Doping of Graphitic Carbon Nitride with Non-Metal Elements and Its Applications in Photocatalysis

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Abstract: This review outlines the latest research into the design of graphitic carbon nitride (g-C3N4) with non-metal elements. The emphasis is put on modulation of composition and morphology of g-C3N4 doped with oxygen, sulfur, phosphor, nitrogen, carbon as well as nitrogen and carbon vacancies. Typically, the various methods of non-metal elements introducing in g-C3N4 have been explored to simultaneously tune the textural and electronic properties of g-C3N4 for improving its response to the entire visible light range, facilitating a charge separation, and prolonging a charge carrier lifetime. The application fields of such doped graphitic carbon nitride are summarized into three categories: CO2 reduction, H2-evolution, and organic contaminants degradation. This review shows some main directions and affords to design the g-C3N4 doping with non-metal elements for real photocatalytic applications.

Keywords: graphitic carbon nitride; doping; non-metals; photocatalysis

1. Introduction

Graphitic carbon nitride has been of interest since Wang et al. published their paper about its ability of photocatalytic water splitting in 2009 [1]. It is a two-dimensional (2D) metal-free semiconducting material with the ability to absorb visible light due to the band gap energy of 2.7 eV. Other interesting properties, such as high thermal, physical, chemical, and photochemical stability, predetermines it for solar cell fabrications, imaging, sensing of some compounds, and also for photocatalysis [2–10]. On the other hand, there are some problems connected to fast recombination of photoinduced electrons and holes and low specific surface area, which must be solved.

Introducing non-metal elements into the g-C3N4 framework modulates its surface morphology, size of particles, electronic and optical properties, and other physico-chemical properties. Since bare g-C3N4 absorbs light up to 420 nm, the non-metal incorporation allows us to extend absorption of visible irradiation and to reduce recombination of photoinduced electrons and holes. Over the past few years, a lot of articles on non-metal doping have been published. This literature review is focused on recent progress in the synthesis and design of non-metal doped g-C3N4 for applications in photocatalysis.

2. Oxygen-Doped g-C3N4

The most common ways to introduce elemental oxygen into g-C3N4 (Table 1) are oxidation methods, such as oxidation of g-C3N4 with acids [11–13], thermal oxidation [14–23], oxidation with...
hydrogen peroxide H$_2$O$_2$ [24–29], hydrothermal treatment [30–32], pretreatment of synthetic precursors followed by thermal oxidation [33–37], and solvothermal methods [38–40].

Putri et al. performed the doping with oxygen atoms via hydrothermal treatment of bulk g-C$_3$N$_4$ with H$_2$O$_2$ at 120 °C [24]. The concentration of H$_2$O$_2$ influenced the specific surface area (SSA) of O-g-C$_3$N$_4$. The highest SSA of O-g-C$_3$N$_4$ was determined to be 85 m$^2$·g$^{-1}$ compared to 75 m$^2$·g$^{-1}$ for pristine g-C$_3$N$_4$. The photocatalytic experiment did not reveal the influence of SSA on activity of O-g-C$_3$N$_4$ photocatalysts. Fourier-transformed infrared spectroscopy (FTIR) allowed authors to get confirmation that the oxygen functionalization of g-C$_3$N$_4$ was achieved by its oxidation with H$_2$O$_2$. The new band at 1070 cm$^{-1}$ was described as vibration of new stretching modes of N-O groups. The insertion of elemental oxygen into g-C$_3$N$_4$ was confirmed by X-ray photoelectron spectroscopy (XPS). The apparent new peak at the binding energy cca 530 eV was ascribed to oxygen doping into the g-C$_3$N$_4$ lattice. The peaks of adhering oxygen atoms directly bound to carbon atoms (C–O) and substitutional O in the form of N–C–O heterocyclic rings of the graphitic structure were observed on a wide scan survey. It was also confirmed that oxygen doping greatly influenced the carbon chemical state. An optical properties study demonstrated that oxygen doping caused band gap narrowing due to the formation of sub-gap impurity states that extend the light absorption of O-g-C$_3$N$_4$ (Figure 1).

![Figure 1](image.png)

**Figure 1.** Mott–Schottky plots for as-synthesized g-C$_3$N$_4$ and O-g-C$_3$N$_4$ samples (a) and postulated band structure of pristine g-C$_3$N$_4$ and increasing oxidation of g-C$_3$N$_4$ (b) Reprinted from [24], Copyright (2020), with permission from Elsevier.

The oxygen groups in the g-C$_3$N$_4$ lattice were supposed to form midgap states, that is, localized states in the band gap. It was observed the decreasing of the midgap energy in the values from 2.30 to 1.80 eV when 10 and 90 cm$^3$ of H$_2$O$_2$ were used. At the same time, for the majority of O-g-C$_3$N$_4$ samples, the intrinsic band gap value was 2.85 eV. The band structure transformation with increasing oxygen doping level in g-C$_3$N$_4$ was suggested to occur according to the scheme presented in Figure 2.

Similar characteristics of O-g-C$_3$N$_4$ were reported by Zhang et al. [41], which performed the oxygen doping in the same way. The reducing of photogenerated carrier recombination was confirmed with photoluminescence (PL) method. The study of optical properties of O-g-C$_3$N$_4$ show that the H$_2$O$_2$ treatment had no effect on the band gap of the catalyst. It caused a significant effect on enlarging a photocatalytic response range of the obtained material and increased its absorption intensity.

Huang et al. performed the oxidative treatment of bulk g-C$_3$N$_4$ with peroxymonosulfate (PMS) at 60 °C [18]. As the SSA of g-C$_3$N$_4$ after the oxidation was approximately unchanged, it was suggested that PMS interacts with the surface groups of g-C$_3$N$_4$ without its exfoliation into a single or few layers. The atomic percentage of oxygen increased on O-g-C$_3$N$_4$ surface to 6.9% in comparison with 1.8% in g-C$_3$N$_4$ as confirmed by XPS. The detailed study of the chemical state of C, N, and O atoms in O-g-C$_3$N$_4$ allowed authors to report that the doped oxygen atoms mainly exist as carbonyl and carboxyl groups. The doping of more oxygen groups in O-g-C$_3$N$_4$ caused a decrease of the optical band gap from 2.82 to
2.79 eV. The doping of oxygen improved the separation of photo-generated carriers that was concluded from the decreasing PL intensity after oxidation of g-C3N4 with PMS.

![Figure 2. Band structure transformation with increasing oxygen doping level in g-C3N4. Reprinted from [24], Copyright (2020), with permission from Elsevier.](image)

Li et al. performed the synthesis of nanostructured O-g-C3N4 with C-O-C and C=O groups by a two-step thermal treatment process [19]. Increase of the O content was observed for every step of the treatment as was determined by elemental analysis (EA). The O content in pristine g-C3N4 and its products of the first and second steps of the treatment were 4.07%, 5.01%, and 8.43%, respectively. The decreasing of N content from 60.30% to 54.18% can be explained by substituting N atoms with O ones in the carbon nitride skeleton. The study of elemental valence state in the samples by XPS revealed that C-O-C groups were introduced into the precursor with copolymerization of urea and ammonium acetate at the first step of synthesis, and the C=O groups were introduced into O-g-C3N4 at the second thermal treatment step. The electron paramagnetic resonance (EPR) signal intensity study of O-g-C3N4 revealed internal electric field between O and tri-s-triazines that caused the remarkable enhancement of visible-light photocatalytic pollutant degradation. The presence of two types of oxygen functional groups caused the polarization of charge distribution, which formed an internal electric field. The negative pole played the oxygen-containing zone and the positive pole played the tri-s-triazine part.

The strategy of another group of researchers concerned the development of purposefully designing precursor for the further thermal treatment [42]. A new hydroxylated and carbonylated melamine for synthesis of porous O-g-C3N4 nanosheets (OCNNS) was obtained by a hydrothermally ethanol-assisted reforming of melamine at 200 °C. During the polymerization of the precursor, oxygen atoms of anchored hydroxyl groups contributed to oxygen doping, while alternative oxygen atoms in anchored carbonyl groups were simultaneously removed in the form of water forming porous nanostructures. The porous OCNNS demonstrated the increased specific surface area (67.4 m²·g⁻¹) providing more active sites, and enhanced the transfer and separation of charges. The C–O bond formation in O-g-C3N4 was demonstrated with XPS. C–O peaks exhibited a progressively increased intensity with increasing amount of ethanol used for the precursor synthesis. The band gaps of O-g-C3N4 and g-C3N4 were determined to be 2.67 eV and 2.60 eV, respectively. It was established that O-g-C3N4 satisfied with the thermodynamic condition for photocatalytic H₂ production, and its conduction band energy was upshifted, confirming the increasing of photoreduction capability.

The solvothermal method was applied by Wei et al. to fabricate a series of O-doped g-C3N4 photocatalyst [22]. The copolymerization of 1,3,5-trichlorotriazine and various amounts of dicyandiamide was performed at a relatively low temperature. The absorption band of ultraviolet-visible (UV-Vis) diffuse reflectance (DR) spectra of O-g-C3N4 was red-shifted, which evidenced that introducing oxygen extended the sensitivity of obtained materials to a wider range of light. Compared to pristine g-C3N4 with a band gap of 2.73 eV, O-g-C3N4 demonstrated narrowing of the band gap from 2.54 to 2.09 eV.
Table 1. Synthetic methods, applications, and photocatalytic efficiency of O-doped g-C₃N₄.

| Precursor          | Synthetic Method | C/O Ratio, Doped (Pristine) | Photocatalytic Process | Conditions of the Process | Efficiency Doped/Pristine | References |
|--------------------|------------------|-----------------------------|------------------------|--------------------------|---------------------------|------------|
| Urea               | H₂O₂ hydrothermal treatment, 120 °C | Surface O at.% in O-doped g-C₃N₄ 3.23–6.59 by XPS 3.16%/2.73% | H₂ evolution | 500 W Xe lamp, simulate solar irradiation; 30 vol% triethanolamine (TEOA) | 408.4 µmol·g⁻¹/317.9 µmol·g⁻¹ | [24] |
| Melamine           | PMS hydrothermal treatment, 60 °C | 1.8%/2.8% by XPS | Rhodamine B (RhB) destruction | 500 W halogen lamp, filter λ > 420 nm | 0.079 min⁻¹/0.0032 min⁻¹ | [17] |
| Urea               | H₂O₂ hydrothermal treatment, 120 °C | — | RhB, Methyl orange (MO) destruction bisphenol A (BPA), phenol (Ph), 2-chlorophenol (2-Ph), diphenhydramine destruction (DP) | 500 W Xe lamp, simulated solar irradiation | RhB:0.1074 h⁻¹/0.0170 h⁻¹ MO: 0.2287 h⁻¹/0.0095 h⁻¹ | [41] |
| Urea, ammonium acetate | two-step thermal treatment | 4.3/8.8 by elemental analysis (EA) | Light-emitting diode (LED) lamp, λ = 420–780 nm | Total organic carbon (TOC) removal rate: BPA 72.79%/9.27%; Ph 67.3%, 2-Ph 61.5%, DP 55.0% | BPA 72.79%/9.27%; Ph 67.3%, 2-Ph 61.5%, DP 55.0% | [19] |
| Melamine, ethanol  | Thermal polymerization | Atom.% (O) 3.25/- by XPS | H₂ evolution | 350 W Xe lamp, filter λ > 420 nm, 10% vol% TEOA, Pt co-catalyst (1 wt.%) | 64.30 µmol·h⁻¹/3.6 µmol·h⁻¹ | [42] |
| 1,3,5-Trichloro-triazine, dicyandiamide | Solvothermal method, 200 °C | C:N:O 1.08:1.02/0.59:1.03 by XPS | H₂ evolution; RhB destruction | 3174 µmol·h⁻¹·g⁻¹/846 µmol·h⁻¹·g⁻¹ | H₂ evolution: | [22] |
| Melamine           | Thermal polycondensation | 12.5/trace by XPS | CO₂ reduction | 350 W Xe lamp, filter λ > 420 nm | 0.249 min⁻¹/0.007min⁻¹ | CH₃OH production 0.88 µmol·g⁻¹·h⁻¹/0.17 µmol·g⁻¹·h⁻¹ | [43] |
| Dicyandia-midine   | Hydrothermal followed by calcination | O content (wt.%) 5.23/0.17 by EA | N₂ fixation | 500 W Xenon lamp filter λ > 420 nm, 10 vol.% methanol as sacrificial agents | 118.8 mg·l⁻¹·h⁻¹·gcat⁻¹/5.86 mg·l⁻¹·h⁻¹·gcat⁻¹ | [18] |
3. Nitrogen-Doped g-C$_3$N$_4$

The number of publications on obtaining nitrogen-doped graphitic carbon nitride (N-g-C$_3$N$_4$) is much lower in comparison with the number of publications on carbon, oxygen, phosphorus, and sulfur doped g-C$_3$N$_4$. The reason for the limited production of N-g-C$_3$N$_4$ is the application of non-environmentally friendly precursors, such as hydroxylammonium chloride and hydrazine hydrate. Some processes of the N-g-C$_3$N$_4$ synthesis generally contain complicated and long-lasting steps. The presented reports on the synthesis and characterization of N-g-C$_3$N$_4$ and its application in photocatalysis inspired researchers to develop appropriate methods of introducing nitrogen into the g-C$_3$N$_4$ lattice (Table 2). Different reaction paths were applied to increase the N content in g-C$_3$N$_4$ by introducing nitrogen atoms into g-C$_3$N$_4$ matrices [44–55] and by the modification of g-C$_3$N$_4$ surface [56–61].

An extremely rapid method of the high-nitrogen content carbon nitride production was offered by Miller et al. [44–46]. They decomposed a single molecular precursor, trichloromelamine, which briefly generated internal temperatures near 400 °C and resulted in amorphous C$_3$N$_{4x}$, where 0.5 < x < 0.8. According to the report the carbon centers of the obtained materials primarily had sp$^2$ hybridization, the layered structure consisted of triazine (C$_3$N$_3$) rings, and nitrogen species bound the triazines. The N-g-C$_3$N$_4$ was thermally stable up to 600 °C, possessed a moderately porous structure with nanospherical morphologies, and demonstrated a blue photoluminescence.

The various nitrogen-rich compounds were used as the precursors of N-g-C$_3$N$_4$. Huynh et al. synthesized 3,6-di(aazido)-1,2,4,5-tetrazine for obtaining nitrogen-rich carbon nitrdes C$_3$N$_4$ and C$_3$N$_5$ [47]. The high-nitrogen contained nitrdes were also synthesized by thermal decomposition of 2,4,6-triazido-1,3,5-triazine [48], 2,5,8 triazido-s-heptazine [44–46]. However, these types of precursors are often thermodynamically unstable, shock and impact sensitive, and should be handled with caution.

Several groups reported on obtaining the nitrogen doped graphitic carbon nitride (C$_3$N$_4$+$x$) [49–52,62]. Fang et al. performed the thermal condensation of precursor with hydrazine hydrate [49]. They confirmed that the nitrogen atom substitutes the sp$^2$ carbon atom in the resultant N-g-C$_3$N$_4$. According to EA the N/C mass ratio was 1.68 for C$_3$N$_{4+x}$, that is, higher than that (1.60) of pristine g-C$_3$N$_4$.

N-g-C$_3$N$_4$ with the high SSA was obtained by Xu et al. via secondary calcinations of g-C$_3$N$_4$ at different temperatures [50]. The highest nitrogen doping ratio and the largest SSA was observed for g-C$_3$N$_4$ that was post treated at 590 °C, which was confirmed with XPS, X-ray diffraction (XRD), and energy dispersion spectroscopy (EDS) methods. The XPS analysis allowed authors to conclude that the sp$^2$ C atom was replaced by the nitrogen atom. According to the EDS analysis, the highest value of N content in the N-g-C$_3$N$_4$ was 57.57 at.%, and the lowest for undoped g-C$_3$N$_4$ was 56.88 at.%. The secondary calcination at 590 °C caused the SSA to increase of about 27 times (from 4.62 to 128.06 m$^2$·g$^{-1}$ for non-treated and post thermal treated g-C$_3$N$_4$, respectively). The enhanced visible light absorption capacity was confirmed with UV-Vis DR spectra, which demonstrated the absorption edge red shift from 464 nm to 515 nm with the secondary calcination temperature increasing. The authors suggested that the shift was caused by the change of electronic structure due to the nitrogen doping. The bandgap of g-C$_3$N$_4$ narrowed from 2.67 to 2.41 eV after the secondary calcination step.

Jiang et al. used the same precursor as Xu et al. [50] for obtaining of g-C$_3$N$_4$, which they modified with N-N dimethylformamide (DMF) and then treated at 550 °C for 4 h under static air [52]. The SSA of g-C$_3$N$_4$ modified with DMF (g-C$_3$N$_4$/DMF) was 42.18 m$^2$·g$^{-1}$ in comparison with 18.36 m$^2$·g$^{-1}$ for non-treated g-C$_3$N$_4$. The further increasing of the specific surface area to 74.79 m$^2$·g$^{-1}$ was reached after the thermal treatment of g-C$_3$N$_4$ with DMF for 4 h. The porous nanosheet architecture of N-g-C$_3$N$_4$ caused the increasing of SSA confirmed with transmission electron microscopy (TEM) and atomic force microscopy (AFM). The C/N molar ratios were 0.692, 0.679, and 0.674 for the pristine g-C$_3$N$_4$, g-C$_3$N$_4$/DMF, and exfoliated N-g-C$_3$N$_4$, respectively. The authors proposed the copolymerization route of dicyandiamide and DMF. According to the XPS analysis the substitution of carbon with nitrogen was concluded to occur. The quantitative XPS analysis showed that the C/N molar ratio of N-g-C$_3$N$_4$ was 0.67, and for pristine it was 0.76. The N doping and nanosheet construction of g-C$_3$N$_4$ expanded.
an absorption band of obtained materials and enhanced its ability to harvest visible light. The band gaps of pristine and N-g-C$_3$N$_4$ were estimated to be 2.51 eV and 2.54 eV, respectively. The transfer and separation efficiency of charge carries in N-g-C$_3$N$_4$ materials were studied with PL spectroscopy. The decreasing of PL intensity of N-g-C$_3$N$_4$ in comparison with g-C$_3$N$_4$ was explained by the presence of midgap states produced by the N doping. They served as separation centers to capture photoexcited electrons averting recombination processes.

Guo et al. synthesized N-doped porous g-C$_3$N$_4$ with enhanced ability of photocatalytic H$_2$ production through the one-step thermal copolymerization of urea and DMF [51]. No influence of DMF on the original graphitic C-N network was revealed with FTIR spectroscopy. According to XPS and EA g-C$_3$N$_4$, that which was obtained by the copolymerization of urea and DMF, was enriched with nitrogen. The results of $^{13}$C nuclear magnetic resonance (NMR) and Raman analysis allowed the authors to conclude that the replacement of C atoms in triazine with N atoms occurred. The modification with DMF promoted the increasing of light absorption in visible region. The obvious red-shift of the absorption edge of N-g-C$_3$N$_4$ was suggested to be the result of incorporated N atoms that caused increased delocalization of $\pi$-electrons. The analysis of UV-Vis DR spectra of N-g-C$_3$N$_4$ revealed the narrowing of band gap to 2.69 eV compared to 2.75 eV of pristine g-C$_3$N$_4$.

The supramolecular self-assembly strategy for obtaining of porous N-g-C$_3$N$_4$ nanotubes with the high adsorption of CO$_2$ was offered by Mo et al. [62]. In the first step, melamine and hydroxylammonium chloride were used to obtain a supramolecular intermediate at 120 °C (Figure 3a). Secondly, the supramolecular intermediate was heated at 520 °C under NH$_3$, air, Ar, and N$_2$ atmospheres. From the scanning electron microscopy (SEM) analysis of N-g-C$_3$N$_4$ obtained under the thermal treatment in various gases, the authors revealed the porous structure only in g-C$_3$N$_4$ prepared under the NH$_3$ atmosphere (Figure 3b–d). The sharp increase of SSA was observed for the N-g-C$_3$N$_4$ materials. The determined values of the SSA of bulk g-C$_3$N$_4$ and materials, which were obtained by treatment in Ar, air, N$_2$, and NH$_3$, were 8.6, 56.9, 78.6, 82.3, and 108.9 m$^2$·g$^{-1}$, respectively. The highest content of amino groups grafted into g-C$_3$N$_4$ nanotubes during the time of the supramolecular intermediate polymerization process was observed for the porous materials treated under NH$_3$ (g-C$_3$N$_4$/NH$_3$). The EA results indicated a significantly lower C/N atomic ratio of g-C$_3$N$_4$/NH$_3$ than those of g-C$_3$N$_4$ samples synthesized under other atmospheres. The determined C/N atomic ratio for the pristine g-C$_3$N$_4$ and materials obtained in NH$_3$, Ar, and N$_2$, air were 0.69, 0.55, 0.59, 0.58, and 0.58 m$^2$·g$^{-1}$, respectively. Based on the XPS analysis, the authors concluded that in the NH$_3$ atmosphere, amino defects corresponding to terminal isolated amino groups were produced as a result of the opening of C-N bonds. The influence of amino groups on the adsorption of CO$_2$ and desorption of CO was studied with density functional theory (DFT) calculations. The DFT calculations demonstrated that g-C$_3$N$_4$/NH$_3$ not only increased the CO$_2$ adsorption energy, but also decreased the CO desorption energy that caused the higher photocatalytic CO$_2$ reduction activity.

Hao at al. incorporated nitrogen atoms into g-C$_3$N$_4$ by the hydrothermal treatment of exfoliated material using DMF [57] according to the scheme presented in Figure 4. The X-ray diffraction (XRD) and FTIR analysis of the obtained 2D g-C$_3$N$_4$ nanosheets revealed that the basic characteristics of g-C$_3$N$_4$ structure were not influenced by the surface nitrogen modification. Formation of new C-N bonds due to N atoms insertion into the g-C$_3$N$_4$ lattice by filling of removed oxygen atom seats was confirmed by XPS. The authors distinguished three types of the sp$^2$ hybridized nitrogen: Pyridinic nitrogen (N=N=C), tertiary nitrogen (N-C$_3$), and noncondensing amino group (C-N-H), respectively. They confirmed the highest content of pyridinic N atoms in N-g-C$_3$N$_4$ that is beneficial to the photocatalytic production of hydrogen. According to XPS, no new N-O bonds were formed. The EDS elemental mapping allowed the authors to evidence the increased nitrogen content in the surface of N-g-C$_3$N$_4$. The nitrogen-doped g-C$_3$N$_4$ demonstrated enhanced visible absorption ability and the increasing lifetime of its excited state.
The ratio of amino groups in the treated sample was shown to be obviously higher due to the introduction of MEA molecules. Nearly the same absorption edges of amine-functionalized g-C\textsubscript{3}N\textsubscript{4} evidenced the absence of any doping effect and thus changes in the intrinsic electronic structure of g-C\textsubscript{3}N\textsubscript{4}. The amine-functionalized materials demonstrated the increased adsorption of CO\textsubscript{2} caused by the chemical interaction between CO\textsubscript{2} and amino groups. The treatment of g-C\textsubscript{3}N\textsubscript{4} with MEA resulted in the stronger adsorption of hydroxyl ions caused decreasing of zeta potentials in aqueous solutions. The zeta potential at pH = 7 of the amine-functionalized and pristine g-C\textsubscript{3}N\textsubscript{4} were 31.67 mV, respectively. They confirmed the highest content of noncondensing amino group (C-N-H), respectively. They suggested that citric acid was a carbon source and formation of new C-N bonds due to N atoms insertion into the g-C\textsubscript{3}N\textsubscript{4} lattice by the reaction mixture. The authors applied a NH\textsubscript{4}Cl-assisted chemical blowing method to prepare nitrogen-rich N-g-C\textsubscript{3}N\textsubscript{4} sample. Reprinted from [57], Copyright (2018), with permission from Elsevier.

Figure 3. Formation and characterization of g-C\textsubscript{3}N\textsubscript{4}/NH\textsubscript{3}. Schematic illustration of the synthetic process (a), SEM images (b,c), TEM images (d,e), scanning tunneling electron microscopy (STEM) image (f), and energy dispersive X-ray (EDX) maps of the g-C\textsubscript{3}N\textsubscript{4}/NH\textsubscript{3} nanotubes (TCN (NH\textsubscript{3})) (g,h). Reprinted from [62], Copyright (2019), with permission from Elsevier.

Figure 4. Scheme of the formation process from the bulk-C\textsubscript{3}N\textsubscript{4} to the g-C\textsubscript{3}N\textsubscript{4} nanosheets (NCNS) sample. Reprinted from [57], Copyright (2018), with permission from Elsevier.

Amine-functionalized g-C\textsubscript{3}N\textsubscript{4} was obtained by its treatment with monoethanolamine (MEA) [58]. The ratio of amino groups in the treated sample was shown to be obviously higher due to the introduction of MEA molecules. Nearly the same absorption edges of amine-functionalized g-C\textsubscript{3}N\textsubscript{4} evidenced the absence of any doping effect and thus changes in the intrinsic electronic structure of g-C\textsubscript{3}N\textsubscript{4}. The amine-functionalized materials demonstrated the increased adsorption of CO\textsubscript{2} caused by the chemical interaction between CO\textsubscript{2} and amino groups. The treatment of g-C\textsubscript{3}N\textsubscript{4} with MEA resulted in the stronger adsorption of hydroxyl ions caused decreasing of zeta potentials in aqueous solutions. The zeta potential at pH = 7 of the amine-functionalized and pristine g-C\textsubscript{3}N\textsubscript{4} were 31.67 mV, respectively. They confirmed the highest content of noncondensing amino group (C-N-H), respectively. They suggested that citric acid was a carbon source and formation of new C-N bonds due to N atoms insertion into the g-C\textsubscript{3}N\textsubscript{4} lattice by the reaction mixture. The authors applied a NH\textsubscript{4}Cl-assisted chemical blowing method to prepare nitrogen-rich N-g-C\textsubscript{3}N\textsubscript{4} sample. Reprinted from [57], Copyright (2018), with permission from Elsevier.

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in the stronger adsorption of hydroxyl ions caused decreasing of zeta potentials in aqueous solutions. The zeta potential at pH = 7 of the amine-functionalized and pristine g-C\textsubscript{3}N\textsubscript{4} were −19.44 mV and −31.67 mV, respectively.

Yan et al. applied a NH\textsubscript{4}Cl-assisted chemical blowing method to prepare nitrogen-rich graphitic carbon nitride nanosheets [59]. They revealed that under the thermal treatment of a NH\textsubscript{4}Cl and melamine mixture, generated gases detached g-C\textsubscript{3}N\textsubscript{4} sheets from each other and decreased the polymerization of carbon nitride precursor subsequently forming nitrogen-doped nanosheets. The content of nitrogen in the obtained materials was higher (47.32 at.\% ) in comparison with pristine g-C\textsubscript{3}N\textsubscript{4} (45.59 at.\%). The band gaps calculated from UV-Vis DR spectra increased from 2.73 eV for g-C\textsubscript{3}N\textsubscript{4} to 2.79 eV for N-g-C\textsubscript{3}N\textsubscript{4}. It was shown that the photoluminescence intensity of these materials was diminished when the morphology changed from bulky to nanosheet-like, due to suppression of electron–hole recombination in nanosheets.

Zhou et al. synthesized N-g-C\textsubscript{3}N\textsubscript{4} by the hydrothermal treatments of urea with small amount of citric acid [63]. The authors suggested that citric acid was a carbon source and promoted the formation of N-g-C\textsubscript{3}N\textsubscript{4} by the reaction with urea. Changes in the structure, SSA, and elemental compositions of obtained N-g-C\textsubscript{3}N\textsubscript{4} were not observed. N-g-C\textsubscript{3}N\textsubscript{4} demonstrated a little red shift of the intrinsic absorption edge in comparison with that of g-C\textsubscript{3}N\textsubscript{4}. The color of the materials changed from light to brown yellow with increase of the citric acid content in the reaction mixture. The authors suggested a lone pair electron on g-C\textsubscript{3}N\textsubscript{4} may trigger $\pi$-electron delocalization in this conjugated system. This material also demonstrated fluorescence quenching that evidenced the suppressed recombination of photogenerated charge carriers.

Wang et al. tried to dope g-C\textsubscript{3}N\textsubscript{4} with nitrogen by the thermal polymerization of urea under the nitrogen atmosphere [53]. The obtained N-g-C\textsubscript{3}N\textsubscript{4} demonstrated the decreasing C/N ratio 0.71 compared to 0.73 of g-C\textsubscript{3}N\textsubscript{4} as was revealed by the XPS analysis. The authors suggested that the decreasing of C/N ratio in N-g-C\textsubscript{3}N\textsubscript{4} occurred due to the formation of carbon vacancies that promoted the formation of tri-s-triazine subunits. The intrinsic bandgaps of N-g-C\textsubscript{3}N\textsubscript{4} obtained in the nitrogen atmosphere increased to 2.70 eV from 2.58 eV of g-C\textsubscript{3}N\textsubscript{4} obtained in air.

Tian et al. discovered that the pre-hydrothermal treatment of urea and melamine mixture (molar ratio of urea:melamine = 3:1) at 180 °C promoted an irreversible monoclinic to orthorhombic melamine phase transformation, calcination of which caused the formation of mesoporous g-C\textsubscript{3}N\textsubscript{4} with enhanced photocatalytic activity [64]. The formation of ultrathin N-g-C\textsubscript{3}N\textsubscript{4} nanosheets with a thickness of ~3 nm that consisted of 7 or 8 at. layers were confirmed with AFM. The SSA of N-g-C\textsubscript{3}N\textsubscript{4} was 39.1 m\textsuperscript{2}\cdot g\textsuperscript{−1} with an average pore diameter of 46.1 nm, which was 9 times higher than pristine g-C\textsubscript{3}N\textsubscript{4}. The introduction of N atoms into the g-C\textsubscript{3}N\textsubscript{4} matrices was confirmed with the EA and XPS analyses. The band gap of N-g-C\textsubscript{3}N\textsubscript{4} decreased to 2.47 eV in comparison with pristine g-C\textsubscript{3}N\textsubscript{4} (2.70 eV). The multiple reflection of incident light across the porous open network structure of the N-rich materials caused their stronger light harvesting capability that appeared as enhanced photo-absorption below 450 nm.
Table 2. Synthetic methods, applications, and photocatalytic efficiency of N-doped g-C₃N₄.

| Precursor                      | Synthetic Method                                      | C/N Atomic Ratio, Doped (Pristine) | Photocatalytic Process | Conditions of the Process | Efficiency Doped/Pristine | References |
|-------------------------------|------------------------------------------------------|------------------------------------|------------------------|--------------------------|---------------------------|------------|
| Melamine, N-N dimethylformamide (DMF) | Hydrothermal treatment | 0.407 (0.540) by EDS, 0.457 (0.575) by Organic Elemental Analysis (OEA) | H₂ evolution | 300W Xe lamp, filter λ > 400 nm, co-catalysts Pt nanoparticles, triethanolamine (TEOA) as a hole quencher | 128.5 h⁻¹/ 58.6 h⁻¹ | [57] |
| Melamine, hydrazine hydrate   | Thermal condensation | 0.67 (0.73) by elemental analysis | H₂ evolution | 300W Xe lamp, filter λ > 400 nm, TEOA (10 vol.%, Pt co-catalyst (5 wt.%)) | 44.28 μmol·h⁻¹ | [49] |
| Dicyandiamide, urea, hydrazine hydrate | Secondary calcination | 0.57 (0.66) at.% by EDS | methylene blue degradation | 300W Xe lamp, filter λ > 420 nm | 0.0235 min⁻¹ | [50] |
| Dicyandiamide, DMF            | Thermal copolymerization | 0.67 (0.76) by XPS | Tetracycline (TC) degradation | 300W Xe lamp, filter λ > 420 nm | 76.78 (52.21)% of TC was degraded in 60 min | [52] |
| Urea, DMF                     | Thermal copolymerization | 0.74 (0.59) at.% by organic elemental analysis | H₂ evolution | 300W Xe lamp, filter λ > 400 nm, TEOA (10 vol.%), Pt co-catalyst (3 wt.%) | 3579 μmol g⁻¹ h⁻¹/ 0.26 μmol h⁻¹ g⁻¹ | [51] |
| Urea, monoethanolamine        | Amine functionalization of g-C₃N₄ | — | CO₂ reduction | 300W Xe lamp, gas phase reaction | 5268 μmol g⁻¹ h⁻¹/ 0.34 μmol h⁻¹ g⁻¹/trace; CH₃OH: 0.26 μmol h⁻¹ g⁻¹/ 0.26 μmol h⁻¹ g⁻¹ | [58] |
| Melamine, NH₄Cl               | Thermal polymerization | N content (at.%) doped 47.32 doped; 45.59 pristine | RbB degradation | 300W Xe lamp, 420 nm cutoff filter, 0.01954 min⁻¹ | 0.00391 min⁻¹ | [59] |
| Melamine, NH₄Cl               | Second-calcination approach | 1.14 (1.63) by XPS analysis | H₂ evolution | 420-nm LED, lactic acid (10 vol%) solution, (Pt co-catalyst (1 wt%)) | 15.5 mmol h⁻¹ | 7.5 mmol h⁻¹ | [65] |
| Melamine, NH₄Cl               | Precursor formation by hydrothermal method; thermal polymerization in NH₃, N₂, Ar, air | 0.55-0.59 (0.69) by elemental analysis | CO₂ reduction | 300 W Xe lamp, CoCl₂, 2,2-bipyridine, TEOA and methyl cyanide | 103.6 μmol g⁻¹ h⁻¹/ 6.1 μmol g⁻¹ h⁻¹ | [62] |
| Citric acid, urea             | Thermal polymerization | — | H₂ evolution | 300W Xe lamp, 420 nm cutoff filter, Pt nanoparticles (3 wt.%), triethanolamine as a hole quencher | 64 μmol h⁻¹/15 μmol h⁻¹ | [63] |
| Dicyandiamide, citric acid, urea | Thermal polymerization | — | Indomethacine degradation | 350 W xenon lamp with 420 nm cutoff filter; 500 W mercury lamp; 350 W xenon lamp with a 290 nm cut-off filter | Photocatalytic activity was 1.1 (UV light irradiation), 1.8 (simulated sunlight), and 13.6 (visible light irradiation) times higher than that of pristine g-C₃N₄ | [66] |
| Melamine, urea                | Hydrothermal treatment | C:N mass ratio doped 0.53/0.73 by OEA; C:N atomic ratio 0.47/0.72 by quantitative XPS | H₂ evolution | 300W Xe lamp, 420 nm cutoff filter, Pt nanoparticles (1 wt.%), 20% vol. lactic acid | 3579 μmol h⁻¹ g⁻¹/ 147 μmol h⁻¹ g⁻¹ | [64] |
| Urea, N₂                      | Thermal polymerization | doped 0.71/0.73 by XPS | Bisphenol A oxidation; Cr(VI) reduction | 300W Xe lamp, 420 nm cutoff filter | Complete degradation of BPA 60 min/90 min; Photoreduction of Cr(VI) over 120 min: 10%/60% | [34] |
4. Carbon-Doped g-C3N4

It has been proposed that g-C3N4-carbonaceous compound hybrids can enhance visible-light absorption and improve photoinduced charge separation efficiency. The various allotropes and hetero-structures of carbon were used for incorporation into g-C3N4 to optimize its conductivity and photocatalytic activity [67–79] (Table 3). The workable and effective way to design the surface structures and electronic properties of g-C3N4 can also be provided by the self-doping of g-C3N4 [80–87].

The carbon doped g-C3N4 (C-g-C3N4) composite was fabricated by Cao et al. in a facile one-pot way by the calcination of dicyanamide and small amounts of dimethylformamide as a cost-effective carbon source [71]. The increasing C/N mass ratio determined by EA of 0.61 for C-g-C3N4 in comparison with 0.59 for pristine g-C3N4 evidenced successful carbon incorporation. The substitution of C atoms on original sites of bridging N was confirmed by the XPS study. The authors found that the content of bridging N in C-g-C3N4 decreased from 17.28% to 16.95% due to replacement of bridging nitrogen by carbon atoms. C-g-C3N4 contained the higher content of C=N=C groups (71.17%) compared with pristine g-C3N4 (70.75%), which benefited the formation of π-conjugated system. The C-doping caused a minor increasing of SSA from 16.63 m²·g⁻¹ for g-C3N4 to 17.80 m²·g⁻¹ for C doped g-C3N4. Typical semiconductor intrinsic absorption in UV range was observed for both g-C3N4. At the same time, the edge of C-g-C3N4 absorption band demonstrated some red shifts with respect to the pristine material. Additionally, remarkable enhancing of the absorption intensity of C-g-C3N4 in visible-light region was observed. The values of band gap of pristine g-C3N4 and C-g-C3N4 calculated by Tauc plots were 2.72 eV and 2.66 eV, respectively. The values of conduction band (CB) determined with the photoelectrochemical method were −1.21 V and −0.94 V (vs. Ag/AgCl electrode) for pristine g-C3N4 and C-g-C3N4, respectively. The valence band (VB) of C-doped g-C3N4 1.92 eV was shifted on 0.21 eV with respect to g-C3N4 (1.71 eV). The influence of C-doping on PL of g-C3N4, which was originated from recombination of holes at valence band and electrons at conduction band, was studied. C-g-C3N4 demonstrated the higher intensity of PL emission with respect to the pristine one. The authors concluded that C-g-C3N4 behaves as an electron buffer that effectively speeds up excited electrons and delocalization of π-electrons in the conjugated system causing the separation ability of photo-excited holes and electrons. C-g-C3N4 demonstrated 4.3 times higher photocurrent density compared with pristine g-C3N4 under visible light.

A facile one-step thermal condensation method using an agar melamine gel (AMG) as the precursor was offered by Wang et al. to synthesize mesoporous C-g-C3N4 ultrathin nanosheets (C/CNNS) [79]. The agar was applied as a soft template, which was carbonized between g-C3N4 layers during the thermal polymerization. The ultrathin nanosheet structures and the typical wrinkled morphology was found on TEM images. The AFM analysis evidenced that C/CNNS consisted of approximately 10 single layers of g-C3N4. The absorption edge of C/CNNS was shifted to the longer wavelengths with the increasing carbon content. Similarly, the color of the C/CNNS nanosheets was changed from light yellow to dark grey (Figure 5a). The values of band gap energies determined by the Tauc method were 2.62 eV and 2.56 eV for bulk g-C3N4 and C/CNNS, respectively (Figure 5b). The CB edge potential −0.61 eV of C/CNNS was negatively shifted in relation to the CB edge potential −0.42 eV of g-C3N4 (Figure 5c,d). The observed decreasing of PL intensity for C/CNNS compared to pristine g-C3N4 evidenced the suppressing of electron–hole pairs recombination induced by the carbon doping.

Ran et al. performed a simple thermal polymerization method to obtain C-g-C3N4 photocatalysts with high NO removal efficiency under visible light [82]. C-g-C3N4 prepared by the co-pyrolysis of urea and saccharose possessed high SSA: 81 and 118 m²·g⁻¹, for bulk and C-g-C3N4, respectively. It improved the photocatalytic performance due to the formation of more active sites to assist the transfer of reactants. The substitution of N with C favored charge transportation and was observed by room temperature, solid-state electron paramagnetic resonance (EPR). The PL intensity greatly decreased with the increasing of carbon amount confirming that the carbon substitution suppressed photogenerated electron–hole recombination. The C-g-C3N4 samples demonstrated improved visible-light absorption and narrowed band gap in comparison with pristine g-C3N4. The values of band gap were 2.71 eV for
pristine and 2.65 eV C-g-C_3N_4, respectively. The authors demonstrated that C-g-C_3N_4 promoted the reactants activation, improved photo-generated charges separation, and assisted generation of radicals for the NO oxidation under visible light.

Figure 5. Ultra-violet diffuse-reflectance spectra of bulk g-C_3N_4, C/CNNS-x (x = 0.1, 0.3, 0.4, 0.5, 1.0, 2.0) (a), the band gap plots (b), valence band (VB) XPS spectra (c), and the band structure diagrams of bulk g-C_3N_4 and C/CNNS-0.5 photocatalysts (d). Reprinted from [79], Copyright (2019), with permission from Elsevier.

Long et al. obtained C_60/g-C_3N_4 nanowire composites for the photocatalytic H_2 evolution process by the thermal treatment of urea and C_60 nanorods mixture [76]. The insignificant increasing of SSA from 104.77 m²·g⁻¹ (for pristine g-C_3N_4) to 117.47 m²·g⁻¹ was observed. Both samples were mesoporous with the main pore width of 2-6 nm. The incorporation of C_60 nanorods in g-C_3N_4 improved visible light absorbance. The band gap of the C_60/g-C_3N_4 photocatalyst was narrower (2.57 eV) compared to pristine g-C_3N_4 (2.75 eV). The improved ability of C_60/g-C_3N_4 to separate photogenerated electron–hole pairs was concluded from g-C_3N_4 fluorescence quenching due to modification with C_60. The C_60/g-C_3N_4 nanocomposite produced more photogenerated electrons as demonstrated by the highest transient photocurrent responses compared to pristine g-C_3N_4. The improvement of C_60/g-C_3N_4 photocatalytic H_2 production was explained by synergy of g-C_3N_4 and C_60, which allowed the photogenerated charges separation.
Table 3. Synthesis methods, applications, and photocatalytic efficiency of C-doped g-C$_3$N$_4$.

| Precursor | Synthetic Method | C/N Doped (Pristine) | Photocatalytic Process | Conditions of the Process | Efficiency Doped/Pristine | References |
|-----------|------------------|----------------------|------------------------|---------------------------|---------------------------|------------|
| Dicyanamide, dimethylformamide | Thermal copolymerization | C/N mass ratio 0.61(0.59) by elemental analysis | H$_2$ evolution | 300W Xe lamp, filter $\lambda > 400$ nm, Pt co-catalyst (1 wt.%), triethanolamine (TEOA) as a hole quencher | 35.5 $\mu$mol/6.78 $\mu$mol in 8 h | [71] |
| Melamine, cellulose | thermal treatment | C/N mass ratio 33.39 (30.12) by elemental analysis | H$_2$ evolution | 300W Xe lamp, filter $\lambda > 420$ nm, Pt (3%), TEOA (10 vol%) | 1024 $\mu$mol·g$^{-1}$·h$^{-1}$/59.6 $\mu$mol·g$^{-1}$·h$^{-1}$ | [68] |
| Melamine, Urea, phenylmaleic acid | Precursor copolymerization on the surface of g-C$_3$N$_4$ | C/N at. Ratio 68.9 (43.0) | bisphenol A destruction | 300W Xe lamp, filter $\lambda > 420$ nm, Pt (3%), TEOA (10 vol%) | BPA destruction: 0.0507 min$^{-1}$/0.0038 min$^{-1}$; H$_2$ evolution: 31 $\mu$mol·h$^{-1}$/10 $\mu$mol·h$^{-1}$ | [73] |
| Cyanuric acid, ethylene glycol, melamine | microwave treatment of supramolecular aggregates | C/N at. Ratio 0.688 (0.669) C, %: 39.98 (39.51) | N$_2$ photofixation | 250W high-pressure Na lamp (400 < $\lambda$ < 800 nm) | 5.3 mg·L$^{-1}$·gcat$^{-1}$/0.48 mg·L$^{-1}$·gcat$^{-1}$ | [88] |
| Urea, C$_{40}$ nanorods | liquid-liquid interfacial precipitation method | - | H$_2$ evolution | 500 W Xe lamp, filter $\lambda > 420$ nm, Pt (3%), TEOA (17 vol%) | 8.7 $\mu$mol·h$^{-1}$/1.85 $\mu$mol·h$^{-1}$ | [76] |
| Agar-melamine gel | one-step thermal condensation method | C/N at. Ratio 0.69 (0.67) C, %: 34.9 (35.33) by elemental analysis | RhB, Phenol, BPA, Phe destruction | 300 W Xe lamp, filter $\lambda > 420$ nm | RhB destruction 0.042 min$^{-1}$/0.016 min$^{-1}$ BPA destruction 0.145 min$^{-1}$/0.113 min$^{-1}$ | [79] |
| Urea, sacharose | Thermal polymerization | C/N at. Ratio 0.58 (0.57) C, %: 34.83 (34.81) by XPS analysis | NO removal | Xe lamp, filter $\lambda > 420$ nm | NO removal ratio 56.77%/50.89% | [82] |
| Melamine, carbon dots (CD) combining g-C$_3$N$_4$ treated with H$_2$O$_2$ and CD | - | C wt.%: 46.77(39.78) by EDX | MB, RhB, fuchsine, Phe destruction; Cr(VI) photoreduction | 50 W LED lamp, visible light irradiation | RhB destruction 0.0675 min$^{-1}$/0.0019 min$^{-1}$ | [67] |
The combination of carbon dots (CDs) with g-C_3N_4 (CDs/g-C_3N_4) activated by hydrogen peroxide allowed Asadzadeh et al. to obtain photocatalysts with exceptional activity upon visible-light irradiation [67]. The activation of g-C_3N_4 with H_2O_2 increased its SSA from 14.6 to 45.1 m^2·g^{-1} due to exfoliation during the treatment process. However, the adhering of CDs blocked micropores of the treated g-C_3N_4 that caused the SSA decrease to 19.7 m^2·g^{-1}. The homogeneous dispersion of CDs on the surface of activated g-C_3N_4 was confirmed by the EDS analysis. The EDS elemental mappings of CDs/g-C_3N_4 demonstrated the uniform distribution of C, N, and O elements evidencing the binary nanocomposite formation. The presence of two components in CDs/g-C_3N_4 was also confirmed by high-resolution TEM (HRTEM) images. The d-spacing of g-C_3N_4 was determined to be 0.326 nm, corresponding to the lattice fringe of (002) planes, while the spacing of 0.320 nm corresponded to the (002) plane of CDs. The absorption band of the pristine g-C_3N_4 edge at 460 nm and was red shifted to 475 nm in the spectrum of the H_2O_2 activated g-C_3N_4. The absorbance of CDs/g-C_3N_4 demonstrated a slight shift to the visible region. The as-synthesized CDs demonstrated PL emissions located at 504 nm that shifted when excited by various wavelength lights (from 500 to 900 nm).

The authors suggested a multiphoton active process took place, in which absorption of two or more photons occurred simultaneously and caused emission of light at a shorter wavelength compared to their corresponding excitations.

5. Sulfur-Doped g-C_3N_4

The doping of g-C_3N_4 with sulfur (S-g-C_3N_4) caused changes in its electronic structure, adjustment to the position of CB and VB, carrier mobility enhancing, and as a result, improvement of photocatalytic activity (Table 4). The incorporation of S into g-C_3N_4 was performed by the thermal treatment under H_2S [89], the thermal polymerization of S-containing precursors [90–93], the thermal copolymerization with S-containing compounds [94–105], by a gas-templating method [106], and by sulfuring and treatment of g-C_3N_4 [107].

Li et al. applied thioacetamide (TAA) as a sulfur source for obtaining S-doped terminal-methylated g-C_3N_4 (SM-g-C_3N_4) nanosheets by a one-pot copolymerization process [103]. The thioacetamide also performed a blocking function during the polymerization to generate structure edge defects, which caused enlargement of SSA. The highest SSA of SM-g-C_3N_4 was 90.5 m^2·g^{-1} compared to 42.6 m^2·g^{-1} of pristine g-C_3N_4. The XPS analysis revealed the increased C/N ratio in SM-g-C_3N_4 (1.26) compared to g-C_3N_4 (0.81) that the authors associated with methyl groups introducing. The increased number of the C-NH_{x} (x = 1, 2) groups that were not involved in the polymerization due to a blocking effect of terminal methyl was confirmed with XPS. The remarkable shift of absorption edge to near-infrared region was observed in the UV-vis DR spectra of SM-g-C_3N_4 samples with the increasing amount of TAA used for sulfur incorporation. The band gaps of SM-g-C_3N_4 nanosheets decreased from 2.62 (for g-C_3N_4) to 1.85 eV (the optimum photocatalyst). The doping of sulfur into methylated melon units was confirmed with DFT calculation to promote the valence band splitting near the Fermi level and caused a midgap electronic state formation. As a result, a significant decrease of bandgap about 0.7 eV occurred. The band structures of the SM-g-C_3N_4 nanosheets were calculated based on the band gaps obtained from UV-vis DRS. The enhancement of non-radiative recombination rates after introducing sulfur and terminal methyl groups in melon was concluded from the PL study. From DFT calculations it was concluded that an internal electric field was formed due to changes in local charges allocation and lattices strain in melon units of SM-g-C_3N_4 nanosheets and thus the separation of electron–hole pairs was improved.

Lv et al. combined doping of sulfur into g-C_3N_4 in situ and thermal oxidative etching treatment of obtained S-g-C_3N_4 [90]. The thermal oxidative etching caused the breaking of H-bonds between layers of g-C_3N_4 nanosheets and decreased their thickness to 4.0 nm. S-g-C_3N_4 nanosheets treated over 3 h demonstrated increased SSA to 226.9 m^2·g^{-1} compared to 16.6 m^2·g^{-1} for pristine g-C_3N_4.
An apparent blue shift of absorption band edge from 470 to 420 nm was demonstrated compared to pristine g-C$_3$N$_4$. However, in comparison with the analog without sulfur, the absorption band edge of S-g-C$_3$N$_4$ nanosheets was red-shifted by 5-10 nm. The band gap of pristine g-C$_3$N$_4$ and the nanosheets with and without S-doping was calculated to be 2.28, 2.73, and 2.85 eV. The mass percent of the S atom in the samples estimated by XPS demonstrated that thermal oxidative etching treatment caused the increased S content in g-C$_3$N$_4$. The content of S in the S-g-C$_3$N$_4$ nanosheets and S-g-C$_3$N$_4$ was calculated to be 1.58 and 0.51 wt.%, respectively. The analysis of the O/C and N/C ratios in the S-g-C$_3$N$_4$ before and after oxidative etching treatment revealed the formation of more surface O species and surface N defects after the etching treatment. It was also suggested that the doping of sulfur was favorable to the formation of surface N defects and O species. The S-g-C$_3$N$_4$ nanosheets demonstrated highest capability for the separation of photogenerated charge carrier and this material was stable for up to 36 h during the photocatalytic H$_2$ evolution.

Ke et al. synthesized the graphene-like S-g-C$_3$N$_4$ by the thermal treatment of a urea and benzyl disulfide mixture at 560–650 °C in the Ar flow [101]. The pronounced increase of SSA was observed from 20.2 m$^2$·g$^{-1}$ of pristine g-C$_3$N$_4$ to 298.2 m$^2$·g$^{-1}$ of S-g-C$_3$N$_4$. The XPS analysis allowed the authors to evidence the formation of C–S bonding by replacing the latticed N with S, and the presence of C–SO$_x$–C bond. The transformation of g-C$_3$N$_4$ to graphene-like S-g-C$_3$N$_4$ was achieved by weakening planar H-bonding when S partially replaced N. An obvious red shift of the absorption edges of S-g-C$_3$N$_4$ to 530 nm compared with that of g-C$_3$N$_4$ at 458 nm was observed (Figure 6a). Accordingly, the band gap energy decreased from 2.74 eV (g-C$_3$N$_4$) to 2.10 eV (S-g-C$_3$N$_4$) (Figure 6b). The calculation of band potentials of the samples vs. standard hydrogen electrode evidenced the formation of electronic structures with the elevated CB and VB potentials in S-g-C$_3$N$_4$ (Figure 6c). The as-designed S-g-C$_3$N$_4$ demonstrated the high photocatalytic elimination efficiency of UO$_2^{2+}$ under visible-light illumination.

Fan et al. constructed S-g-C$_3$N$_4$ rods with increased SSA and tuned their band gap to enhance photocatalytic activity [95]. They conducted the pyrolysis of supramolecular melamine-trithiocyanuric acid complexes (MT) at 500–650 °C (Figure 7). S-g-C$_3$N$_4$ demonstrated the increased SSA of 52 m$^2$·g$^{-1}$ compared to pristine g-C$_3$N$_4$ (15 m$^2$·g$^{-1}$). The composition study by the elemental analysis showed similar atomic C/N ratios (0.67–0.69) of S-g-C$_3$N$_4$ with that of pristine g-C$_3$N$_4$ (0.65). The presence of about 2% of hydrogen in pristine g-C$_3$N$_4$ was attributed to the un-condensed amino groups. With the increasing temperature of the treatment, the H content decreased due to the higher condensation yield. The content of S in S-g-C$_3$N$_4$ decreased from 0.63 to 0.27 wt.% with the increasing synthesis temperature. The sulfur oxide species formed during the calcination were found. The improved optical absorption in the range of 450–600 nm was observed for all S-g-C$_3$N$_4$ rods. The corresponding band gaps estimated from the absorption spectra decreased after the S-doping from 2.70 eV of pristine g-C$_3$N$_4$ to 2.56 eV of S-g-C$_3$N$_4$. The decreasing of fluorescence intensity was observed for S-g-C$_3$N$_4$ evidencing enhancement of the separation efficiency of photogenerated electron–hole pairs. The S-g-C$_3$N$_4$ rods demonstrated the high adsorption and photocatalytic activity on the RhB decomposition under visible light.
the samples vs. standard hydrogen electrode evidenced the formation of electronic structures with the elevated CB and VB potentials in S-g-C3N4 (Figure 6c). The as-designed S-g-C3N4 demonstrated the high photocatalytic elimination efficiency of UO22+ under visible-light illumination. The narrowed band gap with upshifting of CB and VB potentials, and the excellent efficiency of charge transfer and carrier utilization, caused the remarkable photoactivity of S-g-C3N4.

![Figure 6](image-url). Optical absorption spectra of g-C3N4 and S-g-C3N4 (SC3N4) samples (a); plots of $(\alpha h\nu)^{1/2}$ vs. photon energy $(h\nu)$ (b) and electrochemical Mott–Schottky plots of g-C3N4 and S-g-C3N4 samples (c). Reprinted from [101] Copyright (2017), with permission from Elsevier.

Fan et al. constructed S-g-C3N4 rods with increased SSA and tuned their band gap to enhance photocatalytic activity [95]. They conducted the pyrolysis of supramolecular melamine-trithiocyanuric acid complexes (MT) at 500-650 °C (Figure 7). S-g-C3N4 demonstrated the increased SSA of 52 m²·g⁻¹ compared to pristine g-C3N4 (15 m²·g⁻¹). The composition study by the elemental analysis showed similar atomic C/N ratios (0.67–0.69) of S-g-C3N4 with that of pristine g-C3N4 (0.65). The presence of about 2% of hydrogen in pristine g-C3N4 was attributed to the un-condensed amino groups. With the increasing temperature of the treatment, the H content decreased due to the higher condensation yield. The content of S in S-g-C3N4 decreased from 0.63 to 0.27 wt.% with the increasing synthesis temperature. The sulfur oxide species formed during the calcination were found. The improved optical absorption in the range of 450–600 nm was observed for all S-g-C3N4 rods. The corresponding band gaps estimated from the absorption spectra decreased after the S-doping from 2.70 eV of pristine g-C3N4 to 2.56 eV of S-g-C3N4. The decreasing of fluorescence intensity was observed for S-g-C3N4 evidencing enhancement of the separation efficiency of photogenerated electron−hole pairs. The S-g-C3N4 rods demonstrated the high adsorption and photocatalytic activity on the RhB decomposition under visible light.

![Figure 7](image-url). Scheme of the formation of melamine-trithiocyanuric acid (MT) complex and S-g-C3N4. Reprinted from [95] Copyright (2017), with permission from Elsevier.
Table 4. Synthetic methods, applications, and photocatalytic efficiency of S-doped g-C₃N₄.

| Precursor                  | Synthetic Method                                      | Content of Sulfur | Photocatalytic Process                                      | Conditions of the Process | Efficiency Doped/Pristine | References |
|----------------------------|-------------------------------------------------------|-------------------|------------------------------------------------------------|---------------------------|---------------------------|------------|
| Melamine, sulfur           | Thermal polycondensation, 520 °C                      | -                 | O₂ evolution; scheme H₂O splitting; bactericidal activity  | 400 W halide lamp (λₘₐₓ = 360 nm), 150 W Xe lamp, filter λ > 400 nm | O₂ evolution: 40.3 µmol·h⁻¹·g⁻¹ | [96]       |
| Urea, thiouacamide         | One-pot copolymerization                              | 0.1 at.% S        | Procion Red MX-5B degradation                               | 350 W Xe lamp, filter λ > 420 nm, 10% vol% TEOA, Pt co-catalyst (1 wt.%) | H₂ evolution | [103]      |
| Thiourea                   | Thermal polycondensation followed by thermal oxidative etching | S content: 0.45 by OEA, 1.58 by XPS | Phenol degradation; H₂ evolution | 300 W Xe lamp, 5% vol% TEOA, Pt co-catalyst (1 wt.%) | 75% of Phenol was decomposed; H₂ evolution: 127.4 µmol·h⁻¹; 0.5 µmol·h⁻¹ | [90]       |
| Thiourea, mesyl chloride   | Post-synthetic derivatization of g-C₃N₄              | -                 | Acid Orange 7 dye degradation                               | UVA tube lamp, λₘₐₓ = 368 nm | 0.113 min⁻¹; 0.022 min⁻¹ | [99]       |
| 1,3,5-trichlorotriazine    | Solvothermal condensation process, 180 °C            | -                 | Cr(VI) reduction                                            | Irradiation with λ > 420 nm | 1.85 min⁻¹; 0.03 min⁻¹ | [104]      |
| Melamine, Trithiocyanuric acid | Thermal polycondensation of the supramolecular complex | S (wt%): 0.63     | RhB degradation                                             | 500 W Xe lamp, filter λ > 420 nm | 0.0167 min⁻¹; 0.0013 min⁻¹ | [95]       |
| Melamine, Trithiocyanuric acid | Thermal polycondensation                              | -                 | Reduction elimination of UO₂²⁻                            | 350 W Xe lamp, λ ≥ 420 nm | 0.16 min⁻¹; 0.07 min⁻¹ | [101]      |
| Urea, benzyl disulfide     | Thermal polycondensation, 520 °C                      | -                 | H₂ evolution                                               | 300 W Xe lamp, filter λ > 420 nm, 10% vol% TEOA | 95.3 µmol·h⁻¹; 36.4 µmol·h⁻¹ | [100]      |
| Urea, thiourea             | Thermal polycondensation, 550 °C                      | -                 | 4-nitrophenol degradation                                   | 500 W Xe lamp, filter λ > 400 nm | 3.47 × 10⁻² min⁻¹; 7.04 × 10⁻⁴ min⁻¹ | [107]      |
| Melamine, sulfuric acid    | Sulfuring and sonicating bulk g-C₃N₄                 | -                 | CO₂ reduction                                              | 300 W Xe lamp, Pt co-catalyst (1 wt.%) | CH₃OH formation: 1.12 µmol·g⁻¹; 0.81 µmol·g⁻¹ | [98]       |
| Thiourea                   | Thermal polycondensation, 520 °C                      | S atomic% 0.05 by EA | CO₂ reduction                                              | 300 W Xe lamp, Pt co-catalyst (1 wt.%) | CH₃OH formation: 1.12 µmol·g⁻¹; 0.81 µmol·g⁻¹ | [97]       |
6. P-Doped g-C\textsubscript{3}N\textsubscript{4}

To overcome the inherent drawbacks of g-C\textsubscript{3}N\textsubscript{4} and to promote its photocatalytic activity, the doping of phosphorus into g-C\textsubscript{3}N\textsubscript{4} (P-g-C\textsubscript{3}N\textsubscript{4}) was performed recently by many researchers [108–121]. The band gap structure regulation and the improvement of carrier separation efficiency were reached (Table 5). The most commonly used method for obtaining of P-g-C\textsubscript{3}N\textsubscript{4} was the thermal modification of pristine g-C\textsubscript{3}N\textsubscript{4} with sources of P [109,115,117] and their thermal condensation [108,110,118,119,122–124].

Su et al. performed the thermal condensation of adenosine phosphate and urea followed by thermal exfoliation to obtain porous P-g-C\textsubscript{3}N\textsubscript{4} nanosheets [118]. The increasing of SSA to 84.8 m\textsuperscript{2}g\textsuperscript{-1} was reached compared to 66.6 m\textsuperscript{2}g\textsuperscript{-1} of pristine g-C\textsubscript{3}N\textsubscript{4}. The XPS analysis indicated the presence of P in the nanosheets in terms of P=N and P–N bonds. According to EA the content of P was 2.17 atomic\%. The lower C/N ratio of 0.71 of P-g-C\textsubscript{3}N\textsubscript{4} compared to 0.75 of pristine g-C\textsubscript{3}N\textsubscript{4} was observed. The increasing of the O atomic\% from 2.8\% of pristine to 7.65\% of the P-g-C\textsubscript{3}N\textsubscript{4} nanosheets was ascribed to the higher content of C–OH bonds in the edge of g-C\textsubscript{3}N\textsubscript{4} as a result of the thermal exfoliation. The authors suggested the replacement of C atoms with P ones. The lowest photogenerated electron–hole pairs recombination rate of the nanosheets was revealed by PL study. The midgap states and the expansion of π-electron conjugated system by P atom introduction in g-C\textsubscript{3}N\textsubscript{4} was suggested due to the red shift of emission peaks about 70 nm compared to pristine g-C\textsubscript{3}N\textsubscript{4}. The more effective photoinduced carrier separation was confirmed by the fluorescence decay study and the quantitative confirmation of PL quenching. The P-g-C\textsubscript{3}N\textsubscript{4} nanosheets demonstrated significant enhancement of visible-light absorption in the region of 450-750 nm. The nanosheets demonstrated a distinct Urbach tail absorption band, which the authors attributed to the n→π* electron transition from lone electron pairs of edge nitrogen atoms in the heptazine parts due to the formation of incompletely symmetric planar modes. The transition energy was estimated at 1.91 eV based on the Urbach tail absorption, which is associated with midgap states. The calculated band gaps of undoped and P-g-C\textsubscript{3}N\textsubscript{4} was 2.73 and 2.56 eV, respectively. It was shown that the P-doping changed the original band gap structure due to the formation of impurity level between VB and CB. Decrease in the VB position from 1.7 to 1.57 eV was suggested as a result of defects generation under the thermal exfoliation. The greatly improved photocatalytic H\textsubscript{2} evolution was reached using the with P-g-C\textsubscript{3}N\textsubscript{4} nanosheets.

The nano-structuring and P-doping strategy was implemented by Zhao et al. via a one-pot process for improvement of the g-C\textsubscript{3}N\textsubscript{4} photocatalytic hydrogen evolution activity under visible light [121]. The aqueous solution of dicyandiamide, NH\textsubscript{4}Cl (gas-template), and (NH\textsubscript{4})\textsubscript{2}HPO\textsubscript{4} (P dopant) was freeze-dried and the obtained material was calcined at 550 °C over 4 h. The SSA of P-g-C\textsubscript{3}N\textsubscript{4} was determined to be 36.4 m\textsuperscript{2}g\textsuperscript{-1}, which is higher than 5.5 m\textsuperscript{2}g\textsuperscript{-1} of pristine g-C\textsubscript{3}N\textsubscript{4}. The authors confirmed that the successful nano-structuring of g-C\textsubscript{3}N\textsubscript{4} was due to the gas-template application. The XPS analysis evidenced the successful doping of P element in g-C\textsubscript{3}N\textsubscript{4} and the probable replacement of C with P forming P-N bonds. P-g-C\textsubscript{3}N\textsubscript{4} contained 2.05 wt.\% of P, which was determined by XPS.

In contradiction to the previous study, Su et al. [118] found the incorporation of P caused the blue shift of intrinsic absorption edge of g-C\textsubscript{3}N\textsubscript{4} from 458 nm to 440 nm. Accordingly, the band gap was changed from 2.74 eV to 2.90 eV. The band gap enlargement was explained by the quantum size effect. The PL study revealed that the recombination of photo-induced charge carriers in g-C\textsubscript{3}N\textsubscript{4} was efficiently diminished due to the P-doping and the nano-structure formation. The photocurrent density test was applied to confirm the efficiency of charge separation and migration in P-g-C\textsubscript{3}N\textsubscript{4}. The photocurrent density of P-g-C\textsubscript{3}N\textsubscript{4} was 0.51 μmol·g\textsuperscript{-1}·h\textsuperscript{-1}·μA\textsuperscript{-1} compared to 0.06 μmol·g\textsuperscript{-1}·h\textsuperscript{-1}·μA\textsuperscript{-1} of pristine g-C\textsubscript{3}N\textsubscript{4}.

P-doped tubular g-C\textsubscript{3}N\textsubscript{4} (PT-g-C\textsubscript{3}N\textsubscript{4}) with surface defects was obtained by Guo et al. through a phosphorus-contained compounds-assisted hydrothermal method [125]. The melamine was used as a raw material. Sodium pyrophosphate, ammonium phosphate, sodium hypophosphite, and sodium phosphite were used as P-containing compounds. A hexagonal tube-shaped nanostructure of PT-g-C\textsubscript{3}N\textsubscript{4} demonstrated the increasing of SSA from 8.6 to 24.5-32.4 m\textsuperscript{2}g\textsuperscript{-1} of pristine g-C\textsubscript{3}N\textsubscript{4} and PT-g-C\textsubscript{3}N\textsubscript{4}.
from various P sources, respectively. According to the XPS analysis, the replacement of C in the triazine moieties with P to form P-N bonds during synthesis was suggested. The content of P in PT-g-C$_3$N$_4$ varied from 0.32 to 0.87 wt.%. The highest P ratio was reached using sodium pyrophosphate. The XPS study also revealed decreasing of the C/N surface atom ratio from 0.74 (PT-g-C$_3$N$_4$) to 0.69 (g-C$_3$N$_4$) due to carbon defects formation during the synthesis. It was also established that carbon defects exist only on the surface of g-C$_3$N$_4$ as the C/N mass ratio determined for pristine and PT-g-C$_3$N$_4$ samples demonstrated the same value of 0.68. The P-doping and the tube structure expanded the visible-light absorption due to numerous reflections of light within the PT-g-C$_3$N$_4$ tubes. The band gap of PT-g-C$_3$N$_4$ obtained from ammonium phosphate was calculated at 2.63 eV compared to 2.75 eV of g-C$_3$N$_4$. The PL and photocurrent measurements confirmed the decrease of photo-induced electrons and holes recombination rate. A low resistance for interfacial charge transfer from the g-C$_3$N$_4$ photocatalysts to reacting molecules was observed for the PT-g-C$_3$N$_4$ samples using electrochemical impedance spectroscopy (EIS).

Zhou et al. reported on the synthesis of P-g-C$_3$N$_4$ by the thermal copolymerization of hexachlorocyclotriphosphazene and guanidinium hydrochloride, a non-expensive and environmentally friendly compound [126]. The obtained P-doped photocatalysts showed the high photocatalytic performance both in the H$_2$ evolution and the photodecomposition of organic dyes. The synthesized P-g-C$_3$N$_4$ demonstrated the increased SSA of 40.5 m$^2$·g$^{-1}$ compared to 26.86 m$^2$·g$^{-1}$ of pristine g-C$_3$N$_4$. The optical properties study revealed that the P-g-C$_3$N$_4$ possessed a little bit wider band gap (2.71 eV) compared to 2.69 eV of g-C$_3$N$_4$. The VB maximum for pristine and P-doped g-C$_3$N$_4$ were found to be 2.07 eV, and 2.12 eV, respectively. The C/N molar ratio determined with EA was 0.79 and 0.85 for P-doped and pristine g-C$_3$N$_4$ that corresponded to non-perfect framework structures of both products. From the XPS analysis of C, N and P spectra the incorporation of P-atoms by the replacement of C-ones was concluded. XPS and $^{31}$P NMR data revealed the P atoms location at corner-carbon and bay-carbon sites of g-C$_3$N$_4$. The authors suggested the formation of electron-rich state of P-g-C$_3$N$_4$, which was confirmed by the measurement of zeta potentials of aqueous sample suspensions. After the P-doping, the charge of surface was changed from +7.3 mV (for g-C$_3$N$_4$) to −33.5 mV. The negatively charged surface of P-g-C$_3$N$_4$ promoted the adsorption of the cationic dye RhB. The authors suggested the formation of Lewis acid sites ($P^+$ centers) and intrinsic Lewis base sites (amine or imine groups) (Figure 8) in g-C$_3$N$_4$ should promote the rapid separation of photogenerated electrons and holes and, thus, favoring the photocatalytic activity of H$_2$ evolution and RhB degradation.

Figure 8. Scheme of a possible existing form of P atoms in the framework of g-C$_3$N$_4$ and its effect on the electronic and chemical properties of g-C$_3$N$_4$. The dark blue P atom refers to the corner site and the red one is the bay site. Reproduced from [126] Copyright (2015), with permission from The Royal Society of Chemistry.
| Precursor | Synthetic Method | C/Doping Element Atomic Ratio, Doped (Pristine) | Photocatalytic Process | Conditions of the Process | Efficiency Doped/Pristine | References |
|-----------|-----------------|-----------------------------------------------|-----------------------|--------------------------|---------------------------|-----------|
| g-C3N4, P powder | Thermal modification | P 2p signal at around 133.7 eV | H2 evolution | 300 W Xe lamp (λ > 300 nm), filter λ > 420 nm, 10% vol% TEOA, Pt co-catalyst (3 wt.%) | 261.2 µmol·g⁻¹·h⁻¹/81.6 µmol·g⁻¹·h⁻¹ (λ > 300 nm) | [109] |
| Urea, phosphonitrilic chloride | Thermal condensation | 4.4 atomic% by EDS 5.72 atomic% by XPS | H2O2 generation | Visible light irradiation (420 nm ≤ λ ≤ 700 nm) | 1968 µmol·g⁻¹·h⁻¹/68 µmol·g⁻¹·h⁻¹ | [108] |
| NH4SCN, NH4PF6 | Thermal condensation | — | RhB destruction | 300 W Xe lamp, filter λ > 420 nm | 0.09856 min⁻¹/0.03679 min⁻¹ | [110] |
| g-C3N4, phosphorene | Mechanically mixing | 1.8 wt.% | H2 evolution | 300 W Xe lamp, filter λ > 400 nm, lactic acid (88 vol%) | 571 µmol·g⁻¹·h⁻¹/43 µmol·g⁻¹·h⁻¹ | [117] |
| g-C3N4, sodium hypophosphite | Thermal treatment method | 13.52 wt.% | RhB destruction | 300 W Xe lamp, λ: 420–780 nm, 300 W Xe lamp, filters | 0.0525 min⁻¹/0.0126 min⁻¹ | [115] |
| Urea, adenosine phosphate | Thermal condensation followed by thermal exfoliation method | 2.17 atomic% | H2 evolution | λ: 400, 420, 435, 450, 550 nm; 10% vol% TEOA, Pt co-catalyst (3 wt.%) | 9523.7 µmol·g⁻¹·h⁻¹/458 µmol·g⁻¹·h⁻¹ | [118] |
| Urea, NH4H2PO2 | Thermal condensation | — | H2 evolution | 300 W Xe lamp, filter λ 400 nm, 20% vol% TEOA, Pt co-catalyst (1 wt.%) | 5.7 times that of pristine | [119] |
| Dicyandiamide, NH4Cl, (NH4)2HPO4 | Thermal condensation | 1.53 wt% by EDS | H2 evolution | 300 W Xe lamp, filter λ 420 nm, 10% vol% TEOA, Pt co-catalyst (3 wt.%) | 33.2 µmol·g⁻¹·h⁻¹/10.7 µmol·g⁻¹·h⁻¹ | [126] |
7. Vacancy-Doped g-C₃N₄

The alternative way to modulate the g-C₃N₄ electronic band structure to favor visible light harvesting, accelerate charge separation, and transport was reported to be homogeneous self-modification with nitrogen [127–138] or carbon [88,139–141] vacancies. Native point defect doping via thermal treatment is an easy and promising method to tune the electrical transport properties of semiconductors made for renewable-energy conversion. By introducing additional energy levels and acting as reactive sites, vacancies can play a significant role in medication of the properties of photocatalysts (Table 6). The most common strategies of synthesis of nitrogen or carbon defective g-C₃N₄ are the post-heat treatment in H₂ or Ar [127,141], the polymerization in various atmospheres [88,128,129], the post-heat treatment with a reducing agent [88,130,131], the thermal copolymerization with agents that deliberates gas [132,133,138], and the quick post-thermal treatment [135,136,139,142].

Wang et al. created N vacancies in g-C₃N₄ by the copolymerization of urea with oxalyl dihydrazide (ODH) as an environmental atmosphere control agent [133]. The thermal destruction of ODH caused the H₂ liberation and produced a certain amount of heat that resulted in the defects formation in g-C₃N₄. The source of H₂ was N₂H₄ as a product of the pyrolysis of ODH and NH₃ (NH₃ was produced by the thermal condensation of urea) at 135–140 °C. The SSA of pristine and modulated with N vacancies g-C₃N₄ (V-g-C₃N₄) were 85.4 and 116.9 m²·g⁻¹, respectively. The progressive increasing of the C/N atomic ratio was observed. The atomic ratio of C/N determined with EA 0.65 for pristine and 0.74 for V-g-C₃N₄ was in agreement with the data from EDS and XPS (Table 4). The formation of C-C bond was confirmed using ¹³C solid-state magic-angle spinning nuclear magnetic resonance (MAS NMR) (Figure 9a) by the appearance of a small peak at 169.5 ppm in g-C₃N₄ modulated with N vacancies that was ascribed to C₂N–C (3). The enhanced ESR signal at g = 1.9997 (Figure 9b) illustrated the presence of unpaired electrons on the C atoms, which appeared due to the loss of N atoms (Figure 9c).

![Figure 9](image)

Figure 9. ¹³C solid-state magic-angle spinning NMR spectra (a), electron paramagnetic resonance (EPR) spectra of g-C₃N₄ (CN) and oxalyl dihydrazide (ODH)-CN2 (b), structure model of ODH-CN with N vacancies (c). Reprinted from [133] Copyright (2020), with permission from Elsevier.

Introduction of N vacancies resulted in increasing of the crystallinity of g-C₃N₄ as was detected by the XRD study. The authors also observed that the absorption band of the N vacancies doped g-C₃N₄ was red shifted compared with pristine g-C₃N₄, resulting in the bandgap narrowing from 2.75 eV to 2.61 eV. The PL, photocurrent, and EIS studies demonstrated that the interface charge transport can be effectively enhanced by the introduction of N vacancies.
The introduction of intra- and inter-triazine N-vacancies into g-C₃N₄ was performed under melamine treatment in various atmospheres by Li et al. [128]. The theoretical DFT calculation and experimental results allowed these authors to determine the type of N-vacancies obtained under various conditions. The inter-triazine N-vacancies were introduced after treating melamine in the CCl₄ atmosphere. The polymerization of melamine in Ar and H₂ resulted in the formation of “vacancy-free” and intra-triazine N-vacancies contained g-C₃N₄, respectively. The DFT calculation and optical properties study demonstrated that the bandgap was only slightly reduced by the inter-triazine N-vacancy but was strongly reduced by the inter-triazine N-vacancy. The band gap values of g-C₃N₄ obtained in CCl₄, Ar, and H₂ were determined to be 2.76, 2.79, and 2.80 eV, respectively. The minor changes in the values of SSA were observed for all samples: 11.2, 12.6, and 16.0 m²·g⁻¹ for g-C₃N₄ treated at CCl₄, Ar, and H₂, respectively. Compared with “vacancy-free” g-C₃N₄, the EPR signals of g-C₃N₄ with inter- and intra-triazine N-vacancies were much enhanced, indicating the existence of more unpaired electrons. The efficient separation of photogenerated carriers was confirmed by the PL quenching and photocurrent enhancement of both types of nitrogen V-g-C₃N₄ due to the extra channel of electron transfer.

Xie et al. designed g-C₃N₄ with two types of regulatable nitrogen vacancies in a one pot method by the KOH-assisted calcination treatment of pristine g-C₃N₄ for a remarkably high H₂O₂ evolution photoactivity [131]. During the thermal treatment, the formation of N₂C and NHₓ vacancies occurred due to changing molecular structure influenced by KOH. The loss of g-C₃N₄ ordered structure was caused by the treatment as well. The experimental analyses and theoretic DFT calculations revealed that the N₂C vacancies improved the photoexcited charges separation and the NHₓ vacancy activated oxygen in two-electron process. The favorable amount of two types of N vacancies in g-C₃N₄ was determined. The N/C atomic ratios for a sample with an optimal amount of both types of N vacancies decreased compared with pristine g-C₃N₄. The SSA was 71 m²·g⁻¹ and the thermal post treatment of g-C₃N₄ with and without KOH decreased from 48 to 45 m²·g⁻¹, respectively. Due to the efficient carrier separation and oxygen activation processes, the nitrogen defective g-C₃N₄ demonstrated a 15-fold enhancement of H₂O₂ evolution (152.6 µmol·h⁻¹) and superior stability over 52 h.

The carbon vacancies were prepared in the g-C₃N₄ framework via magnesium vapor etching by Li et al. [88]. They calcined a mixture of pristine g-C₃N₄ and magnesium powders to get magnesium vapor that etched the N-(C)₃, C–N=C, or C=C lattice sites resulting in the vacancies. The applied method allowed the authors to increase the SSA from 58.5 m²·g⁻¹ of g-C₃N₄ to 70.6 m²·g⁻¹ of V-g-C₃N₄ that can supply more active centers for photocatalytic process. The decreased C/N atomic ratio from 0.78 of g-C₃N₄ to 0.51 of V-g-C₃N₄ was determined by the EDS analysis. The further evidence of carbon vacancies in g-C₃N₄ framework after etching was confirmed by the XPS analysis. The smaller C/N atomic ratio of V-g-C₃N₄ and the disappearance of the deconvoluted peak of C=C group in the high-resolution C 1s spectrum of V-g-C₃N₄ evidenced the origin of C vacancies from the destruction of C–C groups. A slight blue-shift of the absorption threshold and the absorption intensity enhancement from 450 nm to 800 nm was observed by DRS of V-g-C₃N₄. The calculated band-gap values were 2.87 eV and 2.98 eV for pristine and C vacancies-doped g-C₃N₄. The significant decrease of the V-g-C₃N₄ PL compared to pristine g-C₃N₄ confirmed its ability to inhibit charge recombination due to the capture of electrons by C vacancies. V-g-C₃N₄ also demonstrated the higher charge separation efficiency. The transient photocurrent responses under irradiation in an on-and-off cycle mode of carbon V-g-C₃N₄ was larger than that of pristine g-C₃N₄. As a result, V-g-C₃N₄ demonstrated the significant improvement of photocatalytic H₂ generation performance.
Table 6. Synthetic methods, applications, and photocatalytic efficiency of vacancy-doped g-C₃N₄.

| Precursor                          | Synthetic Method                        | C/N Element Atomic Ratio, Doped (Pristine) | Photocatalytic Process                                      | Conditions of the Process                                                                 | Efficiency Doped/Pristine | References |
|-----------------------------------|----------------------------------------|-------------------------------------------|------------------------------------------------------------|----------------------------------------------------------------------------------------|--------------------------|------------|
| Urea, oxalyl dihydrazide (ODH)    | Thermal copolymerization                | 0.74 (0.65) by elemental analysis; 0.67 (0.61) by XPS | Tetracycline hydrochloride (TC-HCl) and sulfamethoxazole (SMZ) destruction; H₂ evolution | 300 W Xe lamp, filter λ > 420 nm, Pt co-catalyst (1wt.%), TEOA                         | SMZ destruction: 0.0203 min⁻¹ / 0.0066 min⁻¹; H₂ evolution: 5833.1 µmol h⁻¹ g⁻¹ / 1458.2 µmol g⁻¹ | [133]      |
| Urea, dicyandiamide               | Post-thermal treatment of g-C₃N₄       | —                                         | H₂ evolution                                               | Visible light irradiation                                                              | 6.5 µmol·g⁻¹ / 2.1 µmol·g⁻¹ | [137]      |
| Melamine                          | Polymerization in atmosphere of: CCl₄; H₂; Ar | 0.61 (0.65) by elemental analysis          | H₂ evolution                                               | 3000 W Xe lamp, filter λ > 420 nm, Pt (3%), TEOA (10 vol%)                           | 0.079 min⁻¹ / 0.0032 min⁻¹ | [128]      |
| Urea                              | KOH-assisted calcination treatment      | 1.45 (1.51) by organic elemental analysis | H₂O₂ production                                            | simulated sunlight lamp 20 vol% ethanol                                               | 152.6 µmol·h⁻¹ / 10.2 µmol·h⁻¹ | [131]      |
| Dicyandiamide, NH₄Cl, 3-amino-1,2,4-triazole | Thermal polymerization with post treatment in N₂ | 1.260 (1.489) by element analysis          | H₂ evolution                                               | 3000 W Xe lamp, filter λ > 400 nm, Pt (3%), TEOA (10 vol%) | 3882.5 µmol·h⁻¹·g⁻¹ / 85.0 µmol·h⁻¹·g⁻¹ | [134]      |
| Urea, Mg powder                   | magnesium vapor etching                | 0.51 (0.78) by EDX                        | H₂ evolution                                               | 3000 W Xe lamp, filter λ > 400 nm, Pt (3%), TEOA (10 vol%) | 450 µmol·h⁻¹·g⁻¹ / 225 µmol·h⁻¹·g⁻¹ | [88]       |
| Dicyandiamide                     | two-step calcination                   | 0.81 (0.85) by XPS                        | N₂ fixation                                                | 300 W Xe lamp                                                                       | NH₄⁺ formation: 54 mmol·L⁻¹ / 24 mmol·L⁻¹ | [139]      |
| Urea, melamine                    | precursor preprocessing and thermolysis in N₂ | —                                         | NO oxidation                                              | LED lamp (λ ≥ 448 nm)                                                                | the NO oxidation in 30 min of irradiation 47.7% / 22% | [140]      |
Zhang et al. prepared porous ultrathin carbon defective g-C3N4 by the thermal treatment of g-C3N4 in two steps [139]. The obtained V-g-C3N4 possessed lower crystallinity compared to pristine g-C3N4 due to the formation of vacancies in the C3N4 structure. The two-step thermal treatment promoted the formation mesoporous structure with the increased SSA from 2.06 m² g⁻¹ to 162.57 m² g⁻¹. The formation of carbon defects was evidenced by the reduced C/N ratio from 0.85 to 0.81 determined by XPS. The enhanced EPR signal of V-g-C3N4 corresponded to the presence of C vacancies. The absorption edge of V-g-C3N4 was blue-shifted due to thermal oxidation of pristine g-C3N4. The band gap values were 2.74 and 3.02 eV for the pristine and carbon defective g-C3N4, respectively. The VB potentials of pristine and thermally exfoliated carbon V-g-C3N4 (determined by XPS) were 2.24 eV and 2.40 eV, respectively. The conduction bands were −0.50 eV and −0.62 eV, respectively. As the reduction potential of N₂ to NH₄⁺ was more positive than the CB potentials of both g-C₃N₄, the authors predicted the ability to reduce nitrogen under irradiation. The PL study of pristine g-C₃N₄ and V-g-C₃N₄ was not in agreement with other reports on doped g-C₃N₄ [88,139]. The authors attributed the longer lifetime of excited state of V-g-C₃N₄ to the decreasing of the recombination rate of electron–hole pairs. The confirmation of efficient charge carrier separation was obtained by the strong increasing of photocurrent response intensity of carbon V-g-C₃N₄ compared to g-C₃N₄. The capacity of V-g-C₃N₄ to transport charge carriers was suggested to be due to its porous structure as a result of carbon vacancies, which also promoted nitrogen fixation in a water environment.

8. Photocatalytic Applications of Non-Metal Elements Doped g-C₃N₄

Graphitic carbon nitride as a promising photocatalyst found applications in many photocatalytic processes, such as CO₂ reduction, hydrogen evolution, pollutants degradation, and so forth [124,142–147]. The variety of strategies are offered to optimize photocatalytic processes by the modulation of g-C₃N₄-based photocatalysts composition and morphology to enlarge the range of absorbed light, promote charge carrier separation, and increase specific surface area.

8.1. Photocatalytic CO₂ Reduction

The nanostructured graphitic carbon nitrides were suggested to be the perspective materials for CO₂ capture and transformation into fine chemicals due to perfect semiconducting band gap with suitable band edges (Figure 10a–c).

![Figure 10. Schematic illustration of CO₂ capture and conversion to organic fuels using carbon nitride nanostructures (a), molecular structure (b) and band structure (c) of g-C₃N₄. Reproduced with permission [145], Copyright 2019, with permission from John Wiley and Sons.](image-url)
The hierarchical O-g-C$_3$N$_4$ nanotubes obtained by thermal polycondensation of melamine exhibited significantly improved the photocatalytic CO$_2$ reduction performance under visible light irradiation in comparison with pristine g-C$_3$N$_4$ [43]. Compared with pristine g-C$_3$N$_4$, O-g-C$_3$N$_4$ nanotubes have the following advantages: (1) Larger SSA and more photoactive sites; (2) wider visible-light absorption range and suitable band structure; (3) improved separation efficiency of charge carriers; and (4) high CO$_2$ uptake capacity. The photocatalytic activity was evaluated by the generation rates of CH$_3$OH as it was the main product of photocatalytic performance on both g-C$_3$N$_4$ and the nanotubes. The average CH$_3$OH generation rate of 0.88 µmol·g$^{-1}$·h$^{-1}$ was about five times higher than that produced by g-C$_3$N$_4$ (0.17 µmol·g$^{-1}$·h$^{-1}$). The CH$_3$OH generation rate was approximately the same in three cycles (3 h). Thus, it was concluded that the highly active and stable O-g-C$_3$N$_4$ nanotubes are the promising photocatalysts for hydrocarbon fuel generation by the photocatalytic CO$_2$ reduction under visible light irradiation.

The direction for the design and synthesis of low-cost N-g-C$_3$N$_4$ materials for the photocatalytic CO$_2$ reduction under UV light was proposed by Mo et al. [62]. As photocatalysts they used N-g-C$_3$N$_4$ nanotubes obtained by the heating of supramolecular intermediate under NH$_3$, air, Ar, and N$_2$ atmospheres. The influence of the porous structures and surface amino groups on the photocatalytic process was investigated. The main reaction products were determined to be CO and a small amount of H$_2$. The highest CO formation rate of 103.6 µmol·g$^{-1}$·h$^{-1}$ was observed for pristine g-C$_3$N$_4$ (NH$_3$) that was obtained by the precursor thermal treatment in the NH$_3$ atmosphere. This rate was 17.0, 1.8, 2.7, and 2.8 times higher than that with g-C$_3$N$_4$ and the N-g-C$_3$N$_4$ materials, which were obtained by the thermal treatment in air, Ar, and N$_2$, respectively. The high photocatalytic activity of g-C$_3$N$_4$ (NH$_3$) catalyst was explained by the peculiar porous nanotube structure and by the increased quantity of amino groups. The porous 1D tubular structure improved the charge separation efficiency and provided numerous active sites for the surface reaction. The modification of g-C$_3$N$_4$ with amino groups not only extended the lifetime of excited species, but also caused the strong Lewis basicity, which was beneficial for the CO$_2$ adsorption with further promotion of the CO$_2$ photoreduction. The CO formation rates with g-C$_3$N$_4$ (NH$_3$) photocatalyst was 15 and 13 times higher than those of TiO$_2$ (P25) and black phosphorus, respectively. The nitrogen-doped sp$^2$-carbon (graphitic)-rich electrodes demonstrated high selectivity for the CO$_2$ reduction reaction products [148]. The authors evidenced that the host structure of nitrogen dopants was crucial for the catalytic activity observed.

The photocatalytic CO$_2$ reduction of amine-functionalized g-C$_3$N$_4$ obtained by its treatment with monoethanolamine was evaluated under UV light [58]. The amine-modified g-C$_3$N$_4$ demonstrated the considerable enhancement in the CO$_2$ conversion in comparison with pristine g-C$_3$N$_4$. The main products were found to be CH$_3$OH and CH$_4$. The pristine g-C$_3$N$_4$ was reported to have the photocatalytic CH$_3$OH-production rate of 0.26 µmol·h$^{-1}$·g$^{-1}$ and only trace amount of CH$_4$, while the optimal amine-functionalized sample provided the similar CH$_3$OH production rate of 0.28 µmol·h$^{-1}$·g$^{-1}$ and, further, the CH$_4$-production rate of 0.34 µmol·h$^{-1}$·g$^{-1}$. Similar to Mo et al. [62], the high activity of the amine-functionalized photocatalyst was attributed to the enhancement of CO$_2$ adsorption and destabilization ability of g-C$_3$N$_4$ after the amine-functionalization treatment. The authors assumed that CO$_2$ was adsorbed on the surface of amine-functionalized g-C$_3$N$_4$ through acid-base interactivity with amino groups and formed HCO$_3^−$. As HCO$_3^−$ was more active than linear CO$_2$ it promoted the formation of CH$_4$ [149]. It was shown that under the same conditions, CO$_2$ molecules formed CH$_3$OH [98]. Similar to Mo et al. [62], it was established that the exorbitant surface amine functionalization caused the decrease of photocatalytic activity due to reducing surface-active sites.

S-g-C$_3$N$_4$ fabricated by the thermal polycondensation of thiourea demonstrated enhanced activity in the photocatalytic reduction of CO$_2$ into hydrocarbon fuels under UV–Vis light irradiation in comparison with pristine g-C$_3$N$_4$ [98]. The main product of photocatalytic CO$_2$ reduction was CH$_3$OH. The CH$_3$OH yield with S-g-C$_3$N$_4$ was determined to be 1.12 µmol·g$^{-1}$, whereas for pristine g-C$_3$N$_4$ it was 0.81µmol·g$^{-1}$. The photogenerated electrons captured in these defects can promote the charge
transfer and separation. The inhibition of the electron–hole recombination and prolongation of the lifetime of charge carriers occurs.

Overall, the O, N, S, and P-doped g-C3N4 demonstrated the enhanced activity in the CO2 photocatalytic reduction by improving the energy band structure that allowed more effective light trapping in the visible light region of spectra. The nonmetal element doping caused the formation of an impurity level in g-C3N4, which favored the charge transfer. Moreover, the surface groups, which are introduced by the doping process, enhanced the CO2 adsorption due to acid–base interactivity.

8.2. H2-Evolution

The graphitic carbon nitride presents a great potential for realizing hydrogen evolution reactions. The introduction of non-metal elements caused the exfoliation of bulk g-C3N4 into ultrathin nanosheets, activated the basal plane of g-C3N4, and improved the intrinsic electronic conductivity, thus implementing the facilitated H2 production.

The activity of the C-g-C3N4 composite fabricated by Cao et al. was evaluated by the production of H2 under visible light irradiation and compared with pristine g-C3N4 [71]. The H2 evolution rate using C-g-C3N4 (8.88 μmol/h) was 5.2 times higher that of g-C3N4 (1.70 μmol·h−1) due to the improvement of separation of photoexcited carriers and the enhanced utilization of visible light efficiency. The advantages of C-g-C3N4 were responsible for its drastic photocatalytic activity, such as the ability to separate more photoinduced electrons of CB and holes of VB under irradiation and the presence of delocalized π bonds, which reduce the barrier of carrier transfer and enhance electron transportation (Figure 11). The bridging nitrogen atoms of pristine g-C3N4 are unable to form conjugation with ambient carbon atoms due to inconsequent and small area of π conjugated system in pristine g-C3N4. Thus, under irradiation of C-g-C3N4, more and faster electrons were formed to participate in the process of hydrogen evolution.

![Figure 11. Proposed mechanism for Pt-deposited g-C3N4 (CN) and C-g-C3N4 (CD-CN) of visible-light photocatalytic performance; TEOA is triethanolamine and D is oxidation products. Reprinted from [71] Copyright (2020), with permission from Elsevier.](image-url)

O-g-C3N4 with the various content of oxygen was tested for the photocatalytic hydrogen evolution reactions to study the dependence of photocatalytic activity of O-g-C3N4 on oxygen coverage [24]. The reaction was performed at atmospheric pressure using N2 as a gas carrier in the presence of a hole scavenger and Pt cocatalyst under irradiation by a Xe lamp fitted with a filter to simulate solar light. The increasing of the O-g-C3N4 photocatalytic activity was observed in the sequence of surface O at.% compositions 3.6 > 3.2 > 0 > 5.4 > 6.6. The authors observed a competing dual effect of oxygen doping
on the photocatalytic activity. On one hand, the enhanced light harvesting capability was influenced by the higher porosity of O-g-C₃N₄ and sub-gap impurity states formed by oxygen in its electronic band structure. Although, at the lower oxygen levels the dopant effectively captured and mediated the interfacial charge transfer that promoted the H₂ evolution. On the other hand, the impurity levels from high-density oxygen groups become detrimental to the photocactivity of O-g-C₃N₄. These levels acted as recombination centers due to their positions closer to central position of the band gap.

O-g-C₃N₄ obtained by the thermal polymerization of a purposefully designed precursor with increased photoreduction capability demonstrated the notable enhancement of hydrogen evolution under visible light irradiation [42]. The average hydrogen evolution rate was 64.30 µmol·h⁻¹, which is 17.8 times higher in comparison with pristine g-C₃N₄.

C₆₀-g-C₃N₄ nanowire composites obtained by Long et al. through the calcination of urea and a C₆₀ nanorods mixture demonstrated the higher activity in the photocatalytic H₂ evolution process compared to pristine g-C₃N₄ [76]. Due to the band gap of g-C₃N₄ reduced by incorporation of C₆₀, the charge carriers of C₆₀-g-C₃N₄ nanowire composites became easily excited with visible light. The delocalized π structure of C₆₀ promoted the photoinduced electron transfer and acted as effective electron acceptor. The irradiation of C₆₀-g-C₃N₄ composites caused the CB photogenerated electrons transfer to C₆₀, which resulted in the effective hole–electron separation. These separated charges were trapped by surface adsorbates to produce highly reactive radicals. The proton reduction to H₂ occurred with electrons accumulated on C₆₀, thus optimizing the H₂ production. The H₂ evolution rate for the C₆₀-g-C₃N₄ nanowire composite was about 4.7 times higher than for pristine g-C₃N₄. The hydrogen was produced with the rate of 8.73 µmol·h⁻¹ at 5.10% of quantum efficiency in the presence of C₆₀-g-C₃N₄.

The H₂ evolution under visible light-inducing water splitting was performed to study the photocatalytic activity of N-g-C₃N₄ [63]. The authors used 3 wt.% Pt as a co-catalyst and 10 vol% triethanolamine as a hole sacrificial agent. The hydrogen evolution performance of N-g-C₃N₄ was 4.3 times higher in comparison with pristine g-C₃N₄. The doped N atoms were supposed to promote the separation and transfer of charge carriers and inhibit their recombination. N-g-C₃N₄ demonstrated its high stability after four cycles of the photocatalytic experiments.

Guo et al. suggested the improved optical absorption properties of N-g-C₃N₄ that was obtained by the copolymerization of urea with DMF and the decreased band-gap facilitated harvesting of visible light and increased photocatalytic activity [51]. The more negative conduction band potential of obtained N-g-C₃N₄ resulted in the improved reducing ability of photoelectrons, thus promoting the photocatalytic water splitting for H₂ evolution. The rate of photocatalytic hydrogen production was 14 times higher than that of pristine g-C₃N₄.

Tian et al. studied the photocatalytic performance of mesoporous N-g-C₃N₄ materials obtained via the pre-hydrothermal treatment of urea and melamine for the photocatalytic H₂ production under visible light irradiation [64]. The authors used 20 vol% lactic acid as a sacrificial agent and 1% Pt as a co-catalyst. The increased H₂ evolution activity was observed for all the doped samples. The positive effect of melamine phase-transformation was observed even for N-g-C₃N₄ obtained without urea that demonstrated the photocatalytic H₂ production rate of 1.7 times higher than that of pristine g-C₃N₄. The highest photocatalytic performance with the H₂ evolution rate of 3579 µmol·h⁻¹·g⁻¹ was observed for the sample with the molar ratio of urea: melamine = 3:1, which was 23 times higher than that of g-C₃N₄. Consistent results were also obtained for the H₂ evolution in the absence of Pt while maintaining other conditions to be similar. The sample with the molar ratio of urea: melamine = 0:1 and 3:1 demonstrated the H₂ evolution rate of 1.9 and 15 times higher than that of pristine g-C₃N₄.

The authors identified three factors that caused the high photocatalytic activity of the 3D ultrathin porous N-g-C₃N₄ materials: Firstly, the increased specific surface area originated from porous nanosheets that contained more reaction sites. Secondly, the narrowed band gap allowed more visible-light absorption and improved the H₂ evolution ability. Thirdly, the significant reduction of recombination rate of photogenerated electrons and holes by porous structure of N-g-C₃N₄ improved
the charge separation and rapid movement of charge carriers to the surface of photocatalyst where the reduction process occurred.

N vacancies-doped g-C$_3$N$_4$ with increased crystallinity and boosted visible-light harvesting demonstrated improved performance of the photocatalytic H$_2$ evolution [133]. The hydrogen evolution rate 5833.1 $\mu$mol·h$^{-1}$·g$^{-1}$ compared to 1447.8 $\mu$mol·h$^{-1}$·g$^{-1}$ of pristine g-C$_3$N$_4$. The V-g-C$_3$N$_4$ photocatalyst had high chemical stability even after five cycles of the continuous photocatalytic reaction.

The theoretical and experimental study of the effect of intra- and inter-triazine N-vacancies in g-C$_3$N$_4$ on the photocatalytic H$_2$ evolution activity was carried out by Li et al. [88]. The singly occupied defect states, which were formed in the band gap of g-C$_3$N$_4$ by both types of N vacancies, trapped the photogenerated electrons and served as centers of the H$^+$ reduction. The most efficient H$_2$ evolution was observed for V-g-C$_3$N$_4$ with the inter-triazine vacancies compared to V-g-C$_3$N$_4$ with the intra-triazine vacancies due to stronger electron localization. The normalized reaction rate of inter-triazine V-g-C$_3$N$_4$ was 9 times higher than that of “vacancy-free” g-C$_3$N$_4$, and 2.2 times higher than that of intra-triazine V-g-C$_3$N$_4$.

The SM-g-C$_3$N$_4$ nanosheets demonstrated enhanced activity in the photocatalytic H$_2$ production compared to pristine g-C$_3$N$_4$ [103]. The average H$_2$ evolution rate was 3.80 times higher than that of g-C$_3$N$_4$. The study of H$_2$ production under irradiation with the wavelengths of 420, 450, 475, and 520 nm demonstrated that the activity of SM-g-C$_3$N$_4$ corresponded to the optical absorption of the photocatalyst due to the band gap excitation. The only trace amount of H$_2$ was produced with pristine g-C$_3$N$_4$ when the irradiation light with the wavelength longer than 450 nm was applied.

In other research, the drastic increase of H$_2$ evolution was reached with S-g-C$_3$N$_4$ nanosheets [90]. The obtained S-doped materials possessed the increased SSA, higher efficiency in charge carrier separation, and enlarged band gap energy with the upward shift of the CB potential and the downward shift of the VB potential. These factors caused the high H$_2$ production rate of 127.4 $\mu$mol·h$^{-1}$, which is about 250 times higher than that of pristine g-C$_3$N$_4$. There was a stronger reduction ability observed for the hydrogen evolution of electrons in the CB of S-g-C$_3$N$_4$.

The S-doping effect of pristine g-C$_3$N$_4$ and P-g-C$_3$N$_4$ was evaluated by Li et al. [88]. The singly occupied defect states, which were formed in the band gap of g-C$_3$N$_4$ by both types of N vacancies, trapped the photogenerated electrons and served as centers of the H$^+$ reduction. The most efficient H$_2$ evolution was observed for V-g-C$_3$N$_4$ with the inter-triazine vacancies compared to V-g-C$_3$N$_4$ with the intra-triazine vacancies due to stronger electron localization. The normalized reaction rate of inter-triazine V-g-C$_3$N$_4$ was 9 times higher than that of “vacancy-free” g-C$_3$N$_4$, and 2.2 times higher than that of intra-triazine V-g-C$_3$N$_4$.

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The great increase of photocatalytic activity in the H$_2$ evolution under the visible-light irradiation was reached for the porous P-g-C$_3$N$_4$ nanosheets [118]. The total H$_2$ production for 4 h was 1813 and 30,281 $\mu$mol for pristine g-C$_3$N$_4$ and P-g-C$_3$N$_4$, respectively. The photocatalytic H$_2$ evolution rate was 458 and 9524 $\mu$mol·h$^{-1}$·g$^{-1}$, respectively. The obtained P-g-C$_3$N$_4$ was stable over the five test cycles. The apparent quantum efficiency was calculated to be 5.49%, 2.67%, 1.01%, and 0.17% at irradiation with $\lambda = 400$, 420, 450, and 550 nm, respectively. The enhancing of photocatalytic activity was reached due to the increased number of active sites for the photocatalytic H$_2$ evolution provided by the porous structure and P-doping, the extending of light absorption range, and the improvement of hydrophilicity for easier water molecules adsorption via introducing OH groups. Additionally, the P-doping changed the excitation process and improved the efficiency of the charge separation.

The O, N, S, and P doping is a useful strategy to modify the electronic structure of g-C$_3$N$_4$ and to enhance the photocatalytic effect of hydrogen production. When the non-metal elements were applied to dope g-C$_3$N$_4$, the H$_2$ generation was increased due to the lowering of the charge recombination rate and accelerated charge mobility.

8.3. Degradation of Dyes and Organic Pollutants

The photocatalytic activity of O-g-C$_3$N$_4$ was evaluated by the degradation of organic dyes Rhodamine B (RhB) and Methyl Orange (MO) under irradiation with simulated solar light [35]. Ninety-five percent of RhB (10 mg/L) was degraded in 20 min and 70% of MO (10 mg/L) in 4 h in the presence of O-g-C$_3$N$_4$. The determined rate constants were 65 times and 24 times higher than those of g-C$_3$N$_4$, for RhB and MO degradation, respectively. The significant improvement of photocatalytic activity was explained by the porous layered structure of O-g-C$_3$N$_4$, its ability to reduce the recombination of photogenerated carriers, and increased absorption of visible light. Among the
possible active species (O$_{2}^{•−}$, OH$^{•−}$, h$^{+}$) O$_{2}^{2−}$ and h$^{+}$ were main active species of the photocatalytic degradation of RhB that was confirmed by using sacrificial agents.

The photocatalytic decomposition of RhB under visible light was performed to determine the influence of oxidative treatment of g-C$_{3}$N$_{4}$ with PMS [17]. The dependence of the photocatalytic activity of the resulting O-g-C$_{3}$N$_{4}$ on the amount of oxidant was found. Huang et al. determined the optimal amount of PMS for obtaining the O-g-C$_{3}$N$_{4}$ photocatalyst with the highest activity for the decomposition of RhB under visible light. The mechanism of RhB decomposition is not the same as for non-selective degradation of the chromophore in RhB by hydroxyl radicals described in the papers [34,35]. It was found that the RhB photocatalytic degradation by O-g-C$_{3}$N$_{4}$ occurred through N-deethylation pathways. The study of the RhB degradation in the presence of various inhibitors of photoactive species formation confirmed that O$_{2}^{•−}$ was the dominant oxidant in the studied photocatalytic system (Figure 12).

A dual oxygen group (C-O-C and C=O) doped carbon nitride prepared by a two-step thermal treatment process demonstrated the remarkably enhanced visible-light photocatalytic performance for pollutant degradation [19]. Compounds, such as bisphenol, phenol, 2-chlorophenol, and diphenhydramine, were decomposed in their aqueous solutions using g-C$_{3}$N$_{4}$. The improvement of the degradation rate occurred due to the formation of an internal electric field and strong interactions between the photocatalyst and organic contaminant. The authors proposed a possible electron transfer pathway for enhanced pollutant photodegradation. Photoexcited electrons moved to the dual oxygen groups together with further generation of O$_{2}^{•−}$ that decomposed the pollutants. The pollutant adsorption caused the enhancement of internal electric field and greatly increased photogenerated e$^{−}$/h$^{+}$ separation and transfer. As a result, the oxidation with h$^{+}$ and the generation of O$_{2}^{•−}$ became more facile.

In other research, 49.3 times higher photocatalytic degradation efficiency of 4-nitrophenol using S-g-C$_{3}$N$_{4}$ than that with pristine g-C$_{3}$N$_{4}$ under visible light irradiation (>400 nm) was demonstrated [107]. The enhanced photocatalytic activity was attributed to the nanosheets formation and sulfur modification. Chrysanthemum-like nanosheet structures of S-g-C$_{3}$N$_{4}$ presented more active sites and improved its photochemical response. The sulfur modification induced the energy structure changes and lattice distortion. It was confirmed that the photocatalytic degradation of 4-nitrophenol by S-g-C$_{3}$N$_{4}$ was greatly influenced by oxidative species, such as singlet oxygen.

The high photocatalytic activities toward removing organic pollutants were demonstrated for mesoporous C-g-C$_{3}$N$_{4}$ ultrathin nanosheets synthesized through a facile one-step thermal condensation method with an agar-melamine gel precursor [79]. The more efficient ability of the nanosheets to remove RhB, phenol, Bisphenol A, and Phenanthrene compared to bulk g-C$_{3}$N$_{4}$ under
visible-light irradiation was reported. The C-g-C3N4 ultrathin nanosheets demonstrated improved photoelectrochemical properties due to the strong enhancing of the photo-excited carriers’ separation and migration. It was found that O2•− as well as OH• radicals were responsible for the strong oxidative capacity of the carbon doped photocatalysts, while for the pristine g-C3N4 only O2•− radicals oxidized the pollutants. The abundant holes of the VB h+ directly oxidized the pollutants. The great improvement photocatalytic activity was assigned to synergy of doped carbon and ultrathin nanosheets structure. The incorporated carbon strengthened visible-light absorbance, promoted charge separation, and prevented the photogenerated carriers’ recombination. The C-g-C3N4 nanosheets provided more active sites for photocatalytic reactions.

The photocatalytic performance of SM-g-C3N4 nanosheets under the visible light irradiation was tested for the degradation of dichlorotriazine dye used in textile crafts (Procion Red MX-5B) [103]. The highest activity in the process was observed for a sample with the highest SSA and narrowest bandgap. To determine the mechanism of the photocatalytic process the degradation of Procion Red MX-5B was performed with the most active photocatalysts in the presence of hole, OH, and O2•− scavengers. The most active species in the photocatalytic decomposition of the dichlorotriazine dye was determined to be the O2•−.

P-g-C3N4 obtained by the thermo-induced copolymerization method from a low cost and environmentally friendly P precursor were tested in the RhB degradation under irradiation with visible light. Due to significant changes in the electronic, surface, and semiconductor properties of g-C3N4 after P-doping the improved photocatalytic performance of RhB degradation was confirmed [126]. RhB in the solution (10 mg·L−1) was completely decomposed within 10 min while the decomposition of RhB solution of the same concentration lasted 30 min with pristine g-C3N4. The high ability of P-g-C3N4 to adsorb RhB also influenced the improvement of photocatalytic performance.

The presented research reports demonstrated that the photocatalytic activity of non-metal element-doped g-C3N4 has been greatly improved over pristine g-C3N4, and the degradation rates of organic dyes and pollutants have been enhanced to varying degrees. The doping of g-C3N4 with O, N, C, S, and P elements resulted in materials with stronger light absorbance, faster charge migration rate, and more photoreaction sites, providing the increased photocatalytic reaction rate. The comparison of the photocatalytic activity of doped g-C3N4 in the reported processes can be done generally by the comparison of the photocatalytic rate constants. Because absorption of photons plays a key role in photocatalytic processes, the apparent quantum yield must be used for reporting and comparing photocatalytic activities, which corresponds to lower limits of the quantum yield [150].

9. Conclusions

In this review, we summarized the recent research progress in the non-metal doping of graphitic carbon nitride used mostly for photocatalysis. The overview was focused on the modulation of composition and morphology of g-C3N4 with chemical doping with oxygen, sulfur, phosphor, nitrogen, carbon, as well as nitrogen and carbon vacancies. The efforts of various research groups to improve the photocatalytic activity of g-C3N4 in processes of the CO2 reduction, H2-evolution, and organic contaminants degradation by its non-metal doping were successful. Their results confirmed that g-C3N4 is a universal, environmentally friendly, low-price, and stable material for creating new photocatalysts with targeted properties.

One of targets of the incorporation of non-metallic dopants into g-C3N4 is the narrowing of the band gap, extending the sensitivity to the light of visible region as well as the reducing of recombination rate of electron–hole pairs for efficient charge separation that caused the enhancement of photocatalytic performances. However, in very few studies, a significant band gap reduction was observed after doping/modification with nonmetal atoms. In some cases, the efforts to modify pristine g-C3N4 caused even band gap enlargement. It is important to perform the doping of non-metal atoms into g-C3N4 matrices to reach the effective band gap narrowing. The surface doping can only cause the formation of some band gap localized states.
The prominent decreasing of the PL intensity of the majority of O-, C-, N-, S-, P-, and vacancy-doped g-C₃N₄ compared to the pristine g-C₃N₄ confirmed their ability to inhibit charge recombination due to the capture of electrons by the dopants. However, the study of PL decay is rarely used for g-C₃N₄ materials. Data on PL quenching can give quantitative characteristic of charge recombination inhibition processes. The creation of g-C₃N₄ materials with a strong visible light absorption and extremely low radiative recombination of excited charge carriers is still the target of future investigations.

It is well known that SSA has important characteristics of solid catalysts as it influences a number of reaction sites and the ability to absorb reaction products. The effect of active sites on the activity of g-C₃N₄-based photocatalysts is unquestionable. The higher SSA of the materials provides more active sites, and enhances the transfer and separation of charges in photocatalytic processes. The SSA of pristine g-C₃N₄ was strongly affected by synthesis methods. In some cases, the modification with non-metal atoms caused the increasing of SSA that enhanced their photocatalytic activity.

It should be mentioned that the relation between acid–base properties of g-C₃N₄ and non-metal elements doping and its influence on photocatalytic activity was not enlightened enough in the literature. The Bronsted and Lewis base centers are formed in the frame of g-C₃N₄ by uncondensed primary and tertiary amino groups, and aromatic amino groups of the three-s-triazine moieties. The presence of Lewis acid and base centers affected its application as active materials for dark catalysis and photocatalysis. The study of the connection between kinds of non-metal element doping and the acid–base properties of doped g-C₃N₄ will allow us to develop new materials with targeted properties for the appropriate photocatalytic process.

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