

Recent Advances in g-C₃N₄-Based Photocatalysts for NO_x Removal

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Abstract: Nitrogen oxides (NO_x) pollutants can cause a series of environmental issues, such as acid rain, ground-level ozone pollution, photochemical smog and global warming. Photocatalysis is supposed to be a promising technology to solve NO_x pollution. Graphitic carbon nitride (g-C₃N₄) as a metal-free photocatalyst has attracted much attention since 2009. However, the pristine g-C₃N₄ suffers from poor response to visible light, rapid charge carrier recombination, small specific surface areas and few active sites, which results in deficient solar light efficiency and unsatisfactory photocatalytic performance. In this review, we summarize and highlight the recent advances in g-C₃N₄-based photocatalysts for photocatalytic NO_x removal. Firstly, we attempt to elucidate the mechanism of the photocatalytic NO_x removal process and introduce the metal-free g-C₃N₄ photocatalyst. Then, different kinds of modification strategies to enhance the photocatalytic NO_x removal performance of g-C₃N₄-based photocatalysts are summarized and discussed in detail. Finally, we propose the significant challenges and future research topics on g-C₃N₄-based photocatalysts for photocatalytic NO_x removal, which should be further investigated and resolved in this interesting research field.

Keywords: photocatalysis; g-C₃N₄; NO_x; mechanism; modification strategy



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1. Introduction

With the fast development of the economy and modern industrialization, environmental pollution and the energy crisis have become the two major challenges in the world [1–7]. Air pollution is one of the serious environmental problems [8,9]. There are a variety of air pollutants including sulfur oxides (SO_x), nitrogen oxides (NO_x), carbon monoxide (CO) and so on [10,11]. Air pollution would bring about a number of environmental issues: it can damage and corrode buildings and equipment; it is harmful to human beings, animals and vegetables; and it can lead to ecological deterioration of the environment. NO_x is especially serious among air pollutants [12–18]. To be more specific, as shown in Figure 1, NO_x pollutants result in ground-level ozone pollution, acid rain, photochemical smog, global warming and so on. Moreover, it could cause damage to human health and increase the risk of diseases such as emphysema, bronchitis and respiratory disease. If human beings want to realize sustainable development and have a bright future, we must solve air pollution as soon as possible.

An enormous amount of research work has been carried out to deal with NO_x pollution [19–22]. For example, traditional adsorption, filtration and selective catalytic reduction technologies have been extensively used to solve NO_x pollution [23–25]. However, these technologies have low efficiency to remove the low-concentration NO_x pollutants and also have disposal and regeneration issues [26]. Recently, photocatalysis as a green technology has attracted a substantial amount of attention [8,27]. Compared with traditional

physical or chemical methods, photocatalytic NO_x removal technology is more efficient and environment-friendly with a semiconductor as the photocatalyst and solar energy as the driving force. Photocatalytic technology can convert the low concentration of NO_x in the atmosphere into non-toxic products without disposal and regeneration issues. The greatest challenge in the photocatalytic process is to develop low-cost and highly efficient photocatalysts, which can make full use of solar energy to remediate environmental problems. Unveiling the photocatalytic mechanism is the premise of developing highly effective photocatalysts. Since Fujishima and Honda reported photoelectrochemical water splitting in 1972 [28], great progress has been made to unravel the photocatalysis mechanism [29–31]. Typically, as shown in Scheme 1, the photocatalytic process includes three consecutive steps [32–34]: (1) light harvesting using a semiconductor photocatalyst for charge carrier excitation; (2) photogenerated electron-hole pairs separation and migration and (3) surface reduction and oxidation reactions. It should be pointed out that a large number of photogenerated electrons and holes recombine during the charge carrier separation and migration process, i.e., volume recombination and surface recombination. Only the effective charge carriers, in other words, the remaining charge carriers, can attend the surface reduction and oxidation reactions [35–37]. Therefore, if we attempt to improve the photocatalytic performance of the photocatalysts, we can enhance the light-harvesting capability, promote the charge carrier separation efficiency and facilitate the surface reduction and oxidation reactions.

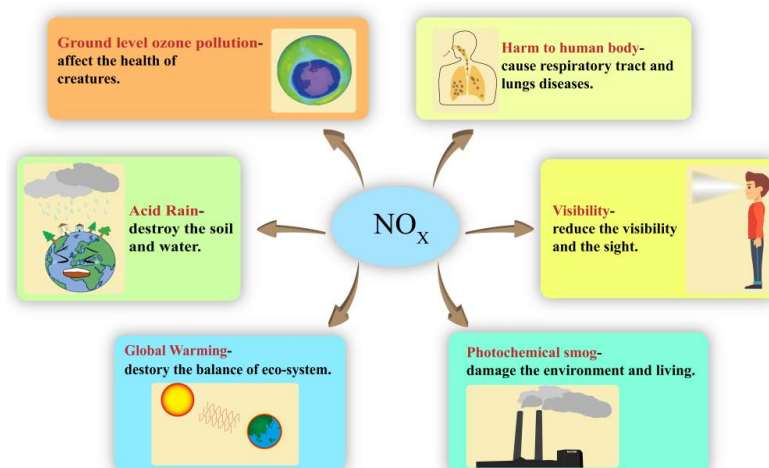
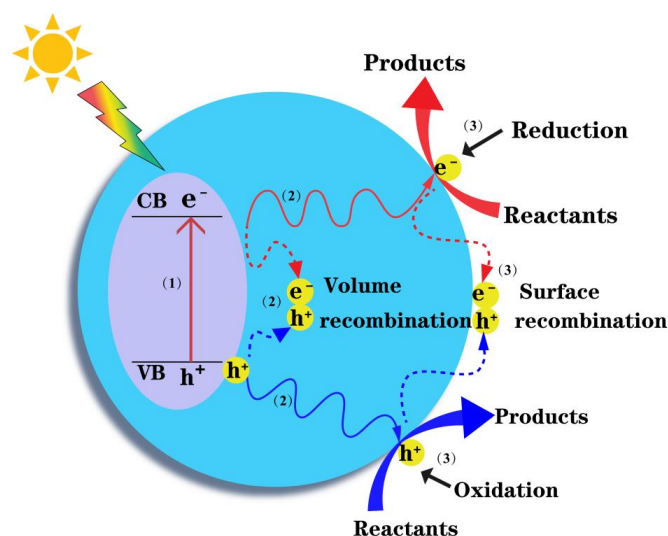
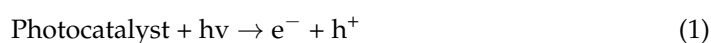


Figure 1. The environmental issues caused by NO_x pollutants.



Scheme 1. The basic principle of photocatalysis over semiconductor photocatalyst.

As one of the typical photocatalytic processes, the reaction mechanism of photocatalytic NO_x removal has been carefully discussed. When the photocatalyst is irradiated by light with equal or greater energy than the bandgap energy of the photocatalyst, the electrons (e[−]) can be excited from the valence band to the conduction band, resulting in positive holes (h⁺) in the valence band [8,38]. It is well-understood that oxygen molecules are the second most abundant gases, consisting of 21% of the atmosphere. The oxygen molecules absorbed on the surface would be reduced, which brought about the superoxide anion radicals (·O₂[−]) [39]. At the same time, holes (h⁺) in the valence band can oxidize the water molecules and hydroxide ion (OH[−]) to obtain hydroxyl radicals (·OH) [10,39]. It should be noted that these radicals play significant roles during the photocatalytic NO_x removal process. To be more specific, the NO absorbed on the surface of a photocatalyst would be oxidized by superoxide radicals (·O₂[−]) and/or hydroxyl radicals (·OH) and/or positive holes (h⁺) to become the final products of the nitrate ion (NO₃[−]), through the formation of intermediates related to NO₂ and HNO₂. These series of reactions are illustrated as follows [10,24,39–42]:



It is universally acknowledged that the key point of photocatalysis is to develop highly effective and stable photocatalysts. Since the pioneering work of Fujishima and Honda in 1972 [28], a great number of photocatalysts have developed to be used in energy conversion and environmental remediation [1,21,43–50]. The reported photocatalysts include metal oxides such as Fe₂O₃ [51,52], WO₃ [53], TiO₂ [54] and ZnO [55]; metal sulfides such as ZnS [56], CdS [57] and CuS [58]; bismuth-based photocatalysts such as BiOX (X = I, Br, Cl) [59] and Bi₂MO₆ (M = Mo, W) [60]; metal-organic frameworks (MOFs) [61]; covalent organic frameworks (COFs) [62] and many more. Among these semiconductor photocatalysts, TiO₂ is considered the most classical photocatalyst owing to its many advantages such as non-toxicity, low cost, long-term stability and so on [63,64]. However, the wide bandgap of TiO₂ (3.0–3.2 eV) constrains the photocatalytic response to only ultraviolet (UV) light [65]. As we know, the full solar spectrum consists of a near-infrared region (52%), a visible-light region (43%) and a UV region (5%) [66]. Therefore, metal and non-metal doping are performed to reduce the bandgap to make the best use of solar energy [67,68].

Recently, graphitic carbon nitride (g-C₃N₄), as a metal-free semiconductor photocatalyst, has attracted much attention since Wang et al. reported it could be used for H₂ production in 2009 [31]. The g-C₃N₄ exhibited outstanding optical, electrical and structural properties, such as visible-light response due to the suitable bandgap (2.7 eV), nanoscale thickness and high surface-to-volume ratio owing to the two-dimensional (2D) structure, facile synthesis with a cheap precursor, such as melamine, dicyandiamide, urea thiourea and cyanamide (Figure 2a,b), high thermal and chemical stability and nontoxic nature [32,38]. What is more, the electronic structures of the 2D materials could be modulated by controlling the thickness or doping strategy. Thanks to its excellent advantages, g-C₃N₄ has been used in different fields including energy issues and environmental remediation. To be more specific, it has been reported in supercapacitors [69], electrocatalysis [70], photo-electro catalytic reactions [71], N₂ fixation [72], pollutant degradation [73], CO₂ reduction [74], water splitting [30], organic catalysis [75] and sensing [76].

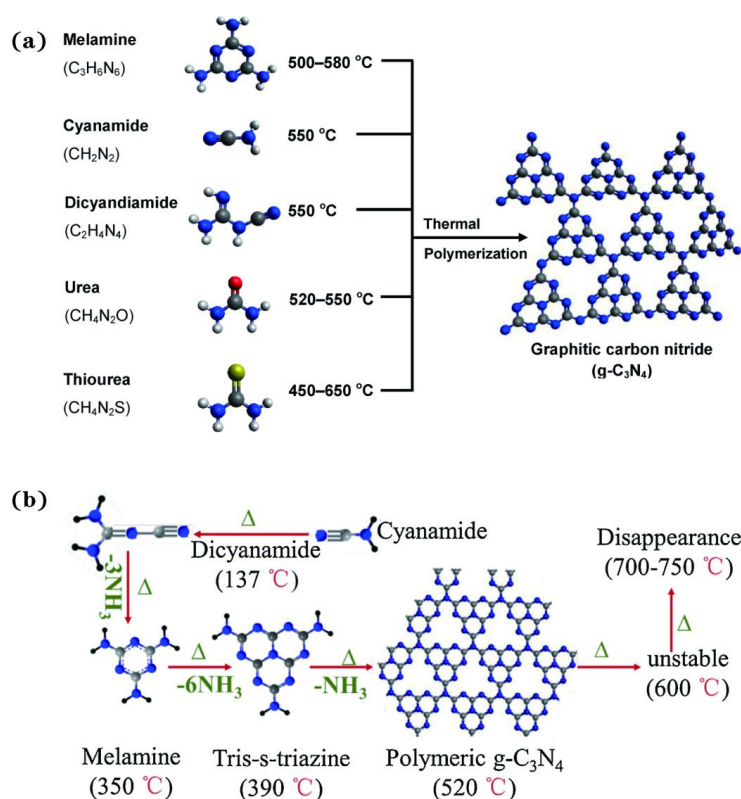


Figure 2. (a) Synthesis of $g-C_3N_4$ using thermal polymerization with different precursors [32]. Copyright 2016, American Chemical Society. (b) reaction pathway of $g-C_3N_4$ using cyanamide as a precursor [38]. Copyright 2017, Elsevier.

The long history of $g-C_3N_4$ could trace back to 1834 when Berzelius and Liebig prepared it by igniting mercuric thiocyanate [77,78]. Since then, $g-C_3N_4$ has become a hot research area. $g-C_3N_4$ is normally considered as three basic structures: triazine-based $g-C_3N_4$, heptazine-based $g-C_3N_4$ and triazine and heptazine mixed $g-C_3N_4$ [32,38]. Figure 3a,b shows the typical structures of triazine-based $g-C_3N_4$ and heptazine-based $g-C_3N_4$, respectively. However, it should be noted that heptazine-based $g-C_3N_4$ is the most stable phase at ambient conditions according to the first-principles density functional theory (DFT) calculations carried out by Kroke et al. [79]. Therefore, more and more researchers and scientists tend to recognize heptazine as the building block for the formation of $g-C_3N_4$.

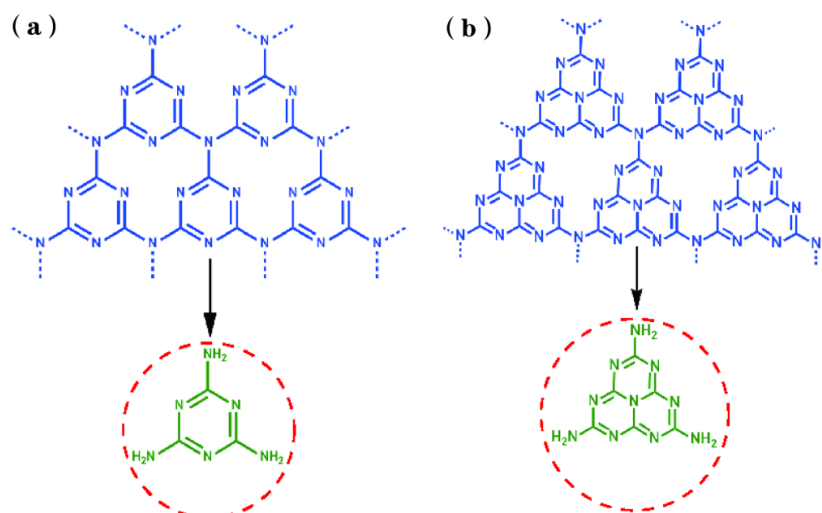


Figure 3. (a) Triazine and (b) tris-s-triazine (heptazine) structures of $g-C_3N_4$.

2. Modification Strategies of Pristine g-C₃N₄

g-C₃N₄, as the significant metal-free semiconductor photocatalyst, holds great potential in the application of the photocatalytic 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-C₃N₄ 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-C₃N₄, a variety of modification strategies have been developed including metal doping, non-metal doping, defect engineering, crystallinity optimization, morphology controlling and heterojunction construction.

2.1. Morphology Controlling

Morphology controlling is considered a promising strategy to improve the photocatalytic performance of bulk g-C₃N₄ [80]. Since bulk g-C₃N₄ 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-C₃N₄ exhibits a longer charge carrier migration distance, and thus the photogenerated electron and hole pairs achieve rapid charge recombination. In addition, bulk g-C₃N₄ is unfavorable for molecular mass transport, surface redox reactions and light harvesting in comparison with porous g-C₃N₄ [32,81]. 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-C₃N₄ into nanosheets, template strategy including hard-template and soft-template and supramolecular preorganization method.

2.1.1. Nanosheets Structure

Inspired by the preparation of graphene nanosheets [82,83], scientific researchers attempt to exfoliate bulk g-C₃N₄ into nanosheets. Compared with bulk g-C₃N₄, g-C₃N₄ 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-C₃N₄ 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-C₃N₄ nanosheets leads to enhanced oxidation potential energy and reduced potential energy, which is useful for surface reactions.

Generally, the g-C₃N₄ nanosheet structures could be achieved using two different strategies, i.e., liquid exfoliation of bulk g-C₃N₄ and thermal exfoliation of bulk g-C₃N₄. Various solvents with suitable surface energy, such as water, methanol, ethanol, N-methylpyrrolidone (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-C₃N₄ 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 (Figure 4) [84]. 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 H₂SO₄ (98%) assisted liquid exfoliation strategy to fabricate a single atomic layer of g-C₃N₄ ultrathin nanosheets [85]. 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.

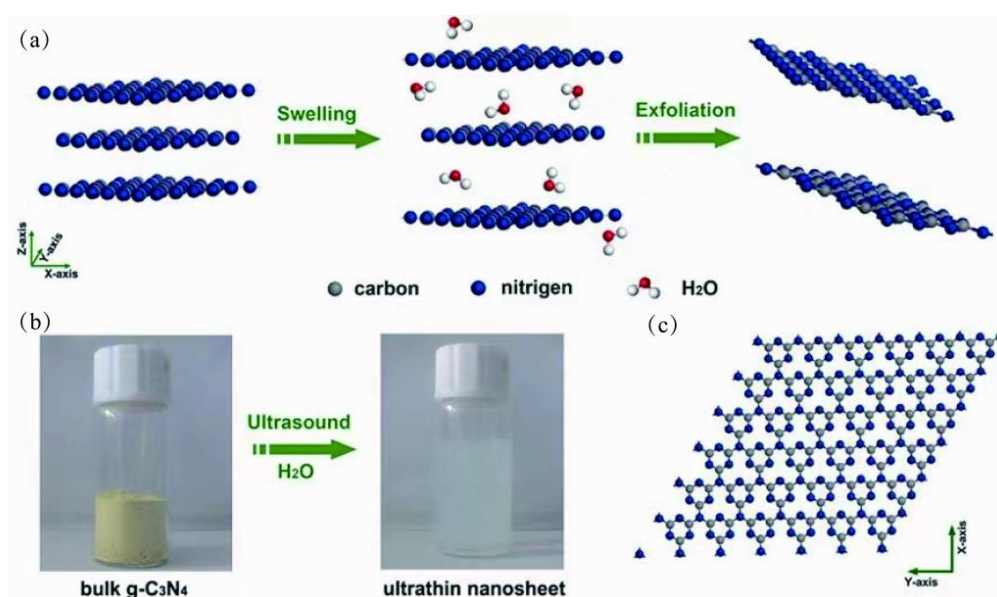


Figure 4. (a–c) Schematic illustration for the liquid-exfoliation process of bulk g-C₃N₄ [84]. Copyright 2012, American Chemical Society.

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 [86]. 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 [87]. 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 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. This research work provides new insight into the thermal exfoliation approach for enhancing the photocatalytic NO_x removal performance.

2.1.2. 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 [88,89]. 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 [89]. 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 [90].

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 [91]. 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 [92]. The hollow nanospheres of g-C₃N₄ displayed excellent photocatalytic H₂ evolution performance due to the hollow sphere structure. However, the biggest drawback of the silica-based hard template involves toxic reagents, such as ammonium hydrogen difluoride (NH₄HF₂), when we remove the silica-based hard template. Recently, Zhang et al. demonstrated that low-cost calcium carbonate (CaCO₃) is a promising environmentally friendly hard template [93]. 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 [94]. 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 [32,38]. The soft templates provide a facile and more environmentally friendly strategy to prepare nanostructured g-C₃N₄ [95]. Very recently, supramolecular preorganization has become an interesting topic to prepare nanostructured g-C₃N₄. Figure 5 shows the formation of the self-assembled structures used to prepare nanostructured g-C₃N₄ [75]. 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 (Figure 6a) [96]. 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 (Figure 6b,c). The enhanced photocatalytic NO_x removal performance was ascribed to the unique microstructure and prolonged lifetime of the charge carriers.

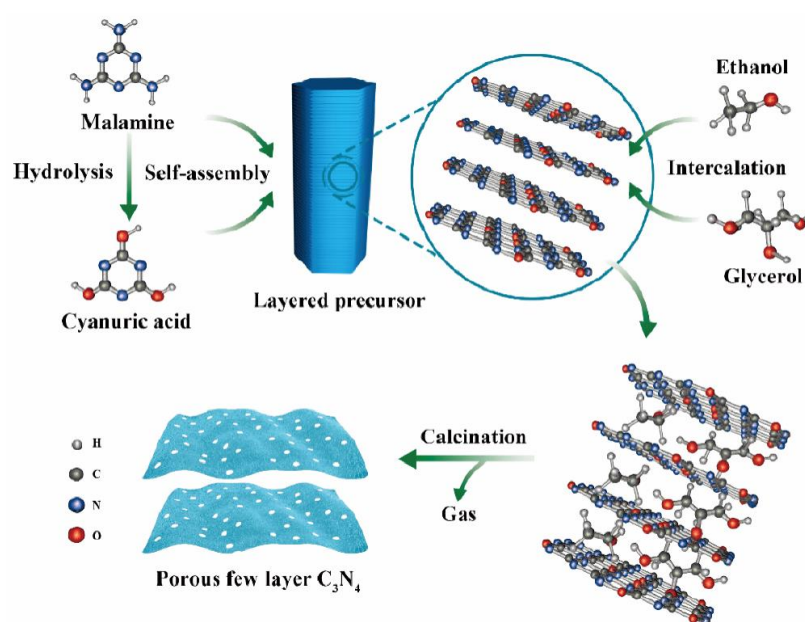


Figure 5. Schematic illustration for the self-assembled method to prepare few-layer porous structures of g-C₃N₄ [75]. Copyright 2019, American Chemical Society.

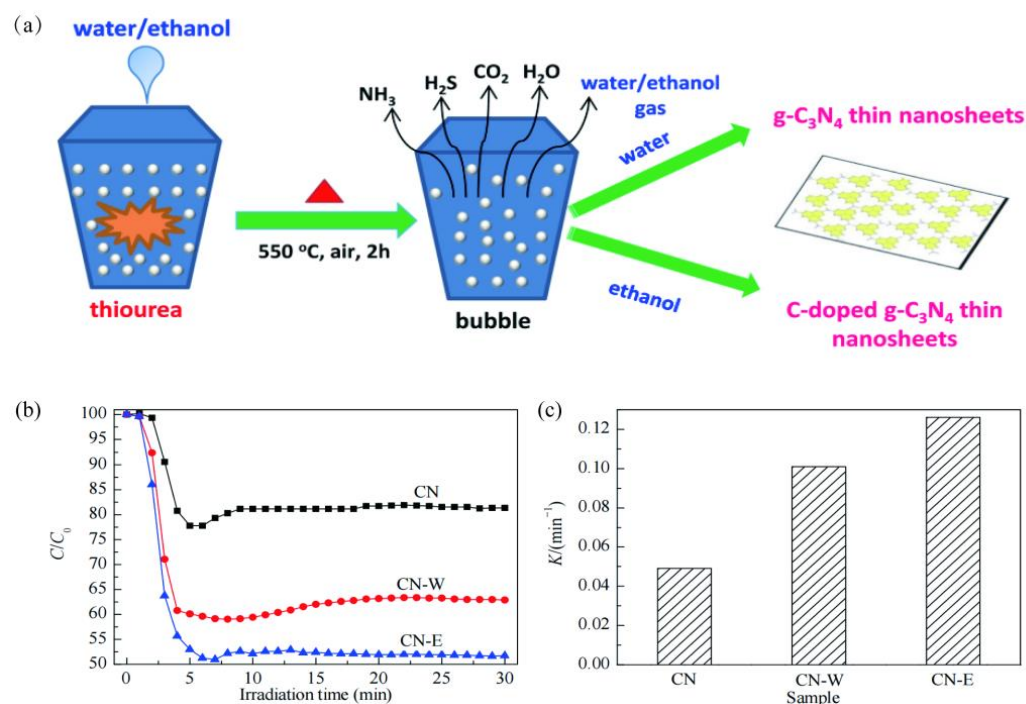


Figure 6. (a) Schematic illustration for preparation of porous g-C₃N₄ with the addition of water and ethanol. Photocatalytic performance (b) and Arrhenius rate constants (c) of g-C₃N₄, g-C₃N₄-W and g-C₃N₄-E for the removal of NO irradiated under visible light [96]. Copyright 2017, Elsevier.

2.2. 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-C₃N₄. The strategies of band structure engineering can be roughly divided into two categories: metal element doping and non-metal element doping [38].

2.2.1. Metal Element Doping

A series of metal cations have been used to modulate the band structure of pristine g-C₃N₄. There are two kinds of metal element doping related to g-C₃N₄, which are cave doping and interlayer doping. The metal cations can be introduced into the triangular pores of g-C₃N₄ between the heptazine structures [33]. The strong coordination interaction between the metal cations and g-C₃N₄ matrix and negatively charged nitrogen atoms can realize cave doping [38]. 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 [32,38]. 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-C₃N₄ [97]. Ding et al. also demonstrated that Fe, Mn, Co and Ni could be incorporated into the g-C₃N₄ 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 [98].

In addition, according to the first principle DFT calculation, Pan et al. predicted that the incorporation of Pt and Pd into the g-C₃N₄ 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 [99]. 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 (Figure 7) [100]. 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 [101].

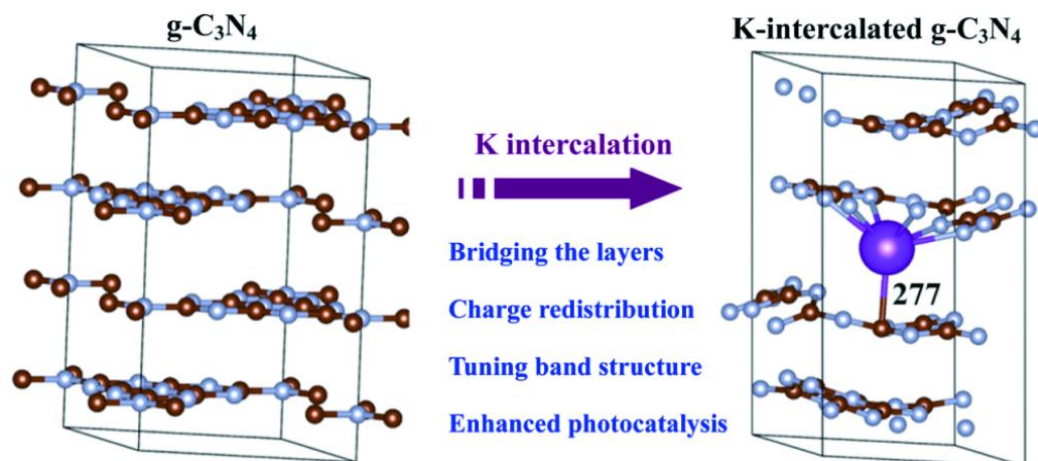


Figure 7. The proposed mechanism of K intercalation to improve photocatalytic performance of $g\text{-C}_3\text{N}_4$ [100]. Copyright 2016, American Chemical Society.

2.2.2. 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. As shown in Figure 8 [38], 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 [102]. 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 (Figure 9a). 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 (Figure 9b,c). 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 (Figure 9d).

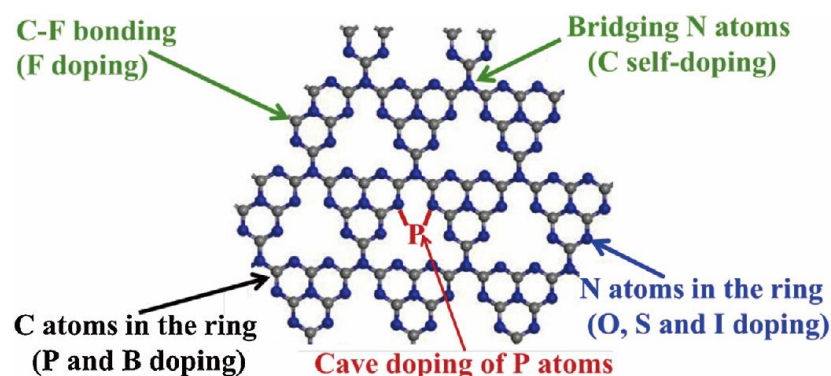


Figure 8. Schematic illustration of the non-metal doping of the g-C₃N₄ framework [38]. Copyright 2017, Elsevier.

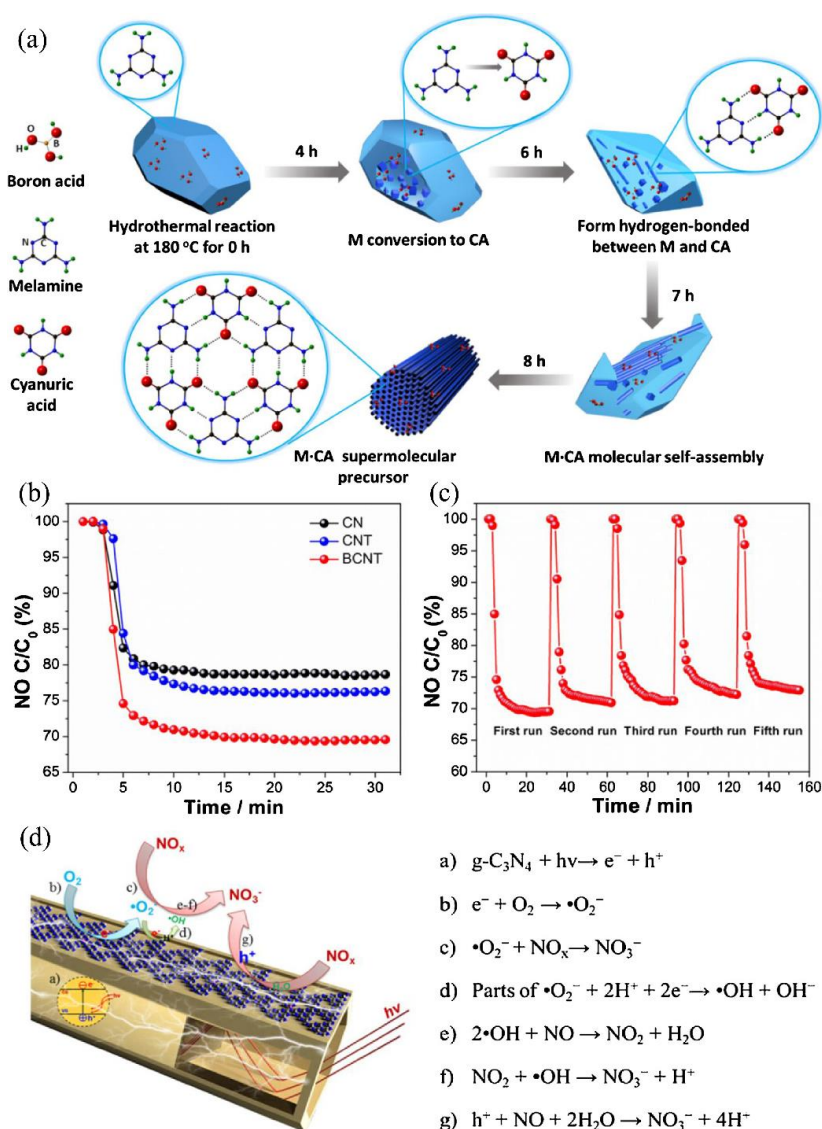


Figure 9. (a) Schematic illustration for the preparation of B-doped g-C₃N₄ hollow tubes. (b) Photocatalytic performance of bulk g-C₃N₄, g-C₃N₄ tubes and B-doped g-C₃N₄ tubes for the removal of NO irradiated under visible light. (c) Stability test of B-doped g-C₃N₄ tubes. (d) The proposed mechanism of B-doped g-C₃N₄ tubes to improve the photocatalytic performance of g-C₃N₄ [102]. Copyright 2018, Elsevier.

2.3. 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 [103–106]. For example, the band structures and optical properties of pristine TiO_2 could be tuned by oxygen vacancies [107,108]. 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 (Figure 10a) [109]. 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 curial roles of nitrogen vacancies. As shown in Figure 10b–g, 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 $g\text{-C}_3\text{N}_4$ under visible-light irradiation. Li et al. successfully synthesized carbon vacancies-modified $g\text{-C}_3\text{N}_4$ nanotubes by calcining the hydrolyzed melamine–urea mixture [110]. The EPR spectra confirmed the formation of carbon vacancies in $g\text{-C}_3\text{N}_4$ nanotubes because the EPR signal of carbon vacancies-modified $g\text{-C}_3\text{N}_4$ decreased significantly due to the fewer unpaired electrons.

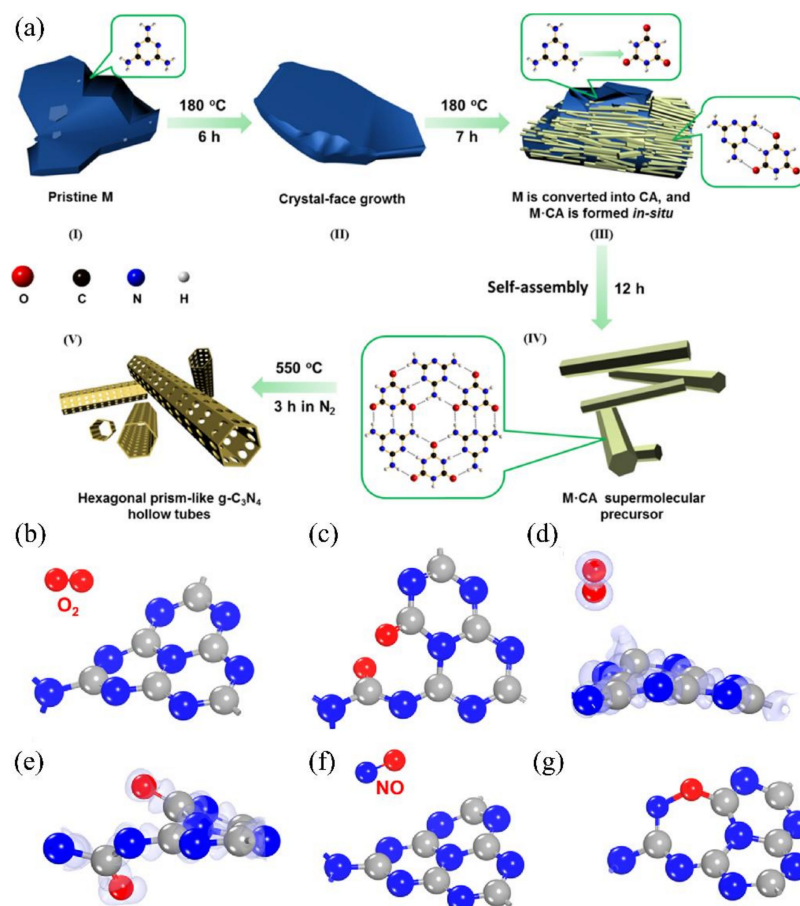


Figure 10. (a) Schematic illustration for the preparation of nitrogen vacancies–mediated $g\text{-C}_3\text{N}_4$ microtubes. (b–g) Schematic illustration for the nitrogen vacancies in $g\text{-C}_3\text{N}_4$ photocatalysts for the enhanced adsorption behavior [109]. Copyright 2019. American Chemical Society.

Gu et al. reported that the carbon vacancies and hydroxyls co-modified g-C₃N₄ were successfully prepared using a post-hydrothermal treatment [111]. 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 (Figure 11a). 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 (Figure 11b). 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 (Figure 11c).

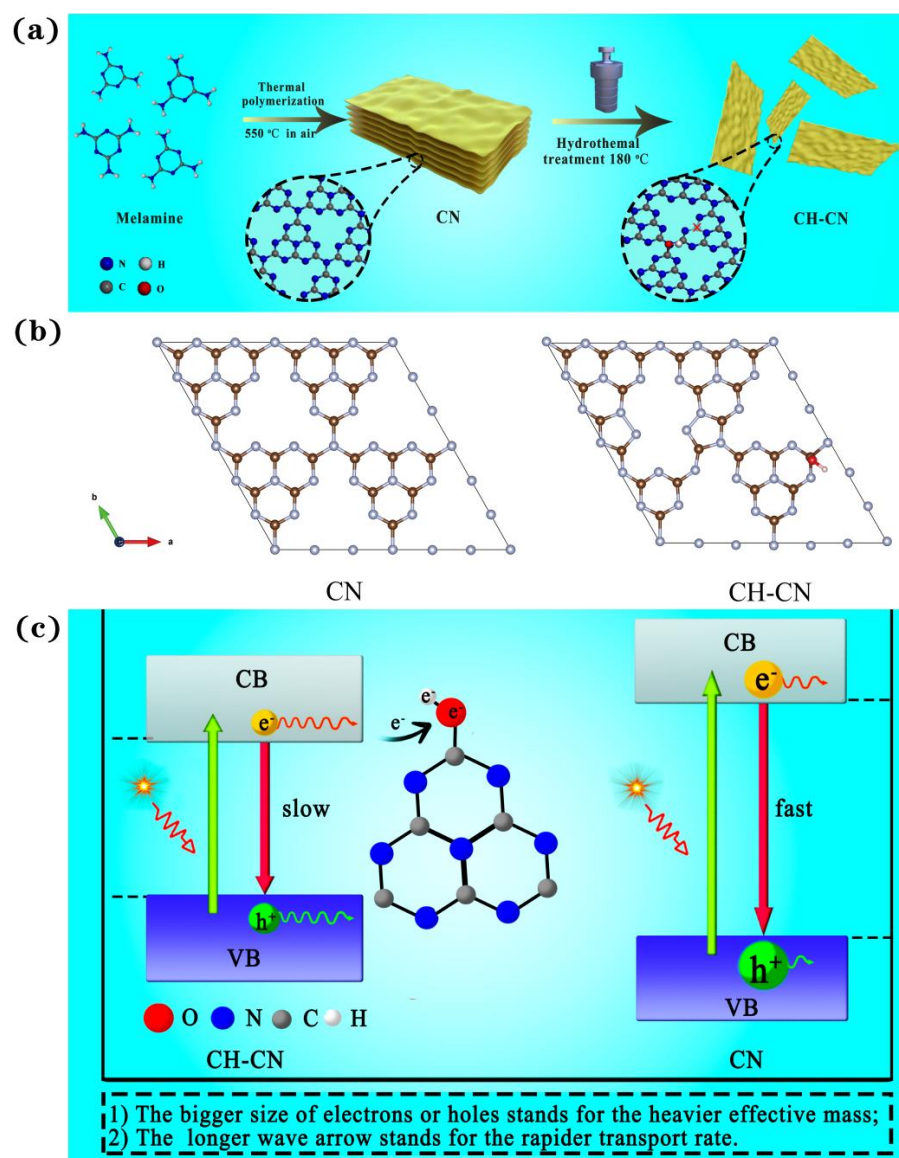


Figure 11. (a) Schematic illustration for the preparation of carbon vacancies and hydroxyls co-modified g-C₃N₄. (b) Schematic illustration for the g-C₃N₄ and carbon vacancies and hydroxyls co-modified g-C₃N₄. (c) The proposed mechanism of carbon vacancies and hydroxyls co-modified g-C₃N₄ for improved photocatalytic performance of g-C₃N₄ [111]. Copyright 2020, Elsevier.

2.4. Crystallinity Optimization

Recently, the crystallinity optimization strategy has attracted much attention for improving the photocatalytic activity of pristine $g\text{-C}_3\text{N}_4$ [78]. It is well-understood that kinetic hindrance is the major issue in the traditional high-temperature solid-state synthesis of pristine $g\text{-C}_3\text{N}_4$, 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 $g\text{-C}_3\text{N}_4$ was successfully synthesized with the ionothermal method using the eutectic mixture of LiCl/KCl as a high-temperature solvent [112].

Up to the present, a great deal of research work has been carried out to prepare crystalline $g\text{-C}_3\text{N}_4$ for enhancing photocatalytic performance. For example, Wang et al. prepared heptazine-based crystalline $g\text{-C}_3\text{N}_4$ 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 [113]. Then, the mixtures were calcined again in a muffle furnace to prepare heptazine-based crystalline $g\text{-C}_3\text{N}_4$. Detailed experimental characterization and theoretical simulation showed that heptazine-based crystalline $g\text{-C}_3\text{N}_4$ displayed higher photocatalytic performance than triazine-based crystalline $g\text{-C}_3\text{N}_4$ owing to the enhanced light-harvesting property and increased mobility of photogenerated charge carriers. In addition, Wang et al. studied the crystallization process of $g\text{-C}_3\text{N}_4$ using different precursors of the melem-based oligomer and melon-based polymer with a molten salts method (Figure 12a) [114]. The melem-based oligomer and melon-based polymer represented different polymerization degrees of $g\text{-C}_3\text{N}_4$, which were calcined at 450 °C and 550 °C in a muffle furnace, respectively. Xiang et al. demonstrated that the crystallinity of crystalline $g\text{-C}_3\text{N}_4$ synthesized using the molten salts method could be further improved by hydrochloric acid treatment (Figure 12b) [115].

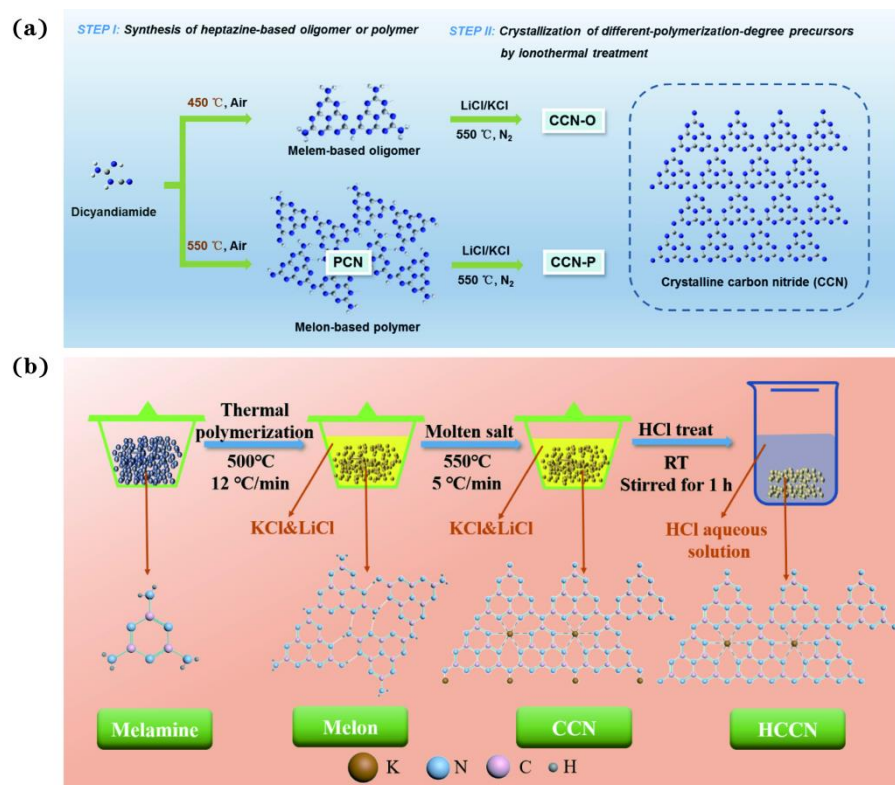


Figure 12. (a) Schematic illustration for the crystallization process of $g\text{-C}_3\text{N}_4$ [114]. Copyright 2020, Elsevier. (b) Schematic illustration for improving the crystallinity of $g\text{-C}_3\text{N}_4$ using hydrochloric acid treatment [115]. Copyright 2020, Elsevier.

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 (Figure 13a) [116]. 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 (Figure 13b,c). 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 (Figure 13d–k).

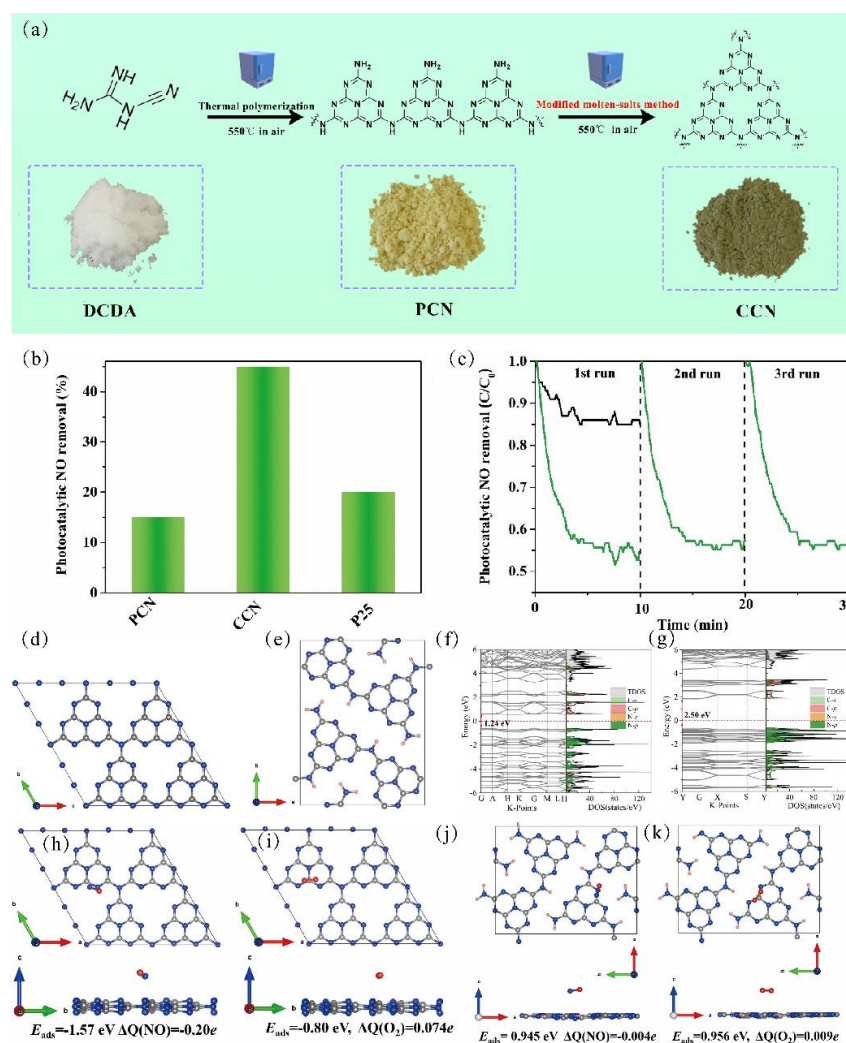


Figure 13. (a) Schematic illustration for the preparation of crystalline g-C₃N₄ using a modified molten salt method under ambient pressure. (b) Photocatalytic performance of pristine g-C₃N₄, crystalline g-C₃N₄ and P25 for the removal of NO irradiated under visible light. (c) Stability test of crystalline g-C₃N₄. (d–g) Schematic illustration for crystallinity in g-C₃N₄ photocatalysts for the enhanced light-harvesting properties. (h–k) Schematic illustration for crystallinity in g-C₃N₄ photocatalysts for the enhanced adsorption behavior [116]. Copyright 2021, Elsevier.

2.5. 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 [117–120]. 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 [121]. 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 [70]. 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 [122]. 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%.

Recently, direct Z-scheme heterojunction has become a research hotspot [37,123]. The direct Z-scheme heterojunction is totally different from the all-solid-state Z-scheme because there is no intermediate, either Au or Ag nanoparticles, used in the direct Z-scheme heterojunction [25,122,124]. To describe the photocatalytic mechanism of the direct Z-scheme heterojunction clearly and vividly, the Yu group first nominated the direct Z-scheme heterojunction for a step-scheme (S-scheme) heterojunction [125,126]. Yu et al., for the first time, reported the g-C₃N₄-TiO₂ direct Z-scheme heterojunction using the facile calcination method. Moreover, they found that the g-C₃N₄-TiO₂ direct Z-scheme heterojunction was largely dependent on the content of g-C₃N₄ [54]. To be more specific, if the surface of TiO₂ was partially covered by the g-C₃N₄, the g-C₃N₄-TiO₂ direct Z-scheme heterojunction would be obtained; if the content of g-C₃N₄ was too much, the traditional type-II heterojunction would be obtained. Lu et al. reported an α -Fe₂O₃/g-C₃N₄ direct Z-scheme heterojunction prepared using an impregnation-hydrothermal method (Figure 14a) [52]. The unique direct Z-scheme heterojunction brought about wide visible-light absorption and facilitated charge carrier separation efficiency (Figure 14b) [52]. The α -Fe₂O₃/g-C₃N₄ direct Z-scheme heterojunction displayed approximately 1.78 times higher photocatalytic NO removal performance than pristine g-C₃N₄. As for the S-scheme heterojunction, Yu et al., for the first time, designed and constructed the S-scheme heterojunction of WO₃/g-C₃N₄ using an electrostatic self-assembly strategy [126]. After that, a great number of

S-scheme heterojunctions have been reported for improving photocatalytic performance. For example, Zhang et al. reported a $\text{Sb}_2\text{WO}_6/\text{g-C}_3\text{N}_4$ S-scheme heterojunction prepared using an ultrasound-assisted strategy for improved visible-light photocatalytic NO removal performance. In addition, Cao et al. successfully reported a 2D/0D $\text{g-C}_3\text{N}_4/\text{SnO}_2$ S-scheme heterojunction using a hydrothermal and annealing strategy toward visible-light-driven NO degradation (Figure 15a) [127]. The S-scheme charge transfer mechanism was revealed using the Density-Functional Theory (DFT) calculation, trapping experiments and EPR spectra. Because of the unique structural features, the $\text{g-C}_3\text{N}_4/\text{SnO}_2$ S-scheme photocatalysts displayed a photocatalytic NO removal percentage of 40% irradiated under visible light (Figure 15b).

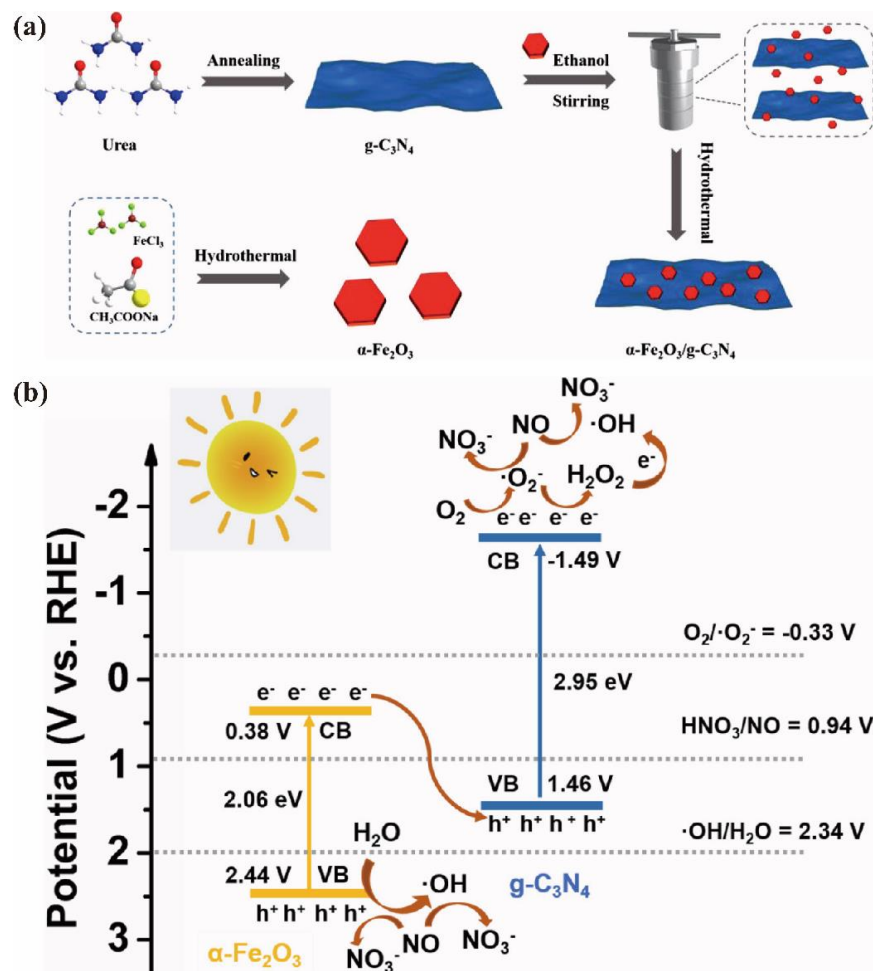


Figure 14. (a) Schematic illustration for the preparation of $\alpha\text{-Fe}_2\text{O}_3/\text{g-C}_3\text{N}_4$ direct Z-scheme heterojunction prepared using an impregnation–hydrothermal method. (b) The proposed mechanism of direct Z-scheme heterojunction to improve the photocatalytic performance of $\alpha\text{-Fe}_2\text{O}_3/\text{g-C}_3\text{N}_4$ [52]. Copyright 2021, Elsevier.

Carbon materials including graphene have brought about widespread attention in the field of photocatalysis owing to their outstanding physical and chemical properties including excellent electron conductivity, good light harvesting properties, large specific surface areas, low cost and high stability [128–130]. Constructing a $\text{g-C}_3\text{N}_4/\text{carbon}$ heterojunction can take advantage of carbon materials to improve the photocatalytic performance of pristine $\text{g-C}_3\text{N}_4$. Firstly, coupling carbon materials with the $\text{g-C}_3\text{N}_4$ can significantly extend the light-harvesting range to near-infrared. Secondly, carbon materials can facilitate the photogenerated charge carrier separation efficiency since it acts as conductive channels for electron transfer. Lastly, the large specific surface areas of carbon materials can provide plentiful of supporting sites for $\text{g-C}_3\text{N}_4$. For example, Gu et al. reported an alkali-

assisted hydrothermal method to prepare g-C₃N₄/reduced graphene oxide (g-C₃N₄/rGO) nanocomposites (Figure 16a) [131]. During the hydrothermal process, the NaOH could improve the reduction of GO to increase the conductivity of rGO and etch the pristine g-C₃N₄ into nanosheets to enlarge the specific surface areas. The g-C₃N₄/rGO nanocomposites displayed 2.7 times higher photocatalytic NO_x removal performance than pristine g-C₃N₄. The distinctly enhanced photocatalytic performance of g-C₃N₄/rGO nanocomposites is ascribed to the improved light-harvesting property, increased specific surface areas and active sites and facilitated charge carrier separation efficiency.

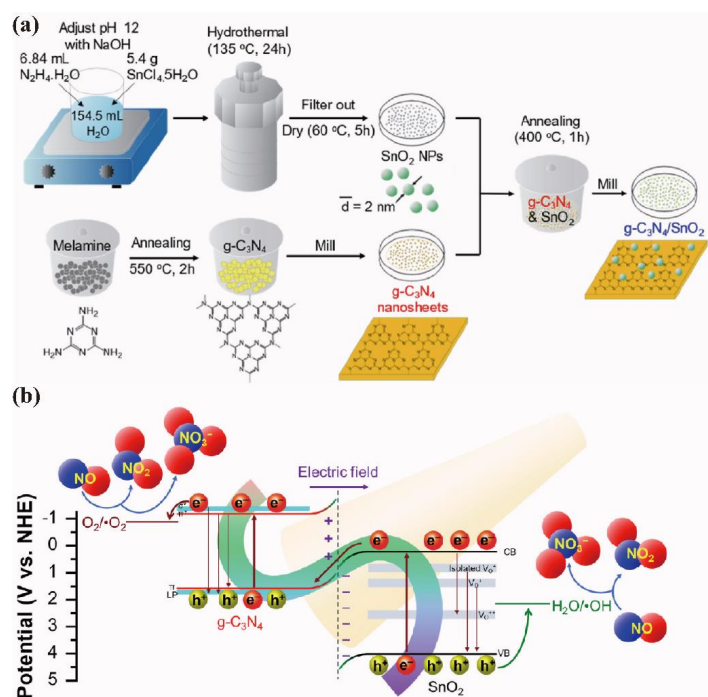


Figure 15. (a) Schematic illustration for the preparation of g-C₃N₄/SnO₂ S-scheme heterojunction using a hydrothermal and annealing strategy. (b) The proposed mechanism of S-scheme to improve the photocatalytic performance of g-C₃N₄/SnO₂ [127]. Copyright 2021, Elsevier.

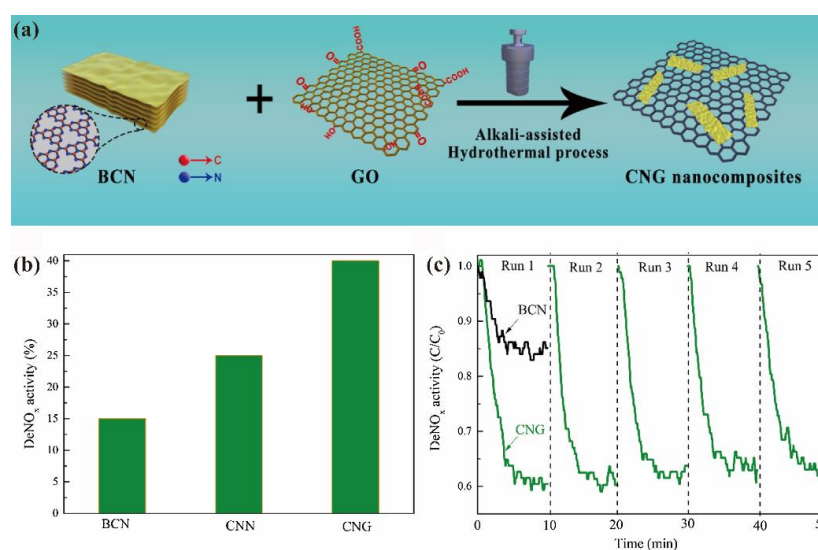


Figure 16. (a) Schematic illustration for the preparation of g-C₃N₄/rGO nanocomposites using an alkali-assisted hydrothermal method. (b) Photocatalytic performance of pristine g-C₃N₄ and g-C₃N₄ treated using an alkali-assisted process and g-C₃N₄/rGO for the removal of NO irradiated under visible light. (c) Stability test of g-C₃N₄/rGO [122]. Copyright 2020, Elsevier.

3. Conclusions and Prospects

In conclusion, photocatalysis is an environmentally friendly and low-cost technology to solve NO_x pollution. As a typical 2D metal-free semiconductor, the $\text{g-C}_3\text{N}_4$ photocatalyst has drawn great attention owing to its outstanding physical and chemical properties including visible light response, adjustable band structure, low cost, facile synthesis, high stability and so on. Therefore, the $\text{g-C}_3\text{N}_4$ photocatalyst possesses great potential for application in the photocatalytic NO_x removal process. However, pristine $\text{g-C}_3\text{N}_4$ synthesized using the traditional high-temperature solid reaction suffers from small specific surface areas and low crystallinity, which results in few reactive sites, limited light-harvesting capacity, rapid recombination of photogenerated charge carriers and unsatisfactory photocatalytic NO_x removal performance. In this review, we briefly summarize the recent advances in $\text{g-C}_3\text{N}_4$ -based photocatalysts for the NO_x removal process. Various modification strategies are discussed including morphology controlling, band structure engineering, crystallinity optimization, defect engineering and heterojunction construction (Figure 17). The different modification strategies play different roles in improving the photocatalytic NO_x removal performance of pristine $\text{g-C}_3\text{N}_4$. Specifically, morphology controlling can not only enlarge the specific surface areas and increase the actives, but also shorten the charge carrier migration distance and thus suppress the photogenerated electron and hole pairs recombination. Band structure engineering can be achieved using metal and non-metal doping, which can reduce the bandgap and extend the light-harvesting range. As for defect engineering, it can modify the electronic structures and improve the molecules to be adsorbed on the surface of pristine $\text{g-C}_3\text{N}_4$. The crystallinity optimization strategy can increase the crystallinity of pristine $\text{g-C}_3\text{N}_4$ and decrease its band gap. In addition, it increases the conductivity to improve the photogenerated charge carrier separation efficiency. When it comes to the heterojunction construction, it mainly promotes charge carrier separation efficiency through efficient charge transfer across the interface between the two semiconductors. Up to now, great progress has been made to enhance the photocatalytic NO_x removal performance of $\text{g-C}_3\text{N}_4$. However, from our perspective, there are still some significant challenges for us to solve.

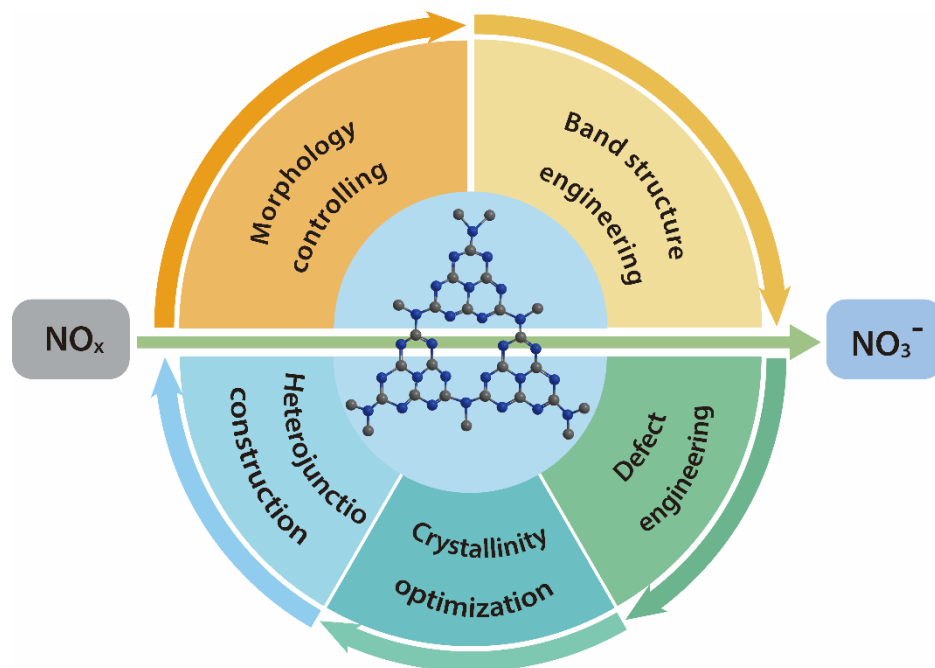


Figure 17. The different modification strategies to improve the photocatalytic NO_x removal performance of $\text{g-C}_3\text{N}_4$.

First of all, although a variety of modification strategies were developed to enhance the photocatalytic NO_x removal performance of $\text{g-C}_3\text{N}_4$, many of them are carried out under

harsh conditions even involving toxic reagents. For example, dangerous hydrofluoric acid is used to remove the silica-based hard templates for preparing different nanostructured g-C₃N₄. Therefore, in the near future, the environmentally friendly and low-cost synthesis process which is suitable for large-scale production needs to be exploited for fabricating hollow or porous nanostructured g-C₃N₄.

Secondly, collaborative strategies should be adopted to modify pristine g-C₃N₄ for improving the photocatalytic NO_x removal performance. The majority of research works involve the single modification strategy, i.e., the element doping strategy, morphology control strategy, crystallinity optimization, defect engineering and heterojunction construction. The single modification strategy can enhance the photocatalytic activity of pristine g-C₃N₄ remarkably, but there is room for improvement. We can employ collaborative strategies to improve the photocatalytic NO_x removal performance of pristine g-C₃N₄. For instance, we can optimize the crystallinity and introduce nitrogen simultaneously to enhance the photocatalytic activity of pristine g-C₃N₄. Collaborative strategies extend the visible light response range, promote charge carrier separation efficiency and activate the reactants molecules, resulting in excellent photocatalytic performance.

Thirdly, g-C₃N₄-based photocatalysts with full-spectrum-activated photocatalytic activities from UV to near-infrared still remains a great challenge. It is well-understood that pristine g-C₃N₄ cannot harvest near-infrared (NIR) light, which accounts for 50% of the full solar spectrum. In order to make full use of solar energy, it is urgent to develop full-spectrum responsive g-C₃N₄-based photocatalysts for photocatalytic NO_x removal. Heterojunction construction with narrow optical materials, the combination of up-conversion materials and plasmonic materials and element doping collaboration with crystallinity optimization can be used to extend the light absorption of g-C₃N₄ to NIR light region.

Finally, the photocatalytic NO_x removal process is very complicated, and the related catalytic mechanism is not thoroughly studied or understood. Therefore, advanced characterization techniques and theoretical simulations are recommended for revealing the photocatalytic NO_x removal mechanism. Steady-state photoluminescence spectra and time-resolved photoluminescence spectra show the photogenerated charge carrier separation efficiency. The in situ infrared absorption spectroscopic analysis helps us to understand the mechanism of ROS generation and conversion. At the same time, the theoretical calculation should be widely used to analyze the effects of metal or non-metal doping on the band structure and the effects of carbon or nitrogen vacancies on the reactant molecule activation. Only when we clarify the photocatalytic NO_x removal mechanism comprehensively can we synthesize highly efficient g-C₃N₄-based photocatalysts for the photocatalytic NO_x removal process.

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