



Review Recent Advances of Doping and Surface Modifying Carbon Nitride with Characterization Techniques

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Abstract: As a non-metallic organic semiconductor photocatalyst, graphitic carbon nitride ($g-C_3N_4$, CN) has become a research hotspot due to its excellent performance in organic degradation, CO₂ reduction and water splitting to produce hydrogen. However, the high recombination rate of electronhole pairs, low specific surface area and weak light absorption of bulk CN synthesized by the traditional one-step thermal polymerization method seriously restrict its photocatalytic performance and practical application. To enhance the photocatalytic performance of CN, doping and surface modification strategies are usually employed to tune the band gap of carbon nitride and improve the separation of carriers. In this paper, the research progress of different methods to modify CN in recent years is introduced, and the mechanisms of improving the photocatalytic performance are mainly analyzed. Typical modification methods are mainly divided into metal doping, non-metal doping, co-doping and surface-functionalized modification. Some characterization methods that can analyze the doping state and surface modification are also discussed as examples. Finally, the difficulties that need to be addressed through modified CN photocatalysts and the directions for future research are pointed out.

Keywords: photocatalysis; carbon nitride; doping; surface modification; characterization methods; visible light

1. Introduction

With the rapid development of human society and the extensive use of fossil energy, energy crisis and environmental pollution problems have become increasingly serious, forcing human beings to address such issues [1–3]. Solar energy is a clean and pollution-free green energy, and its effective use has become an ideal strategy to solve energy and environmental problems [4,5]. Semiconductor-based photocatalytic technology can transform solar energy to new energy and degrade pollutants, such as splitting water [6], reducing carbon dioxide to fuel [7], removing nitrogen oxides [8] and so on. In 1972, TiO₂ was reported to be able to split water under illumination, and it became a widely studied major photocatalyst [9–11]. However, TiO₂ has a wide band gap and can only be excited by UV light. UV light only accounts for a small fraction of solar radiation energy, which greatly limits the practical application of TiO₂ [12,13]. Therefore, the exploration of efficient and inexpensive visible light—responsive photocatalysts is still a research hotspot in the field of photocatalysis, such as cadmium sulfide (CdS) [14], carbon nitride [15], etc.

As a non-metallic organic polymer semiconductor photocatalyst, graphitic carbon nitride $(g-C_3N_4, CN)$ has been widely studied due to its excellent performance in organic degradation, CO₂ reduction and water splitting to produce hydrogen [16–18]. In 2009, Wang et al. reported that carbon nitride was used in photocatalytic water splitting for hydrogen production [19]. CN has a layered structure similar to graphite. Each layer



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). consists of sp²-hybridized tri-s-triazine repeating units, and the layers are connected by van der Waals forces. Compared with TiO₂, conventional CN has a more suitable band gap of 2.7-2.8 eV, and photoelectron excitation can also occur under visible light irradiation [19–23]. Traditional bulk graphitic carbon nitride (BCN) can be obtained from nitrogen-rich precursors by a simple one-step calcination method, such as melamine, cyanamide, dicyanamide, urea and thiourea (Figure 1a). In fact, different CN precursors and different polymerization temperatures will also affect the physical and chemical properties of CN [20]. For example, calcining melamine at different temperatures will change the C/N ratio and band gap of the resulting CN [24]. Using urea as a precursor led to higher hydrogen production performance than thiourea – and dicyandiamide-derived CN under visible light irradiation, which can be attributed to the higher specific surface area and porosity of CN obtained by calcining urea [25]. However, traditional BCN has many defects, a high charge recombination rate and a low specific surface area, which seriously restrict the photocatalytic performance and practical application of CN [26,27]. To enhance the photocatalytic performance of CN, various modification strategies have been explored, such as element doping [28,29], construction of heterojunctions [30,31], loading of co-catalysts [1,32] and structural nanoscale methods [33].



Figure 1. (a) Schematic illustration of the synthesis process of CN by polymerization of different precursors [20]. (b) Number of annual publications using "photocatalytic" and "carbon nitride" as topic keywords since 2012. (c) Number of annual publications using "photocatalytic", "carbon nitride" and "doping" as topic keywords since 2012. Adapted from ISI Web of Science, dated August 2022.

It is a common and effective method to improve the photocatalytic performance of catalysts by doping metal elements, non-metal elements or functional groups. Different doping methods and doping elements may bring about completely different doping results. Impurity atoms can not only replace the C atoms or N atoms in the CN conjugated skeleton, but in some cases, the dopant atoms can also enter and exist in the cavities of π -conjugate planes or be present in the CN interlayer [34,35]. The lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) of CN can be effectively regulated by doping. Element doping enables photogenerated electrons to easily transition from impurity energy levels to conduction band (CB) or from valence band (VB) to impurity energy levels by introducing impurity energy levels in the middle of the forbidden band, thereby enhancing light absorption and optimizing charge transfer. In addition, doping can also change the potential values of VB and CB, thereby tuning the photocatalytic oxidation or reduction ability of CN [36–38].

Since Wang et al. reported the photocatalytic hydrogen production of CN in 2009, there has been a surge in its research in the field of photocatalysis. Modification methods for CN are also becoming more and more prosperous. As can be seen from Figure 1b,c, in the past decade, the number of publications on carbon nitride photocatalysis has increased dramatically, and the articles describing doping with CN account for a considerable part. This shows the importance and development potential of doping modification in this field. In this review, we focus on recent research progress in doped and surface-modified CN. In recent years, there have been some excellent reviews on doped CN for photocatalysis. For example, Patnaik et al. analyzed the research progress of anion-doped CN photocatalysts [39]. The classification and discussion of various types of anion-doped CN, such as S, P, B, O, etc., has also be considered. As another example, Bai et al. analyzed the synthesis, structure and application of various types of metal-doped CN [40]. However, few works have comprehensively analyzed the various doping methods of CN and discussed the commonly used characterization methods. This work classifies and discusses the methods for the doping and surface modification of CN and its characterization methods from a more comprehensive perspective. Doping of CN is divided into metal doping, non-metal doping and co-doping. The effects and mechanisms of different modification methods on the performance of CN catalysts are also analyzed. In this review, we also highlight some common characterization methods that can be demonstrated for doped g-CN, such as X-ray photoelectron spectroscopy, solid-state nuclear magnetic resonance, Fourier transform infrared spectra, elemental mapping images and X-ray absorption spectroscopy. The method by which each characterization technique is used to demonstrate doping is briefly described with examples. The advantages and limitations of different representations are also pointed out. Finally, some suggestions are put forward for the challenges and development directions of modified CN.

2. Doped CN Systems

The photoreactivity of CN is sensitive to the doped elements. The doping of CN can be divided into metal doping, non-metal doping and co-doping. Table 1 summarizes the effects of dopants on the improvement of CN's photocatalytic performance, including H_2 evolution, H_2O_2 production, CO_2 reduction and organic degradation. Although the photoreactivity of the photocatalyst is sensitive to many parameters, such as the light source (wavelength and power), the distance between the lamp and the reactor, the shape of the reactor and reaction temperature, it can still be observed that the photoreactivity of CN can be improved to a higher level when doping with transitional metals, especially noble metals such as Pt (entry 2), compared to that doped with nonmetals such as S (entry 7), P (entry 8) and N (entry 9).

Entry	Catalysts	Dopant Source	Application	Activity	Rate Enhanced	Ref.
1	Pt-CN	H ₂ PtCl ₆	H_2 evolution	$318 \ \mu mol \ h^{-1}$	50	[41]
2	Pt-CN	H_2PtCl_6	H ₂ evolution	$14.7 \ { m mmol} \ { m h}^{-1} \ { m g}^{-1}$	1340	[42]
3	Pd_{1+NPs}/C_3N_4	Pd(acac) ₂	CO_2 reduction	20.3 μ mol CH ₄ g ⁻¹ h ⁻¹	-	[43]
4	CN-K	KBr	NO removal	around 40%	-	[35]
5	CCN	KCl	H ₂ evolution	1356 μ mol h $^{-1}$ g $^{-1}$	22	[44]
6	PCNNs-IHO	NaCl	CH ₃ SH mineralization	_	-	[45]
7	S-CN	thiourea	CH ₃ OH production	$1.12 \ \mu mol \ g^{-1}$	1.38	[46]
8	P-CN	HCCP	H ₂ evolution	$50.6 \text{ mmol } \text{h}^{-1}$	2.9	[47]
9	$C-C_3N_4$	glucose	H ₂ evolution	6545.8 μ mol g ⁻¹	3	[48]
10	C_3N_{4+x}	hydrazine hydrate	H ₂ evolution	44.28 mmol h^{-1}	4.6	[49]
11	RPCN	2,4,6-triamine-pyrimidine + KCl	H_2 evolution	640 μmol h ⁻¹ g ⁻¹ 500~780 nm	-	[50]
12	Co/V-g-C ₃ N ₄	vanadyl acetylacetonate + cobalt acetate	TC-HCl degradation	$0.0108 \ { m min}^{-1}$	4	[51]
13	Co/Ru–CN	$RuCl_3 + Co(NO_3)_2 \cdot 6H_2O$	CO_2 reduction	95.6 μmol g ⁻¹	3	[52]
14	$Na/g-C_3N_4$	NaCl	H_2O_2 production	7.01 mM	220	[53]

Table 1. Summary of the photocatalytic activity of modified CN.

The following sections contain detailed discussions of doped CN systems from the perspectives of metal doping, non-metal doping and co-doping.

2.1. Metal Doping

In the CN catalytic system, the introduction of metal impurities in general can generate additional binding energy, on the one hand, thereby shortening the band gap, and, on the other hand, can coordinate with N atoms to optimize the carrier behavior [54,55]. Usually, calcination can be carried out by homogeneously mixing the precursor of CN with the soluble salt. In this way, the metal heteroatoms will be simultaneously doped into the CN matrix during the heating copolymerization.

It has been confirmed that noble metals as co-catalysts can promote the separation of charge carriers and provide active sites for photocatalytic reactions. Many recent studies have shown that CN supported with single-atom co-catalysts can maximize atom utilization and exhibit excellent photocatalytic performance [56–58]. For CN, it has a good structural basis for metal ion doping. Metal ions can be located in the cavity surrounded by six N atoms in the tri-s-triazine unit, and the abundant lone pair electrons in the cavity can also coordinate with the metal ions [2,40,59,60]. Li et al. synthesized single-atom supported photocatalysts by a mild method (entry 1) [41]. After stirring CN and H₂PtCl₆ in the liquid phase, Pt–CN was prepared by annealing at 125 °C. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) was used to find that Pt atoms do not agglomerate on CN, but exist in the form of isolated single atoms. Moreover, through extended X-ray absorption fine structure (EXAFS) analysis of the bonding distance, it is concluded that Pt atoms are dispersed at the top of the five-membered ring of CN (Figure 2a).

To further explore the mechanism of single-atom metal doping to enhance the performance of CN, Zhang et al. used simultaneous illumination X-ray photoelectron spectroscopy (SI-XPS) to reveal the charge transfer and chemical bond evolution in single-atom Pt/CN (entry 2) [42]. When the single-atom Pt/CN is in the ground state, a single Pt atom is doped in the tri-s-triazine ring cavity and forms bonds with N atoms. The electron transfer from the Pt atom to the N atom leads to the appearance of the Pt²⁺ oxidation state. After excitation by light, Pt²⁺ can effectively absorb the electrons of C₃N₄, the Pt–N bond is broken and converted into Pt⁰, and the C–N bond of CN is converted into a C=N bond at the same time (Figure 2b–d). Electron-rich Pt⁰ and hole-rich C₃N₄ can serve as reduction and oxidation sites for water, respectively. When the illumination ends, the catalyst system returns to the ground state. The hydrogen evolution activity of the single-atom Pt/CN catalyst is significantly improved, which is 20 times that of C_3N_4 modified with Pt particles. It can be found that the performance improvement of single-atom noble metal-supported CN is significant, which is mainly attributed to its ability to promote charge separation and maximize the utilization of atoms. This work demonstrates the dynamic evolution of catalysts for photocatalytic applications from an atomic perspective. It provides inspiration for the preparation of efficient single-atom catalysts.



Figure 2. (a) Schematic models of Pt–CN [41]. (b,c) High-resolution SI-XPS of single-atom Pt/CN. (d) Illustration of charge transfer and bond variation on single-atom Pt/CN for photocatalytic H₂ evolution [42]. (e) The reaction mechanism for photocatalytic conversion of CO₂ to CH₄ over Pd_{1+NPs}/C₃N₄. (f) Production rates of CO₂ photoreduction over C₃N₄, Pd₁/C₃N₄, Pd_{1+NPs}/C₃N₄ and Pd_{NPs}/C₃N₄ [43].

Recently, Liu et al. constructed CN (Pd_{1+NPs}/C_3N_4) with bifunctional centers of singleatom Pd and Pd nanoparticles (Figure 2e) (entry 3) [43]. Under the premise of maintaining high CO₂ reduction activity, the catalyst has selectivity of 97.8% to methane, which is significantly higher than that of Pd_1/C_3N_4 and Pd_{NPs}/C_3N_4 (Figure 2f). The experimental results and theoretical calculations reveal the mechanism by which the Pd bifunctional centers synergistically promote the highly selective production of methane. The Pd₁ site mainly activates CO₂, while the Pd_{NPs} site promotes the dissociation of water and migrates the generated H* to the Pd₁ site, which promotes the protonation of *CO to CH₄. Although the photocatalytic performance of Pd_{1+NPs}/C_3N_4 is not significantly improved compared with that of Pd_1/C_3N_4 , it significantly improves the selectivity to methane on the basis of maintaining high activity, which has certain significance for promoting the practical application of photocatalytic carbon dioxide reduction. In recent years, some breakthroughs have been made in the research of alkali metal ion-modified CN. Alkali metal ions are coordinated into the CN framework, which can significantly improve the transfer, separation and distribution of charge carriers, thereby enhancing the photocatalytic reaction ability [61]. Xiong et al. synthesized K-doped CN (CN–K) and Na-doped CN(CN–Na) by a simple one-step thermal polymerization method: mixed calcined thiourea and XBr (X = Na, K) (entry 4) [35]. Density functional theory (DFT) calculations show that K or Na doping can narrow the band gap of CN, but the positions of the two when doped into the CN framework are different (Figure 3a). Na atoms are doped into the CN plane layer and increase the in-plane electron density, resulting in a high recombination rate of carriers and reduced photocatalytic performance; K atoms are mainly inserted between the layers of CN, and are coordinately bonded to the atoms of the two adjacent layers, connecting the layers and transporting electrons in them, which promotes the transfer and separation of carriers (Figure 3b,c).



Figure 3. (a) Calculated crystal structures, (b) photocatalytic oxidation of NO activity and (c) transient photocurrent responses of CN, CN–K and CN–Na [35]. (d) Schematic diagram and (e) HRTEM image of CCN prepared by solid KCl method [44]. (f) Illustration of the synthesis process of PCNNs-IHO [45].

In addition, alkali metal ions are also of great help for the preparation of highly crystalline carbon nitride (CCN). Due to the defects of a large number of amino groups, hydrogen bonds and folded structures in BCN synthesized by the traditional one-step thermal polymerization method, it will hinder the conduction of electrons on the plane. At the same time, an electron–hole recombination center is formed, which limits the electron–

hole separation of CN in photocatalysis [45,62,63]. Xu et al. used solid KCl as a template, mixed it with the preheated product of melamine and then calcined it to obtain CN with satisfactory crystallinity (Figure 3d) (entry 5) [44]. The precursors of CN were reorganized and ordered in the confined space provided by solid KCl. The obvious lattice fringes in the high-resolution transmission electron microscope (HRTEM) images in Figure 3e show its highly crystalline properties [64–66]. Potassium ions are doped between the melon chains as a "binder" and provide an electron transport channel, improving the separation and migration of carriers. Its photocatalytic hydrogen production shows a nearly 20-fold improvement compared to BCN. In another work, Guo et al. found that CN nanosheets with a highly ordered structure (PCNNs-IHO) were successfully prepared by calcining a mixture of melamine and sodium chloride at 650 °C (Figure 3f) (entry 6) [45]. NaCl crystal has high surface energy, which can promote the adsorption and activation of melamine on its crystal surface. This is beneficial to promote its polymerization kinetics and generate long-range ordered structures between the tri-s-triazine units. In addition, the interaction between NaCl and CN precursors controlled the growth direction of CN to a certain extent, resulting in two-dimensional CN nanosheets assembled on NaCl. After washing with water to remove salt, the obtained CN exhibited excellent photocatalytic performance for CH_3SH mineralization under visible light irradiation, even higher than P25 and CCN prepared by the LiCl/KCl molten salt method. It is not difficult to find that the preparation of CCN from alkali metal salts is a new modification method of CN, which allows a significant improvement in the hydrogen production performance of CN. It would be interesting for future work to focus on the modification of CCN, such as the construction of heterojunctions and single-atom loading, but the effect of alkali metal ions on the polymerization of CN and how to improve its stability need to be further explored.

2.2. Non-Metal Doping

Non-metal anion doping can maintain the metal-free properties of CN, and S [67], P [68], B [69], etc., have been studied. Anions have high ionization potential and electronegativity, and can obtain electrons from other substances and form covalent bonds, so as to achieve the purpose of doping [70,71]. Doping anions at the atomic level can easily tune the VB and CB structures of the catalysts. When the CB minimum value increases, the photoreduction ability of the catalyst can be enhanced and the charge separation can be improved. Moreover, broad VB can enhance the photo-oxidation efficiency by increasing the mobility of holes [72–75].

Wang et al. focused on the preparation of S-doped CN by the calcination of thiourea, and studied the theoretical partial DOS of pure CN and S-doped CN by DFT calculations (entry 7) [46]. It was found that impurity states were generated in the S-doped CN samples, which made it easy for photoelectrons to transition from the VB to the impurity state or from the impurity state to the CB. For S-doped CN, the fundamental composition states of CB and VB do not change. However, the spin-up and spin-down states of the samples are not uniform, indicating that the extra electrons introduced by the S atoms lead to spin polarization (Figure 4a–c). In addition, impurity energy levels composed of S 3p, N 2p and C 2p states appeared below the BCB, which can be attributed to the doped S atoms affecting the atomic structure of CN and forming bonds with C and N atoms, resulting in p orbital hybridization between C, N and S atoms. The total energy level of S-doped CN is the same as the Eg value of pure CN, both being 1.18 eV. However, due to the existence of the impurity level, the E_{max} (maximum energy gap) is reduced to 1.02 eV, and the Fermi level is also shifted down (Figure 4d). Macroscopically, this results in a shortened CN band gap and enhanced light absorption.



Figure 4. (**a**–**c**) Partial DOS of the S-doped CN. (**d**) Schematic of band structure of pure CN and S-doped CN [46]. (**e**) Schematic diagram of possible existing forms of P atoms in CN and their effects on electronic properties. (**f**) Zeta potentials of the pure CN (P0-550) and P-doped CN (P10-550, P10-600) [47].

Many papers have reported the method of doping P atoms into the CN framework to change its photoelectrochemical properties. The optional doping P source is very rich, and a large number of compounds are used as dopants, such as polyphosphate cyanogen [76], phosphorous acid [77], hexachlorocyclotriphosphazene [47], sodium hypophosphite monohydrate [78] and BmimPF6 [79], etc. Generally, when a P atom is doped into the CNconjugated framework, it can form a chemical bond with the adjacent N atom and induce in-plane coordination. Meanwhile, P possesses five free electrons, four of which coordinate with adjacent N atoms to form covalent bonds. The remaining one electron keeps the Pdoped CN in an electron-rich state and facilitates charge transfer. In addition, lone electron delocalization and P-N bond polarization can also lead to the generation of P⁺ centers (Lewis acid site), which, together with Lewis base sites (–NH₂), are theoretically beneficial for the separation of photogenerated carriers (Figure 4c) [38,47,80]. Zhou et al. successfully synthesized P-doped CN by copolymerizing guanidine hydrochloride (CN precursor) and hexachlorocyclotriphosphazene (HCCP, P source) (entry 8). The chemical composition and chemical environment of the material were analyzed by solid-state nuclear magnetic resonance (NMR) and X-ray photoelectron spectroscopy (XPS), and it was verified that P can replace C atoms (corner-carbon and bay-carbon sites). The zeta potential of the

samples in water was tested, and, as shown in Figure 4f, the P-doped CN was negatively charged, while the pure CN was positively charged. This indicates that the introduction of P atoms generates additional electrons and places CN in an electron-rich state. This work explains the effect of P-doped CN on charge transfer from the atomic point of view, and has certain guiding significance for the mechanism of doping atoms to promote the performance improvement.

Although the doping of heteroatoms can promote light absorption and improve carrier dynamics, excessive generation of impurities or defects may act as carrier recombination centers, especially at high doping concentrations. This is mainly attributed to the structural asymmetry and the deformation of the planar conjugated skeleton upon heteroatom doping. Accordingly, self-doping modification strategies have been proposed. The self-doping method can tune the electronic structure while avoiding the disadvantage of heteroatoms acting as recombination centers [36,81,82].

The introduction of C self-doping can form delocalized π bonds and promote the transfer of delocalized electrons. Wang et al. explored a secondary calcination method to prepare C self-doped CN nanosheets (C–C₃N₄ NS), in order to improve the photocatalysis performance of CN (entry 9) [48]. In the second calcination process, glucose was added as a C source to achieve the purpose of doping, and the bulk CN was also peeled off into a flake-like morphology due to thermal oxidation etching. By infrared NMR and XPS analysis, it was found that the doped C atoms replaced the N atoms bridging the tri-s-triazine unit and maintained the original 2D conjugated tri-s-triazine unit structure of CN (Figure 5a). Benefiting from C doping, the band gap of CN is shortened. Compared with CN nanosheets (C3N4 NS), the valence band of C doping does not change, but due to the existence of the C doping energy level, the position of the conduction band is shifted positively (Figure 5b). Finally, the self-doped CN showed a nearly three-fold improvement in hydrogen production activity compared to pure CN NS.



Figure 5. (a) Atomic structure and (b) bond structure of CN and C–C3N4 NS [48]. (c) Schematic of the structure and (d) EPR spectra for C3N4 and C3N_{4+x} [49].

There are a few studies on the synthesis of N-rich CN. Fang et al. reported, for the first time, that N self-doped CN (C_3N_{4+x}), which is higher than that of pure C_3N_4 without pretreatment, was used for visible light catalytic H₂ production by pretreatment of melamine with hydrazine hydrate, which absorbed more visible light, simultaneously promoting the charge and transfer process, and the performance was enhanced (entry 10) [49]. The elemental analysis results show that the N/C mass ratio of C_3N_{4+x} is 1.68, which is higher than that of pure C_3N_4 (1.60) without pretreatment, and the existence of N–N bonds analyzed by XPS can lead to the conclusion that N self-doped CN was successfully synthesized. Analysis

shows that replacing C atoms with N atoms results in electron asymmetry in the system, and electrons are more easily released to the conduction band after being excited by visible light. The electron paramagnetic resonance (EPR) signal detected by C_3N_{4+x} also increased (Figure 5c,d). In fact, this proves that CN self-doping is more difficult than hetero-doping, and it needs more comprehensive characterization techniques to be achieved.

2.3. Co-Doping

Although single-element doping has become a general and effective strategy for photocatalyst modification, it usually suffers from the problem of incomplete performance improvement and even adverse effects in some aspects. In order to further improve the photocatalytic performance of CN on the basis of single-element doping, the multi-element co-doping method has been explored to combine the advantages of single dopants, which can complement or jointly promote each other from various aspects to further improve the photocatalytic activity [76,83,84]. The choice of co-doping elements is abundant. In recent years, many works have explored co-doping.

For example, Xu et al. used KCl and 2,4,6-triamine-pyrimidine as a K source and C source, respectively, and synthesized C/K co-doped red CN (RPCN) by copolymerization with melamine (entry 11) [50]. The uniform doping of C and K significantly narrows the band gap of CN (1.7 eV), and its corresponding range of photocatalytic activity covers almost the entire wavelength range. Moreover, the apparent quantum efficiency at 700 \pm 10 nm is also as high as 0.84%. In addition, due to the positive effect of the solid-state template KCL during the calcination process, the crystallinity of CN is also significantly improved on the basis of co-doping, which is beneficial to the transport and separation of carriers (Figure 6).



Figure 6. (a) Physical photo of red RPCN and a schematic diagram of the atomic structure. (b) UV-vis DRS spectra, (c) Kubelka-Munk plots, (d) XRD patterns and (e) electrochemical impedance spectra of PCN and RPCN [50].

Bimetallic co-doped CN has also been investigated. A Co/V co-doped CN was synthesized by using vanadyl acetylacetonate solution and cobalt acetate as V and Co sources, respectively (entry 12) [51]. DFT studies show that the band gaps of Co–g–C₃N₄, V–g–C₃N₄ and Co/V–g–C₃N₄ are reduced from 1.30 eV in pure g–C₃N₄ to 0.90, 0.61 and 0.61 eV, respectively. Moreover, the CB of Co/V–g–C₃N₄ becomes wider, which indicates that the synergistic effect of Co/V co-doping has a further influence on the electronic structure. Co/V co-doping promoted the transfer and separation of photogenerated carriers,

and the activity of the photocatalytic removal of tetracycline hydrochloride (TC–HCl) was significantly improved, which was 4.00, 4.70 and 3.48 times higher than that of $g-C_3N_4$, Co– $g-C_3N_4$ and V– $g-C_3N_4$, respectively (Figure 7a,b). In another work, Cheng et al. introduced atomically dispersed metallic elements Co and Ru, with different specific functions, into porous CN polymers (Figure 7c) (entry 13) [52]. The results of time-resolved PL spectroscopy show that the fluorescence lifetimes of Ru-doped CN (Ru–HCNP) (0.37 ns) and CN (0.38 ns) are almost the same; however, with the introduction of Co atoms, the fluorescence lifetime of CN is significantly reduced to 0.33 ns (Co–HCNP) and 0.32 ns (CoRu–HCNP). It is shown that the main influence on the carrier behavior is the Co atom. In the CO2 adsorption experiment, it was found that Ru atoms have a strong CO2 adsorption capacity, which can promote the formation of the intermediate COOH* and the dissociation of CO* in the photocatalytic reaction (Figure 7d). It is not difficult to see that Co and Ru play different roles in the diatomic doped system. Co atoms promote charge transfer, while Ru atoms promote the adsorption of CO2 on the surface. The coordinated

action of the two results in a high photocatalytic CO2 reduction rate with an apparent



Figure 7. (a) The possible charge transfer behavior and reaction mechanism of Co/V–g– C_3N_4 . (b) Kinetic curves of TC–HCl degradation over the different samples [51]. (c) Schematic illustration of doping structure and proposed dynamic photocarrier transfer mechanism in bimetallic Co-Ru-doped CN. (d) Comparison of CO₂ adsorption isotherms with different doped CN [52].

3. Surface-Functionalized Modification

quantum efficiency (AQE) of 2.8% at 385 nm.

It is recognized that in the unmodified intrinsic π -conjugated CN system, electron transfer among the tri-s-triazine units is random and uncontrolled, resulting in inefficient charge separation. In some cases, molecules or functional groups introduced into the CN framework can establish a donor-acceptor (D-A) structure in the molecule, which can not only suppress the recombination of electron-hole pairs by the directional transfer of photoelectrons between the tri-s-triazine unit and the doping unit, but also tune the energy band structure of the catalyst [85–89]. For example, Che et al. synthesized an ultrathin benzene ring skeleton modified CN (UCN-BI_x) -conjugated polymer by heating copolybenzoyl isothiocyanate (BI) and urea (Figure 8a) [90]. Due to the positive effect of the D-A structure, UCN-BI_x obtained significantly enhanced photocatalytic hydrogen evolution

activity and AQE (Figure 8b,c). The as-synthesized CN with the D-A structure effectively promotes the directional separation of charges and enhances the light absorption range. Furthermore, the modification of the benzene ring also makes the UCN-BI_x conduction band (CB) site more negative compared to pure CN, which also enhances its photocatalytic H_2 production capability (Figure 8d).



Figure 8. (a) Schematic illustration of the possible reaction path for fabrication of UCN-BIX D-A conjugated copolymers. (b) Photocatalytic H₂ evolution rate and (c) AQE of UCN-BI D-A conjugated copolymers. (d) Band alignment of pure $g-C_3N_4$ and UCN-BI400 [90]. Free energy diagrams for (e) the reduction of O₂ to H₂O₂ and (f) H₂O dehydrogenation to •H on the pristine CN and $g-C_3N_4-NH-CH_2-OH$ [91]. (g) Schematic of proposed structure of CN with Na doping and N≡C defect [53].

In addition to changing the charge behavior by constituting the D-A polymer, the insertion of functional groups can also improve the surface properties of the photocatalyst. Liu et al. successfully introduced a $-NH-CH_2-OH$ group on the surface of CN (g-C₃N₄-NH-CH₂-OH) by reacting formaldehyde with the $-NH_2$ group in the CN structure and used it for the photocatalytic production of H_2O_2 [91]. The presence of hydroxyl groups enhances the hydrophilicity of CN and facilitates the mass transfer between water molecules and CN. The experimental results and theoretical calculations show that the introduction of $-NH-CH_2-OH$ groups does not significantly change the microscopic morphology, light absorption or charge transfer properties of CN, but improves the hydrophilicity and O₂ adsorption properties of CN. The free energy of O₂ reduction to H_2O_2 and H_2O dehydrogenation over $g-C_3N_4-NH-CH_2-OH$ is lower, indicating that it is kinetically more favorable for the reduction of O_2 to H_2O_2 (Figure 8e,f). The activity of $g-C_3N_4-NH-CH_2-OH$ to generate H_2O_2 in a pure water system is significantly improved, which is 12.8 times that of pure CN.

Sometimes, the doping of elements also introduces special functional groups and achieves the effect of co–doping. For example, Na–doped porous CN was successfully synthesized using NaCl and DCDA as precursors (entry 14) [53]. In Fourier transform infrared spectroscopy (FT–IR), a new, strong peak appeared at 2180 cm⁻¹, which corre-

sponded to the cyano group ($-C\equiv N$), indicating that NaCl also introduced a new functional group (Figure 8g). Benefiting from Na doping and the introduction of cyano groups, CN exhibits significantly enhanced photocatalytic activity for H₂O₂ production and selectivity as high as 93%, which is approximately 220 times that of pure CN. DRS and DOS results show that the introduction of Na and cyano groups in CN will generate intermediate energy levels and shorten the band gap. According to the O₂ adsorption model calculated by DFT, the cyano group affects the charge distribution and polarizes the charge, promoting O₂ adsorption and protonation. Moreover, Na⁺ promotes the transfer of electrons to O₂ to generate a superoxide radical (\bullet O₂), which is an intermediate product of the synthesis of H₂O₂. In addition, the stronger H_a peak of CN in the solid-state NMR spectra and the smaller contact angle with H₂O indicate that the co-doping of Na and cyano groups also improves the surface environment of CN, making the surface very hydrophilic and easily adsorbing water molecules to form hydrogen bonds.

4. Characterization of Modified CN

Since the doping of foreign elements or functional groups in CN cannot be observed with the naked eye or by means of electron microscopy, in general, some characterization methods, such as X-ray photoelectron spectroscopy, solid-state nuclear magnetic resonance, Fourier transform infrared spectra, elemental mapping images and X-ray absorption spectroscopy, are needed to analyze the element doping. Some commonly used characterization methods to prove CN doping are listed below (Table 2) and analyzed via examples.

Characterization Techniques	Information	Limitations	
XPS	elemental composition, chemical structure, bonding environment	surface characterization techniques	
NMR	chemical environment	limited sensitivity, difficult for quantitative analysis	
FT-IR	functional groups triggering new vibrational modes	only sensitive to organic groups, not for detection of trace elements directly	
Elemental mapping	intuitive display of the presence of foreign elements	only reflects the spatial distribution of the element, without considering the chemical environment	
XAS	coordination environment and electronic state of single atomic CN	only reflects the average information of all species in the catalyst	

Table 2. Summary of the characterization of modified CN.

4.1. X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) is a technique for analyzing the chemical properties of the surfaces of substances. According to the position, intensity and area of the measured spectral peaks, the elemental composition, chemical structure, bonding and other information about the CN surface doped with hetero-elements can be obtained. For example, Wang et al. used XPS to analyze the structural information of CN containing C defects (V_C-OCN) (Figure 9a–c) [76]. It can be found that in the C 1s high-resolution XPS spectra, in addition to the basic impurity C atom peak (C–C), the N–C=N peak in the tri-s-triazine ring and edge amino (–NH_x), the modified CN also has a new peak at 289.0 eV that can be attributed to C–O. The calculated proportion of N–C=N in the total C atoms decreased to 38.2% compared with CN (61.7%), and the proportion of C–NHx increased significantly, which can be speculated to be caused by the absence of C atoms in the tri-s-triazine ring. In addition, in the N 1s and O 1s high-resolution XPS spectra, the ratio of the C–N=C peak area decreased and the new peak C–O–C appeared, further proving that some O atoms were bound to sp2 hybrid C by substituting N atoms.



Figure 9. The high-resolution XPS spectra of C 1s (a), N 1s (b) and O 1s (c) of the samples [76]. The high-resolution XPS spectra of C 1s (d), N 1s (e) and S 2p (f) of the samples, and (g) the proposed theoretical atomic structure of $Mo/S/g-C_3N_4$ [92].

Similarly, Li et al. analyzed the coordination environment of Mo and S co-doped CN $(Mo/S/g-C_3N_4)$ (Figure 9d–f) [92]. Due to the relatively small doping content of impurity elements, the existence of doping elements could not be observed in the XPS total spectrum. However, in the N 1s high-resolution spectrum, a peak at 397.8 eV corresponding to the N–Mo bond can be deconvoluted, indicating that the Mo element is successfully doped and forms a bond with the N atom. The two peaks decomposed in the S 2p spectrum correspond to S–Mo and S–C, respectively, and it can be speculated that the S atom replaces the N atom and forms bonds with the Mo and C atoms. At the same time, when Mo and S are doped, two new peaks appear in the C 1s spectra, corresponding to C–OH and C–NH groups. This may be due to the weakening of the van der Waals forces between the CN layers by the dopants, leading to the formation of C–OH and C–NH groups. According to this, the theoretical atomic structure of Mo/S/g–C₃N₄ was drawn, as shown in Figure 9g.

4.2. Solid-State NMR

Nuclear magnetic resonance (NMR) spectroscopy can be used to analyze the chemical environment of CN and doping elements. Luo et al. synthesized S-doped CN (S–CN)

and demonstrated S doping by ¹³C solid-state NMR spectroscopy (Figure 10a) [93]. For pure CN (U–CN), two characteristic peaks at 157.3 ppm and 165.1 ppm are assigned to the C atom of N–C=N and C–NH_x. However, in the S-doped CN, a new shoulder peak at 162.7 ppm indicates a significant change in the chemical state of C, with a higher electron density around the C–NH_x. This peak can be attributed to a C atom bonded to an S atom. Similar methods were also used to demonstrate C vacancies and O doping sites in CN (V_C–OCN₁₅) [76]. As shown in Figure 10b, the C1-to-C2 intensity ratio of the modified CN is slightly weaker than that of CN, implying that the C at the C_{3N} site is missing. Three new, weak signals were also found in the modified CN, indicating the existence of three new C species in V_C–OCN₁₅, namely the C atoms (C3, 163.6 ppm) connecting –NH_x around the C vacancy and the two C atoms (C4, 161.2 ppm and C5, 154.5 ppm) in C–O–C.



Figure 10. (a) Solid-state ¹³C NMR of U–CN and S–CN [93]. (b) ¹³C CP-MAS NMR spectra of CN and VC-OCN₁₅ [76]. (c) 13C NMR spectra of the prepared samples [94]. (d) FT-IR spectra of pristine g–C₃N₄ and CNO [95]. (e) FT-IR spectra of g–C₃N₄ and a-C₃N₄ [96]. (f) FT-IR spectra of g–C₃N₄ and O–CN [97].

Figure 10c shows the ¹³C NMR spectra of P-doped CN versus ordinary CN [94]. It can be seen that in addition to the characteristic signals of CN at 156.4 and 164.5 ppm, a new signal appears at 151.8 ppm for the modified sample (CN-NB, carbon nitride nanobelt; P–CN–NB, P-doped carbon nitride nanobelt), which can be attributed to C_3 atoms (C– C_1). It is particularly noted that no signal peak of P–C is observed on P-CN-NB, which can be attributed to the substitution of C atoms by dopant atoms to form P–N bonds instead of the substitution of N atoms.

4.3. Fourier Transform Infrared Spectra

When surface-functionalized modification in CN induces new vibrational modes, they can be characterized by FT-IR. For example, Wang et al. synthesized an oxidized graphitic carbon nitride (CNO) and characterized it by FT-IR (Figure 10d) [95]. The new peaks at 1720, 1385, 1080 and 970 cm⁻¹ of CNO are attributed to the vibrations of C=O, $-NO_2$, C=O and C=O-C, respectively, which confirm the doping of oxygen-containing functional groups. In another example, Xu et al. synthesized modified CN (a-C₃N₄) by base-assisted synthesis. The peak at 2178 cm⁻¹ in FT–IR and attributed to the cyano group ($-C\equiv N$) vibration proved the introduction of $-C\equiv N$ (Figure 10e) [96].

While FT–IR can characterize new vibrational modes, elemental doping cannot be demonstrated. When an element is doped into CN in the form of a single atom, it usually does not change the structure of CN so as to be indistinguishable in FT-IR. For example, an O-doped CN was synthesized and its FT-IR spectrum is shown in Figure 10f [97]. It

can be found that the FT-IR spectra of $g-C_3N_4$ and O–CN exhibit similar characteristic vibrational modes. Compared with $g-C_3N_4$, the FT-IR spectrum of O–CN undergoes some changes, such as the attenuation of the peak intensity at 807 cm⁻¹ and the shift in the peak position at 1235 cm⁻¹. This may be attributed to the perturbation effect of heteroatoms on the structure, but no obvious new peaks were found, i.e., the existence of trace doping elements could not be directly detected.

4.4. Elemental Mapping

Elemental mapping can provide the most intuitive proof of element doping, showing the type and distribution of elements in the form of dots. Most of the elements can be displayed in the mapping. For example, Figure 11a,b show that elements such as Ga [98], Co and Ru [52] are doped into CN and evenly distributed. However, only the distribution of element species and the approximate doping amount can be seen, and the element coordination and chemical bonding cannot be analyzed. Uniformly distributed elemental spots are also observed when CN and other materials are compounded but not doped. For example, Figure 11c,d show the elemental mapping and TEM of a ternary composite $TiO_2/Ti_3C_2/CN$ [21], where uniformly distributed Ti, C and N element spots can be observed, but not doped. In addition, the self-doped CN cannot be proven by elemental mapping.



Figure 11. Elemental mapping images of (a) Ga-doped CN [98], (b) Co/Ru-doped CN [52] and (c) $TiO_2/Ti_3C_2/CN$ triple Z-scheme compound heterojunction. (d) TEM images of $TiO_2/Ti_3C_2/CN$ [21].

4.5. X-ray Absorption Spectroscopy

X-ray absorption spectroscopy (XAS) is divided into X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS), which can provide valuable information about the coordination environment and the chemical state of the probed atoms. The coordination environment and electronic state of dopant elements in CN can be analyzed by XAS. Wang et al. used XANES spectroscopy to analyze the valence state of Cu doped in CN (Cu SAs/p-CNS) [99]. The XANES spectra of the Cu k-edge in Figure 12a show that the absorption edge of Cu SAs/p-CNS is located between the Cu foil and CuO, indicating that the valence state of Cu is between 0 and +2. In the EXAFS spectra (Figure 12b), the peak around 1.5A corresponds to the Cu–N connection, which illustrates the coordination environment of Cu. Unlike the Cu foil, no peak for Cu-Cu coordination was observed at 2.2A, indicating that Cu was incorporated into the CN as a single atom, without aggregation. Similarly, the coordination mode of W atoms supported on CN was also demonstrated by EXAFS (Figure 12c) [100]. The fitting results show that the W atom is attached to the CN structure alone in a W–N coordination manner and there is no W-W connection. Moreover, the EXAFS fitting results show that each W single atom is coordinated with four N atoms with a bond length of 1.773 ± 0.136 Å. The atomic structure of the sample was determined as the W–N4 model, as shown in Figure 12d.



Figure 12. (a) XANES and (b) EXAFS spectra of Cu k-edge of Cu SAs/p-CNS, Cu foil, CuO and CuPc [99]. (c) FT-EXAFS curves of W-SA-PCN-7.5 and the references. (d) Atomic structure model of W-SA-PCN-7.5 [100]. (e) N K-edge and (f) C K-edge XANES spectra of g–C₃N₄, CN–B, CN–H and BH400 [101].

In addition to analyzing the valence state and coordination environment of doped metal elements in CN, XAS of the C k-edge and N k-edge can also be used to analyze defects and doping in CN [101]. Figure 12e shows the N K-edge XANES of pure g-C3N4, B-doped CN (CN–B), defective N-deficient CN (CN–H) and both boron-doped and nitrogendeficient CN (BH400). It can be found that all CN have two typical π^* resonances at 400.3 and 403.3 eV, corresponding to C-N=C and N-3C, respectively. The peak intensities of the N K-edge can correspond to the amount of different N atoms or unoccupied N 2p states, respectively. The ratio of the two peak intensities of CN–B is almost the same as that of g-C3N4, indicating that CN-B does not introduce N deficiency. However, the K-edge intensities of CN–H and BH400 are lower than that of g-C3N4 and the peak intensities of C–N=C/N–3C are higher than that of g–C3N4, revealing that CN–H and BH400 have more N-3C defects. From the C K-edge XANES spectrum (Figure 12f), it can be found that all samples also have two peaks located at approximately 285.5 eV and 288.4 eV. The Ca peaks correspond to defect structures, and all modified CN have higher Ca peak intensities than pure CN, indicating more defect structures. A drop in peak Cb usually indicates disorder of the structure. BH400 exhibits a lower peak Cb intensity, indicating that, with the introduction of B doping and N defects, conjugated in-plane structural disorder is induced.

5. Summary and Outlook

In the context of increasingly serious environmental and energy issues, graphitic carbon nitride has shown promising application as a non-metallic organic semiconductor photocatalyst. CN has the advantages of a visible light response, good stability, non-toxicity and good redox ability. The redox ability obtained by CN absorbing visible light can be applied to various fields, such as pollutant degradation, water splitting to produce hydrogen, sterilization and CO_2 reduction. However, the problems of easy carrier recombination and low specific surface area in conventional BCN limit its photocatalytic performance and practical application. To enhance the photocatalytic efficiency of CN, doping and surface modification strategies are often used to tune the electronic band structure of carbon nitride and improve the separation of carriers. In this paper, the research progress regarding modification strategies for carbon nitride in recent years is reviewed. Metal elements are usually doped between the conjugated planes or in the heptazine ring voids located in the planes to stimulate the carrier separation/migration. Non-metal element doping can maintain the metal-free properties of $g-C_3N_4$, including hetero-doping and self-doping. Among them, hetero-doping can change the electronic energy band structure by replacing C or N atoms. Self-doping can adjust the electronic structure without introducing heteroatoms as recombination centers. Co-doping combines the advantages of single dopants to jointly promote the improvement of photocatalytic activity from various aspects. Surface-functionalized modification can facilitate carrier separation or improve catalyst surface properties. Moreover, some characterization methods that can prove the existence of doping and analyze the doping state are also discussed with examples, such as XPS, solid-state NMR, FT-IR, elemental mapping images and XAS.

Although many achievements have been made in the doping and surface modification of CN, there are still many problems that need to be solved in the future:

- (1) The typically used characterization methods are non-real-time processes. Therefore, the results cannot reflect the real state of the photocatalyst during photoreaction. To account for the effects of doping and surface modification on the photocatalytic performance of CN, more in situ characterization techniques besides in situ DRIFTs are needed.
- (2) Some have reported the decomposition of pristine CN during the photocatalytic reaction. The question of how to improve the photostability of doped/surface-modified CN should be carefully considered, as it is of great importance to its practical applications.
- (3) As for co-doping methods, it is difficult to control the location of the dopants. Much work should be done to adjust the doping structure to better exploit the synergistic effect.

In order to further improve the photocatalytic performance of carbon nitride, future development can be explored according to the following directions.

- (1) Doping carbon nitride to form a heterojunction with other semiconductor materials is a worthwhile research direction, particularly the new S-scheme heterojunction scheme, which can not only promote the separation of electron-hole pairs, but also maintain the strong redox ability of the catalyst.
- (2) The doping of single-atom noble metals can maximize the atom utilization and significantly enhance the photoreactivity. Recently, the synergistic effect of single-atom noble metals and metal particles has become a popular research direction.
- (3) Recently, the fabrication of crystalline CN (CCN) has attracted much attention due to its good crystallization, which provides an opportunity to further improve the photocatalytic activity of CCN photocatalysts by using doping and surface modification approaches.
- (4) Guiding practice with theory can also be used in photocatalyst design. Before preparation of the CN photocatalyst, DFT calculations can be used in advance for photocatalyst screening by predicting the effects of doping and surface modification on the electronic structure, interfacial charge transfer and energy band structure of CN.

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Abbreviations

CN	Carbon nitride
BCN	Bulk graphitic carbon nitride
HAADF-STEM	High-angle annular dark-field scanning transmission electron microscopy
CCN	Crystalline carbon nitride
НССР	Hexachlorocyclotriphosphazene
D-A	Donor-acceptor
XAS	X-ray absorption spectroscopy
XANES	X-ray absorption near-edge structure
EXAFS	Extended X-ray absorption fine structure

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