

Modification Strategies of Pristine Graphitic Carbon Nitride

Subjects: Crystallography

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Graphitic carbon nitride ($g\text{-C}_3\text{N}_4$), as the significant metal-free semiconductor photocatalyst, holds great potential in the application of the photocatalytic nitrogen oxides (NO_x) removal process due to its plentiful extraordinary advantages, such as visible light response properties, mild bandgap, low cost, facile preparation and high thermal stability. However, pristine $g\text{-C}_3\text{N}_4$ prepared using the traditional high-temperature solid reaction suffers from low specific surface areas and low crystallinity owing to kinetic hindrance, which results in small specific surface areas, few reactive sites, limited light-harvesting capacity, rapid recombination of photogenerated charge carriers and unsatisfactory photocatalytic NO_x removal performance. In order to improve the photocatalytic performance of pristine $g\text{-C}_3\text{N}_4$, a variety of modification strategies have been developed including metal doping, non-metal doping, defect engineering, crystallinity optimization, morphology controlling and heterojunction construction.

Keywords: photocatalysis ; $g\text{-C}_3\text{N}_4$; NO_x ; mechanism

1. Morphology Controlling

Morphology controlling is considered a promising strategy to improve the photocatalytic performance of bulk graphitic carbon nitride ($g\text{-C}_3\text{N}_4$)^[1]. Since bulk $g\text{-C}_3\text{N}_4$ is synthesized using the high-temperature solid reaction, it suffers from low specific surface areas and few active sites, which is detrimental to photocatalytic performance. Moreover, bulk $g\text{-C}_3\text{N}_4$ exhibits a longer charge carrier migration distance, and thus the photogenerated electron and hole pairs achieve rapid charge recombination. In addition, bulk $g\text{-C}_3\text{N}_4$ is unfavorable for molecular mass transport, surface redox reactions and light harvesting in comparison with porous $g\text{-C}_3\text{N}_4$ ^{[2][3]}. In order to enlarge the specific surface areas, increase the active sites, promote the charge carrier separation efficiency and facilitate the molecular mass transport, much progress has been made such as the exfoliation of bulk $g\text{-C}_3\text{N}_4$ into nanosheets, template strategy including hard-template and soft-template and supramolecular preorganization method.

1.1. Nanosheets Structure

Inspired by the preparation of graphene nanosheets^{[4][5]}, scientific researchers attempt to exfoliate bulk $g\text{-C}_3\text{N}_4$ into nanosheets. Compared with bulk $g\text{-C}_3\text{N}_4$, $g\text{-C}_3\text{N}_4$ nanosheets exhibit a great deal of distinct benefits owing to morphology changes. It not only enlarges the specific surface areas and increases the active sites but also shortens the charge carrier's transport distance, improves the solubility and modifies the electronic structures owing to the famous quantum confine effect. More specifically, the photogenerated electrons and holes coming from the $g\text{-C}_3\text{N}_4$ nanosheets can easily migrate to the surface of the photocatalysts to attend the surface reactions through the shortened paths. This phenomenon is instrumental in facilitating the charge carrier separation efficiency to improve photocatalytic performance. In addition, the enlarged bandgap of $g\text{-C}_3\text{N}_4$ nanosheets leads to enhanced oxidation potential energy and reduced potential energy, which is useful for surface reactions.

Generally, the $g\text{-C}_3\text{N}_4$ nanosheet structures could be achieved using two different strategies, i.e., liquid exfoliation of bulk $g\text{-C}_3\text{N}_4$ and thermal exfoliation of bulk $g\text{-C}_3\text{N}_4$. Various solvents with suitable surface energy, i.e., such as water, methanol, ethanol, N-methyl-pyrrolidone (NMP), 1-isopropanol (IPA), acetone and their mixtures, have been used to overcome the weak van der Waals forces between the two adjacent layers of bulk $g\text{-C}_3\text{N}_4$ using facile sonification. For example, Xie et al. reported a green liquid exfoliation strategy to obtain ultrathin nanosheets using cheap and environmentally friendly water as the solvent^[6]. The thickness of the exfoliated nanosheet is about 2.5 nm in height (around seven layers) with the size distribution ranging from 70 nm to 160 nm. In addition, Zhu et al. reported a concentrated H_2SO_4 (98%) assisted liquid exfoliation strategy to fabricate a single atomic layer of $g\text{-C}_3\text{N}_4$ ultrathin nanosheets^[7]. The intercalation of

concentrated H₂SO₄ (98%) into the interplanar spacing of bulk g-C₃N₄ resulted in the graphene-like single-layer g-C₃N₄ structure with a small thickness of 0.4 nm and a large size of micrometers.

Compared with the liquid exfoliation strategy, thermal exfoliation is more facile and more environmentally friendly because it does not involve toxic solutions such as aqueous ammonia, hydrochloric acid and concentrated H₂SO₄ (98%). The thermal exfoliation approach is fast, low-cost and low-pollution. However, the largest drawback of the thermal exfoliation strategy is the low yield due to thermal oxidation and thermal etching. For instance, Niu et al. obtained g-C₃N₄ nanosheets with a thickness of 2 nm (about six to seven layers) using the thermal exfoliation strategy [8]. The synthesized g-C₃N₄ nanosheets exhibited enhanced photocatalytic H₂ evolution under simulated solar light irradiation. The excellent photocatalytic H₂ production of the obtained g-C₃N₄ nanosheets was ascribed to the large specific surface area, low sheet thickness, enlarged band gap, increased electron-transport ability and prolonged lifetime of the charge carriers. In addition, Gu et al. reported that bulk g-C₃N₄ could be exfoliated into nanosheets to increase the specific surface areas and active sites using facile post-thermal treatment [9]. At the same time, the electronic structure of bulk g-C₃N₄ was optimized during the calcination process. The valence band of g-C₃N₄ nanosheets was increased owing to the quantum confinement effect and nitrogen vacancy, which led to the higher thermodynamic driving force during the photocatalytic nitrogen oxides (NO_x) removal process. The g-C₃N₄ nanosheets showed about 3.0 times higher photocatalytic NO_x removal performance than pristine g-C₃N₄ owing to the enlarged specific surface areas and optimized electronic structure. In addition, the impact of calcination temperature, calcination time and sample amount on the photocatalytic NO_x removal performance and the yield of g-C₃N₄ nanosheets were systematically studied.

1.2. Porous Structure

The template strategy is an effective approach to fabricating porous nanostructured g-C₃N₄, which can increase the specific surface areas and active sites of bulk g-C₃N₄ [10][11]. Moreover, the high porosity of nanostructured g-C₃N₄ is beneficial for mass and gas transport. In addition, the voluminous void space in nanostructured g-C₃N₄ can enhance the light absorption efficiency owing to the light trapping effect. These plentiful advantages can bring about outstanding photocatalytic performance in comparison with the bulk counterpart [11]. In general, the template method is based on the use of inorganic or organic nanostructures as a template, i.e., a hard template and a soft template [12].

A hard template is a controllable and precious strategy to prepare nanostructured g-C₃N₄. The hard template method, in other words, solid material nano-casting, is performed using a physical structure agent to control the porous nanostructured g-C₃N₄. Up to now, a large number of hard templates have been studied. For example, Zhang et al. used HCl-treated SBA-15 silica as a hard template to prepare ordered mesoporous g-C₃N₄ [13]. The obtained mesoporous g-C₃N₄ displayed significantly enlarged specific surface area and pore volume, which were 517 m² g⁻¹ and 0.49 cm³ g⁻¹, respectively. Similarly, Sun et al. reported hollow nanospheres of g-C₃N₄ when using a silica-based hard template [14]. The hollow nanospheres of g-C₃N₄ displayed excellent photocatalytic H₂ evolution performance due to the hollow sphere structure. Recently, Zhang et al. demonstrated that low-cost calcium carbonate (CaCO₃) is a promising environmentally friendly hard template [15]. After the CaCO₃ is removed using hydrochloric acid treatment, porous g-C₃N₄ was successfully prepared.

Since hard templates involve hazardous fluoride-containing reagents, a tremendous amount of work has been completed on the soft template [16]. The key point of a soft template is the molecular self-assembly process, which can chemically tailor the porosity and morphology of pristine g-C₃N₄. Various templates, such as non-ionic surfactants and amphiphilic block polymers, could be chosen as soft templates. In addition, ionic liquids have demonstrated an effective soft template [2][17]. The soft templates provide a facile and more environmentally friendly strategy to prepare nanostructured g-C₃N₄ [18]. Very recently, supramolecular preorganization has become an interesting topic to prepare nanostructured g-C₃N₄. To some extent, the supramolecular preorganization strategy is similar to the soft template strategy. However, this strategy is based on the supramolecular interactions of g-C₃N₄ monomers, including hydrogen bonds, the π-π bond and so on. For instance, Zhang et al. reported a solvent-assisted strategy to prepare porous g-C₃N₄ with enhanced visible-light photocatalytic NO removal performance [19]. g-C₃N₄ prepared with the addition of water and ethanol exhibited significantly improved visible-light photocatalytic performance, with NO removal percentages of 37.2% and 48.3%, respectively. The enhanced photocatalytic NO_x removal performance was ascribed to the unique microstructure and prolonged lifetime of the charge carriers.

2. Band Structure Engineering

The band structure of photocatalysts plays a crucial role in the photocatalytic process. The optimized band structure can absorb more solar energy to generate more electron-hole pairs; improve the charge carrier separation efficiency to obtain

more effective electrons and holes for the surface reactions; and optimize the reaction sites and promote the adsorption of intermediates to improve the surface reactions. Up to now, tremendous efforts have been devoted to modulating the electronic structure of $g\text{-C}_3\text{N}_4$. The strategies of band structure engineering can be roughly divided into two categories: metal element doping and non-metal element doping [17].

2.1. Metal Element Doping

A series of metal cations have been used to modulate the band structure of pristine $g\text{-C}_3\text{N}_4$. There are two kinds of metal element doping related to $g\text{-C}_3\text{N}_4$, which are cave doping and interlayer doping. The metal cations can be introduced into the triangular pores of $g\text{-C}_3\text{N}_4$ between the heptazine structures [20]. The strong coordination interaction between the metal cations and $g\text{-C}_3\text{N}_4$ matrix and negatively charged nitrogen atoms can realize cave doping [17]. According to previous literature, the transition metal elements including Fe, Mn, Co, Ni and Zn have been demonstrated to be effective at optimizing the electronic structure [2][17]. For example, Wang et al. showed that the band gap could be reduced to enhance the visible-light harvesting capability using Fe and Zn doping into $g\text{-C}_3\text{N}_4$ [21]. Ding et al. also demonstrated that Fe, Mn, Co and Ni could be incorporated into the $g\text{-C}_3\text{N}_4$ framework to extend the visible-light absorption range and improve the separation efficiency of the photogenerated electrons and holes, which resulted in enhanced photocatalytic performance [22].

In addition, according to the first principle density functional theory (DFT) calculation, Pan et al. predicted that the incorporation of Pt and Pd into the $g\text{-C}_3\text{N}_4$ framework could promote the charge carrier transport rate to improve the charge carrier separation efficiency and reduce the band gap to improve the light absorption, which played positive effects in improving the photocatalytic activity [23]. Recently, Dong et al. found that K atoms brought about interlayer doping instead of caving doping in the $g\text{-C}_3\text{N}_4$ matrix. Pristine $g\text{-C}_3\text{N}_4$ displayed a limited photocatalytic NO removal rate of 16%. The K-doped $g\text{-C}_3\text{N}_4$ exhibited approximately 2.3 times higher photocatalytic NO removal performance than pristine $g\text{-C}_3\text{N}_4$. The outstanding photocatalytic performance of K-doped $g\text{-C}_3\text{N}_4$ was ascribed to the benefits of K intercalation including bridging the layers, charge redistribution, facilitating the charge carrier separation and tuning band structure [24]. In addition, Zhu et al. revealed that K doping could decrease the VB level of $g\text{-C}_3\text{N}_4$, leading to the promoted separation and transportation of photo-induced electrons and holes under visible light irradiation [25].

2.2. Non-Metal Element Doping

Compared with metal doping, the strategy of non-metal doping may be more popular because it not only tunes the electronic structure but also retains the metal-free property. So far, many non-metal elements such as S, P, B, O, C and I have been demonstrated to be effective for band-gap engineering using chemical substitution. C atom self-doping can substitute the bridging N atoms while O, S and I atoms tend to replace the N atoms in the aromatic heptazine rings. Thanks to non-metal doping, the delocalization of the π -conjugated electrons is enhanced to improve the conductivity, mobility and separation of the charge carriers, which is beneficial for improving the photocatalytic performance. As for the P and B atoms, they are inclined to substitute the C atoms. For instance, Wang et al. successfully synthesized B-doped $g\text{-C}_3\text{N}_4$ hollow tubes for improved photocatalytic NO_x removal performance [26]. The B-doped $g\text{-C}_3\text{N}_4$ hollow tubes were fabricated by calcining the assembly supramolecular precursors, which were obtained using the self-conversion of melamine with the aid of boric acid. The B-doped $g\text{-C}_3\text{N}_4$ hollow tubes displayed the best photocatalytic NO_x removal performance (30.4%), which was 1.5 and 1.3 times higher than pristine $g\text{-C}_3\text{N}_4$ (20.8%) and $g\text{-C}_3\text{N}_4$ hollow tubes (22.9%), respectively. The excellent photocatalytic NO_x removal performance of B-doped $g\text{-C}_3\text{N}_4$ hollow tubes was attributed to the extended light-harvesting range and enhanced charge carrier efficiency.

3. Defect Engineering

At the same time, defect engineering is also an effective strategy to improve the photocatalytic performance of pristine $g\text{-C}_3\text{N}_4$. The defect engineering strategy is premature to modify the electronic structures of pristine TiO_2 , which may be due to the fact that TiO_2 is the most classical and fully-studied photocatalyst [27][28][29][30]. For example, the band structures and optical properties of pristine TiO_2 could be tuned by oxygen vacancies [31][32]. The oxygen vacancies-mediated TiO_2 can extend the visible-light range, enhance the charge carrier separation efficiency and improve the molecules to be adsorbed on the surface of the photocatalysts, which would result in excellent photocatalytic performance.

Inspired by the oxygen vacancies-mediated TiO_2 , a defect engineering strategy is used to improve the photocatalytic performance of pristine $g\text{-C}_3\text{N}_4$. For example, Wang et al. reported the nitrogen vacancies-mediated $g\text{-C}_3\text{N}_4$ microtubes synthesized using a simple and green hydrothermal process [33]. The nitrogen vacancies-mediated $g\text{-C}_3\text{N}_4$ microtubes displayed significantly enhanced NO removal performance due to the enlarged specific surface areas and the crucial roles of nitrogen vacancies. The nitrogen vacancies-mediated $g\text{-C}_3\text{N}_4$ was beneficial for NO and O_2 adsorption, which

contributed to attending the surface reactions. The enhanced surface reactions and increased active sites resulted in improved photocatalytic NO removal performance in comparison with pristine g-C₃N₄ under visible-light irradiation. Li et al. successfully synthesized carbon vacancies-modified g-C₃N₄ nanotubes by calcining the hydrolyzed melamine–urea mixture [34]. The EPR spectra confirmed the formation of carbon vacancies in g-C₃N₄ nanotubes because the EPR signal of carbon vacancies-modified g-C₃N₄ decreased significantly due to the fewer unpaired electrons.

Gu et al. reported that the carbon vacancies and hydroxyls co-modified g-C₃N₄ were successfully prepared using a post-hydrothermal treatment [35]. Pristine g-C₃N₄ was first prepared using the thermally induced polymerization of melamine. Then a green hydrothermal treatment was employed to introduce the carbon vacancies and hydroxyls. During the hydrothermal process, the water could induce the pristine g-C₃N₄ to partially hydrolyze, which introduced the carbon vacancies and hydroxyls into the pristine g-C₃N₄ simultaneously. The obtained carbon vacancies and hydroxyls co-modified g-C₃N₄ showed 2.2 times higher photocatalytic NO removal activities than pristine g-C₃N₄. With the aid of DFT calculations and experimental calculations, Gu et al. revealed that carbon vacancies and hydroxyls played significant roles in enhancing the photocatalytic NO removal performance due to a synergistic effect. The carbon vacancies narrowed the band gap to extend the light-harvesting range and the hydroxyls could form the covalent bond acting as electron transport channels to facilitate the charge carrier separation efficiency.

4. Crystallinity Optimization

Recently, the crystallinity optimization strategy has attracted much attention for improving the photocatalytic activity of pristine g-C₃N₄ [36]. It is well-understood that kinetic hindrance is the major issue in the traditional high-temperature solid-state synthesis of pristine g-C₃N₄, which results in semi-crystalline or amorphous structures and limited photocatalytic performance. Since kinetic hindrance is a great problem in traditional high-temperature solid-state reactions, a novel liquid reaction synthesis technology was developed to solve this problem. Bojdys et al. first reported that triazine-based crystalline g-C₃N₄ was successfully synthesized with the ionothermal method using the eutectic mixture of LiCl/KCl as a high-temperature solvent [37].

Up to the present, a great deal of research work has been carried out to prepare crystalline g-C₃N₄ for enhancing photocatalytic performance. For example, Wang et al. prepared heptazine-based crystalline g-C₃N₄ with the molten salt method using preheated melamine as precursors. The melamine was first heated at 500 °C in a muffle furnace and the preheated melamine was mixed with KCl and LiCl [38]. Then, the mixtures were calcined again in a muffle furnace to prepare heptazine-based crystalline g-C₃N₄. Detailed experimental characterization and theoretical simulation showed that heptazine-based crystalline g-C₃N₄ displayed higher photocatalytic performance than triazine-based crystalline g-C₃N₄ owing to the enhanced light-harvesting property and increased mobility of photogenerated charge carriers. In addition, Wang et al. studied the crystallization process of g-C₃N₄ using different precursors of the melon-based oligomer and melon-based polymer with a molten salts method [39]. The melon-based oligomer and melon-based polymer represented different polymerization degrees of g-C₃N₄, which were calcined at 450 °C and 550 °C in a muffle furnace, respectively. Xiang et al. demonstrated that the crystallinity of crystalline g-C₃N₄ synthesized using the molten salts method could be further improved by hydrochloric acid treatment [40].

It is important to point out that these reported molten salt methods were carried out under an inert gas atmosphere in a muffle furnace, which limited the large-scale production of crystalline g-C₃N₄. To solve this drawback, Gu et al. developed a modified molten salt method under ambient pressure using dicyanamide (DCDA) as the initial precursor [41]. The molten salts played two roles in the post-calcination process. One was improving the crystallinity of pristine g-C₃N₄ acting as the high-temperature solution, the other was protecting pristine g-C₃N₄ from contact with air since the pristine g-C₃N₄ was immersed in the solution. The crystalline g-C₃N₄ exhibited 3.0 times higher photocatalytic NO removal activity than pristine g-C₃N₄ under visible-light irradiation, with high stability under the cycling test. The detailed experimental characterization and DFT calculation demonstrated that the optimized crystallinity played important roles in improving the photocatalytic NO removal activity of crystalline g-C₃N₄. The optimized crystallinity could decrease the band gap to extend the light-harvesting range, increase the conductivity to promote the photogenerated charge carrier separation efficiency and reduce the adsorption energy of NO and O₂ molecules to activate the surface reactions, which led to the significantly enhanced photocatalytic NO removal performance.

5. Heterojunction Construction

Charge carrier transport and separation is decisive in the photocatalytic process. A large number of photogenerated electrons and holes suffered from volume recombination and surface recombination, which result in unsatisfactory photocatalytic performance [42][43][44][45]. Constructing a g-C₃N₄-based heterojunction is an effective strategy to improve

photocatalytic performance. The spatial separation of photogenerated electron-hole pairs can be achieved with efficient charge transfer across the interface between the two semiconductors. At the same time, the g-C₃N₄-based heterojunction can display the advantages of the counterpart. In other words, the g-C₃N₄-based heterojunction has both benefits of the two components. Up to the present, several types of g-C₃N₄-based heterojunction have attracted much attention including the traditional type-II heterojunction, all-solid-state Z-scheme heterojunction, step-scheme (S-scheme) heterojunction and g-C₃N₄/carbon heterojunction.

The traditional type-II heterojunction is facile constructed, and much progress has been made in this field. For example, Koci et al. reported that a series of TiO₂/g-C₃N₄ heterojunction photocatalysts were easily prepared using mechanical mixing of TiO₂ and g-C₃N₄ in a water suspension followed by calcination in a muffle furnace [46]. The TiO₂/g-C₃N₄ heterojunction with the optimal weight ratio of TiO₂ and g-C₃N₄ has shifted absorption edge energy towards longer wavelengths and decreased the recombination rate of charge carriers compared to pure g-C₃N₄.

Even though the traditional type-II heterojunction can improve the charge carrier separation efficiency to improve the photocatalytic performance, it sacrifices the oxidation potential energy and reduction potential energy. To overcome this drawback, the all-solid-state Z-scheme was developed inspired by the photosynthesis of plants [47]. The photosynthesis of plants consists of two isolated reactions of water oxidation and CO₂ reduction, which are linked together through redox mediators. Thanks to the unique structure, it keeps the strong redox ability, improves the charge carrier separation efficiency and results in enhanced photocatalytic performance. For instance, Zhang et al. reported an all-solid-state Z-scheme g-C₃N₄/Au/ZnIn₂S₄ heterojunction photocatalyst for enhanced photocatalytic NO removal performance [48]. The noble Au nanoparticles played an important role in the charge carrier transfer process, which acted as an electron acceptor and conductive channel for enhancing the charge carrier separation efficiency. Additionally, the all-solid-state Z-scheme heterojunction exhibited oxidation potential energy and reduction potential energy during the photocatalytic NO removal process. Therefore, the optimized Z-scheme g-C₃N₄/Au/ZnIn₂S₄ heterojunction photocatalyst showed photocatalytic NO removal efficiency of up to 59.7%.

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