Review

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_2O_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 $\text{g-C}_3\text{N}_4$ with H_2O_2 at 120 °C [24]. The concentration of H_2O_2 influenced the specific surface area (SSA) of $\text{O-g-C}_3\text{N}_4$. The highest SSA of $\text{O-g-C}_3\text{N}_4$ was determined to be $85 \text{ m}^2\cdot\text{g}^{-1}$ compared to $75 \text{ m}^2\cdot\text{g}^{-1}$ for pristine $\text{g-C}_3\text{N}_4$. The photocatalytic experiment did not reveal the influence of SSA on activity of $\text{O-g-C}_3\text{N}_4$ photocatalysts. Fourier-transformed infrared spectroscopy (FTIR) allowed authors to get confirmation that the oxygen functionalization of $\text{g-C}_3\text{N}_4$ was achieved by its oxidation with H_2O_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 $\text{g-C}_3\text{N}_4$ 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 $\text{g-C}_3\text{N}_4$ 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 $\text{O-g-C}_3\text{N}_4$ (Figure 1).

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

The oxygen groups in the $\text{g-C}_3\text{N}_4$ 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_2O_2 were used. At the same time, for the majority of $\text{O-g-C}_3\text{N}_4$ samples, the intrinsic band gap value was 2.85 eV. The band structure transformation with increasing oxygen doping level in $\text{g-C}_3\text{N}_4$ were suggested to occur according to the scheme presented in Figure 2.

Similar characteristics of $\text{O-g-C}_3\text{N}_4$ 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 $\text{O-g-C}_3\text{N}_4$ show that the H_2O_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 $\text{g-C}_3\text{N}_4$ with peroxymonosulfate (PMS) at 60 °C [18]. As the SSA of $\text{g-C}_3\text{N}_4$ after the oxidation was approximately unchanged, it was suggested that PMS interacts with the surface groups of $\text{g-C}_3\text{N}_4$ without its exfoliation into a single or few layers. The atomic percentage of oxygen increased on $\text{O-g-C}_3\text{N}_4$ surface to 6.9% in comparison with 1.8% in $\text{g-C}_3\text{N}_4$ as confirmed by XPS. The detailed study of the chemical state of C, N, and O atoms in $\text{O-g-C}_3\text{N}_4$ allowed authors to report that the doped oxygen atoms mainly exist as carbonyl and carboxyl groups. The doping of more oxygen groups in $\text{O-g-C}_3\text{N}_4$ 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.

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	H ₂ O ₂ hydrothermal treatment, 120 °C	Surface O at.% in O-doped g-C ₃ N ₄ 3.23–6.59 by XPS 3.16%/2.73%	H ₂ 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	by Energy-Dispersive X-Ray Spectroscopy (EDS) 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	H ₂ O ₂ hydrothermal treatment, 120 °C	—	RhB, Methyl orange (MO) destruction	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)	bisphenol A (BPA), phenol (Ph), 2-chlorophenol (2-Ph), diphenhydramine destruction (DP)	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%	[19]
Melamine, ethanol	Thermal polymerization	Atom.% (O) 3.25/- by XPS	H ₂ 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 1.08:1:0.23/ 0.69:1:0.03 by XPS	H ₂ evolution; RhB destruction	Visible light, λ > 420, Pt co-catalyst (0.3 wt.%)	H ₂ evolution: 3174 µmol·h ⁻¹ g ⁻¹ /846 µmol·h ⁻¹ ·g ⁻¹ RhB degradation: 0.249 min ⁻¹ /0.007min ⁻¹	[22]
Melamine	Thermal polycondensation	12.5/trace by XPS	CO ₂ reduction	350 W Xe lamp, filter λ > 420 nm	CH ₃ OH production 0.88 µmol·g ⁻¹ ·h ⁻¹ / 0.17 µmol·g ⁻¹ ·h ⁻¹	[43]
Dicyandiamide	Hydrothermal followed by calcination	O content (wt.%) 5.23/0.17 by EA	N ₂ 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-C₃N₄

The number of publications on obtaining nitrogen-doped graphitic carbon nitride (N-g-C₃N₄) is much lower in comparison with the number of publications on carbon, oxygen, phosphorus, and sulfur doped g-C₃N₄. The reason for the limited production of N-g-C₃N₄ is the application of non-environmentally friendly precursors, such as hydroxylammonium chloride and hydrazine hydrate. Some processes of the N-g-C₃N₄ synthesis generally contain complicated and long-lasting steps. The presented reports on the synthesis and characterization of N-g-C₃N₄ and its application in photocatalysis inspired researchers to develop appropriate methods of introducing nitrogen into the g-C₃N₄ lattice (Table 2). Different reaction paths were applied to increase the N content in g-C₃N₄ by introducing nitrogen atoms into g-C₃N₄ matrices [44–55] and by the modification of g-C₃N₄ 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 C₃N_{4+x}, where 0.5 < x < 0.8. According to the report the carbon centers of the obtained materials primarily had sp² hybridization, the layered structure consisted of triazine (C₃N₃) rings, and nitrogen species bound the triazines. The N-g-C₃N₄ 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-C₃N₄. Huynh et al. synthesized 3,6-di(azido)-1,2,4,5-tetrazine for obtaining nitrogen-rich carbon nitrides C₃N₄ and C₃N₅ [47]. The high-nitrogen contained nitrides 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 (C₃N_{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 sp² carbon atom in the resultant N-g-C₃N₄. According to EA the N/C mass ratio was 1.68 for C₃N_{4+x}, that is, higher than that (1.60) of pristine g-C₃N₄.

N-g-C₃N₄ with the high SSA was obtained by Xu et al. via secondary calcinations of g-C₃N₄ at different temperatures [50]. The highest nitrogen doping ratio and the largest SSA was observed for g-C₃N₄ 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 sp² C atom was replaced by the nitrogen atom. According to the EDS analysis, the highest value of N content in the N-g-C₃N₄ was 57.57 at.% and the lowest for undoped g-C₃N₄ 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 m²·g^{−1} for non-treated and post thermal treated g-C₃N₄, 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-C₃N₄ 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-C₃N₄, 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-C₃N₄ modified with DMF (g-C₃N₄/DMF) was 42.18 m²·g^{−1} in comparison with 18.36 m²·g^{−1} for non-treated g-C₃N₄. The further increasing of the specific surface area to 74.79 m²·g^{−1} was reached after the thermal treatment of g-C₃N₄ with DMF for 4 h. The porous nanosheet architecture of N-g-C₃N₄ 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-C₃N₄, g-C₃N₄/DMF, and exfoliated N-g-C₃N₄, 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-C₃N₄ was 0.67, and for pristine it was 0.76. The N doping and nanosheet construction of g-C₃N₄ expanded

an absorption band of obtained materials and enhanced its ability to harvest visible light. The band gaps of pristine and N-g-C₃N₄ were estimated to be 2.51 eV and 2.54 eV, respectively. The transfer and separation efficiency of charge carries in N-g-C₃N₄ materials were studied with PL spectroscopy. The decreasing of PL intensity of N-g-C₃N₄ in comparison with g-C₃N₄ 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-C₃N₄ with enhanced ability of photocatalytic H₂ 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-C₃N₄, that which was obtained by the copolymerization of urea and DMF, was enriched with nitrogen. The results of ¹³C 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-C₃N₄ was suggested to be the result of incorporated N atoms that caused increased delocalization of π -electrons. The analysis of UV-Vis DR spectra of N-g-C₃N₄ revealed the narrowing of band gap to 2.69 eV compared to 2.75 eV of pristine g-C₃N₄.

The supramolecular self-assembly strategy for obtaining of porous N-g-C₃N₄ nanotubes with the high adsorption of CO₂ 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 NH₃, air, Ar, and N₂ atmospheres. From the scanning electron microscopy (SEM) analysis of N-g-C₃N₄ obtained under the thermal treatment in various gases, the authors revealed the porous structure only in g-C₃N₄ prepared under the NH₃ atmosphere (Figure 3b–d). The sharp increase of SSA was observed for the N-g-C₃N₄ materials. The determined values of the SSA of bulk g-C₃N₄ and materials, which were obtained by treatment in Ar, air, N₂, and NH₃, were 8.6, 56.9, 78.6, 82.3, and 108.9 m²·g^{−1}, respectively. The highest content of amino groups grafted into g-C₃N₄ nanotubes during the time of the supramolecular intermediate polymerization process was observed for the porous materials treated under NH₃ (g-C₃N₄/NH₃). The EA results indicated a significantly lower C/N atomic ratio of g-C₃N₄/NH₃ than those of g-C₃N₄ samples synthesized under other atmospheres. The determined C/N atomic ratio for the pristine g-C₃N₄ and materials obtained in NH₃, Ar, and N₂, air were 0.69, 0.55, 0.59, 0.58, and 0.58 m²·g^{−1}, respectively. Based on the XPS analysis, the authors concluded that in the NH₃ 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 CO₂ and desorption of CO was studied with density functional theory (DFT) calculations. The DFT calculations demonstrated that g-C₃N₄/NH₃ not only increased the CO₂ adsorption energy, but also decreased the CO desorption energy that caused the higher photocatalytic CO₂ reduction activity.

Hao et al. incorporated nitrogen atoms into g-C₃N₄ 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-C₃N₄ nanosheets revealed that the basic characteristics of g-C₃N₄ structure were not influenced by the surface nitrogen modification. Formation of new C-N bonds due to N atoms insertion into the g-C₃N₄ lattice by filling of removed oxygen atom seats was confirmed by XPS. The authors distinguished three types of the sp² hybridized nitrogen: Pyridinic nitrogen (C-N=C), tertiary nitrogen (N-C₃), and noncondensing amino group (C-N-H), respectively. They confirmed the highest content of pyridinic N atoms in N-g-C₃N₄ 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-C₃N₄. The nitrogen-doped g-C₃N₄ demonstrated enhanced visible absorption ability and the increasing lifetime of its excited state.

Figure 3. Formation and characterization of $g\text{-C}_3\text{N}_4/\text{NH}_3$. 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 $g\text{-C}_3\text{N}_4/\text{NH}_3$ nanotubes (TCN (NH_3)) (g,h). Reprinted from [62], Copyright (2019), with permission from Elsevier.

Figure 4. Scheme of the formation process from the bulk- C_3N_4 to the $g\text{-C}_3\text{N}_4$ nanosheets (NCNS) sample. Reprinted from [57], Copyright (2018), with permission from Elsevier.

Amine-functionalized $g\text{-C}_3\text{N}_4$ 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 $g\text{-C}_3\text{N}_4$ evidenced the absence of any doping effect and thus changes in the intrinsic electronic structure of $g\text{-C}_3\text{N}_4$. The amine-functionalized materials demonstrated the increased adsorption of CO_2 caused by the chemical interaction between CO_2 and amino groups. The treatment of $g\text{-C}_3\text{N}_4$ 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-C₃N₄ were −19.44 mV and −31.67 mV, respectively.

Yan et al. applied a NH₄Cl-assisted chemical blowing method to prepare nitrogen-rich graphitic carbon nitride nanosheets [59]. They revealed that under the thermal treatment of a NH₄Cl and melamine mixture, generated gases detached g-C₃N₄ 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-C₃N₄ (45.59 at.%). The band gaps calculated from UV-Vis DR spectra increased from 2.73 eV for g-C₃N₄ to 2.79 eV for N-g-C₃N₄. 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-C₃N₄ 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-C₃N₄ by the reaction with urea. Changes in the structure, SSA, and elemental compositions of obtained N-g-C₃N₄ were not observed. N-g-C₃N₄ demonstrated a little red shift of the intrinsic absorption edge in comparison with that of g-C₃N₄. 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-C₃N₄ may trigger π -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-C₃N₄ with nitrogen by the thermal polymerization of urea under the nitrogen atmosphere [53]. The obtained N-g-C₃N₄ demonstrated the decreasing C/N ratio 0.71 compared to 0.73 of g-C₃N₄ as was revealed by the XPS analysis. The authors suggested that the decreasing of C/N ratio in N-g-C₃N₄ occurred due to the formation of carbon vacancies that promoted the formation of tri-s-triazine subunits. The intrinsic bandgaps of N-g-C₃N₄ obtained in the nitrogen atmosphere increased to 2.70 eV from 2.58 eV of g-C₃N₄ 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-C₃N₄ with enhanced photocatalytic activity [64]. The formation of ultrathin N-g-C₃N₄ nanosheets with a thickness of ~3 nm that consisted of 7 or 8 at. layers were confirmed with AFM. The SSA of N-g-C₃N₄ was 39.1 m²·g^{−1} with an average pore diameter of 46.1 nm, which was 9 times higher than pristine g-C₃N₄. The introduction of N atoms into the g-C₃N₄ matrices was confirmed with the EA and XPS analyses. The band gap of N-g-C₃N₄ decreased to 2.47 eV in comparison with pristine g-C₃N₄ (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)	H ₂ evolution	300W Xe lamp, filter $\lambda > 400$ 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	H ₂ evolution	300W Xe lamp, filter $\lambda > 400$ nm, TEOA (10 vol.%, Pt co-catalyst (3 wt.%))	44.28 $\mu\text{mol}\cdot\text{h}^{-1}$ / 7.86 $\mu\text{mol}\cdot\text{h}^{-1}$	[49]
dicyandiamide	Secondary calcination	57.57 (56.88) at.% by EDS	methylene blue degradation	300W Xe lamp, filter $\lambda > 420$ nm	0.02355 min ⁻¹ / 0.00829 min ⁻¹	[50]
Dicyandiamide, DMF	Thermal copolymerization	0.67 (0.76) by XPS	Tetracycline (TC) degradation	300W Xe lamp, filter $\lambda > 420$ 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	H ₂ evolution	300W Xe lamp, filter $\lambda > 400$ nm, TEOA (10 vol.%), Pt co-catalyst (3 wt.%)	5268 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ / 3579 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$	[51]
Urea, monoethanolamine	Amine functionalization of g-C ₃ N ₄	—	CO ₂ reduction	300W Xe lamp, gas phase reaction	CH ₄ : 0.34 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$ /trace; CH ₃ OH: 0.26 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$ / 0.26 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	[58]
Melamine, NH ₄ Cl	Thermal polymerization	N content (at.%) doped 47.32 doped; 45.59 pristine	RhB degradation	300W Xe lamp, 420 nm cutoff filter,	0.01954 min ⁻¹ / 0.00391 min ⁻¹	[59]
Melamine, NH ₄ Cl	Second-calcination approach	1.14 (1.63) by XPS analysis	H ₂ 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, NH ₄ Cl	Precursor formation by hydrothermal method; thermal polymerization in NH ₃ , N ₂ , Ar, air	0.55-0.59 (0.69) by elemental analysis	CO ₂ reduction	300 W Xe-lamp, CoCl ₂ , 2,2-bipyridine, TEOA and methyl cyanide	103.6 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ / 6.1 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$	[62]
Citric acid, urea	Thermal polymerization	without change	H ₂ evolution	300W Xe lamp, 420 nm cutoff filter, Pt nanoparticles (3 wt.%), triethanolamine as a hole quencher	64 $\mu\text{mol}\cdot\text{h}^{-1}$ /15 $\mu\text{mol}\cdot\text{h}^{-1}$	[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-C ₃ N ₄	[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	H ₂ evolution	300W Xe lamp, 420 nm cutoff filter, Pt nanoparticles (1 wt.%), 20% vol. lactic acid	3579 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$ / 147 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	[64]
Urea, N ₂	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 allotropies 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-C₃N₄, respectively. The authors demonstrated that C-g-C₃N₄ 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-C₃N₄, 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-C₃N₄ and C/CNNS-0.5 photocatalysts (d). Reprinted from [79], Copyright (2019), with permission from Elsevier.

Long et al. obtained C₆₀/g-C₃N₄ nanowire composites for the photocatalytic H₂ evolution process by the thermal treatment of urea and C₆₀ nanorods mixture [76]. The insignificant increasing of SSA from 104.77 m²·g^{−1} (for pristine g-C₃N₄) to 117.47 m²·g^{−1} was observed. Both samples were mesoporous with the main pore width of 2–6 nm. The incorporation of C₆₀ nanorods in g-C₃N₄ improved visible light absorbance. The band gap of the C₆₀/g-C₃N₄ photocatalyst was narrower (2.57 eV) compared to pristine g-C₃N₄ (2.75 eV). The improved ability of C₆₀/g-C₃N₄ to separate photogenerated electron–hole pairs was concluded from g-C₃N₄ fluorescence quenching due to modification with C₆₀. The C₆₀/g-C₃N₄ nanocomposite produced more photogenerated electrons as demonstrated by the highest transient photocurrent responses compared to pristine g-C₃N₄. The improvement of C₆₀/g-C₃N₄ photocatalytic H₂ production was explained by synergy of g-C₃N₄ and C₆₀, which allowed the photogenerated charges separation.

Table 3. Synthetic methods, applications, and photocatalytic efficiency of C-doped g-C₃N₄.

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 $\mu\text{mol}/$ 6.78 μmol 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 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}/$ 59.6 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$	[68]
Melamine, Urea, phenylmalonic acid	Precursor copolymerization on the surface of g-C ₃ N ₄	C/N at. Ratio 68.9 (43.0) C, % 33.52 (33.45) by elemental analysis	bisphenol A (BPA) destruction H ₂ evolution	300W Xe lamp, filter $\lambda > 420$ nm, Pt (3%), TEOA (10 vol%)	BPA destruction: 0.0507 $\text{min}^{-1}/0.0038 \text{ min}^{-1};$ H ₂ evolution: 31 $\mu\text{mol}\cdot\text{h}^{-1}/10 \mu\text{mol}\cdot\text{h}^{-1}$	[73]
Cyanuric acid, ethylene glycol, melamine	microwave treatment of supramolecular aggregates	C/N at. Ratio 0.688 (0.669) C, %: 39.98 (39.51) by elemental analysis	N ₂ photofixation	250W high-pressure Na lamp (400 < λ < 800 nm)	5.3 $\text{mg}\cdot\text{L}^{-1}\cdot\text{gcat}^{-1}/$ 0.48 $\text{mg}\cdot\text{L}^{-1}\cdot\text{gcat}^{-1}$	[88]
Urea, C ₆₀ nanorods	liquid-liquid interfacial precipitation method	-	H ₂ evolution	500 W Xe lamp, filter $\lambda > 420$ nm, Pt (3%), TEOA (17 vol%)	8.7 $\mu\text{mol}\cdot\text{h}^{-1}/$ 1.85 $\mu\text{mol}\cdot\text{h}^{-1}$	[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 C/N at. Ratio 0.90 (0.87) by XPS C/N at. Ratio 0.58 (0.57) C, %: 34.83 (34.81) by XPS analysis	RhB, Phenol, BPA, Phe destruction	300 W Xe lamp, filter $\lambda > 420$ nm	RhB destruction 0.042 $\text{min}^{-1}/$ 0.016 min^{-1} BPA destruction 0.145 $\text{min}^{-1}/$ 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 $\text{min}^{-1}/$ 0.0019 min^{-1}	[67]

The combination of carbon dots (CDs) with g-C₃N₄ (CDs/g-C₃N₄) activated by hydrogen peroxide allowed Asadzadeh et al. to obtain photocatalysts with exceptional activity upon visible-light irradiation [67]. The activation of g-C₃N₄ with H₂O₂ increased its SSA from 14.6 to 45.1 m²·g^{−1} due to exfoliation during the treatment process. However, the adhering of CDs blocked micropores of the treated g-C₃N₄ that caused the SSA decrease to 19.7 m²·g^{−1}. The homogeneous dispersion of CDs on the surface of activated g-C₃N₄ was confirmed by the EDS analysis. The EDS elemental mappings of CDs/g-C₃N₄ demonstrated the uniform distribution of C, N, and O elements evidencing the binary nanocomposite formation. The presence of two components in CDs/g-C₃N₄ was also confirmed by high-resolution TEM (HRTEM) images. The d-spacing of g-C₃N₄ 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-C₃N₄ edge at 460 nm and was red shifted to 475 nm in the spectrum of the H₂O₂ activated g-C₃N₄. The absorbance of CDs/g-C₃N₄ 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 the excitation wavelength. The PL study of CDs/g-C₃N₄ was not reported. The thermal decomposition of the CDs/g-C₃N₄ occurred at lower temperatures than that of pristine g-C₃N₄ due to the promoted exfoliation and integrated CDs.

5. Sulfur-Doped g-C₃N₄

The doping of g-C₃N₄ with sulfur (S-g-C₃N₄) 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-C₃N₄ was performed by the thermal treatment under H₂S [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-C₃N₄ [107].

Li et al. applied thioacetamide (TAA) as a sulfur source for obtaining S-doped terminal-methylated g-C₃N₄ (SM-g-C₃N₄) 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-C₃N₄ was 90.5 m²·g^{−1} compared to 42.6 m²·g^{−1} of pristine g-C₃N₄. The XPS analysis revealed the increased C/N ratio in SM-g-C₃N₄ (1.26) compared to g-C₃N₄ (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-C₃N₄ samples with the increasing amount of TAA used for sulfur incorporation. The band gaps of SM-g-C₃N₄ nanosheets decreased from 2.62 (for g-C₃N₄) 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-C₃N₄ 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-C₃N₄ nanosheets and thus the separation of electron-hole pairs was improved.

Lv et al. combined doping of sulfur into g-C₃N₄ in situ and thermal oxidative etching treatment of obtained S-g-C₃N₄ [90]. The thermal oxidative etching caused the breaking of H-bonds between layers of g-C₃N₄ nanosheets and decreased their thickness to 4.0 nm. S-g-C₃N₄ nanosheets treated over 3 h demonstrated increased SSA to 226.9 m²·g^{−1} compared to 16.6 m²·g^{−1} for pristine g-C₃N₄.

An apparent blue shift of absorption band edge from 470 to 420 nm was demonstrated compared to pristine g-C₃N₄. However, in comparison with the analog without sulfur, the absorption band edge of S-g-C₃N₄ nanosheets was red-shifted by 5–10 nm. The band gap of pristine g-C₃N₄ 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-C₃N₄. The content of S in the S-g-C₃N₄ nanosheets and S-g-C₃N₄ 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-C₃N₄ 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-C₃N₄ nanosheets demonstrated highest capability for the separation of photogenerated charge carrier and this material was stable for up to 36 h during the photocatalytic H₂ evolution.

Ke et al. synthesized the graphene-like S-g-C₃N₄ 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 m²·g^{−1} of pristine g-C₃N₄ to 298.2 m²·g^{−1} of S-g-C₃N₄. 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-C₃N₄ to graphene-like S-g-C₃N₄ was achieved by weakening planar H-bonding when S partially replaced N. An obvious red shift of the absorption edges of S-g-C₃N₄ to 530 nm compared with that of g-C₃N₄ at 458 nm was observed (Figure 6a). Accordingly, the band gap energy decreased from 2.74 eV (g-C₃N₄) to 2.10 eV (S-g-C₃N₄) (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-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.

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

Figure 7. 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	-	O ₂ evolution; scheme H ₂ O splitting; bactericidal activity	400 W halide lamp ($\lambda_{\max}$ = 360 nm), 150 W Xe lamp, filter λ > 400 nm [Co(bpy) ₃]SO ₄ as electron mediator, Ru/SrTiO ₃ :Rh as cocatalyst	O ₂ evolution: 40.3 $\mu\text{mol}\cdot\text{h}^{-1}/$ - Z-scheme H ₂ O splitting: 29.3 $\mu\text{mol}\cdot\text{h}^{-1}/$ -; 70% of bacteria were killed	[96]
Melamine, (NH ₄) ₂ SO ₄	Upgraded gas templating method	—	H ₂ evolution	350 W Xe lamp, filter λ > 420 nm, 10% vol% TEOA, Pt co-catalyst (1 wt.%)	572 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}/$ 78 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	[106]
Urea, thioacetamide	One-pot copolymerization	0.1 at.% S 0.2 by XPS	Procion Red MX-5B degradation H ₂ evolution	500 W Xe lamp, monochromic light provided by using a 420 $\pm$ 15, 450 $\pm$ 15, 475 $\pm$ 15 and 520 $\pm$ 15 nm band pass filter TEOA, Pt co-catalyst (1 wt.%)	Dye degradation 0.072 min ⁻¹ /0.024 min ⁻¹ H ₂ evolution 3.17 mmol·g ⁻¹ ·h ⁻¹ / 0.84 mmol·g ⁻¹ ·h ⁻¹ 75%/100% of Phenol was decomposed;	[103]
Thiourea	Thermal polycondensation followed by thermal oxidative etching	S content: 0.45 by OEA, 1.58 by XPS	Phenol degradation; H ₂ evolution	300 W Xe lamp, 5% vol% TEOA, Pt co-catalyst (1 wt.%)	H ₂ evolution: 127.4 $\mu\text{mol}\cdot\text{h}^{-1}/$ 0.5 $\mu\text{mol}\cdot\text{h}^{-1}$	[90]
Thiourea, mesyl chloride	Post-synthetic derivatization of g-C ₃ N ₄	-	Acid Orange 7 dye degradation	UVA tube lamp, $\lambda_{\max}$ = 368 nm	0.113 min ⁻¹ /0.022 min ⁻¹	[99]
1,3,5-trichlorotriazine, Melamine, Trithiocyanuric acid	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]
Urea, benzyl disulfide	Thermal polycondensation, 520 °C	-	Reduction elimination of UO ₂ ²⁺	350 W Xe lamp, $\lambda \geq$ 420 nm	0.16 min ⁻¹ /0.07 min ⁻¹	[101]
Urea, thiourea	Thermal polycondensation, 550 °C	-	H ₂ evolution	300 W Xe lamp, filter λ > 420 nm, 10% vol% TEOA	95.3 $\mu\text{mol}\cdot\text{h}^{-1}/$ 36.4 $\mu\text{mol}\cdot\text{h}^{-1}$	[100]
Melamine, sulfuric acid	Sulfuring and sonicating bulk g-C ₃ N ₄	-	4-nitrophenol degradation	500 W Xe lamp, filter λ > 400 nm	3.47×10^{-2} min ⁻¹ / 7.04×10^{-4} min ⁻¹	[107]
Thiourea	Thermal polycondensation, 520 °C	S atomic% 0.05 by EA	CO ₂ reduction	300 W Xe lamp, Pt co-catalyst (1 wt.%)	CH ₃ OH formation: 1.12 $\mu\text{mol}\cdot\text{g}^{-1}/0.81 \mu\text{mol}\cdot\text{g}^{-1}$	[98]

6. P-Doped g-C₃N₄

To overcome the inherent drawbacks of g-C₃N₄ and to promote its photocatalytic activity, the doping of phosphorus into g-C₃N₄ (P-g-C₃N₄) 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-C₃N₄ was the thermal modification of pristine g-C₃N₄ 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-C₃N₄ nanosheets [118]. The increasing of SSA to 84.8 m²·g^{−1} was reached compared to 66.6 m²·g^{−1} of pristine g-C₃N₄. 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-C₃N₄ compared to 0.75 of pristine g-C₃N₄ was observed. The increasing of the O atomic% from 2.8% of pristine to 7.65% of the P-g-C₃N₄ nanosheets was ascribed to the higher content of C–OH bonds in the edge of g-C₃N₄ 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-C₃N₄ was suggested due to the red shift of emission peaks about 70 nm compared to pristine g-C₃N₄. The more effective photoinduced carrier separation was confirmed by the fluorescence decay study and the quantitative confirmation of PL quenching was obtained. The P-g-C₃N₄ 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 $n \rightarrow \pi^*$ 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-C₃N₄ 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 H₂ evolution was reached using the with P-g-C₃N₄ nanosheets.

The nano-structuring and P-doping strategy was implemented by Zhao et al. via a one-pot process for improvement of the g-C₃N₄ photocatalytic hydrogen evolution activity under visible light [121]. The aqueous solution of dicyandiamide, NH₄Cl (gas-template), and (NH₄)₂HPO₄ (P dopant) was freeze-dried and the obtained material was calcined at 550 °C over 4 h. The SSA of P-g-C₃N₄ was determined to be 36.4 m²·g^{−1}, which is higher than 5.5 m²·g^{−1} of pristine g-C₃N₄. The authors confirmed that the successful nano-structuring of g-C₃N₄ was due to the gas-template application. The XPS analysis evidenced the successful doping of P element in g-C₃N₄ and the probable replacement of C with P forming P–N bonds. P-g-C₃N₄ 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-C₃N₄ 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-C₃N₄ 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-C₃N₄. The photocurrent density of P-g-C₃N₄ was 0.51 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}\cdot\mu\text{A}^{-1}$ compared to 0.06 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}\cdot\mu\text{A}^{-1}$ of pristine g-C₃N₄.

P-doped tubular g-C₃N₄ (PT-g-C₃N₄) 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-C₃N₄ demonstrated the increasing of SSA from 8.6 to 24.5–32.4 m²·g^{−1} of pristine g-C₃N₄ and PT-g-C₃N₄

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-C₃N₄ 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-C₃N₄) to 0.69 (g-C₃N₄) due to carbon defects formation during the synthesis. It was also established that carbon defects exist only on the surface of g-C₃N₄ as the C/N mass ratio determined for pristine and PT-g-C₃N₄ 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-C₃N₄ tubes. The band gap of PT-g-C₃N₄ obtained from ammonium phosphate was calculated at 2.63 eV compared to 2.75 eV of g-C₃N₄. 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-C₃N₄ photocatalysts to reacting molecules was observed for the PT-g-C₃N₄ samples using electrochemical impedance spectroscopy (EIS).

Zhou et al. reported on the synthesis of P-g-C₃N₄ 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 H₂ evolution and the photodecomposition of organic dyes. The synthesized P-g-C₃N₄ demonstrated the increased SSA of 40.5 m²·g^{−1} compared to 26.86 m²·g^{−1} of pristine g-C₃N₄. The optical properties study revealed that the P-g-C₃N₄ possessed a little bit wider band gap (2.71 eV) compared to 2.69 eV of g-C₃N₄. The VB maximum for pristine and P-doped g-C₃N₄ 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-C₃N₄ 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 ³¹P NMR data revealed the P atoms location at corner-carbon and bay-carbon sites of g-C₃N₄. The authors suggested the formation of electron-rich state of P-g-C₃N₄, 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-C₃N₄) to −33.5 mV. The negatively charged surface of P-g-C₃N₄ 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-C₃N₄ should promote the rapid separation of photogenerated electrons and holes and, thus, favoring the photocatalytic activity of H₂ evolution and RhB degradation.

Figure 8. Scheme of a possible existing form of P atoms in the framework of g-C₃N₄ and its effect on the electronic and chemical properties of g-C₃N₄. 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.

Table 5. Synthetic methods, applications, and photocatalytic efficiency of P-doped g-C₃N₄.

Precursor	Synthetic Method	C/Doping Element Atomic Ratio, Doped (Pristine)	Photocatalytic Process	Conditions of the Process	Efficiency Doped/Pristine	References
g-C ₃ N ₄ , P powder	Thermal modification	P 2p signal at around 133.7 eV	H ₂ evolution	300 W Xe lamp ($\lambda > 300$ nm), filter $\lambda > 420$ nm, 10% vol% TEOA, Pt co-catalyst (3 wt.%)	$\lambda > 300$ nm 261.2 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ / 81.6 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ $\lambda > 420$ nm 171.6 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ / 81.6 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$	[109]
Urea, phosphonitrilic chloride	Thermal condensation	4.4 atomic% by EDS 5.72 atomic% by XPS	H ₂ O ₂ generation	Visible light irradiation (420 nm $\leq \lambda \leq 700$ nm)	1968 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ / 68 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$	[108]
NH ₄ SCN, NH ₄ PF ₆	Thermal condensation	—	RhB destruction	300 W Xe lamp, filter $\lambda > 420$ nm	0.09856 min ⁻¹ / 0.03679 min ⁻¹	[110]
g-C ₃ N ₄ , phosphorene	Mechanically mixing	1.8 wt. %	H ₂ evolution	300 W Xe lamp, filter $\lambda > 400$ nm, lactic acid (88 vol%)	571 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ / 43 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$	[117]
g-C ₃ N ₄ , sodium hypophosphite	Thermal treatment method	13.52 wt. %	RhB destruction	300 W Xe lamp, λ : 420–780 nm,	0.0525 min ⁻¹ / 0.0126min ⁻¹	[115]
Urea, adenosine phosphate	Thermal condensation followed by thermal exfoliation method	2.17 atomic%	H ₂ evolution	300 W Xe lamp, filters λ : 400, 420, 435, 450, 550 nm; 10% vol% TEOA, Pt co-catalyst (3 wt.%)	9523.7 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ / 458 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$	[118]
Urea, NH ₄ H ₂ PO ₂	Thermal condensation	—	H ₂ 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, NH ₄ Cl, (NH ₄) ₂ HPO ₄	Thermal condensation	1.53 wt% by EDS	H ₂ evolution	300 W Xe lamp, filter λ 420 nm, 10% vol% TEOA, Pt co-catalyst (3 wt.%)	33.2 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ / 10.7 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$	[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 C_{2N-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. 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 intra-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 NH_x 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 NH_x 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 element analysis; 0.67 (0.61) by XPS 1.87 (1.09) by EDX	Tetracycline hydrochloride (TC-HCl) and sulfamethoxazole (SMZ) destruction; H ₂ evolution	300 W Xe lamp, filter $\lambda > 420$ nm, Pt co-catalyst (1wt.%), TEOA	SMZ destruction: 0.0203 min ⁻¹ / 0.0066 min ⁻¹ ; H ₂ evolution: 5833.1 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$ / 1458.2 $\mu\text{mol}\cdot\text{g}^{-1}$	[133]
Urea, dicyandiamide	Post-thermal treatment of g-C ₃ N ₄	—	H ₂ evolution	Visible light irradiation	6.5 $\mu\text{mol}\cdot\text{g}^{-1}$ / 2.1 $\mu\text{mol}\cdot\text{g}^{-1}$	[137]
Melamine	Polymerization in atmosphere of: CCl ₄ ; H ₂ ; Ar	0.61 (0.65) by elemental analysis	H ₂ evolution	300W Xe lamp, filter $\lambda > 420$ 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 1.32 (1.64) by XPS	H ₂ O ₂ production	simulated sunlight lamp 20 vol% ethanol	152.6 $\mu\text{mol}\cdot\text{h}^{-1}$ / 10.2 $\mu\text{mol}\cdot\text{h}^{-1}$	[131]
Dicyandiamide, NH ₄ Cl, 3-amino-1,2,4-triazol	Thermal polymerization with post treatment in N ₂	1.260 (1.489) by element analysis	H ₂ evolution	300W Xe lamp, filter $\lambda > 400$ nm), Pt (3%), TEOA (10 vol%)	3882.5 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$ / 85.0 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	[134]
Urea, Mg powder	magnesium vapor etching	0.51 (0.78) by EDX 0.92 (1.14) by XPS	H ₂ evolution	300W Xe lamp, filter $\lambda > 400$ nm), Pt (3%), TEOA (10 vol%)	450 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$ / 225 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	[88]
Dicyandiamide	two-step calcination	0.81 (0.85) by XPS	N ₂ fixation	300W Xe lamp	NH ₄ ⁺ formation: 54 mmol·L ⁻¹ / 24 mmol·L ⁻¹	[139]
Urea, melamine	precursor preprocessing and thermolysis in N ₂	—	NO oxidation	LED lamp ($\lambda \geq 448$ 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.

The hierarchical O-g-C₃N₄ nanotubes obtained by thermal polycondensation of melamine exhibited significantly improved the photocatalytic CO₂ reduction performance under visible light irradiation in comparison with pristine g-C₃N₄ [43]. Compared with pristine g-C₃N₄, O-g-C₃N₄ 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 CO₂ uptake capacity. The photocatalytic activity was evaluated by the generation rates of CH₃OH as it was the main product of photocatalytic performance on both g-C₃N₄ and the nanotubes. The average CH₃OH generation rate of 0.88 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ was about five times higher than that produced by g-C₃N₄ (0.17 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$). The CH₃OH generation rate was approximately the same in three cycles (3 h). Thus, it was concluded that the highly active and stable O-g-C₃N₄ nanotubes are the promising photocatalysts for hydrocarbon fuel generation by the photocatalytic CO₂ reduction under visible light irradiation.

The direction for the design and synthesis of low-cost N-g-C₃N₄ materials for the photocatalytic CO₂ reduction under UV light was proposed by Mo et al. [62]. As photocatalysts they used N-g-C₃N₄ nanotubes obtained by the heating of supramolecular intermediate under NH₃, air, Ar, and N₂ 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 H₂. The highest CO formation rate of 103.6 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ was observed for pristine g-C₃N₄ (NH₃) that was obtained by the precursor thermal treatment in the NH₃ atmosphere. This rate was 17.0, 1.8, 2.7, and 2.8 times higher than that with g-C₃N₄ and the N-g-C₃N₄ materials, which were obtained by the thermal treatment in air, Ar, and N₂, respectively. The high photocatalytic activity of g-C₃N₄ (NH₃) 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-C₃N₄ with amino groups not only extended the lifetime of excited species, but also caused the strong Lewis basicity, which was beneficial for the CO₂ adsorption with further promotion of the CO₂ photoreduction. The CO formation rates with g-C₃N₄ (NH₃) photocatalyst was 15 and 13 times higher than those of TiO₂ (P25) and black phosphorus, respectively. The nitrogen-doped sp²-carbon (graphitic)-rich electrodes demonstrated high selectivity for the CO₂ reduction reaction products [148]. The authors evidenced that the host structure of nitrogen dopants was crucial for the catalytic activity observed.

The photocatalytic CO₂ reduction of amine-functionalized g-C₃N₄ obtained by its treatment with monoethanolamine was evaluated under UV light [58]. The amine-modified g-C₃N₄ demonstrated the considerable enhancement in the CO₂ conversion in comparison with pristine g-C₃N₄. The main products were found to be CH₃OH and CH₄. The pristine g-C₃N₄ was reported to have the photocatalytic CH₃OH-production rate of 0.26 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$ and only trace amount of CH₄, while the optimal amine-functionalized sample provided the similar CH₃OH production rate of 0.28 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$ and, further, the CH₄-production rate of 0.34 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$. Similar to Mo et al. [62], the high activity of the amine-functionalized photocatalyst was attributed to the enhancement of CO₂ adsorption and destabilization ability of g-C₃N₄ after the amine-functionalization treatment. The authors assumed that CO₂ was adsorbed on the surface of amine-functionalized g-C₃N₄ through acid-base interactivity with amino groups and formed HCO₃[−]. As HCO₃[−] was more active than linear CO₂ it promoted the formation of CH₄ [149]. It was shown that under the same conditions, CO₂ molecules formed CH₃OH [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-C₃N₄ fabricated by the thermal polycondensation of thiourea demonstrated enhanced activity in the photocatalytic reduction of CO₂ into hydrocarbon fuels under UV-Vis light irradiation in comparison with pristine g-C₃N₄ [98]. The main product of photocatalytic CO₂ reduction was CH₃OH. The CH₃OH yield with S-g-C₃N₄ was determined to be 1.12 $\mu\text{mol}\cdot\text{g}^{-1}$, whereas for pristine g-C₃N₄ it was 0.81 $\mu\text{mol}\cdot\text{g}^{-1}$. 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 $\mu\text{mol/h}$) was 5.2 times higher than that of g-C₃N₄ (1.70 $\mu\text{mol}\cdot\text{h}^{-1}$) 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 charge 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.

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 photoactivity 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 $\mu\text{mol}\cdot\text{h}^{-1}$, which is 17.8 times higher in comparison with 3.60 $\mu\text{mol}/\text{h}$ of 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 $\mu\text{mol}/\text{h}$ 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 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$ 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 $g\text{-C}_3\text{N}_4$ with increased crystallinity and boosted visible-light harvesting demonstrated improved performance of the photocatalytic H_2 evolution [133]. The hydrogen evolution rate $5833.1 \mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$ compared to $1447.8 \mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$ of pristine $g\text{-C}_3\text{N}_4$. The V- $g\text{-C}_3\text{N}_4$ 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 $g\text{-C}_3\text{N}_4$ 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 $g\text{-C}_3\text{N}_4$ 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- $g\text{-C}_3\text{N}_4$ with the inter-triazine vacancies compared to V- $g\text{-C}_3\text{N}_4$ with the intra-triazine vacancies due to stronger electron localization. The normalized reaction rate of inter-triazine V- $g\text{-C}_3\text{N}_4$ was 9 times higher than that of “vacancy-free” $g\text{-C}_3\text{N}_4$, and 2.2 times higher than that of intra-triazine V- $g\text{-C}_3\text{N}_4$.

The SM- $g\text{-C}_3\text{N}_4$ nanosheets demonstrated enhanced activity in the photocatalytic H_2 production compared to pristine $g\text{-C}_3\text{N}_4$ [103]. The average H_2 evolution rate was 3.80 times higher than that of $g\text{-C}_3\text{N}_4$. The study of H_2 production under irradiation with the wavelengths of 420, 450, 475, and 520 nm demonstrated that the activity of SM- $g\text{-C}_3\text{N}_4$ 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 $g\text{-C}_3\text{N}_4$ 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- $g\text{-C}_3\text{N}_4$ 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 VB potential. These factors caused the high H_2 production rate of $127.4 \mu\text{mol}\cdot\text{h}^{-1}$, which is about 250 times higher than that for pristine $g\text{-C}_3\text{N}_4$. There was a stronger reduction ability observed for the hydrogen evolution of electrons in the CB of S- $g\text{-C}_3\text{N}_4$.

The great increase of photocatalytic activity in the H_2 evolution under the visible-light irradiation was reached for the porous P- $g\text{-C}_3\text{N}_4$ nanosheets [118]. The total H_2 production for 4 h was 1813 and 30,281 μmol for pristine $g\text{-C}_3\text{N}_4$ and P- $g\text{-C}_3\text{N}_4$, respectively. The photocatalytic H_2 evolution rate was 458 and 9524 $\mu\text{mol}^{-1}\cdot\text{h}^{-1}$, respectively. The obtained P- $g\text{-C}_3\text{N}_4$ 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 $g\text{-C}_3\text{N}_4$ and to enhance the photocatalytic effect of hydrogen production. When the non-metal elements were applied to dope $g\text{-C}_3\text{N}_4$, 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- $g\text{-C}_3\text{N}_4$ 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- $g\text{-C}_3\text{N}_4$. The determined rate constants were 65 times and 24 times higher than those of $g\text{-C}_3\text{N}_4$, for RhB and MO degradation, respectively. The significant improvement of photocatalytic activity was explained by the porous layered structure of O- $g\text{-C}_3\text{N}_4$, its ability to reduce the recombination of photogenerated carriers, and increased absorption of visible light. Among the

possible active species ($O_2^{\bullet-}$, $OH^\bullet$, h^+) $O_2^{\bullet-}$ 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_3N_4 with PMS [17]. The dependence of the photocatalytic activity of the resulting O-g- C_3N_4 on the amount of oxidant was found. Huang et al. determined the optimal amount of PMS for obtaining the O-g- C_3N_4 photocatalyst with the highest activity for the decomposition of RhB under visible light. The mechanism of RhB degradation 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_3N_4 occurred through N-deethylation pathways. The study of the RhB degradation in the presence of various inhibitors of photoactive species formation confirmed that $O_2^{\bullet-}$ was the dominant oxidant in the studied photocatalytic system (Figure 12).

Figure 12. The scheme of the RhB photocatalytic degradation in the presence of O-g- C_3N_4 . Reprinted from [17].

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_3N_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 $O_2^{\bullet-}$ 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 $O_2^{\bullet-}$ became more facile.

In other research, 49.3 times higher photocatalytic degradation efficiency of 4-nitrophenol using S-g- C_3N_4 than that with pristine g- C_3N_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_3N_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_3N_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_3N_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_3N_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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References

1. Wang, X.; Maeda, K.; Thomas, A.; Takanabe, K.; Xin, G.; Carlsson, J.M.; Domen, K.; Antonietti, M. A metal-free polymeric photocatalyst for hydrogen production from water under visible light. *Nat. Mater.* **2009**, *8*, 76–80. [[CrossRef](#)] [[PubMed](#)]
2. Dong, G.; Zhang, Y.; Pan, Q.; Qiu, J. A fantastic graphitic carbon nitride (g-C₃N₄) material: Electronic structure, photocatalytic and photoelectronic properties. *J. Photochem. Photobiol. C Photochem. Rev.* **2014**, *20*, 33–50. [[CrossRef](#)]
3. Kroke, E. Novel group 14 nitrides. *Coord. Chem. Rev.* **2004**, *248*, 493–532. [[CrossRef](#)]
4. Ong, W.-J.; Tan, L.-L.; Ng, Y.H.; Yong, S.-T.; Chai, S.-P. Graphitic Carbon Nitride (g-C₃N₄)-Based Photocatalysts for Artificial Photosynthesis and Environmental Remediation: Are We a Step Closer To Achieving Sustainability? *Chem. Rev.* **2016**, *116*, 7159–7329. [[CrossRef](#)] [[PubMed](#)]
5. Hasija, V.; Raizada, P.; Sudhaik, A.; Sharma, K.; Kumar, A.; Singh, P.; Jonnalagadda, S.B.; Thakur, V.K. Recent advances in noble metal free doped graphitic carbon nitride based nanohybrids for photocatalysis of organic contaminants in water: A review. *Appl. Mater. Today* **2019**, *15*, 494–524. [[CrossRef](#)]
6. Zhou, Z.; Zhang, Y.; Shen, Y.; Liu, S.; Zhang, Y. Molecular engineering of polymeric carbon nitride: Advancing applications from photocatalysis to biosensing and more. *Chem. Soc. Rev.* **2018**, *47*, 2298–2321. [[CrossRef](#)]
7. Wang, A.; Wang, C.; Fu, L.; Wong-Ng, W.; Lan, Y. Recent Advances of Graphitic Carbon Nitride-Based Structures and Applications in Catalyst, Sensing, Imaging, and LEDs. *Nano-Micro Lett.* **2017**, *9*, 47. [[CrossRef](#)]
8. Masih, D.; Ma, Y.; Rohani, S. Graphitic C₃N₄ based noble-metal-free photocatalyst systems: A review. *Appl. Catal. B Environ.* **2017**, *206*, 556–588. [[CrossRef](#)]
9. Fu, J.; Yu, J.; Jiang, C.; Cheng, B. g-C₃N₄-Based Heterostructured Photocatalysts. *Adv. Energy Mater.* **2018**, *8*, 1701503, (1–31). [[CrossRef](#)]

10. Zhao, Z.; Sun, Y.; Dong, F. Graphitic carbon nitride based nanocomposites: A review. *Nanoscale* **2015**, *7*, 15–37. [\[CrossRef\]](#)
11. Chen, W.; Jiang, D.; Zhu, M.Y.; Shi, T.Y.; Li, H.N.; Wang, K. An effective strategy for fabricating highly dispersed nanoparticles on O-C₃N₄ with enhanced electrocatalytic activity and stability. *J. Alloy. Compd.* **2018**, *741*, 1203–1211. [\[CrossRef\]](#)
12. Yousefi, M.; Villar-Rodil, S.; Paredes, J.I.; Moshfegh, A.Z. Oxidized graphitic carbon nitride nanosheets as an effective adsorbent for organic dyes and tetracycline for water remediation. *J. Alloy. Compd.* **2019**, *809*, 11. [\[CrossRef\]](#)
13. Zhu, W.R.; Hao, N.; Lu, J.W.; Dai, Z.; Qian, J.; Yang, X.D.; Wang, K. Highly active metal-free peroxidase mimics based on oxygen-doped carbon nitride by promoting electron transfer capacity. *Chem. Commun.* **2020**, *56*, 1409–1412. [\[CrossRef\]](#) [\[PubMed\]](#)
14. Chubenko, E.B.; Baglov, A.V.; Leonenya, M.S.; Yablonskii, G.P.; Borisenko, V.E. Structure of Photoluminescence Spectra of Oxygen-Doped Graphitic Carbon Nitride. *J. Appl. Spectrosc.* **2020**, *87*, 9–14. [\[CrossRef\]](#)
15. Denisov, N.M.; Chubenko, E.B.; Bondarenko, V.P.; Borisenko, V.E. Synthesis of Oxygen-Doped Graphitic Carbon Nitride from Thiourea. *Tech. Phys. Lett.* **2019**, *45*, 108–110. [\[CrossRef\]](#)
16. Gao, Y.W.; Zhu, Y.; Lyu, L.; Zeng, Q.Y.; Xing, X.C.; Hu, C. Electronic Structure Modulation of Graphitic Carbon Nitride by Oxygen Doping for Enhanced Catalytic Degradation of Organic Pollutants through Peroxymonosulfate Activation. *Environ. Sci. Technol.* **2018**, *52*, 14371–14380. [\[CrossRef\]](#)
17. Huang, J.; Nie, G.; Ding, Y.B. Metal-Free Enhanced Photocatalytic Activation of Dioxygen by g-C₃N₄ Doped with Abundant Oxygen-Containing Functional Groups for Selective N-Deethylation of Rhodamine B. *Catalysts* **2020**, *10*, 6. [\[CrossRef\]](#)
18. Huang, T.; Pan, S.G.; Shi, L.L.; Yu, A.P.; Wang, X.; Fu, Y.S. Hollow porous prismatic graphitic carbon nitride with nitrogen vacancies and oxygen doping: A high-performance visible light-driven catalyst for nitrogen fixation. *Nanoscale* **2020**, *12*, 1833–1841. [\[CrossRef\]](#)
19. Li, F.; Han, M.E.; Jin, Y.; Zhang, L.L.; Li, T.; Gao, Y.W.; Hu, C. Internal electric field construction on dual oxygen group-doped carbon nitride for enhanced photodegradation of pollutants under visible light irradiation. *Appl. Catal. B Environ.* **2019**, *256*, 10. [\[CrossRef\]](#)
20. Liu, C.Y.; Huang, H.W.; Cui, W.; Dong, F.; Zhang, Y.H. Band structure engineering and efficient charge transport in oxygen substituted g-C₃N₄ for superior photocatalytic hydrogen evolution. *Appl. Catal. B Environ.* **2018**, *230*, 115–124. [\[CrossRef\]](#)
21. Li, Q.; Wang, S.C.; Sun, Z.X.; Tang, Q.J.; Liu, Y.Q.; Wang, L.Z.; Wang, H.Q.; Wu, Z.B. Enhanced CH₄ selectivity in CO₂ photocatalytic reduction over carbon quantum dots decorated and oxygen doping g-C₃N₄. *Nano Res.* **2019**, *12*, 2749–2759. [\[CrossRef\]](#)
22. Wei, F.Y.; Liu, Y.; Zhao, H.; Ren, X.N.; Liu, J.; Hasan, T.; Chen, L.H.; Li, Y.; Su, B.L. Oxygen self-doped g-C₃N₄ with tunable electronic band structure for unprecedentedly enhanced photocatalytic performance. *Nanoscale* **2018**, *10*, 4515–4522. [\[CrossRef\]](#) [\[PubMed\]](#)
23. Chen, H.; Yao, J.H.; Qiu, P.X.; Xu, C.M.; Jiang, F.; Wang, X. Facile surfactant assistant synthesis of porous oxygen-doped graphitic carbon nitride nanosheets with enhanced visible light photocatalytic activity. *Mater. Res. Bull.* **2017**, *91*, 42–48. [\[CrossRef\]](#)
24. Putri, L.K.; Ng, B.J.; Er, C.C.; Ong, W.J.; Chang, W.S.; Mohamed, A.R.; Chai, S.P. Insights on the impact of doping levels in oxygen-doped gC(3)N(4) and its effects on photocatalytic activity. *Appl. Surf. Sci.* **2020**, *504*. [\[CrossRef\]](#)
25. Sun, S.D.; Li, J.; Cui, J.; Gou, X.F.; Yang, Q.; Liang, S.H.; Yang, Z.M.; Zhang, J.M. Constructing oxygen-doped g-C₃N₄ nanosheets with an enlarged conductive band edge for enhanced visible-light-driven hydrogen evolution. *Inorg. Chem. Front.* **2018**, *5*, 1721–1727. [\[CrossRef\]](#)
26. Chen, Y.L.; Liu, X.Q.; Hou, L.; Guo, X.R.; Fu, R.W.; Sun, J.M. Construction of covalent bonding oxygen-doped carbon nitride/graphitic carbon nitride Z-scheme heterojunction for enhanced visible-light-driven H₂ evolution. *Chem. Eng. J.* **2020**, *383*. [\[CrossRef\]](#)
27. Sun, Z.Z.; Wang, W.; Chen, Q.W.; Pu, Y.Y.; He, H.; Zhuang, W.M.; He, J.Q.; Huang, L.M. A hierarchical carbon nitride tube with oxygen doping and carbon defects promotes solar-to-hydrogen conversion. *J. Mater. Chem. A* **2020**, *8*, 3160–3167. [\[CrossRef\]](#)

28. Yuan, X.J.; Xie, R.L.; Zhang, Q.; Sun, L.; Long, X.J.; Xia, D.S. Oxygen functionalized graphitic carbon nitride as an efficient metal-free ozonation catalyst for atrazine removal: Performance and mechanism. *Sep. Purif. Technol.* **2019**, *211*, 823–831. [[CrossRef](#)]
29. Zeng, Y.X.; Liu, X.; Liu, C.B.; Wang, L.L.; Xia, Y.C.; Zhang, S.Q.; Luo, S.L.; Pei, Y. Scalable one-step production of porous oxygen-doped g-C₃N₄ nanorods with effective electron separation for excellent visible-light photocatalytic activity. *Appl. Catal. B Environ.* **2018**, *224*, 1–9. [[CrossRef](#)]
30. Zhang, C.; Zhang, M.Y.; Li, Y.; Shuai, D.M. Visible-light-driven photocatalytic disinfection of human adenovirus by a novel heterostructure of oxygen-doped graphitic carbon nitride and hydrothermal carbonation carbon. *Appl. Catal. B Environ.* **2019**, *248*, 11–21. [[CrossRef](#)]
31. Wang, Y.X.; Wang, H.; Chen, F.Y.; Cao, F.; Zhao, X.H.; Meng, S.G.; Cui, Y.J. Facile synthesis of oxygen doped carbon nitride hollow microsphere for photocatalysis. *Appl. Catal. B Environ.* **2017**, *206*, 417–425. [[CrossRef](#)]
32. Mei, R.G.; Ma, L.; An, L.A.; Wang, F.; Xi, J.J.; Sun, H.Y.; Luo, Z.K.; Wu, Q.X. Layered Spongy-like O-Doped g-C₃N₄: An Efficient Non-Metal Oxygen Reduction Catalyst for Alkaline Fuel Cells. *J. Electrochem. Soc.* **2017**, *164*, F354–F363. [[CrossRef](#)]
33. Wang, C.; Fan, H.Q.; Ren, X.H.; Ma, J.W.; Fang, J.W.; Wang, W.J. Hydrothermally Induced Oxygen Doping of Graphitic Carbon Nitride with a Highly Ordered Architecture and Enhanced Photocatalytic Activity. *Chemsuschem* **2018**, *11*, 700–708. [[CrossRef](#)] [[PubMed](#)]
34. Wang, H.; Guan, Y.H.; Hu, S.Z.; Pei, Y.B.; Ma, W.T.; Fan, Z.P. Hydrothermal Synthesis of Band Gap-Tunable Oxygen-Doped g-C₃N₄ with Outstanding “Two-Channel” Photocatalytic H₂O₂ Production Ability Assisted by Dissolution-Precipitation Process. *Nano* **2019**, *14*. [[CrossRef](#)]
35. Zhang, B.; Li, X.J.; Zhao, Y.; Song, H.; Wang, H. Facile synthesis of oxygen doped mesoporous graphitic carbon nitride with high photocatalytic degradation efficiency under simulated solar irradiation. In *Colloids and Surfaces a-Physicochemical and Engineering Aspects*; Elsevier: Amsterdam, The Netherlands, 2019; Volume 580. [[CrossRef](#)]
36. Zhang, J.W.; Gong, S.; Mahmood, N.; Pan, L.; Zhang, X.W.; Zou, J.J. Oxygen-doped nanoporous carbon nitride via water-based homogeneous supramolecular assembly for photocatalytic hydrogen evolution. *Appl. Catal. B Environ.* **2018**, *221*, 9–16. [[CrossRef](#)]
37. Zhu, K.; Ouyang, J.; Liu, J.M.; Zhu, Y.X.; Zeng, Q.; Cui, Y.J. Preparation and Photocatalytic Hydrogen Evolution from Water of Oxygen Doped Carbon Nitride Nanosheets. *Chin. J. Inorg. Chem.* **2019**, *35*, 1005–1012. [[CrossRef](#)]
38. Zhu, Y.; Chen, Z.H.; Gao, Y.W.; Hu, C. General synthesis of carbon and oxygen dual-doped graphitic carbon nitride via copolymerization for non-photochemical oxidation of organic pollutant. *J. Hazard. Mater.* **2020**, *394*. [[CrossRef](#)]
39. Tang, R.; Ding, R.L.; Xie, X.C. Preparation of oxygen-doped graphitic carbon nitride and its visible-light photocatalytic performance on bisphenol A degradation. *Water Sci. Technol.* **2018**, *78*, 1023–1033. [[CrossRef](#)]
40. Wang, Y.X.; Rao, L.; Wang, P.F.; Guo, Y.; Guo, X.; Zhang, L.X. Porous oxygen-doped carbon nitride: Supramolecular preassembly technology and photocatalytic degradation of organic pollutants under low-intensity light irradiation. *Environ. Sci. Pollut. Res.* **2019**, *26*, 15710–15723. [[CrossRef](#)]
41. Zhang, S.; Liu, Y.; Gu, P.C.; Ma, R.; Wen, T.; Zhao, G.X.; Li, L.; Ai, Y.J.; Hu, C.; Wang, X.K. Enhanced photodegradation of toxic organic pollutants using dual-oxygen-doped porous g-C₃N₄: Mechanism exploration from both experimental and DFT studies. *Appl. Catal. B Environ.* **2019**, *248*, 1–10. [[CrossRef](#)]
42. Song, P.; Liang, S.H.; Cui, J.; Ren, D.; Duan, R.Y.; Yang, Q.; Sun, S.D. Purposefully designing novel hydroxylated and carbonylated melamine towards the synthesis of targeted porous oxygen-doped g-C₃N₄ nanosheets for highly enhanced photocatalytic hydrogen production. *Catal. Sci. Technol.* **2019**, *9*, 5150–5159. [[CrossRef](#)]
43. Fu, J.W.; Zhu, B.C.; Jiang, C.J.; Cheng, B.; You, W.; Yu, J.G. Hierarchical Porous O-Doped g-C₃N₄ with Enhanced Photocatalytic CO₂ Reduction Activity. *Small* **2017**, *13*, 9. [[CrossRef](#)] [[PubMed](#)]
44. Miller, D.R.; Wang, J.J.; Gillan, E.G. Rapid, facile synthesis of nitrogen-rich carbon nitride powders. *J. Mater. Chem.* **2002**, *12*, 2463–2469. [[CrossRef](#)]
45. Miller, D.R.; Swenson, D.C.; Gillan, E.G. Synthesis and structure of 2,5,8-triazido-s-heptazine: An energetic and luminescent precursor to nitrogen-rich carbon nitrides. *J. Am. Chem. Soc.* **2004**, *126*, 5372–5373. [[CrossRef](#)]

46. Miller, D.R.; Holst, J.R.; Gillan, E.G. Nitrogen-rich carbon nitride network materials via the thermal decomposition of 2,5,8-triazido-s-heptazine. *Inorg. Chem.* **2007**, *46*, 2767–2774. [\[CrossRef\]](#)
47. Huynh, M.H.V.; Hiskey, M.A.; Archuleta, J.G.; Roemer, E.L.; Gilardi, R. 3,6-di(azido)-1,2,4,5-tetrazine: A precursor for the preparation of carbon nanospheres and nitrogen-rich carbon nitrides. *Angew. Chem. Int. Edit.* **2004**, *43*, 5658–5661. [\[CrossRef\]](#)
48. Gillan, E.G. Synthesis of nitrogen-rich carbon nitride networks from an energetic molecular azide precursor. *Chem. Mat.* **2000**, *12*, 3906–3912. [\[CrossRef\]](#)
49. Fang, J.W.; Fan, H.Q.; Li, M.M.; Long, C.B. Nitrogen self-doped graphitic carbon nitride as efficient visible light photocatalyst for hydrogen evolution. *J. Mater. Chem. A* **2015**, *3*, 13819–13826. [\[CrossRef\]](#)
50. Xu, Q.X.; Xu, G.Q.; Yu, Q.B.; Yang, K.; Li, H.Q. Nitrogen self-doped high specific surface area graphite carbon nitride for photocatalytic degrading of methylene blue. *J. Nanopart. Res.* **2019**, *21*, 13. [\[CrossRef\]](#)
51. Guo, F.; Wang, L.J.; Sun, H.R.; Li, M.Y.; Shi, W.L. High-efficiency photocatalytic water splitting by a N-doped porous g-C₃N₄ nanosheet polymer photocatalyst derived from urea and N,N-dimethylformamide. *Inorg. Chem. Front.* **2020**, *7*, 1770–1779. [\[CrossRef\]](#)
52. Jiang, L.B.; Yuan, X.Z.; Zeng, G.M.; Liang, J.; Wu, Z.B.; Yu, H.B.; Mo, D.; Wang, H.; Xiao, Z.H.; Zhou, C.Y. Nitrogen self-doped g-C₃N₄ nanosheets with tunable band structures for enhanced photocatalytic tetracycline degradation. *J. Colloid Interface Sci.* **2019**, *536*, 17–29. [\[CrossRef\]](#) [\[PubMed\]](#)
53. Wang, H.H.; Li, Q.; Zhang, S.; Chen, Z.S.; Wang, W.X.; Zhao, G.X.; Zhuang, L.; Hu, B.W.; Wang, X.K. Visible-light-driven N-2-g-C₃N₄ as a highly stable and efficient photocatalyst for bisphenol A and Cr(VI) removal in binary systems. *Catal. Today* **2019**, *335*, 110–116. [\[CrossRef\]](#)
54. Dong, S.S.; Liu, C.; Chen, Y.G. Boosting exciton dissociation and molecular oxygen activation by in-plane grafting nitrogen-doped carbon nanosheets to graphitic carbon nitride for enhanced photocatalytic performance. *J. Colloid Interface Sci.* **2019**, *553*, 59–70. [\[CrossRef\]](#) [\[PubMed\]](#)
55. Qi, H.L.; Liu, Y.N.; Li, C.Y.; Zou, X.H.; Huang, Y.D.; Wang, Y.G. Precursor-reforming protocol to synthesis of porous N-doped g-C₃N₄ for highly improved photocatalytic water treatments. *Mater. Lett.* **2020**, *264*, 4. [\[CrossRef\]](#)
56. Che, H.N.; Che, G.B.; Zhou, P.J.; Liu, C.B.; Dong, H.J.; Li, C.X.; Song, N.; Li, C.M. Nitrogen doped carbon ribbons modified g-C₃N₄ for markedly enhanced photocatalytic H₂-production in visible to near-infrared region. *Chem. Eng. J.* **2020**, *382*, 9. [\[CrossRef\]](#)
57. Hao, Q.G.; Song, Y.H.; Ji, H.Y.; Mo, Z.; She, X.J.; Deng, J.J.; Muhmood, T.; Wu, X.Y.; Yuan, S.Q.; Xu, H.; et al. Surface N modified 2D g-C₃N₄ nanosheets derived from DMF for photocatalytic H₂ evolution. *Appl. Surf. Sci.* **2018**, *459*, 845–852. [\[CrossRef\]](#)
58. Huang, Q.; Yu, J.G.; Cao, S.W.; Cui, C.; Cheng, B. Efficient photocatalytic reduction of CO₂ by amine-functionalized g-C₃N₄. *Appl. Surf. Sci.* **2015**, *358*, 350–355. [\[CrossRef\]](#)
59. Yan, J.; Zhou, C.J.; Li, P.R.; Chen, B.H.; Zhang, S.S.; Dong, X.P.; Xi, F.N.; Liu, J.Y. Nitrogen-rich graphitic carbon nitride: Controllable nanosheet-like morphology, enhanced visible light absorption and superior photocatalytic performance. *Colloids Surf. A Physicochem. Eng. Asp.* **2016**, *508*, 257–264. [\[CrossRef\]](#)
60. Gao, B.R.; Wang, J.; Dou, M.M.; Huang, X.; Yu, X.X. Novel nitrogen-rich g-C₃N₄ with adjustable energy band by introducing triazole ring for cefotaxime removal. *Sep. Purif. Technol.* **2020**, *241*, 9. [\[CrossRef\]](#)
61. Wu, X.H.; Gao, D.D.; Wang, P.; Yu, H.G.; Yu, J.G. NH₄Cl-induced low-temperature formation of nitrogen-rich g-C₃N₄ nanosheets with improved photocatalytic hydrogen evolution. *Carbon* **2019**, *153*, 757–766. [\[CrossRef\]](#)
62. Mo, Z.; Zhu, X.W.; Jiang, Z.F.; Song, Y.H.; Liu, D.B.; Li, H.P.; Yang, X.F.; She, Y.B.; Lei, Y.C.; Yuan, S.Q.; et al. Porous nitrogen-rich g-C₃N₄ nanotubes for efficient photocatalytic CO₂ reduction. *Appl. Catal. B Environ.* **2019**, *256*, 7. [\[CrossRef\]](#)
63. Zhou, Y.J.; Zhang, L.X.; Huang, W.M.; Kong, Q.L.; Fan, X.Q.; Wang, M.; Shi, J.L. N-doped graphitic carbon-incorporated g-C₃N₄ for remarkably enhanced photocatalytic H₂ evolution under visible light. *Carbon* **2016**, *99*, 111–117. [\[CrossRef\]](#)
64. Tian, N.; Zhang, Y.H.; Li, X.W.; Xiao, K.; Du, X.; Dong, F.; Waterhouse, G.I.N.; Zhang, T.R.; Huang, H.W. Precursor-reforming protocol to 3D mesoporous g-C₃N₄ established by ultrathin self-doped nanosheets for superior hydrogen evolution. *Nano Energy* **2017**, *38*, 72–81. [\[CrossRef\]](#)
65. Wu, M.; Gong, Y.S.; Nie, T.; Zhang, J.; Wang, R.; Wang, H.W.; He, B.B. Template-free synthesis of nanocage-like g-C₃N₄ with high surface area and nitrogen defects for enhanced photocatalytic H₂ activity. *J. Mater. Chem. A* **2019**, *7*, 5324–5332. [\[CrossRef\]](#)

66. Wang, F.L.; Chen, P.; Feng, Y.P.; Xie, Z.J.; Liu, Y.; Su, Y.H.; Zhang, Q.X.; Wang, Y.F.; Yao, K.; Lv, W.Y.; et al. Facile synthesis of N-doped carbon dots/g-C₃N₄ photocatalyst with enhanced visible-light photocatalytic activity for the degradation of indomethacin. *Appl. Catal. B Environ.* **2017**, *207*, 103–113. [[CrossRef](#)]
67. Asadzadeh-Khaneghah, S.; Habibi-Yangjeh, A.; Nakata, K. Decoration of carbon dots over hydrogen peroxide treated graphitic carbon nitride: Exceptional photocatalytic performance in removal of different contaminants under visible light. *J. Photochem. Photobiol. A Chem.* **2019**, *374*, 161–172. [[CrossRef](#)]
68. Deng, P.H.; Li, H.Y.; Wang, Z.D.; Hou, Y. Enhanced photocatalytic hydrogen evolution by carbon-doped carbon nitride synthesized via the assistance of cellulose. *Appl. Surf. Sci.* **2020**, *504*. [[CrossRef](#)]
69. Duan, Y.; Deng, L.; Shi, Z.; Liu, X.; Zeng, H.X.; Zhang, H.J.; Crittenden, J. Efficient sulfadiazine degradation via in-situ epitaxial grow of Graphitic Carbon Nitride (g-C₃N₄) on carbon dots heterostructures under visible light irradiation: Synthesis, mechanisms and toxicity evaluation. *J. Colloid Interface Sci.* **2020**, *561*, 696–707. [[CrossRef](#)]
70. Jeong, T.; Piao, H.; Park, S.; Yang, J.H.; Choi, G.; Wu, Q.; Kang, H.; Woo, H.J.; Jung, S.J.; Kim, H.; et al. Atomic and electronic structures of graphene-decorated graphitic carbon nitride (g-C₃N₄) as a metal-free photocatalyst under visible-light. *Appl. Catal. B Environ.* **2019**, *256*, 7. [[CrossRef](#)]
71. Cao, J.S.; Fan, H.Q.; Wang, C.; Ma, J.W.; Dong, G.Z.; Zhang, M.C. Facile synthesis of carbon self-doped g-C₃N₄ for enhanced photocatalytic hydrogen evolution. *Ceram. Int.* **2020**, *46*, 7888–7895. [[CrossRef](#)]
72. Chatzoudis, A.; Giannopoulos, V.; Hollmann, F.; Smonou, I. Surface-Doped Graphitic Carbon Nitride Catalyzed Photooxidation of Olefins and Dienes: Chemical Evidence for Electron Transfer and Singlet Oxygen Mechanisms. *Catalysts* **2019**, *9*, 639. [[CrossRef](#)]
73. Ge, F.Y.; Xu, Y.G.; Zhou, Y.H.; Tian, D.; Huang, S.Q.; Xie, M.; Xu, H.; Li, H.M. Surface amorphous carbon doping of carbon nitride for efficient acceleration of electron transfer to boost photocatalytic activities. *Appl. Surf. Sci.* **2020**, *507*. [[CrossRef](#)]
74. Li, Z.H.; Huang, D.L.; Zhou, C.Y.; Xue, W.J.; Lei, L.; Deng, R.; Yang, Y.; Chen, S.; Wang, W.J.; Wang, Z.W. Metal-free carbon nitride with boosting photo-redox ability realized by the controlled carbon dopants. *Chem. Eng. J.* **2020**, *382*. [[CrossRef](#)]
75. Liu, H.P.; Liang, J.; Fu, S.; Li, L.; Cui, J.H.; Gao, P.H.; Zhao, F.Y.; Zhou, J.G. N doped carbon quantum dots modified defect-rich g-C₃N₄ for enhanced photocatalytic combined pollutions degradation and hydrogen evolution. *Colloids Surf. A Physicochem. Eng. Asp.* **2020**, *591*, 13. [[CrossRef](#)]
76. Long, D.; Chen, W.L.; Rao, X.; Zheng, S.H.; Zhang, Y.P. Synergetic effect of C-60/g-C₃N₄ nanowire composites for enhanced photocatalytic H₂ evolution under visible light irradiation. *ChemCatChem* **2020**, *12*, 2022–2031. [[CrossRef](#)]
77. Meng, L.R.; Yin, W.H.; Wang, S.S.; Wu, X.G.; Hou, J.H.; Yin, W.Q.; Feng, K.; Ok, Y.S.; Wang, X.Z. Photocatalytic behavior of biochar-modified carbon nitride with enriched visible-light reactivity. *Chemosphere* **2020**, *239*. [[CrossRef](#)]
78. Wang, X.F.; Cheng, J.J.; Yu, H.G.; Yu, J.G. A facile hydrothermal synthesis of carbon dots modified g-C₃N₄ for enhanced photocatalytic H₂-evolution performance. *Dalton Trans.* **2017**, *46*, 6417–6424. [[CrossRef](#)] [[PubMed](#)]
79. Wang, Y.M.; Cai, H.Y.; Qian, F.F.; Li, Y.M.; Yu, J.Q.; Yang, X.L.; Bao, M.T.; Li, X.M. Facile one-step synthesis of onion-like carbon modified ultrathin g-C₃N₄ 2D nanosheets with enhanced visible-light photocatalytic performance. *J. Colloid Interface Sci.* **2019**, *533*, 47–58. [[CrossRef](#)] [[PubMed](#)]
80. Huang, Y.Y.; Li, D.; Fang, Z.Y.; Chen, R.J.; Luo, B.F.; Shi, W.D. Controlling carbon self-doping site of g-C₃N₄ for highly enhanced visible-light-driven hydrogen evolution. *Appl. Catal. B Environ.* **2019**, *254*, 128–134. [[CrossRef](#)]
81. Li, X.L.; Bai, J.F.; Li, J.Q.; Li, C.; Zhong, X.Y.; Deng, S.P. The effect of n-pi* electronic transitions on the N-2 photofixation ability of carbon self-doped honeycomb-like g-C₃N₄ prepared via microwave treatment. *RSC Adv.* **2020**, *10*, 7019–7025. [[CrossRef](#)]
82. Ran, M.X.; Li, J.R.; Cui, W.; Li, Y.H.; Li, P.D.; Dong, F. Efficient and stable photocatalytic NO removal on C self-doped g-C₃N₄: Electronic structure and reaction mechanism. *Catal. Sci. Technol.* **2018**, *8*, 3387–3394. [[CrossRef](#)]
83. Xu, Q.L.; Jiang, C.J.; Cheng, B.; Yu, J.G. Enhanced visible-light photocatalytic H₂-generation activity of carbon/g-C₃N₄ nanocomposites prepared by two-step thermal treatment. *Dalton Trans.* **2017**, *46*, 10611–10619. [[CrossRef](#)] [[PubMed](#)]

84. Xu, J.; Huang, J.; Wang, Z.P.; Zhu, Y.F. Enhanced visible-light photocatalytic degradation and disinfection performance of oxidized nanoporous g-C₃N₄ via decoration with graphene oxide quantum dots. *Chin. J. Catal.* **2020**, *41*, 474–484. [\[CrossRef\]](#)
85. Bao, N.; Hu, X.D.; Zhang, Q.Z.; Miao, X.H.; Jie, X.Y.; Zhou, S. Synthesis of porous carbon-doped g-C₃N₄ nanosheets with enhanced visible-light photocatalytic activity. *Appl. Surf. Sci.* **2017**, *403*, 682–690. [\[CrossRef\]](#)
86. Chen, Z.; Fan, T.T.; Yu, X.; Wu, Q.L.; Zhu, Q.H.; Zhang, L.Z.; Li, J.H.; Fang, W.P.; Yi, X.D. Gradual carbon doping of graphitic carbon nitride towards metal-free visible light photocatalytic hydrogen evolution. *J. Mater. Chem. A* **2018**, *6*, 15310–15319. [\[CrossRef\]](#)
87. Luo, L.; Ma, J.N.; Zhu, H.X.; Tang, J.W. Embedded carbon in a carbon nitride hollow sphere for enhanced charge separation and photocatalytic water splitting. *Nanoscale* **2020**, *12*, 7339–7346. [\[CrossRef\]](#)
88. Li, J.X.; Ma, W.Q.; Chen, J.J.; An, N.; Zhao, Y.; Wang, D.J.; Mao, Z.Y. Carbon vacancies improved photocatalytic hydrogen generation of g-C₃N₄ photocatalyst via magnesium vapor etching. *Int. J. Hydrogen Energy* **2020**, *45*, 13939–13946. [\[CrossRef\]](#)
89. Ma, L.; Hu, S.Z.; Li, P.; Wang, Q.; Ma, H.F.; Li, W. In situ synthesis of sulfur doped carbon nitride with enhanced photocatalytic performance using DBD plasma treatment under H₂S atmosphere. *J. Phys. Chem. Solids* **2018**, *118*, 166–171. [\[CrossRef\]](#)
90. Lv, H.Q.; Huang, Y.; Koodali, R.T.; Liu, G.M.; Zeng, Y.B.; Meng, Q.G.; Yuan, M.Z. Synthesis of Sulfur-Doped 2D Graphitic Carbon Nitride Nanosheets for Efficient Photocatalytic Degradation of Phenol and Hydrogen Evolution. *ACS Appl. Mater. Interfaces* **2020**, *12*, 12656–12667. [\[CrossRef\]](#)
91. Wang, W.J.; Zeng, Z.T.; Zeng, G.M.; Zhang, C.; Xiao, R.; Zhou, C.Y.; Xiong, W.P.; Yang, Y.; Lei, L.; Liu, Y.; et al. Sulfur doped carbon quantum dots loaded hollow tubular g-C₃N₄ as novel photocatalyst for destruction of *Escherichia coli* and tetracycline degradation under visible light. *Chem. Eng. J.* **2019**, *378*, 11. [\[CrossRef\]](#)
92. Joseph, S.; Abraham, S.; Priyanka, R.N.; Abraham, T.; Suresh, A.; Mathew, B. In situ S-doped ultrathin gC(3)N(4) nanosheets coupled with mixed-dimensional (3D/1D) nanostructures of silver vanadates for enhanced photocatalytic degradation of organic pollutants. *New J. Chem.* **2019**, *43*, 10618–10630. [\[CrossRef\]](#)
93. Sakthivel, A.; Chandrasekaran, A.; Jayakumar, S.; Manickam, P.; Alwarappan, S. Sulphur Doped Graphitic Carbon Nitride as an Efficient Electrochemical Platform for the Detection of Acetaminophen. *J. Electrochem. Soc.* **2019**, *166*, B1461–B1469. [\[CrossRef\]](#)
94. Fang, Y.X.; Li, X.C.; Wang, Y.; Giordano, C.; Wang, X.C. Gradient sulfur doping along polymeric carbon nitride films as visible light photoanodes for the enhanced water oxidation. *Appl. Catal. B Environ.* **2020**, *268*, 6. [\[CrossRef\]](#)
95. Fan, Q.J.; Liu, J.J.; Yu, Y.C.; Zuo, S.L.; Li, B.S. A simple fabrication for sulfur doped graphitic carbon nitride porous rods with excellent photocatalytic activity degrading RhB dye. *Appl. Surf. Sci.* **2017**, *391*, 360–368. [\[CrossRef\]](#)
96. Lin, Y.R.; Dizon, G.V.C.; Yamada, K.; Liu, C.Y.; Venault, A.; Lin, H.Y.; Yoshida, M.; Hu, C.C. Sulfur-doped g-C₃N₄ nanosheets for photocatalysis: Z-scheme water splitting and decreased biofouling. *J. Colloid Interface Sci.* **2020**, *567*, 202–212. [\[CrossRef\]](#)
97. Lu, C.H.; Zhang, P.; Jiang, S.J.; Wu, X.; Song, S.Q.; Zhu, M.S.; Lou, Z.Z.; Li, Z.; Liu, F.; Liu, Y.H.; et al. Photocatalytic reduction elimination of UO₂²⁺ pollutant under visible light with metal-free sulfur doped g-C₃N₄ photocatalyst. *Appl. Catal. B Environ.* **2017**, *200*, 378–385. [\[CrossRef\]](#)
98. Wang, K.; Li, Q.; Liu, B.S.; Cheng, B.; Ho, W.K.; Yu, J.G. Sulfur-doped g-C₃N₄ with enhanced photocatalytic CO₂-reduction performance. *Appl. Catal. B Environ.* **2015**, *176*, 44–52. [\[CrossRef\]](#)
99. Praus, P.; Smykalova, A.; Foniok, K.; Velisek, P.; Cvejn, D.; Zadny, J.; Storch, J. Post-Synthetic Derivatization of Graphitic Carbon Nitride with Methanesulfonyl Chloride: Synthesis, Characterization and Photocatalysis. *Nanomaterials* **2020**, *10*, 193. [\[CrossRef\]](#)
100. Qin, H.F.; Lv, W.H.; Bai, J.R.; Zhou, Y.; Wen, Y.P.; He, Q.T.; Tang, J.H.; Wang, L.B.; Zhou, Q.F. Sulfur-doped porous graphitic carbon nitride heterojunction hybrids for enhanced photocatalytic H₂ evolution. *J. Mater. Sci.* **2019**, *54*, 4811–4820. [\[CrossRef\]](#)
101. Ke, L.; Li, P.F.; Wu, X.; Jiang, S.J.; Luo, M.B.; Liu, Y.H.; Le, Z.G.; Sun, C.Z.; Song, S.Q. Graphene-like sulfur-doped g-C₃N₄ for photocatalytic reduction elimination of UO₂²⁺ under visible Light. *Appl. Catal. B Environ.* **2017**, *205*, 319–326. [\[CrossRef\]](#)

102. Raziq, F.; Humayun, M.; Ali, A.; Wang, T.T.; Khan, A.; Fu, Q.Y.; Luo, W.; Zeng, H.P.; Zheng, Z.P.; Khan, B.; et al. Synthesis of S-Doped porous g-C₃N₄ by using ionic liquids and subsequently coupled with Au-TiO₂ for exceptional cocatalyst-free visible-light catalytic activities. *Appl. Catal. B Environ.* **2018**, *237*, 1082–1090. [CrossRef]
103. Li, Y.F.; Wang, S.; Chang, W.; Zhang, L.H.; Wu, Z.S.; Song, S.Y.; Xing, Y. Preparation and enhanced photocatalytic performance of sulfur doped terminal-methylated g-C₃N₄ nanosheets with extended visible-light response. *J. Mater. Chem. A* **2019**, *7*, 20640–20648. [CrossRef]
104. Cui, Y.J.; Li, M.; Wang, H.; Yang, C.F.; Meng, S.G.; Chen, F.Y. In-situ synthesis of sulfur doped carbon nitride microsphere for outstanding visible light photocatalytic Cr (VI) reduction. *Sep. Purif. Technol.* **2018**, *199*, 251–259. [CrossRef]
105. Mohammad, A.; Khan, M.E.; Cho, M.H. Sulfur-doped-graphitic-carbon nitride (S-g-C₃N₄) for low cost electrochemical sensing of hydrazine. *J. Alloy. Compd.* **2020**, *816*, 10. [CrossRef]
106. Guo, H.; Shu, Z.; Chen, D.H.; Tan, Y.G.; Zhou, J.; Meng, F.Y.; Li, T.T. One-step synthesis of S-doped g-C₃N₄ nanosheets for improved visible-light photocatalytic hydrogen evolution. *Chem. Phys.* **2020**, *533*, 7. [CrossRef]
107. Xie, L.L.; Dai, Y.R.; Zhou, Y.J.; Chang, X.; Yin, L.F. Sulfur (VI) modified graphite carbon nitride nanosheets with chrysanthemum-like structure and enhanced photocatalytic activity. *Chem. Phys. Lett.* **2018**, *693*, 1–7. [CrossRef]
108. Cao, J.J.; Wang, H.; Zhao, Y.J.; Liu, Y.; Wu, Q.Y.; Huang, H.; Shao, M.W.; Kang, Z.H. Phosphorus-doped porous carbon nitride for efficient sole production of hydrogen peroxide via photocatalytic water splitting with a two-channel pathway. *J. Mater. Chem. A* **2020**, *8*, 3701–3707. [CrossRef]
109. Zhu, Y.K.; Li, J.Z.; Cao, J.M.; Lv, C.X.; Huang, G.Q.; Zhang, G.L.; Xu, Y.; Zhang, S.C.; Meng, P.P.; Zhan, T.R.; et al. Phosphorus-doped polymeric carbon nitride nanosheets for enhanced photocatalytic hydrogen production. *APL Mater.* **2020**, *8*, 7. [CrossRef]
110. Chai, B.; Yan, J.T.; Wang, C.L.; Ren, Z.D.; Zhu, Y.C. Enhanced visible light photocatalytic degradation of Rhodamine B over phosphorus doped graphitic carbon nitride. *Appl. Surf. Sci.* **2017**, *391*, 376–383. [CrossRef]
111. Chegeni, M.; Dehghan, N. Preparation of Phosphorus Doped Graphitic Carbon Nitride Using a Simple Method and Its Application for Removing Methylene Blue. *Phys. Chem. Res.* **2020**, *8*, 31–44. [CrossRef]
112. Huang, J.X.; Li, D.G.; Li, R.B.; Zhang, Q.X.; Chen, T.S.; Liu, H.J.; Liu, Y.; Lv, W.Y.; Liu, G.G. An efficient metal-free phosphorus and oxygen co-doped g-C₃N₄ photocatalyst with enhanced visible light photocatalytic activity for the degradation of fluoroquinolone antibiotics. *Chem. Eng. J.* **2019**, *374*, 242–253. [CrossRef]
113. Huang, J.X.; Li, D.G.; Liu, Y.; Li, R.B.; Chen, P.; Liu, H.J.; Lv, W.Y.; Liu, G.G.; Feng, Y.P. Ultrathin Ag₂WO₄-coated P-doped g-C₃N₄ nanosheets with remarkable photocatalytic performance for indomethacin degradation. *J. Hazard. Mater.* **2020**, *392*, 13. [CrossRef] [PubMed]
114. Kesavan, T.; Partheeban, T.; Vivekanantha, M.; Prabu, N.; Kundu, M.; Premkumar, S.; Umapathy, S.; Vinu, A.; Sasidharan, M. Design of P-Doped Mesoporous Carbon Nitrides as High-Performance Anode Materials for Li-Ion Battery. *ACS Appl. Mater. Interfaces* **2020**, *12*, 24007–24018. [CrossRef]
115. Li, J.J.; Tian, C.; Zhao, H.; Mei, J.; Zhang, J.; Yang, S.J. Controllable fabrication of a red phosphorus modified g-C₃N₄ photocatalyst with strong interfacial binding for the efficient removal of organic pollutants. *J. Alloy. Compd.* **2019**, *810*. [CrossRef]
116. Jolliffe, I.T. Principal Component Analysis. In *Principal Component Analysis*; Springer: New York, NY, USA, 1986; pp. 115–128. [CrossRef]
117. Ran, J.R.; Guo, W.W.; Wang, H.L.; Zhu, B.C.; Yu, J.G.; Qiao, S.Z. Metal-Free 2D/2D Phosphorene/g-C₃N₄ Van der Waals Heterojunction for Highly Enhanced Visible-Light Photocatalytic H₂ Production. *Adv. Mater.* **2018**, *30*, 6. [CrossRef]
118. Su, C.Y.; Zhou, Y.Z.; Zhang, L.L.; Yu, X.H.; Gao, S.; Sun, X.J.; Cheng, C.; Liu, Q.Q.; Yang, J. Enhanced n → pi* electron transition of porous P-doped g-C₃N₄ nanosheets for improved photocatalytic H₂ evolution performance. *Ceram. Int.* **2020**, *46*, 8444–8451. [CrossRef]
119. Sun, Y.J.; He, J.Y.; Zhang, D.; Wang, X.J.; Zhao, J.; Liu, R.H.; Li, F.T. Simultaneous construction of dual-site phosphorus modified g-C₃N₄ and its synergistic mechanism for enhanced visible-light photocatalytic hydrogen evolution. *Appl. Surf. Sci.* **2020**, *517*, 8. [CrossRef]

120. Wang, P.Y.; Guo, C.S.; Hou, S.; Zhao, X.; Wu, L.L.; Pei, Y.Y.; Zhang, Y.; Gao, J.F.; Xu, J. Template-free synthesis of bubble-like phosphorus-doped carbon nitride with enhanced visible-light photocatalytic activity. *J. Alloy. Compd.* **2018**, *769*, 503–511. [[CrossRef](#)]
121. Zhao, Z.L.; Xie, C.; Cui, H.D.; Wang, Q.Y.; Shu, Z.; Zhou, J.; Li, T.T. Scalable one-pot synthesis of phosphorus-doped g-C₃N₄ nanosheets for enhanced visible-light photocatalytic hydrogen evolution. *Diam. Relat. Mat.* **2020**, *104*, 8. [[CrossRef](#)]
122. Deng, Y.C.; Tang, L.; Zeng, G.M.; Zhu, Z.J.; Yan, M.; Zhou, Y.Y.; Wang, J.J.; Liu, Y.N. Insight into highly efficient simultaneous photocatalytic removal of Cr (VI) and 2,4-dichlorophenol under visible light irradiation by phosphorus doped porous ultrathin g-C₃N₄ nanosheets from aqueous media: Performance and reaction mechanism. *Appl. Catal. B Environ.* **2017**, *203*, 343–354. [[CrossRef](#)]
123. Zhu, Y.P.; Ren, T.Z.; Yuan, Z.Y. Mesoporous Phosphorus-Doped g-C₃N₄ Nanostructured Flowers with Superior Photocatalytic Hydrogen Evolution Performance. *ACS Appl. Mater. Interfaces* **2015**, *7*, 16850–16856. [[CrossRef](#)] [[PubMed](#)]
124. He, F.; Wang, Z.X.; Li, Y.X.; Peng, S.Q.; Liu, B. The nonmetal modulation of composition and morphology of g-C₃N₄-based photocatalysts. *Appl. Catal. B Environ.* **2020**, *269*, 21. [[CrossRef](#)]
125. Guo, S.E.; Tang, Y.Q.; Xie, Y.; Tian, C.G.; Feng, Q.M.; Zhou, W.; Jiang, B.J. P-doped tubular g-C₃N₄ with surface carbon defects: Universal synthesis and enhanced visible-light photocatalytic hydrogen production. *Appl. Catal. B Environ.* **2017**, *218*, 664–671. [[CrossRef](#)]
126. Zhou, Y.J.; Zhang, L.X.; Liu, J.J.; Fan, X.Q.; Wang, B.Z.; Wang, M.; Ren, W.C.; Wang, J.; Li, M.L.; Shi, J.L. Brand new P-doped g-C₃N₄: Enhanced photocatalytic activity for H₂ evolution and Rhodamine B degradation under visible light. *J. Mater. Chem. A* **2015**, *3*, 3862–3867. [[CrossRef](#)]
127. Li, X.H.; Zhang, J.; Zhou, F.; Zhang, H.L.; Bai, J.; Wang, Y.J.; Wang, H.Y. Preparation of N-vacancy-doped g-C₃N₄ with outstanding photocatalytic H₂O₂ production ability by dielectric barrier discharge plasma treatment. *Chin. J. Catal.* **2018**, *39*, 1090–1098. [[CrossRef](#)]
128. Li, H.L.; Jin, C.; Wang, Z.Y.; Liu, Y.Y.; Wang, P.; Zheng, Z.K.; Whangbo, M.H.; Kou, L.Z.; Li, Y.J.; Dai, Y.; et al. Effect of the intra- and inter-triazine N-vacancies on the photocatalytic hydrogen evolution of graphitic carbon nitride. *Chem. Eng. J.* **2019**, *369*, 263–271. [[CrossRef](#)]
129. Peng, G.M.; Wu, J.W.; Wang, M.Z.; Niklas, J.; Zhou, H.; Liu, C. Nitrogen-Defective Polymeric Carbon Nitride Nanolayer Enabled Efficient Electrocatalytic Nitrogen Reduction with High Faradaic Efficiency. *Nano Lett.* **2020**, *20*, 2879–2885. [[CrossRef](#)]
130. Li, X.X.; Tan, T.N.; Zhang, J.; Zhang, N.; He, J.W.; Han, W.M.; Wang, Y.D.; Pan, M. Nitrogen Deficient Graphitic Carbon Nitride as Anodes for Lithium-ion Batteries. *J. Wuhan Univ. Technol. Mat. Sci. Edit.* **2020**, *35*, 263–271. [[CrossRef](#)]
131. Xie, Y.; Li, Y.X.; Huang, Z.H.; Zhang, J.Y.; Jia, X.F.; Wang, X.S.; Ye, J.H. Two types of cooperative nitrogen vacancies in polymeric carbon nitride for efficient solar-driven H₂O₂ evolution. *Appl. Catal. B Environ.* **2020**, *265*, 7. [[CrossRef](#)]
132. Wang, J.; Gao, B.; Dou, M.M.; Huang, X.; Ma, Z.K. A porous g-C₃N₄ nanosheets containing nitrogen defects for enhanced photocatalytic removal meropenem: Mechanism, degradation pathway and DFT calculation. *Environ. Res.* **2020**, *184*, 10. [[CrossRef](#)]
133. Wang, Y.X.; Rao, L.; Wang, P.F.; Guo, Y.; Shi, Z.Y.; Guo, X.; Zhang, L.X. Synthesis of nitrogen vacancies g-C₃N₄ with increased crystallinity under the controlling of oxalyl dihydrazide: Visible-light-driven photocatalytic activity. *Appl. Surf. Sci.* **2020**, *505*, 10. [[CrossRef](#)]
134. Yu, W.W.; Shan, X.; Zhao, Z.K. Unique nitrogen-deficient carbon nitride homojunction prepared by a facile inserting-removing strategy as an efficient photocatalyst for visible light-driven hydrogen evolution. *Appl. Catal. B Environ.* **2020**, *269*, 9. [[CrossRef](#)]
135. Li, X.X.; Zhang, K.L.; Zhou, M.; Yang, K.; Yang, S.; Ma, X.H.; Yu, C.L.; Xie, Y.; Huang, W.Y.; Fan, Q.Z. A Novel Approach to Synthesize Nitrogen-Deficient g-C₃N₄ for the Enhanced Photocatalytic Contaminant Degradation and Electrocatalytic Hydrogen Evolution. *Nano* **2020**, *15*, 13. [[CrossRef](#)]
136. Yang, Z.X.; Chu, D.L.; Jia, G.R.; Yao, M.G.; Liu, B.B. Significantly narrowed bandgap and enhanced charge separation in porous, nitrogen-vacancy red g-C₃N₄ for visible light photocatalytic H₂ production. *Appl. Surf. Sci.* **2020**, *504*, 8. [[CrossRef](#)]

137. Huang, J.J.; Du, J.M.; Du, H.W.; Xu, G.S.; Yuan, Y.P. Control of Nitrogen Vacancy in g-C₃N₄ by Heat Treatment in an Ammonia Atmosphere for Enhanced Photocatalytic Hydrogen Generation. *Acta Phys. Chim. Sin.* **2020**, *36*, 8. [CrossRef]
138. Li, W.S.; Guo, Z.; Jiang, L.T.; Zhong, L.; Li, G.N.; Zhang, J.J.; Fan, K.; Gonzalez-Cortes, S.; Jin, K.J.; Xu, C.J.; et al. Facile in situ reductive synthesis of both nitrogen deficient and protonated g-C₃N₄ nanosheets for the synergistic enhancement of visible-light H₂ evolution. *Chem. Sci.* **2020**, *11*, 2716–2728. [CrossRef]
139. Zhang, Y.; Di, J.; Ding, P.H.; Zhao, J.Z.; Gu, K.Z.; Chen, X.L.; Yan, C.; Yin, S.; Xia, J.X.; Li, H.M. Ultrathin g-C₃N₄ with enriched surface carbon vacancies enables highly efficient photocatalytic nitrogen fixation. *J. Colloid Interface Sci.* **2019**, *553*, 530–539. [CrossRef]
140. Li, Y.H.; Gu, M.L.; Shi, T.; Cui, W.; Zhang, X.M.; Dong, F.; Cheng, J.S.; Fan, J.J.; Lv, K.L. Carbon vacancy in C₃N₄ nanotube: Electronic structure, photocatalysis mechanism and highly enhanced activity. *Appl. Catal. B Environ.* **2020**, *262*, 11. [CrossRef]
141. Li, S.N.; Dong, G.H.; Hailili, R.; Yang, L.P.; Li, Y.X.; Wang, F.; Zeng, Y.B.; Wang, C.Y. Effective photocatalytic H₂O₂ production under visible light irradiation at g-C₃N₄ modulated by carbon vacancies. *Appl. Catal. B Environ.* **2016**, *190*, 26–35. [CrossRef]
142. Barrio, J.; Volokh, M.; Shalom, M. Polymeric carbon nitrides and related metal-free materials for energy and environmental applications. *J. Mater. Chem. A* **2020**, *8*, 11075–11116. [CrossRef]
143. Liu, X.L.; Ma, R.; Zhuang, L.; Hu, B.W.; Chen, J.R.; Liu, X.Y.; Wang, X.K. Recent developments of doped g-C₃N₄ photocatalysts for the degradation of organic pollutants. *Crit. Rev. Environ. Sci. Technol.* **2020**, *40*. [CrossRef]
144. Mun, S.J.; Park, S.J. Graphitic Carbon Nitride Materials for Photocatalytic Hydrogen Production via Water Splitting: A Short Review. *Catalysts* **2019**, *9*, 805. [CrossRef]
145. Talapaneni, S.N.; Singh, G.; Kim, I.Y.; AlBahily, K.; Al-Muhtaseb, A.H.; Karakoti, A.S.; Tavakkoli, E.; Vinu, A. Nanostructured Carbon Nitrides for CO₂ Capture and Conversion. *Adv. Mater.* **2020**, *32*, 21. [CrossRef]
146. Wang, Y.Q.; Shen, S.H. Progress and Prospects of Non-Metal Doped Graphitic Carbon Nitride for Improved Photocatalytic Performances. *Acta Phys. Chim. Sin.* **2020**, *36*, 14. [CrossRef]
147. Zhu, A.H.; Qiu, B.C.; Du, M.M.; Ji, J.H.; Nasir, M.; Xing, M.Y.; Zhang, J.L. Dopant-Induced Edge and Basal Plane Catalytic Sites on Ultrathin C₃N₄ Nanosheets for Photocatalytic Water Reduction. *Acs Sustain. Chem. Eng.* **2020**, *8*, 7497–7502. [CrossRef]
148. Wanninayake, N.; Ai, Q.; Zhou, R.; Hoque, M.A.; Herrell, S.; Guzman, M.I.; Risko, C.; Kim, D.Y. Understanding the effect of host structure of nitrogen doped ultrananocrystalline diamond electrode on electrochemical carbon dioxide reduction. *Carbon* **2020**, *157*, 408–419. [CrossRef]
149. Zhao, H.L.; Liu, L.J.; Andino, J.M.; Li, Y. Bicrystalline TiO₂ with controllable anatase-brookite phase content for enhanced CO₂ photoreduction to fuels. *J. Mater. Chem. A* **2013**, *1*, 8209–8216. [CrossRef]
150. Hoque, M.A.; Guzman, M.I. Photocatalytic Activity: Experimental Features to Report in Heterogeneous Photocatalysis. *Materials* **2018**, *11*, 1990. [CrossRef]