Graphitic carbon nitride based (g-C_3N_4) nanocomposites for the photodegradation of organic pollutants under visible light irradiation: progress and future perspectives

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Abstract

Graphitic carbon nitride (g-C_3N_4) has drawn great attention recently because of its visible light response, suitable band gap, good redox ability, and metal-free nature. Compared with common catalyst of TiO_2, g-C_3N_4 owns better photocatalytic ability and more energy-efficienct process as visible light could be directly utilized in g-C_3N_4 catalysis system. Nevertheless, pure g-C_3N_4 still suffers the drawbacks of insufficient light adsorption, small surface area and fast recombination of photogenerated electron and hole pairs. This review summarizes the recent progress in the development of g-C_3N_4 composites to degrade environmental organic pollutants in water. Element doping has been reported to be an efficient method to promote the degradation efficacy and K doping was proven to be better than other metal elements doping. In addition, semiconductor doping usually has a better degradation performance as in the degradation of Ag_3PO_4-g-C_3N_4 which took only 5 min for the complete degrading 10 mg L^{-1} of methyl orange (MO) under visible light irradiation and the *k* is as high as 0.2357 min^{-1}. Moreover, doping with more than one compound defined as co-doping has the ability to deal with more than one pollutant but still exhibited high rate constant. When the stability is taken consideration, most of the g-C_3N_4 composites possess high reusability and immobilization is regarded as a significant method to improve the stability. Future studies should focus on the photocatalysis of persistent organic pollutants (such as POPs) by the g-C_3N_4 in order to make a further evaluation for their catalytic ability and the environmental conditions during the photocatalysis process that need to be provided at the same time.

Keywords: Photocatalysis; g-C_3N_4 composites; Morphology; Co-doping; Immobilization

Contents

1. Introduction

As the world is facing an increasing challenges in the fields of energy and environmental pollution, the use of renewable energy to control of environmental pollution is of high priority. As an inexhaustible and environmental friendly resource, solar energy is considered to be the most ideal power and it makes the photolysis to be a favourable technology for solving the environmental contamination [1, 2]. By comparison, other treatment methods such as electrochemistry [3], filtration [4], biodegradation [5], and membrane bioreactor [6] all have the drawbacks of consuming raw materials. However, for the practical application of photolysis, low efficacy of solar energy utilization is the main obstacle. Thus, photocatalysis, especially semiconductor photocatalysis, becomes popular due to the advantages of using renewable resources, cost-effectiveness, safe, and comparatively high removal efficacy of the pollutants [7]. For example, titanium dioxide (TiO_2) [8], zinc oxide (ZnO) [9], bismuth sulfide (Bi_2S_3) [10], and carbon nitride (C_3N_4) [11] have been reported previous to perform well in photocatalysis. These semiconductors possess the ability to adsorb the light and produce photogenerated electron and hole pairs, which have redox ability to degrade the environmental pollutants. In addition, doping of catalyst such as TiO_2 by Au has enabled the catalyst to perform significantly better under visible light [12].

Notably, C_3N_4 is a non-toxic, abundant and low cost material, and has a metal-free property compared with other common catalysts [13]. In 1996, Teter and Hemley firstly conducted research on the C_3N_4 material and provided five molecular structures: β-C_3N_4, α-C_3N_4, g-C_3N_4, p-C_3N_4, and c-C_3N_4 (**Fig. S1**) [14]. Among them, g-C_3N_4 is most stable at room temperature and atmosphere pressure with the lowest density. From the end of the twentieth century, g-C_3N_4 has been extensively applied in many fields, including fuel cells, photocatalysis, gas storage, reduction of carbon dioxide (CO_2), and splitting water to produce hydrogen (H_2) [15-17]. As a catalyst, g-C_3N_4 has the moderate bandgap energy of 2.65 eV

which ensures it can utilize visible light directly in the 400-800 nm region [18, 19]. Moreover, the redox ability of the transferred photoexcited carriers and excellent chemical stability makes it potentially suitable for the solar energy conversion and pollutants adsorption. Nevertheless, the pristine of g-C_3N_4 still suffers three main disadvantages including insufficient absorption of light source, low surface area and the fast recombination of photogenerate electron and hole pairs, leading to a comparatively low photodegradation efficacy [20, 21]. Therefore, many routes have been developed to solve such problems and promote the photocatalytic activity. For example, non-metal doping, metal doping, and coupling with other semiconductors are known to be the effectiveness methods. The fusion of two π-conjugated systems not only enhances the charge separation of electron and hole from the single material, but also further increases the utilization region of solar spectra [19]. Moreover, morphology controlling is another effective method to promote the degradation efficacy as it could significantly enlarge the surface area of the catalyst so that the adsorption ability of light source and pollutants are both promoted [22].

The g-C_3N_4 and its modified composites have been successfully applied to the remediation of organic pollutants. Basically, the colored dyes such as Rhodamine B (RhB), methyl orange (MO), basic fuchsin (BF) and methylene blue (MB), were treated to evaluate the catalytic ability of as-synthesized g-C_3N_4 composites [23-26]. Because dye pollutants are not only now widely used in the textile, printing and plastic industries, but also hard to be degraded in water due to their complex composition, deep color, and chemical and physical stability. Dyes could absorb visible light irradiation and represent some of the principal pollutants in the wastewater from the textile industry [27]. On the other hand, some other organic compounds such as phenol, atrazine, and humic acid also have been reported to be treated with g-C_3N_4 composites under photocatalysis system, which indicates that g-C_3N_4 owns the photocatalytic ability to deal with different kinds of environmental organic pollutants in water [28-30].

There have been many publications on the application of g-C_3N_4 in water splitting, H_2 production, CO_2 reduction and photocatalysis [31-35]. In this review, we focused on the evaluation of catalytic ability of g-C_3N_4 composites for the environmental organic pollutants removal under visible light irradiation compared with common catalyst of TiO_2 nanoparticles, and photodegradation mechanism. In addition, in order to further promote the degradation efficacy, modifications on the g-C_3N_4 nanomaterials, including element or compound doping and morphology controlling are discussed. Besides, the stability of these as-synthesized g-C_3N_4 catalysts are introduced on the two sides of reusability and immobilization. In future studies, the photocatalysis of different kinds of organic pollutants degraded by g-C_3N_4 is highly recommended, and the effects of environmental conditions on photocatalysis process should be fully investigated.

2. Photocatalysis by g-C_3N_4

Pure g-C_3N_4 has higher photocatalytic ability than TiO_2 when dealing with dye pollutants and its photodegradation mechanism is related to the photoacticed carriers occurring in the photocatalysis system. the mechanisms and efficiency of g-C_3N_4 are discussed below

2.1. Photodegradation mechanism

The photodegradation mechanism of organic pollutants over g-C_3N_4 is provided in **Fig. S2A**. The band gap of g-C_3N_4 is 2.65 eV and its VB and CB potential is –1.09 and 1.56 eV, respectively [36]. So when g-C_3N_4 absorbs *hv* with energy equal to or great than 2.65 eV, the electron in CB will transfer to VB and in the meantime, a hole is generated in the CB. The photogenerated electron and hole pair owns strong redox ability owing to the high VB potential and low CB potential. As a result, the pollutants could be degraded directly by either photogenerated electrons or the holes and the degradation efficacy largely depend on the quantity of the electron-hole pairs and their redox ability. Besides, as the electrons is in a

comparatively low potential of –1.09 eV, they can react with the dissolved oxygen (DO) to produce superoxide radicals ($\bullet O_2^-$), which also could be the active group to degrade pollutants. Taking RhB as an example, the reaction process can be described as follows:

$$g\text{-}C_3N_4 + h\nu \rightarrow e_{CB}^- + h_{VB}^+ \quad (1)$$

$$O_2 + e^- \rightarrow \bullet O_2^- \quad (2)$$

$$RhB + h_{VB}^+/\bullet O_2^- \rightarrow \text{simple molecules} \rightarrow CO_2 + H_2O \quad (3)$$

$$H_2O + h_{VB}^+ \rightarrow \bullet OH + H^+ \quad (4)$$

The photogenerated electron-hole pairs will soon be recombined so that their quantity is reduced and largely limits the degradation efficacy [37]. Thus, inhibition of this recombination would be a significant route to promote the efficacy. In addition, modifying the band gap structure of the catalyst could broaden the range of light adsorption and thus improve the quantity of electron-hole pairs. However, too narrow band gap will lead to the low redox ability of the photogenerated electrons and holes even though they have high quantity [38]. Thus, making the band gap to a suitable structure is the key point when modifying the catalyst. And when the VB is improved to more than 1.99 eV, hole in the VB potential can react with water to produce hydroxyl radicals (•OH) scavenger as in Eq. 4, which also has the ability to degrade pollutants in this system and further promotes the degradation performance. Besides, controlling the morphology to a certain structure would not only extend the specific surface area of g-C_3N_4 which is beneficial for the light adsorption, but may also provide more active sites to contribute the photocatalysis. According to these methods, many research studies have been performed and already got some achievements in promoting degradation efficacy for the organic pollutants by the modification nanocomposites of g-C_3N_4 materials [39-41].

2.2. Photodegradation ability

The photocatalytic activity of the pure g-C_3N_4 was investigated by some researchers and 5 mg L^{-1} of RhB [42], 10 mg L^{-1} of MO [43], 3 mg L^{-1} of MB and 3.5 mg L^{-1} of BF [44]

were chose as the target pollutants to be degraded. The results are provided in **Fig. 1** which indicates that these four organic pollutants all have shown 50% or more degradation within 120 min by pure g-C_3N_4 with visible light irradiation. This process could be considered as a pseudo first-order reaction and its kinetics are calculated by the equation of $-\ln(C/C_0) = kt$, where k (min^{-1}) is the degradation rate constant, C_0 and C (mg L^{-1}) are the absorption equilibrium concentration of RhB and the concentration of the pollution at a reaction time of t (min), respectively. According to this, the degradation efficacy of different pollutants follows the order of k_{RhB} = 0.0139 min^{-1} > k_{MB} =0.0074 min^{-1} > k_{BF} = 0.0062 min^{-1} > k_{MO} = 0.0041 min^{-1}. This difference may be related to the various molecular composition and structure, degree of charge, or adsorption quantity by the catalyst of these pollutants. For a comparison purpose, 5 mg L^{-1} of RhB [42], 5 mg L^{-1} of MO [45], and 10 mg L^{-1} of MB [46] were conducted by TiO_2 nanoparticles photocatalysis as shown in **Fig. 1**. The results suggest that g-C_3N_4 outperformed TiO_2 when dealing with these three pollutants especially RhB and MB, as their k value of g-C_3N_4 is 4.2 and 3.4 times higher than that of TiO_2. Therefore, g-C_3N_4 is proven to be a better catalyst than TiO_2 in degradation of organic pollutants. However, according to the drawbacks mentioned in the photodegradation mechanism, it has much potential to get stronger photocatalytic ability to degrade the environmental pollutants efficiently.

3. Modified g-C_3N_4 nanomaterials and their catalytic ability

Based on the photodegradation mechanism, many novel g-C_3N_4 nanocomposites were synthesized to overcome the drawbacks of the pristine and achieved comparatively high degradation efficacy for the organic pollutants removal. The modification methods include metal and non-metal doping, semiconductor doping, morphology controlling and co-doping.

3.1. Metal and non-metal doping

Metal doping can lower the band gap of the doped g-C_3N_4 composite and promote its absorption of visible light, improve the specific surface area, and inhibit the recombination of photogenerated electron-hole pairs. The reported metal-doped g-C_3N_4 catalysts are summarized in **Table 1** with their characteristics and degradation efficacy [47-52]. The results exhibit that europium (Eu) doped by Xu et al. [46] has the narrowest band gap of 2.41 eV and tungsten (W) doped by Rong et al. [53] extends its surface area 5.5 times than the pristine condition. However, the most effectiveness modification is potassium (K) doping as this composite catalyst could promote the rate constant 6.5 times higher than the value of original one [54]. Thus, it indicates that K is more suitable for enhancing the photocatalytic activity than any other metals, which might be attributed to the following reasons: firstly, Obtaining suitable band gap. Commonly, the lone pair electron of nitrogen has strong influence on the electron density distribution [55], however, metal doping could change the electron density of the N atoms, thus altering the electronic structure and band gap of carbon nitride as shown in **Fig. 2A**. Notably, too high band gap energy will result in adequate quantity of photo-induced electron-hole pairs produced in the catalytic system. On the opposite, too low band gap could lead to the abundant electron-hole pairs but with weak oxidant-reduction ability. Therefore, according to the results of the *k* value provided in **Table 1**, 2.57 eV is the most suitable band gap for the catalyst of K doping. Secondly, K atoms tend to exist in the g-C_3N_4 interlayer via bridging the layers rather than doping into the conjugated plane acting as Na atoms [35]. Meaningfully, such nanostructure can make K atoms chemically bond with atoms at the adjacent two layers which benefit to forming charge delivery channels and bridging the layers, contributing to the transfer and separation of electron-hole pairs (**Fig. S3**). Thirdly, as the CB and VB potentials altered by K doping could be tuned from -1.09 to -0.53 eV and from +1.56 to +2.04 eV, respectively, and hence •OH and $•O_2^-$ could be formed, leading to the improving efficacy of photodegradation (**Fig. 2A**). As a comparison, the CB and VB potentials changed by W doping was –1.13 and +1.57 eV, which is not beneficial for the

production of •OH/OH^- (+1.99 eV). All in all, compared with pure g-C_3N_4, K doping promoted most degrading efficacy of organic pollutants photodegradation than other metal performance.

Although metal doping has many advantages in promoting the catalytic ability, the drawbacks of poor thermal stability of the doped ions and losing metal-free property existed. Thus, non-metal doping has been investigated on their high ionization energy and high electro negative. As a result, no-metal doping could not only avoid the thermal variation of chemical states of doped metal ions, but also keep the metal-free property of g-C_3N_4. **Table 1** provides four kinds of non-metal doping and it shows that B doping promoted the efficacy 3.6 times higher than the value of pure g-C_3N_4 and better than the performance of P, S and C doping [56]. B doped with g-C_3N_4 were first synthesized by Yan et al. via heating the mixture of melamine and boron oxide [57]. Ruan et al. calculated the forming energy of the doped nanomaterial according to the Eq. 5 as follows [58]:

$$E_{form} = E_{tot}(X{:}C_3N_4) - E_{tot} - \mu(X) + \mu(C) \quad (5)$$

where E_{tot} ($X{:}C_3N_4$) is the total energy after element is doped; E_{tot} is the total energy before element is doped; μ (X) is the atomic energy of the doped element; μ (C) is the atomic energy of the alternative element. The results came out that the form energy of B, P and S doped system were –1.76, 2.44 and 3.41 eV, respectively, which indicated that B was easy to be doped in the carbon site as its energy value was negative while P and S were comparatively hard to be doped as their doping process need adsorbing energy. Thus, B is easier to be doped than P and S, which possibly explains the phenomenon that B doping performs best to promote the degradation ability. Besides, recently a new doping method namely self-doping has been investigated which can be defined as reintroducing the existed element of the catalyst to change its nanostructure [59-61]. Dong et al. conducted C self-doping in CN framework which could accelerate the electronic migration due to the formation of conjugate big π bonds and stronger light absorption capacity [62]. As a result, the photo-induced

electron and hole pairs were increasing and their separation effect was better. In effect, C doping promoted 3.0 times of rate constant for RhB degradation than that of origin g-C_3N_4.

Notably, the precursor of CN in the g-C_3N_4 composite catalyst has strong influence on its photocatalytic ability for the organic pollutants removal. **Fig. S4** exhibits the photocatalytic efficacy for RhB removal of g-C_3N_4 synthesized by different CN precursors. The results indicate that urea as the precursor produced g-C_3N_4 with best degradation performance and the order is: urea (k=0.1973 min^{-1}) > melamine (k=0.1890 min^{-1}) > cyanamide (k=0.1863 min^{-1}) > dicyandiamide (k=0.1442 min^{-1}). During the urea reaction process, the step of thermal polycondensation was much complex and many hetero atoms such as H and O were drawn off as the form of small molecules. As a result, the C and N ratios in the products were relatively high, which achieved high purity of g-C_3N_4 product. Therefore, g-C_3N_4 produced by urea has well efficacy during the photocatalysis of RhB. However, its yield is as low as 8% and this defect would lead to a large resource waste [63]. Thus, when both productive yield and degradation efficacy are taken into consideration, melamine is preferable to be chosen as the precursor. Similarly, the same element of metal or non-metal doped g-C_3N_4 from different precursors possesses various morphology and photocatalytic ability as shown in **Table 1**. For example, KOH and KI as precursors produced K-C_3N_4 catalysts with a different band gap of 2.57 and 2.64 eV, respectively [54, 64]. In addition, Fe-C_3N_4 prepared by $FeCl_3$ as precursor had lower band gap of 2.56 and higher improved times efficacy of 5.8 than the one from $Fe(NO_3)_3$•$9H_2O$ precursor[42, 65]. Moreover, P doping synthesized by $(NH_4)_2HPO_4$, NH_4PF_6, and $BmimPF_6$ also have various promoted efficacies [66-68]. Therefore, it may suggest that as the same elements exist in different forms in different precursors, when they are doped in g-C_3N_4 material, they need different extent of energy so that the synthetic effect and morphology would be various. All in all, the precursors are significant factor related to the synthetic catalyst and their photodegradation ability. So according to the data in **Table 1**, it is reasonable to make a hypothesis that K doping with g-C_3N_4 synthesized by KOH and

melamine as the precursors will own the best catalytic ability than other materials shown in table 1, but still needs to be proven by experiments in the future.

3.2. Semiconductor doping

When two semiconductors with different CB and VB potentials are doped together as heterojunction, the photogenerated electrons and holes could transfer from the energy level of one semiconductor to another's. From the **Table 2**, it proves that all the semiconductor doping catalysts of g-C_3N_4 have the improving efficacy of organic pollutants degradation to varying degrees when compared with the performance of pure g-C_3N_4 (k_p) and TiO_2 (k_T) [45, 53, 69-76]. Particularly, CdS-g-C_3N_4 composites synthesized by Fu et al. could degrade MO (5 mg L^{-1}) within 20 min and its k (0.00564 min^{-1}) was 11.2 and 14.0 times higher than that that of the pristine and TiO_2, respectively [77]. Similarly, BiOBr-g-C_3N_4 prepared by Fu et al. degraded 100% RhB (20 mg L^{-1}) within 40 min with the k of 0.0433 min^{-1}, which was almost 7.2 and 8.6 fold higher than that of the pristine and TiO_2 [78]. Degradation by BiOBr-g-C_3N_4 composites (**Fig. S2B**) is performed according to the following mechanism, the electrons generated in the CB of g-C_3N_4 transfer to the CB of BiOBr and in the meantime, holes generated in the VB of BiOBr transfer to the VB of g-C_3N_4. Thus, the photogenerated electron and hole pairs are able to be separated effectively and promote the photodegradation efficacy. Significantly, the band gap of the doped semiconductor is the key factor as it decides the quantity of the transferred electrons and holes from one material to another and thus indirectly influences the recombination rate of electron-hole pairs. As shown in **Fig. 2B**, different semiconductors possess different VB and CB potentials and based on the results, Ag_2O, BiOBr, CdS have comparatively more matched band gap structure in the composite system than other compounds.

On the other hand, Z-Scheme composite doping is defined as that during the photocatalytic procedure, the electrons generated in the CB of g-C_3N_4 transfer to VB of doped compound rather than the same g-C_3N_4 and annihilate the holes in VB of the compound (two

different migration mechanisms of charges shown in **Fig. S2C and D**). Thus, it could inhibit the electron-hole pairs recombination in both g-C_3N_4 and the doped compound. For example, over Z-Scheme Ag_3PO_4-g-C_3N_4 hybrid photocatalysts, it took only 5 min for the complete degradation of MO (10 mg L^{-1}) with visible light irradiation and the *k* is as high as 0.2357 min^{-1} [79]. It may be contributed to the typical Z-scheme mechanism which is favourable for organic pollutant degradation. Specifically, as shown in **Fig. 3D**, the electrons in CB of Ag_3PO_4 migrate to the VB of g-C_3N_4 and combine with the holes there. So the recombination rates of electron-hole in both g-C_3N_4 and Ag_3PO_4 are reduced. Thus, the electrons in CB of g-C_3N_4 has strong reductive ability as its potential is as low as -1.15 eV so they can react with DO to produce $\bullet O_2^-$ which is able to degrade MO. In the meantime, holes in the VB of Ag_3PO_4 own strong oxidation ability because of its high potential (+2.69 eV) and the holes can degrade MO directly. However, if the migration route of the charges follows the conventional heterojunction electron-hole separation, the electrons in the CB of g-C_3N_4 would transfer to the VB of Ag_3PO_4 and it can not produce $\bullet O_2^-$ with O_2 as the CB potential of Ag_3PO_4 is more positive than that of $O_2/\bullet O_2^-$ couple. Moreover, the oxidation power of holes in VB of g-C_3N_4 is decreasing due to the relatively low potentials (1.6 eV). Therefore, theoretically, the Z-Scheme hybrid g-C_3N_4 composites perform better degradation capacity than conventional heterojunction catalysts. According to the results summarized in **Table 2**, when dealing with above 3 mg L^{-1} of MB, Z-scheme WO_3-g-C_3N_4 could degrade almost MB within 120 min with the *k* of 0.0353 min^{-1} while only 90% MO were photodegraded within as long as 300 min by TiO_2-g-C_3N_4 catalyst and its *k* is just 0.007 min^{-1} [44]. In addition, Z-Scheme Bi_2MoO_6 could degrade 90% of 10 mg L^{-1} MO within 40 min and the *k* is 0.0688 min^{-1} [80]. When dealing with 10 mg L^{-1} of RhB, Z-Scheme SnO_{2-x} and Z-Scheme V_2O_5 both could degrade almost of the pollutant within 60 min and their efficacies were better than that of $DyVO_4$ and $GdVO_4$ [81-84]. Thus, based on the mechanism analysis and results comparison, the Z-Scheme catalysts indeed have the better photodegradation ability but when

the cost of light energy and ambient conditions are taken into consideration, further researches need to be done in the future.

3.3. Morphology controlling and co-doping

There is a close connection between the morphological structure of the catalyst and its photocatalytic capacity. Many efforts have been paid on the morphology controlling and until now, various types of the morphology worked out can be concluded as porous[85], mesoporous [86], microspherical [87], and nanosheet g-C_3N_4 [88], etc. Done et al. investigated the morphology controlling of tubular g-C_3N_4 and their visible light photocatalytic properties [89]. The results are provided in **Table 3** and they exhibit that the modified morphology, nanoflake, nanotube, and rod-like g-C_3N_4 all promoted the rate constant to 0.0047, 0.0055, and 0.0058 min^{-1}, which were 1.3, 1.6, and 1.7 times higher than that of the pristine. The Scanning Electron Microscope (SEM) images of the different morphology structure catalyst are shown in **Fig. S5** and their better performance of degradation can be attributed to the increased specific surface area which is suitable for photocatalytic application. Thus, morphology controlling is truly an effective method of modifying g-C_3N_4 to promote the photocatalytic ability. Besides, metal doping such as S and Cu with morphology modification of porous rods and mesoporous, respectively both made the catalysts own a better photocatalytic ability with the *k* values 12.8 and 4.3 times higher than that of the pristine [43, 56].

Furthermore, co-doping is another significant method which could combine the advantages of single material, leading to improved photocatalytic activity. Dual doping, such as metal/non-metal doping or semiconductor doping both have been proved to have better performance as discussed above. Recently, tridoping g-C_3N_4 is developed by combing three different heteroatoms into g-C_3N_4 framework for modification. Moreover, with morphology controlling, these tridoping g-C_3N_4 catalysts possess more benefits for the photodegradation of organic pollutants (**Table 3**) [90, 91]. Notably, Ag@AgCl-g-C_3N_4 porous nanosheets

synthesized by Zhang et al. could degrade RhB, MB, MO, and Phenol as pollutants [92]. Especially, 10 mg L^{-1} of RhB was completely degraded within 30 min with the *k* of 0.1954 min^{-1} and 10 mg L^{-1} of MB and MO both could be 100% degraded within 60 min. Even though with comparatively lower rate constant, 10 mg L^{-1} of Phenol still would be mostly degraded (80%) within 140 min. Thus, this co-doping catalyst with morphology controlling not only can degrade several kinds of dye pollutants, but also have high degradation efficacy when dealing with different target pollutants. The major active species for the photodegradation was identified as the holes and $\bullet O_2^-$. Besides, the holes could oxidize Cl^- ions from AgCl to •Cl, which is also able to degrade dye pollutants as the active radical species. In addition, the synergistic interaction of Ag and polarization field around AgCl and the matching bang gap of AgCl and g-C_3N_4 both contribute to the separation and migration of photogenerated electrons and holes. Moreover, the Ag@AgCl nanoislands on the porous g-C_3N_4 nanosheets could provide many active centers by full exposing the adjacent area of island-sheet interfaces to the pollutants. Similarly, porous N-TiO_2/g-C_3N_4 heterojunctions prepared by Wang et al. degraded 100% RhB and MB within 40 and 60 min, respectively with the *k* of 0.0284 and 0.07 min^{-1} [93]. Other composites such as core-shell nanoplates N-ZnO/g-C_3N_4, nanosheets MoS_2-TiO_2/g-C_3N_4 and so on all promoted the degradation efficacy in some extent compared with the performance of the pristine and TiO_2 as shown in **Table 3** [94-96]. Therefore, a conclusion can be drawn that compounding doping and morphology controlling can effectively modified the g-C_3N_4 to possess higher photocatalytic ability for the organic pollutants removal.

4. Stability of g-C_3N_4 nanocomposites

Besides the photocatalytic ability, the stability of the catalysts performing during the photocatalysis procedure is also important for application on real water treatment. Thus, the

reusability and immobilization of the as-synthesized g-C_3N_4 nanocomposites are discussed in the following section.

4.1. Reusability

In the practical photocatalytic applications in aqueous solution, the recycling of the catalyst is essential task due to the leakage of the individual components during the degradation process. Ag@AgCl-g-C_3N_4 porous nanosheets are taken as the representative example because of comparatively high degradation efficacy and the reusability of this catalyst is evaluated by recycling the photodegradation for RhB removal under visible light. The results shown in **Fig. 3A** exhibit that only a slight decrease was observed after eight consecutive photocatalysis, which proves that this materials have not only possess high photocatalytic ability, but also excellent stability, which both contribute to a promising visible-light driven catalyst on the application of pollutants removal. However, even though the efficacy decrease during the recycling is minimum as shown in **Fig. 3A**, the small loss will be enlarged with the change of catalysts content or the flow rate. Because no research on g-C_3N_4 nanocomposites is conducted to this area, TiO_2 treatment is chose as the potential evidence to be investigated. Li et al. used TiO_2 as catalyst for the continuous photodegradation of dye wastewater and the COD removal rate was detected for the evaluation of degradation efficacy [97]. **Fig. 3B** shows the Dye wastewater COD removed by TiO_2 composites with different catalysts content and flow rates. The COD removal rate increases with an increasing catalyst loading until 6.0 g L^{-1} and subsequently decreases. Thus, it is reasonable to predict that in the application of as-synthesized g-C_3N_4 nanocomposites, the degradation efficacy of the pollutants removal will be decreased with the losing of catalysts content during each cycle. Besides, the COD removal rate decreases with the increase of flow rate, which is mainly caused by the decrease of photocatalytic time. So when the g-C_3N_4 composites deal with large volume of wastewater, the flow rate has an important effect on the target pollutants removal and the efficacy will decreases quickly with the high flow rate.

Overall, the reusability of the as-synthesized catalysts should be further investigated as it is reliant on many environmental factors.

4.2. Immobilization

The immobilization is an effectiveness method to promote the stability of catalysts by providing a carrier according to the following methods: 1) the catalysts are evenly painted on the smooth foundation to form a kind of continuous film; 2) the catalysts are doped with the carrier to get the doping composites. Notably, the carrier should own the properties such as well light transmission, strong binding force with the catalyst, strong adsorption of the pollutants, large specific surface area and chemically inert. For example, Ye et al. fabricated MoS_2/S-doped g-C_3N_4 heterojunction film to enhance photocatalytic degradation of MB with visible light irradiation [98]. The CN film was prepared on the indium-tin oxide (ITO) substrate and showed much stronger absorption with an abrupt gap of 430 nm. In another instance, Dong et al. synthesized polymeric g-C_3N_4 doped on the structured Al_2O_3 ceramic foam as a proper support for practical environmental application [99]. They found that Al_2O_3 ceramic foam were made up of connected arrays of struts and this design enabled the immobilized g-C_3N_4 stable in activity and can be used repeatedly without deactivation. In addition, the specific surface area of immobilized g-C_3N_4 was enlarged more than the pure g-C_3N_4, which also make the Al_2O_3 ceramic foam an ideal carrier for immobilization of g-C_3N_4. Therefore, the carrier could not only provide the immobilization of the catalyst, but also promote the photocatalytic ability, which should be considered as a necessary decoration for the g-C_3N_4 materials when they are applied in real wastewater.

Photocatalytic reactor is designed as the area of the photodegradation process for the pollutants removal from water. As many reactors have been done for TiO_2 immobilization while few are applied for g-C_3N_4, we redesigned these TiO_2 reactors to make them suitable for the well immobilization and photodegradation performance of g-C_3N_4 nanocomposites application. Basically, g-C_3N_4 catalysts only need visible light rather than UV light which is

necessary for TiO_2 due to the different adsorption ability of light source between the two catalysts. Furthermore, pure g-C_3N_4 catalysts own the non-metal property so the leakage and recycle of the metal should not be a problem to be considered. Normally the photocatalytic experiments conducted in the laboratory use the suspension photocatalytic reactor as shown in **Fig. 4A**. This kind of reactor possesses the advantages of simple structure, convenient operation, non-limitation of compound transmission, and high rate of reaction. Nevertheless, it also has several disadvantages; firstly, the particle size has strong influence on the suspended state of the catalyst, namely, too small size would lead to a difficult separation while too large would result in particles deposition. In addition, the particle size also affects the light transmission as large size or high concentration would lead to the turbid solution so that the light transmission will be disturbed and light adsorption is going to be reduced. More important, the catalysts suspending in the solution is hard to be separated and re-used. Thus, the loaded photocatalytic reactor is preferable to be used for the g-C_3N_4 nanocomposites application. As shown in **Fig. 4B**, g-C_3N_4 on structured Al_2O_3 ceramic foam synthesized by Dong et al. could be fixed at one side of the reaction pool and the pollutant water flows from water intake to outlet passing though the loading g-C_3N_4 materials. However, such reactor structure would easily present following two problems: one is the limited reaction area which is just the cross-sectional area of the g-C_3N_4 on the Al_2O_3 foam; the other one is comparatively short stay time of contacting the catalysts, which will lead to the incompletely photodegradation. Accordingly, tubes, fibres, and floated glass balls have been designed for the substitution of the single tiled catalysts. Notably, among them, fibres own the advantages of large reaction area, low catalyst loss during the transmission, and high efficacy of optical transmission. For instance, Hatat-Fraile et al. used the doped TiO_2 coated quartz fibre membranes in a photocatalytic reactor as shown in **Fig. 4C** and it turned out to be durable degradation ability with high efficacy [100]. In the same way, when g-C_3N_4 nanocomposites take the place of TiO_2, it should achieve the similar degradation performance for the

pollutants removal. However, the fibre reactor also owns its drawbacks such as easy broken, expensive, and difficult loading of the catalysts. Therefore, every kind of the photocatalytic reactor should be taken into consideration when dealing with real wastewater.

5. Future perspectives

Although much research has been conducted about the g-C_3N_4 nanocatalysts, the development application in photocatalysis is still at its early stage and there remain many challenges.

5.1. Photocatalysis of POPs

As shown in the **Tables 1–3**, the main target compounds degraded by g-C_3N_4 composites are the dye pollutants such as the most common object of RhB, then MO, and MB. Their molecular structures are provided in **Fig. S6A**. Based on the research of Wang et al. [52], RhB could be degraded into CO_2 and H_2O by g-C_3N_4 nanocomposites under simulated solar light irradiation. So it indicates that the photogenerated electron and hole pairs in the photocatalytic system are able to broke the chemical bond including phenyl C-H bond, C-O bond, and so on as shown in **Fig. S6A**. Notably, the bond dissociation energy (BDE) at 298 K of C-O bond reaches as high as 1077 kJ mol^{-1} and then the BDE of phenyl C-H bond could be 473 kJ mol^{-1}. Therefore, g-C_3N_4 can degrade other POPs existing in environmental with visible light in theory. For example, as a classic kind of perfluoroalkyl substances(PFAS), perfluorooctanoic acid (PFOA) recently draw a great attention as they are potential reproductive and developmental toxins, endocrine disrupters, and carcinogens [101]. More serious, PFOA was detected in high concentration in the environmental media and hard to be degraded due to the strong C-F bond (BDE is 544 kJ mol^{-1}) as shown in the structure (**Fig. S6B**). Li et al. used the commercial In_2O_3 nanocrystals and the results showed that they could degraded 80% PFOA within 180 min under UV irradiation [102]. Besides, Chen et al. successfully synthesized In_2O_3/g-C_3N_4 composites and the as-synthesized catalysts was

proved to be able to degrade almost RhB under visible light irradiation [103]. Thus, it is reasonable to provide a suspicion that In_2O_3/g-C_3N_4 composites can degrade PFOA more efficiently than commercial In_2O_3 or pure g-C_3N_4. The reason may be attributed to that the doping composites should have a better band gap and the recombination of photogenerated electron and hole pairs should be inhibited as the function of composite structure. more details about the specific degradation and simulation process are available in **Eqs. (S1)–(S12)** (See appendix…). Therefore, PFOA photodegraded by In_2O_3/g-C_3N_4 catalysts are worthwhile to be investigated in the future because it could prove a novel materials able to deal with the PFAS efficiently.

5.2. Influence of environmental conditions

Many environmental conditions during the photodegradation process such as solution pH, reaction temperature, DO, and dissolved organic matters (DOM) play the significant factors for the photocatalytic performance while these factors were seldom investigated in the previous research of g-C_3N_4 photocatalysis. The solution pH would influence the ionization degree of the chemical compounds and largely decide their positive or negative charged. The opposite charged of the pollutants and the catalysts could promote the combination between them and thus increase the photodegradation efficacy. In addition, the reaction temperature would lead to a high impact for the photodegradation progress. Because high temperature is able to accelerate the redox reaction, however, too high temperature would change the nanostructure of the catalyst which leads to the catalyst deactivation. Besides, DO plays an important role in degrading the pollutants. As shown in Eq. 2, the oxygen in the solution could react with electron to produce the $\bullet O_2^-$, which has the oxidation ability to deal with the pollutants as the same function of photogenerated h^+ and in the meantime it can inhibit the recombination of electron and hole pairs due to the consumption of electron. Furthermore, DOM normally exists in the real water and considered to have a pronounced effect on photochemical because of the generation of DOM-derived oxidative intermediates or their

physicochemical quenching effects. On one hand, DOM will occupy the surface of the catalysts instead of the target pollutant, which lead to the less adsorption capacity of the catalysts and poor degradation efficacy. Furthermore, DOM such as humid acid in the reaction mixture absorb the photon and generated active groups such as •OH or $•O_2^-$ and thus would affect the photooxidation rate [104]. These environmental conditions have been proven to have significant effect on the catalytic ability of TiO_2 in the previous literatures [104-107]. Therefore, when a new kind of g-C_3N_4 composites is synthesized, pH, reaction temperature, DO, and DOM should be investigated to determinate the best conditions for the photocatalytic performance of the as-synthesized catalysts.

Some other significant points in the future research are including as follows:

- Synthesizing innovative g-C_3N_4 composites which are benefit in the morphology controlling or the new compound doping;
- Investigating the application on the real wastewater and evaluating the photocatalytic ability of different g-C_3N_4 composites, combining with their cost in commercial and energy consuming;
- Designing the suitable material as the carrier to promote the immobilization of g-C_3N_4 composites which can inhibit the catalyst loss during degradation process;
- Investigating other significant persistent organic pollutants (POPs) such as Polybrominated diphenyl ethers (PBDEs) [108, 109], Hexabromocyclododecane (HBCDs) [110], Endocrine disrupting chemicals (EDCs) [111], pharmaceuticals [112], etc. conducted by g-C_3N_4 composites under visible light irradiation and evaluating their photodegradation efficacy.

6. Conclusions

In summary, g-C_3N_4 possesses higher photocatalytic ability than TiO_2 for some organic pollutants, which is probably attributed to the suitable bang gap energy and good

redox ability of the photogenerated carriers. However, owing to the drawbacks of low surface are and fast recombination of photogenerated electron and hole pairs, element and compounding doping are summarized and their degradation efficacy have been compared. As a conclusion, among metal doping, K doping promoted most degrading efficacy with the k value of 0.0110 min^{-1} than other metal performance. And C, as a present of non-metal doping, promoted 3.0 times of rate constant for RhB degradation than origin g-C_3N_4. In addition, when two semiconductors with different CB and VB potentials are doped together as heterojunction, the photogenerated electrons and holes could transfer from the energy level of one semiconductor to another's and thus inhibits the recombination of electron and hole pairs in single material. Notably, Z-Scheme composite doping, such as Z-Scheme Ag_3PO_4-g-C_3N_4, have outstanding degradation efficacy, which could degrade 100% MO within 5 min with *k* of 0.2357 min^{-1} under visible light irradiation. Besides, morphology controlling and co-doping can further promoted the catalytic ability. For example, Ag@AgCl-g-C_3N_4 porous nanosheets degraded degrade RhB, MB, MO, and Phenol all with high *k* value of 0.1954, 0.0258, 0.0260, 0.0128 min^{-1}, respectively. Besides, those reported g-C_3N_4 composites all have well reusability according to the repeated photocatalysis experiments. However, when the catalyst dose or the flow rate of the solution increases, the photodegradation rate would be negatively influenced. Notably, the immobilization is the significant method to promote the stability of the catalyst in application, which mainly includes carriers fabricating and photo reactor designing. And future work should be focus on the other meaningful POPs photodegradation by these as-synthesized g-C_3N_4 composites and environmental conditions discussion during the photocatalysis process. In the meantime, we still have to devote to synthesize more functionalized yet low-cost g-C_3N_4 composites to decompose the environmental organic pollutant with high and stable efficacy.

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