothermal method using pre-prepared g-C₃N₄ and MoS₂ as precursors, followed by further calcination treatment.⁴⁶ Both $g-C_3N_4$ and MoS_2 exhibited layered structures (see Fig. 9a-d), and MoS₂ was attached on the surface of g-C₃N₄ to establish an intimate interface, which provided an efficient charge transfer pathway between MoS₂ and g-C₃N₄, and thus facilitated the electron-hole separation. Furthermore, MoS₂ and g-C₃N₄ have matched band structures to form a heterojunction, in which the CB edge potential of g-C₃N₄ was more negative than that of MoS₂, allowing for the migration of electrons from g-C₃N₄ to MoS₂. In addition, the small amount of MoS₂ on the g-C₃N₄ could also slightly enhance the visible-light absorption of the sample due to its relatively low band gap, and thus induce more electron-hole pairs. As a result, the 0.5 wt% MoS₂-g-C₃N₄ composite photocatalysts loaded with 1.0 wt% Pt (sample G) showed the highest H_2 evolution rate of 23.1 µmol h^{-1} , which was ~11 times higher than that of pure $g-C_3N_4$ loaded with 1.0 wt% Pt (sample D) (see D and G of Fig. 9e). However, further loading of MoS_2 on the g-C₃N₄ led to a reduction of photocatalytic activity. This is because the introduction of excessive black MoS₂ could shield the active sites on the g-C₃N₄ surface, and also weaken the intensity of light through the depth of the reaction solution. Furthermore, two types of electron transfer pathway were proposed to explain the enhanced photocatalytic H₂-production activity (see Fig. 10). In the first, electrons directly migrated to the surface of MoS₂ or Pt to reduce the adsorbed H⁺ and produce H₂, while in the second the electrons were first transferred to Pt nanoparticles, and then accumulated on MoS₂ nanosheets.



Fig. 9 TEM (a–c) and HRTEM (d) images of the MoS₂–g-C₃N₄ composite sample, and comparison of photocatalytic hydrogen production rates of the samples (e): (A) pure MoS₂, (B) pure g-C₃N₄, (C) 0.5 wt% MoS₂/g-C₃N₄ without Pt loading, (D) 1.0 wt% Pt/g-C₃N₄, (E) mechanical mixture of MoS₂ (0.5 wt%) and g-C₃N₄ with 1.0 wt% Pt co-catalyst, (F) 3.0 wt% Pt/g-C₃N₄, and (G) 0.5 wt% MoS₂/g-C₃N₄ photocatalysts loaded with 1.0 wt% Pt. Reprinted with permission from ref. 46. Copyright 2013, Elsevier B.V.



Fig. 10 Proposed mechanism of photocatalytic activity enhancement in the MoS_2-g-C_3N_4 composite system under visible-light irradiation.

Similarly, Hou *et al.* prepared an organic–inorganic layered heterojunction by the gas-controlled growth of thin-layer MoS_2 on the mesoporous g-C₃N₄ (mpg-CN) surface.⁴⁷ It was found

that the analogous layered structures of MoS_2 and mpg-CN were beneficial for building a layered heterojunction. Moreover, the mesoporous structure of mpg-CN facilitated and stabilized the high dispersion of MoS_2 . This unique layered heterojunction ensured a short distance for charge carrier transfer between MoS_2 and mpg-CN, and consequently promoted the charge separation. The high charge separation rate was further confirmed by the electrochemical measurements, in which the MoS_2/mpg -CN showed a much higher electrocatalytic hydrogen evolution activity than the pure mpg-CN, indicating that the heterojunction with close surface contact significantly enhanced the electron-hole separation rate. Simultaneously, the photocatalytic hydrogen evolution activity of MoS_2/mpg -CN was significantly higher than that of pure MoS_2 and mpg-CN, even much higher than that of Pt/g-C₃N₄.

Recently, our group has prepared graphene–g- C_3N_4 composite photocatalysts for photocatalytic hydrogen production by an impregnation–chemical reduction strategy.³¹ The prepared graphene–g- C_3N_4 composite photocatalyst exhibited a close contact between g- C_3N_4 and graphene (see Fig. 11). This unique stacking structure was beneficial for the electron migration from g- C_3N_4 to graphene, thus significantly enhancing the photocatalytic H₂-production activity of the composite samples. Further results indicated that the specific surface areas of the graphene–g- C_3N_4 composite samples increased with increasing amounts of graphene. Usually, an increased specific surface area for hydrogen production. During photocatalytic hydrogen production,



Fig. 11 TEM images of graphene oxide (a) and graphene–g- C_3N_4 composite photocatalyst (b). (c) Illustration of the graphene–g- C_3N_4 composite photocatalyst. Reprinted with permission from ref. 31. Copyright 2011, American Chemical Society.



Fig. 12 Enhanced mechanism of photocatalytic H_2 -production for the graphene-g-C₃N₄-Pt composite.

g-C₃N₄ was used as the photocatalyst, and graphene nanosheets were the co-catalyst and the support for g-C₃N₄. Upon visible light irradiation, photoinduced electron-hole pairs were generated in g-C₃N₄. Normally, these electron-hole pairs quickly recombine and only small amounts of electrons and holes take part in the photocatalytic reaction. With the loading of graphene, the photoinduced electrons in g-C₃N₄ quickly migrated to the graphene and further accumulated on the Pt co-catalyst, and subsequently reduced protons to produce H_2 (see Fig. 12). As a result, the optimal 1.0 wt% graphene loaded g-C3N4 sample exhibited photocatalytic hydrogen production activity 3 times higher than that of pure g-C₃N₄ (see Fig. 13a). However, overloading of graphene caused a rapid reduction of photocatalytic activity. This was due to the increased opacity of the composite that consequently inhibited the light passing through the reaction suspension. Such an observation indicated that an appropriate ratio of graphene to g-C₃N₄ was crucial to maximize the photocatalytic activity of the composite. In addition, the graphene-g-C₃N₄ composite showed excellent photocatalytic stability as shown in Fig. 13b. After 4 cycles totalling 12 h of reaction, the H₂ evolution did not decrease. This work demonstrated a significant approach to enhance the photocatalytic activity of g-C₃N₄ by using graphene as a support, and provided a new insight into the preparation of 2D layered composites for photocatalytic applications.

3.2 Photocatalytic bacterial disinfection

Bacterial disinfection is important in microbiological laboratories and health centers in order to reduce the number of bacteria and prevent the spread of bacteria. The traditional way to resolve this issue is the utilization of aggressive chemicals, which is not effective for long-term treatment. In addition, disinfection with strong ultraviolet light is also widely used. However, the use of ultraviolet light has limitations because the depth of the light penetration is not sufficient to kill all bacteria. Recent studies have indicated that photocatalytic disinfection is one of the best solutions for bacterial disinfection.^{48,49} In fact, the photocatalytic bacterial disinfection by TiO₂ in aqueous solution and gaseous conditions has been well documented.^{10,50} Very recently, the photocatalytic bacterial



Fig. 13 (a) Comparison of photocatalytic H₂-generation activity of the graphene–g-C₃N₄ composite samples with different graphene loading amounts and N-doped TiO₂ in methanol aqueous solution under visible light. (b) Recycling test of photocatalytic hydrogen production over the graphene–g-C₃N₄ sample with optimal graphene loading. Reprinted with permission from ref. 31. Copyright 2011, American Chemical Society.

disinfection using 2D layered composites has also been demonstrated.

Wang *et al.* reported a novel metal-free heterojunction photocatalyst by wrapping graphene and g-C₃N₄ nanosheets on cyclooctasulfur (α -S₈) crystals for photocatalytic disinfection.⁵¹ Two synthetic routes with different wrapping sequences were applied, as shown in Fig. 14a. The first product comprised RGO sandwiched between g-C₃N₄ nanosheets and α -S₈, and was known as CNRGOS₈, while the second product comprised g-C₃N₄ nanosheets sandwiched between the RGO nanosheets and α -S₈, and was known as RGOCNS₈ (see Fig. 14a).

The TEM results (Fig. 14b) further confirmed the formation of the above two kinds of composite heterogeneous structures CNRGOS₈ and RGOCNS₈. Ultraviolet-visible (UV-vis) diffuse reflectance spectra also indicated that the co-wrapping of graphene and g-C₃N₄ nanosheets could obviously enhance the UV and visible-light absorption of α -S₈. The samples were then tested for photocatalytic bacteria inactivation under aerobic conditions using *Escherichia coli* (*E. coli*) K-12, which is a common waterborne microorganism, as the bacteria source (see Fig. 15). It was found that α -S₈ wrapped individually with RGO or g-C₃N₄ could significantly enhance the photocatalytic bacterial inactivation activity. The enhancement shown by graphene wrapped α -S₈ was attributed to the excellent electron



Fig. 14 Schematic illustration (a) of different synthetic pathways for preparing CNRGOS₈ and RGOCNS₈ heterogeneous structures and TEM images (b) of CNRGOS₈ and RGOCNS₈. Reprinted with permission from ref. 51. Copyright 2011, The Royal Society of Chemistry.



Fig. 15 Comparison of photocatalytic *E. coli* K-12 inactivation efficiency (2 \times 10⁶ cfu mL⁻¹, 50 mL) in the presence of the different samples (100 mg L⁻¹) in aerobic conditions under visible-light irradiation for 4 hours.

conductivity of graphene. In particular, the photocatalytic activity of the g-C₃N₄ wrapped α -S₈ was much higher than that of graphene wrapped α -S₈, which could be ascribed to the Type II heterojunction formed between g-C₃N₄ and α -S₈, greatly improving the separation of the electron-hole pairs. Further investigation indicated that the graphene and g-C₃N₄ co-wrapped α -S₈ exhibited much higher photocatalytic bacterial inactivation activity than all the above samples. Interestingly, CNRGOS₈ showed higher activity than RGOCNS₈, due to their different hierarchical structures. As shown in Fig. 14a, for CNRGOS₈, the graphene nanosheets acted as an interlayer of the g-C₃N₄ and α -S₈ heterojunction and significantly improved the charge migration. However, graphene nanosheets as the outer layer in RGOCNS₈ could not mediate the charge migration,

thus resulting in the lower photocatalytic activity of RGOCNS₈. Cycling tests revealed that both CNRGOS8 and RGOCNS8 still retained high activity after 16 h, suggesting their excellent stability for practical bacterial disinfection applications. This work provides new insight into the exploration and understanding of photocatalytic bacterial inactivation by the co-modification of 2D nanolayered structures, graphene and g- C_3N_4 on semiconductor photocatalysts.

3.3 Photocatalytic pollutant degradation

Organic contaminants and biorecalcitrants are common pollutants in air, soil and water, which are mainly released by industrial processes. These pollutants generate serious environmental issues and bring negative effects on human health. A great deal of methods, including physical, chemical and biological techniques have been used in attempts to remove these pollutants. Recently, the photocatalytic degradation of organic contaminants has attracted much attention due to its strong ability to degrade hazardous chemical compounds without creating any harmful by-products.^{52–56} In particular, 2D layered photocatalysts are becoming rising stars in this area due to their unique properties.

Liao and co-workers have prepared a GO-g-C₃N₄ composite photocatalyst by a simple sonochemical approach.⁵⁷ On the basis of TEM observations, they proposed that the GO was overlaid on the surface of g-C₃N₄ to build a close stacking contact between GO and g-C₃N₄, thus promoting the electron migration to the GO surface and allowing for ultrafast electronhole separation. As can be seen from Fig. 16, the obtained GO-g-C₃N₄ composite also showed strong UV and visible-light absorption due to the presence of the black GO. As a result, the GO-g-C₃N₄ composite sample showed 3.8 and 1.3 times higher photocatalytic degradation efficiency on rhodamine (RhB) and 2,4-dichlorophenol (2,4-DCP) under visible-light irradiation as compared to pure $g-C_3N_4$. More importantly, the photocatalytic activity of the composite sample was quite stable and did not change after 750 min continuous testing, which was attributed not only to the chemical and physical inertness of the $g-C_3N_4$ and GO nanosheets, but also the large contact area between the 2D layer of g-C₃N₄ and GO nanosheets. This work suggested



Fig. 16 UV-vis spectra of graphene oxide, $g-C_3N_4$ and graphene oxide– $g-C_3N_4$ composite. Reprinted with permission from ref. 57. Copyright 2011, The Royal Society of Chemistry.

that the 2D layered composites were fascinating long-term and highly active photocatalytic materials for the degradation of organic pollutants.

Furthermore, Park *et al.* also reported hybrid of g- C_3N_4 and rGO synthesized by a simple solution-based process using GO and cyanamide as raw materials.⁵⁸ In this process, the reduction of GO and the GO-assisted generation of g- C_3N_4 occurred concurrently, and a close interaction could be achieved between g- C_3N_4 and rGO, which could not only boost the electron migration but also strengthen the thermal stability of g- C_3N_4 and rGO. The resultant g- C_3N_4 -rGO hybrids exhibited much higher photocatalytic activity towards RhB degradation under one-sun solar light illumination than pristine g- C_3N_4 and GO.

In another study, Zhao and co-workers prepared a series of cross-linked g-C3N4/rGO layered composites with different amounts of rGO by a thermal conversion method.⁵⁹ Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS) results for g-C₃N₄/rGO revealed that almost all of the oxygen-containing functional groups on the GO surface were removed except for the -OH groups. The remaining -OH groups could act as cross-linkers between g-C₃N₄ and rGO and help to generate 2D layered composites with close contacts, which is beneficial for electron-hole separation. TEM observations showed that the g-C₃N₄-rGO composite exhibited a lamellar structure, forming multiple corrugated layers buckled together. Optical studies indicated that the band structure of the resulting g-C₃N₄/rGO could be tuned by controlling the weight ratio of cyanamide to GO in precursor materials, which was also confirmed by further electrochemical measurements. Among all samples, the 2.5% rGO loaded g-C₃N₄ exhibited the most positive VB potential, suggesting stronger oxidation ability compared with other samples. This optimal g-C₃N₄-rGO composite indeed exhibited significant enhancement of the photocatalytic degradation efficiency towards RhB and 4-nitrophenol under visible-light irradiation, which is 3.0 and 2.7 times higher than that of pure g-C₃N₄. Such improved photocatalytic activity could be attributed to the narrower band gap for enhanced visible-light absorption, more positive VB potential for stronger oxidation ability, and close contact between g-C3N4 and rGO for improved electron-hole separation.

Recently, Dong et al. prepared a unique g- C_3N_4/g - C_3N_4 metalfree isotype heterojunction with a simple, cheap and environmentally friendly method using thiourea and urea as precursors.⁶⁰ It was found that g-C₃N₄ prepared using thiourea (CN-T) showed higher VB and CB positions than urea (CN-U). The g-C₃N₄/g-C₃N₄ isotype heterojunction thus formed due to this difference in band structures, and caused the redistribution of the photoinduced electrons and holes to CN-U and CN-T, respectively. As a result, the g-C₃N₄-g-C₃N₄ composite showed higher charge separation efficiency than separate CN-U and CN-T, prolonging the lifetime of the charge carriers. This g-C₃N₄-g-C₃N₄ composite was then evaluated for the photocatalytic NO removal in air under visiblelight irradiation, and was proved to have much higher NO removal capacity than CN-U and CN-T. This work demonstrated the excellent performance of 2D layered composite photocatalysts toward gaseous pollutant removal.

4. Summary and perspectives

In recent years, continuous breakthroughs have been made in the synthesis and application of 2D layered materials such as graphene, g-C₃N₄, MoS₂ and so on. These materials possess many superior properties, including good physical and chemical stability, high electron mobility, large surface area, high adhesive force and abundant surface active sites, thus have stimulated intense study of 2D layered materials in the field of photocatalysis. Moreover, by combining the advantages of different 2D layered materials, band gap tuning and heterojunction formation could be easily achieved in the form of 2D layered composites. A more efficient light absorption with the desired reducing and oxidizing ability, and better charge separation efficiency are consequently obtained. As a result, 2D layered composites such as g-C₃N₄-rGO, graphene-MoS₂ and g-C₃N₄-MoS₂ have shown significant enhancement of photocatalytic performance for hydrogen evolution from water splitting, bacterial disinfection, and degradation of organic pollutants as compared to pristine 2D layered materials.

However, the study of 2D layered composites in the field of photocatalysis is still at the primary stage. There are still several challenges ahead. Firstly, a better fundamental understanding of their physical and chemical properties, as well as their formation mechanisms, is needed, which is beneficial for the purposeful design of high-performance 2D layered composites. This relies not only on advanced material characterization techniques, but also on rigorous theoretical simulation and analysis of different aspects. Secondly, a precise control of the morphologies of 2D layered composites can help to improve the surface contact for better charge migration and separation processes, and to provide more active sites for the surface chemical reaction. However, the previously obtained 2D layered composites were usually grown with irregular morphologies, which limited the photocatalytic performance because of the insufficient utilization of their surface contacts. Therefore, it is necessary to develop novel strategies to fabricate high-quality 2D layered composites with desired morphologies. Third, the modification of 2D layered composites with doping to alter the band structures, and surface engineering to introduce the functional groups, is highly encouraged. Such modification will favor not only the adjustment of redox potential and the enhancement of light harvesting, but also the communication between the 2D layered photocatalysts/co-catalysts and the target reactants. Lastly, the exploration of novel conductive 2D layered materials can also bring new insights into the preparation of different types of 2D layered composites, thus can enrich the 2D layered composite family and provide new options for their applications in various fields. All in all, it is without doubt that there will be many exciting research opportunities related to 2D layered composites, which will require extensive efforts from scientists and researchers all over the world.

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