

Metal-free brush-like 3D carbon nitride delivers efficient red-light-driven photocatalysis

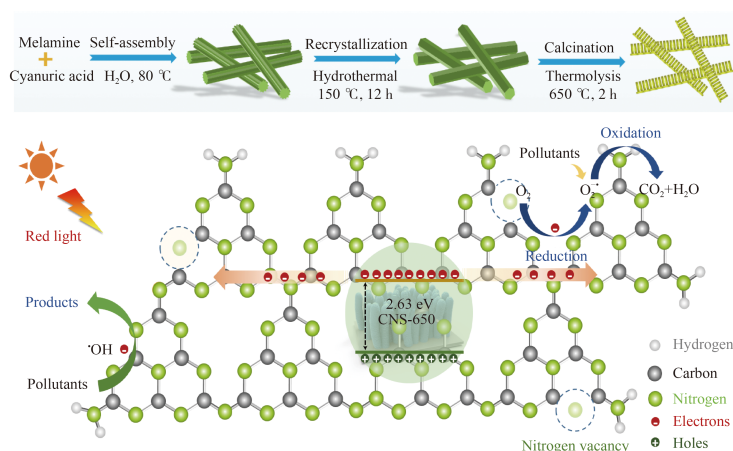
WANG Peng¹, HAN Yanling¹, LIU Yuanyuan^{1,*}, LU Pengfei², LI Xiao^{2,*}

¹ School of Material and Chemical Engineering, Xuzhou University of Technology, Xuzhou 221018, China;

² School of Chemical Engineering and Technology, China University of Mining and Technology, Xuzhou 221116, China

Abstract: In this study, melamine and cyanuric acid were used as precursors to form supramolecular crystals *via* hydrogen-bond-assisted self-assembly followed by hydrothermal treatment. Subsequent high-temperature calcination yielded a novel brush-like three-dimensional carbon nitride. The brush-like 3D architecture was found to expose more accessible active sites, markedly accelerate electron transfer, and suppress the recombination of photogenerated charge carriers. The resulting superoxide ($O_2^{\cdot-}$) and hydroxyl ($\cdot OH$) radicals generated *via* electron reduction were identified as the key reactive species in the photocatalytic process. Moreover, the surface of the brush-like structure is enriched with nitrogen vacancies, which enhance the catalyst's ability to harvest visible light. The photocatalytic performance of the brush-like CNS-650 catalyst was evaluated for rhodamine B (RhB) degradation. Under red-light irradiation (660 nm), its degradation rate was 7.4 times higher than that of bulk CN. This work provides valuable insights into the design and application of efficient metal-free 3D photocatalysts.

Key words: photocatalysis; carbon nitride; three dimensional structure; red-light



Photocatalysis is regarded as an effective approach for energy conversion and environmental remediation^[1–2]. Carbon nitride (CN) is a novel organic, metal-free polymeric semiconductor that exhibits excellent thermal and chemical stability, good biocompatibility, and strong visible-light responsiveness, making it a research hotspot in photocatalysis^[3–5]. However, bulk CN synthesized *via* direct thermal polymerization suffers from several drawbacks, including a low specific surface area, poor visible-light utilization, and low separation efficiency of photogenerated charge carriers^[6–7]. It has been shown that the morphology, size, and structure of photocatalysts significantly influence their catalytic performance, as catalysts with different

morphologies exhibit distinct optical, chemical, and physical properties. Consequently, tailoring the morphology of carbon nitride has become a major focus of research^[8–10].

In studies on the morphological control of CN, its nanostructures can be classified by dimensionality into zero-dimensional quantum dots, one-dimensional rod-like materials, two-dimensional nanosheets, and three-dimensional nanoporous architectures^[11–14]. CN quantum dots possess unique optical properties that enable the conversion of near-infrared light into visible light, playing a crucial role in enhancing light-harvesting capability. However, they have low surface energy, are prone to aggregation, and exhibit poor stability^[15]. One-dimensional

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* Corresponding author. E-mail: liuyuanyuan@xztu.edu.cn, lixiao@cumt.edu.cn.

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rod-like structures, such as nanorods, nanowires, and nanotubes, feature a large specific surface area and high aspect ratio, which enhance light absorption and shorten the transport pathways of charge carriers^[16]. Two-dimensional nanosheets typically exhibit good electrical conductivity, high electron mobility, and excellent chemical stability^[17]. However, the synthesis of ultrathin or even monolayer CN materials usually requires harsh conditions, such as strong acid treatment or chemical exfoliation, which are unsuitable for industrial-scale production and environmentally unfriendly^[18–19]. To overcome these limitations, assembling two-dimensional nanosheets into three-dimensional porous architectures has been demonstrated as an effective and feasible strategy. Three-dimensional porous structures not only exhibit strong light-harvesting ability and a high density of active sites but also provide more selective and shorter charge-transport pathways, all of which markedly enhance photocatalytic performance^[20]. Currently, the synthesis of 3D porous CN materials mainly relies on hard- or soft-template methods. However, template-assisted approaches have inherent drawbacks, including complex procedures, low production efficiency, potential damage to microstructures, and possible introduction of impurities^[21]. Therefore, there is an urgent need to develop green and efficient methods for fabricating three-dimensional CN architectures.

Supramolecules refer to assemblies composed of two or more molecules held together by non-covalent interactions, which self-assemble into stable, ordered aggregates while retaining structural integrity that endows them with well-defined microstructures and macroscopic properties^[22]. Unlike CN materials obtained directly from nitrogen-rich precursors *via* high-temperature thermal polymerization, using supramolecular assemblies as precursors offers distinct advantages for fabricating CN materials with tailored morphologies and has been successfully applied in this context^[23–24]. Among various supramolecular precursors, the most extensively studied are derivatives of melamine and cyanuric acid, which exhibit complementary electronic affinities and form highly ordered melamine-cyanuric acid supramolecular polymers through triple hydrogen bonding. For example, when equimolar amounts of melamine and cyanuric acid are co-precipitated in dimethyl sulfoxide, they form layered, spherical aggregates that, upon calcination, yield mesoporous hollow CN spheres^[25].

Introducing surface defects into the catalyst can create defect states within the semiconductor bandgap, thereby extending its photoresponsive range and enhancing photocatalytic performance^[26–27]. Yang et al.^[28] innovatively synthesized a novel CN semiconductor with excellent light-harvesting capability *via* photoinduced polymerization of triazine subunits. The resulting CN matrix contained abundant nitrogen vacancies, which effectively narrowed the bandgap by introducing vacancy-related localized states. Therefore, in this system, defect engineering of carbon nitride can be achieved by high-temperature calcination of

supramolecular precursors, significantly increasing the surface defect density and enhancing red-light absorption capability.

In this work, melamine-cyanuric acid supramolecular precursor with tunable morphology was employed to synthesize a novel brush-like carbon nitride assembled from nanoribbons. This approach not only endowed the photocatalyst with a unique hierarchical architecture but also enriched its surface with defect sites, thereby enhancing visible-light absorption and significantly improving the separation of photogenerated charge carriers. Various dye solutions were used to simulate wastewater, and the photocatalytic degradation performance of the as-prepared catalysts was systematically evaluated under different light sources. Comprehensive characterizations were conducted to elucidate the effects of morphology modulation on the nanostructure and optical properties of carbon nitride, and the underlying degradation mechanism was thoroughly investigated.

1 Experimental

1.1 Chemicals and reagents

Melamine ($C_3H_6N_6$) and cyanuric acid ($C_3H_3N_3O_3$) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Benzoquinone (BQ), disodium ethylenediamine tetraacetate (EDTA-2Na), and tert-butanol (*t*-BuOH) were obtained from Aladdin Reagent Co., Ltd. (Shanghai, China). Rhodamine B (RhB), methylene blue (MB), and methyl orange (MO) were purchased from Tianjin Chemical Reagent Research Institute (Tianjin, China).

1.2 Catalyst preparation

Preparation of CN: The CN material was obtained through a thermal condensation process. Melamine (30 g) was introduced into a crucible and calcined at 550 °C for 4 h with a heating rate of 5 °C/min.

Preparation of supramolecular crystals: 8 g of melamine and 8 g of cyanuric acid were separately dissolved in 400 mL of deionized water under continuous stirring in a water bath at 80 °C until complete dissolution. The clear and transparent cyanuric acid solution was then mixed with the melamine solution and stirred for an additional 30 min to ensure thorough mixing, followed by cooling to room temperature. This process resulted in the formation of a white precipitate identified as a melamine-cyanuric acid supramolecular complex. The precipitate was centrifuged twice and washed with deionized water. The purified precipitate was redispersed in 400 mL of deionized water to obtain a rod-like supramolecular aggregate solution with a loose structure at a concentration of 20 mg/mL. Subsequently, 60 mL of this solution was transferred into a 100 mL polytetrafluoroethylene reactor and heated at 150 °C in a thermostatic oven for 12 h. After the reaction,

the resulting white precipitate was collected by centrifugation, washed, and freeze-dried for 24 h to obtain the melamine-cyanuric acid supramolecular crystals.

Preparation of CNS: 2 g of melamine-cyanuric acid supramolecular crystals were calcined at 500, 550, 600 and 650 °C for 2 h to obtain photocatalysts. The resulting carbon nitride materials were designated as CNS-500, CNS-550, CNS-600 and CNS-650, respectively. The preparation process of the brush-like carbon nitride is shown in Figure 1.

1.3 Photocatalyst characterization

X-ray diffraction (XRD) measurements were carried out using a Rigaku Ultima IV diffractometer, scanning within the 2θ range of 5° to 85° . Surface morphologies were characterized by scanning electron microscopy (SEM) using a Hitachi SU8600 ultra-high-resolution instrument (Japan). X-ray photoelectron spectroscopy (XPS) analysis was conducted using a 250Xi spectrometer from Thermo Fisher Scientific (USA). To correct for surface charging, all binding energy values were referenced to the C 1s signal at 284.8 eV. N_2 adsorption-desorption isotherms and structural parameters were determined using a Quantachrome Autosorb-iQ2 analyzer (USA). Infrared (IR) spectra were collected using a Bruker Alpha spectrometer (Germany). Photoluminescence (PL) spectra were recorded on a Hitachi F-4600 fluorescence spectrometer (Japan). UV-vis absorption measurements were performed with a PerkinElmer Lambda 750 spectrophotometer (USA). The photoelectrochemical measurements were performed using a CHI660E electrochemical workstation (CH Instruments, USA). An Ag/AgCl electrode and a Pt electrode were used as the reference and counter electrodes, respectively. The working electrode was prepared by dispersing 10 mg of catalyst in a mixture of 500 μ L ethanol, 50 μ L Nafion

solution and 450 μ L deionized water, followed by ultrasonication. The resulting suspension was drop-cast onto FTO glass, covering an area of $1\text{ cm} \times 1\text{ cm}$. A 0.5 mol/L Na_2SO_4 aqueous solution was used as the electrolyte. Linear sweep voltammetry (LSV) curves were recorded at a scan rate of 0.05 V/s. Time-dependent photocurrent responses ($i-t$ curves) were recorded at open-circuit potential, with transient photocurrents measured at 30 s intervals during light on-off cycles. To assess the photoelectrochemical behavior of the prepared electrode materials, electrochemical impedance spectroscopy (EIS) was conducted across a frequency range spanning 0.1 Hz to 100 kHz. Radical species were detected *via* electron paramagnetic/spin resonance (EPR/ESR) spectroscopy using a Bruker EMXPLUS instrument. The CV curves were collected to analyse the electrochemically active surface area (ECSA).

1.4 Photocatalytic activity evaluation

The photocatalytic performance of CN, CNS-500, CNS-550, CNS-600 and CNS-650 were assessed through the degradation of aqueous solutions of rhodamine B (RhB), methylene blue (MB) and methyl orange (MO), each starting at a concentration of 10 mg/L. The experiments were carried out in a custom-designed photoreactor equipped with 50 W LED lamps (Philips) emitting at wavelengths of 420, 575 and 660 nm. In each experiment, 0.03 g of photocatalyst was uniformly dispersed in 20–50 mL of dye solution. Before light irradiation, the mixture was stirred magnetically in the absence of light for 30 min to ensure adsorption-desorption equilibrium was achieved. At intervals of 0.25 or 0.5 h, aliquots were withdrawn, centrifuged to remove solids, and the dye concentration in the supernatant was determined using a UV-vis spectrophotometer (Lambda 750).

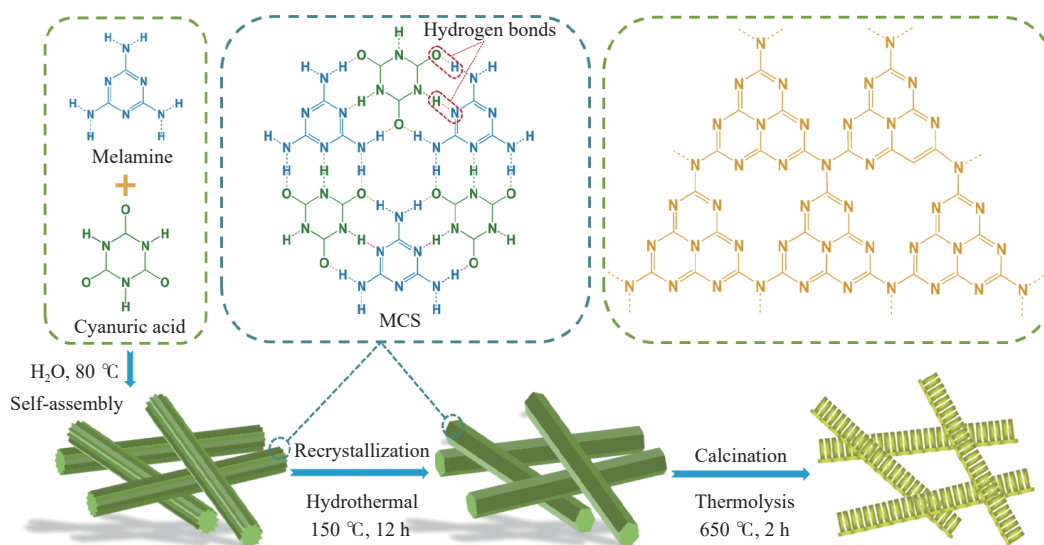


Fig. 1 Schematic illustration for the fabrication of brush-like carbon nitride

2 Results and discussion

2.1 Morphological evolution of photocatalysts

SEM images of CN, CNS-500 and CNS-550 are presented in Figure 2(a)–(c) respectively. While CN exhibits a predominantly bulk-like morphology with an average particle size of about 8.65 μm , the particle sizes of CNS-500 and CNS-550 are markedly reduced to 1.85 and 1.50 μm , respectively. Furthermore, both samples are found to consist of aggregated rod-like structures. With increasing calcination temperature, these rods gradually exfoliate, and the separation of rod-like particles becomes more pronounced in CNS-600 than in CNS-550. This phenomenon can be attributed to the rod-like nature of the supramolecular precursors of the CNS samples. Upon increasing the calcination temperature to 600 $^{\circ}\text{C}$, a significant transformation takes place, characterized by the emergence of abundant clubbed and tubular structures (Figure 2(d)). Notably, further elevating the calcination temperature to 650 $^{\circ}\text{C}$ provides sufficient thermal energy to drive extensive self-assembly and structural reconstruction. As shown in Figure 2(e) and 2(f), the nanorods generated during pyrolysis tend to align vertically along the substrate and ultimately assemble into uniformly oriented, stripe-like arrays. The resulting architecture exhibits a unique “brush-like” 3D morphology, which is markedly different from the conventional bulk $\text{g-C}_3\text{N}_4$ produced *via* thermal polymerization. In this study, the conventional muffle furnace heating method was employed, relying on an outward-to-inward heat conduction mechanism. This approach inherently produces pronounced temperature gradients, leading to uneven heating of the material. Such a non-uniform thermal environment compels the precursor to undergo a gradient-like thermal polycondensation process, resulting in structural residues at the edges and ultimately yielding the distinctive “brush-like” morphology. This hierarchical structure is expected to enhance light-harvesting capability by promoting multiple scattering and extended optical paths for solar irradiation.

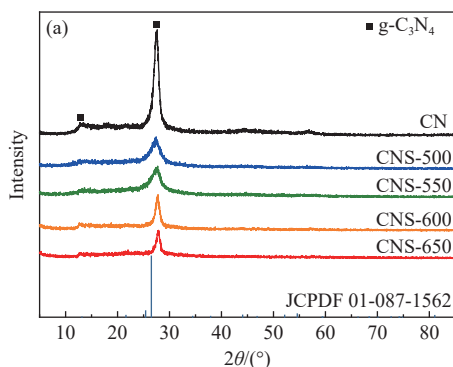


Fig. 3 (a) XRD patterns and (b) nitrogen adsorption-desorption isotherms of the CN, CNS-500, CNS-550, CNS-600 and CNS-650 samples

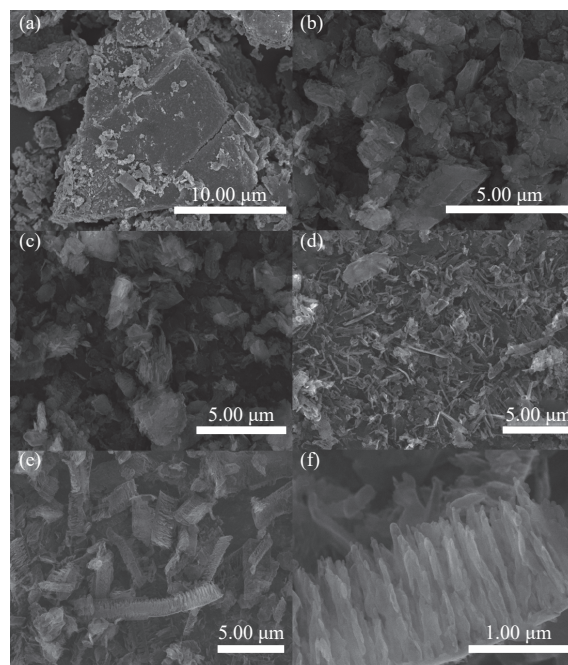
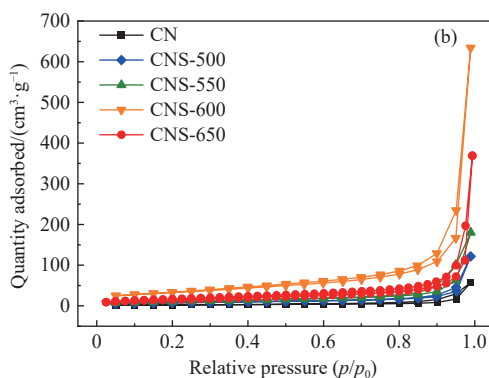


Fig. 2 SEM images of (a) CN, (b) CNS-500, (c) CNS-550, (d) CNS-600, (e) and (f) CNS-650

2.2 Structural and surface composition analysis of the photocatalysts

XRD patterns of the CNS series are shown in Figure 3(a). For the pristine CN sample, the characteristic peak at 13.0 $^{\circ}$ corresponds to the (100) plane, associated with in-plane structural packing of the tri-s-triazine units. The intense peak centered at 27.4 $^{\circ}$ is assigned to the (002) interlayer stacking of conjugated aromatic systems, typical of graphitic carbon nitride frameworks^[29–30]. Notably, CNS-500 and CNS-550 exhibit a broadened (002) peak at 27.4 $^{\circ}$, indicating enlarged interlayer spacing, which can be attributed to thermal exfoliation at elevated temperatures. In contrast, CNS-600 and CNS-650 display significantly sharper and slightly shifted (002) peaks, suggesting the formation of more ordered structures upon higher-temperature calcination, as supported by SEM observations.



The peak at 13.0° reflects the surface crystallinity of the samples, compared with CNS-500 and CNS-550, CNS-600 and CNS-650 exhibit enhanced crystallinity.

The nitrogen adsorption-desorption isotherms of the samples are shown in Figure 3(b). According to the IUPAC classification, all samples exhibit type IV isotherms with pronounced H1 hysteresis loops, indicating the presence of mesoporous structures^[31]. The textural parameters of the samples are summarized in Table 1. As shown, the specific surface area and pore volume of CNS samples increase significantly upon calcination between 500 and 600 °C. CNS-600 displays the highest surface area and pore volume, exceeding those of pristine CN by more than tenfold. In contrast, CNS-650 shows a decrease in surface area. Combined with SEM observations, this trend can be attributed to the formation of hollow tubular structures at 600 °C, while the development of a dense “brush-like” morphology at 650 °C partially reduces the accessible surface area.

The surface elemental composition and oxidation states of the photocatalysts were analyzed using XPS. The elemental distribution of C and N, as well as the

corresponding C/N ratios, are summarized in Table 2. Notably, compared to the bulk CN sample, the CNS materials with different morphologies exhibit significantly increased C/N ratios, suggesting the presence of nitrogen vacancies in the carbon nitride synthesized from supramolecular precursors^[32]. High-resolution N 1s spectra of CNS-500, CNS-550, CNS-600 and CNS-650 are shown in Figure 4. The N 1s peak can be deconvoluted into three components located at approximately 398.7, 399.9 and 401.2 eV, corresponding to sp^2 -hybridized nitrogen in C=N–C, tertiary nitrogen in the ring structure N–(C)₃, and amino functional groups (–NH or –NH₂), respectively^[33–34]. The relative proportions of these nitrogen species were quantitatively analyzed, and the results are presented in Table 3. With increasing calcination temperature, the N_{(2C)/N_(3C)} ratio gradually decreases. These results indicate that nitrogen vacancies in the CNS catalysts predominantly originate from the loss of N_(2C) species.

Electron paramagnetic resonance (EPR) spectroscopy of CN and CNS samples was also employed to further confirm the presence of nitrogen defects. As shown in Figure 5, all the samples exhibit similar Lorentzian signals.

Table 1 Textural properties of the photocatalysts

Sample	BET surface area/(m ² ·g ^{−1})	Pore volume/(cm ³ ·g ^{−1})	Pore diameter/nm
CN	8.510	0.092	3.830
CNS-500	18.195	0.183	3.064
CNS-550	27.492	0.272	3.061
CNS-600	91.002	0.966	3.058
CNS-650	58.903	0.565	2.975

Table 2 Contents of C, N and O atoms in the CN, CNS-500, CNS-550, CNS-600 and CNS-650 samples determined by XPS analysis

Sample	C	N	O	C/N
CN	43.49	53.37	3.13	0.82
CNS-500	47.14	49.8	3.78	0.96
CNS-550	46.05	51.18	2.77	0.90
CNS-600	45.92	52.25	1.83	0.88
CNS-650	45.24	50.81	3.95	0.89

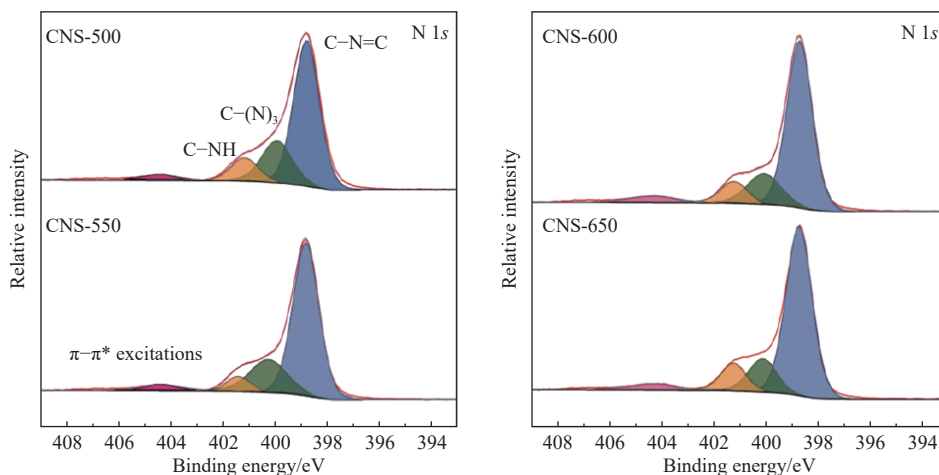


Fig. 4 High-resolution XPS spectra of CNS-500, CNS-550, CNS-600 and CNS-650 samples in regions of N 1s

Table 3 Contents of $N_{(2C)}$, $N_{(3C)}$ and N–H in N 1s obtained via XPS data

Sample	$N_{(2C)}$	$N_{(3C)}$	N–H	$N_{(2C)}/N_{(3C)}$
CNS-500	71.85	22.98	2.13	3.13
CNS-550	69.86	23.68	2.37	2.95
CNS-600	68.33	24.32	2.69	2.81
CNS-650	68.52	25.32	2.35	2.71

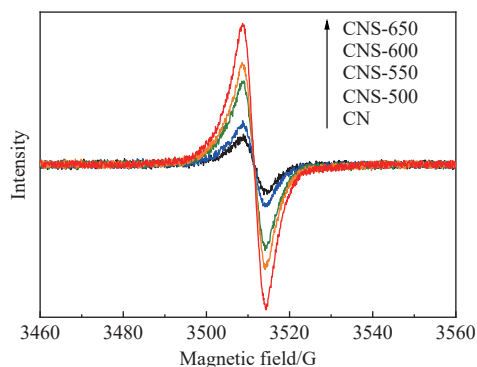


Fig. 5 EPR results of the CN, CNS-500, CNS-550, CNS-600 and CNS-650 samples

As expected, the EPR intensity of the CNS samples gradually increased with increasing calcination temperature. This result reflects the formation of nitrogen defects in the CNS matrix, consistent with the XPS results.

2.3 Studies on the optical properties

FT-IR spectroscopy was employed to investigate the surface functional groups of the catalysts, as shown in Figure 6. The FT-IR spectra of all samples exhibit nearly identical characteristic peaks, indicating that the bonding structure of $g\text{-C}_3\text{N}_4$ remains largely unchanged during catalyst preparation, and the chemical compositions are similar across all samples. The absorption bands are primarily located in three regions: the sharp peak at 813 cm^{-1} corresponds to the out-of-plane bending vibration of triazine rings; the bands within the range of $1240\text{--}1700\text{ cm}^{-1}$ are attributed to typical stretching vibrations of C–N heterocycles; and the broad absorption around

$3000\text{--}3300\text{ cm}^{-1}$ is assigned to N–H and O–H stretching vibrations^[35–37].

The UV-vis diffuse reflectance spectra of all samples are presented in Figure 7(a). The pristine CN sample exhibits an absorption edge at approximately 460 nm. In contrast, the CNS-500, CNS-550 and CNS-600 samples display a pronounced blue shift in the absorption edge, attributable to their morphological and structural evolution. Whereas CN retains a bulk structure, CNS-500 to CNS-600 gradually exfoliate into rod-like morphologies, resulting in smaller and thinner particles. This decrease in thickness and size contributes to the widening of the bandgap^[38–39]. However, a distinct shoulder peak at $500\text{--}660\text{ nm}$ was observed for the CNS-650 sample. As shown in Figure 7(b), the bandgap (E_g) of CN is about 2.70 eV. In contrast, the lower E_g value of CNS-650 (2.63 eV) indicates an improved light-harvesting ability compared with pristine CN. These results suggest that the unique brush-like 3D structure, enriched with defects and vacancies, can effectively tailor the electronic structure of CN, thereby narrowing the bandgap.

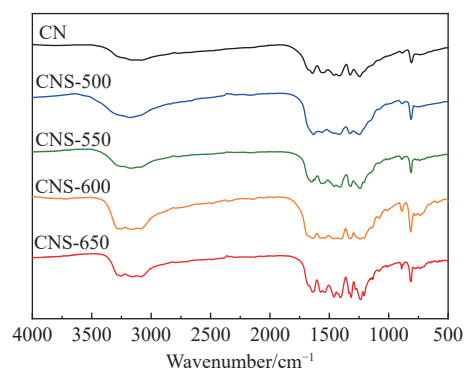


Fig. 6 FT-IR spectra of CNS-500, CNS-550, CNS-600 and CNS-650

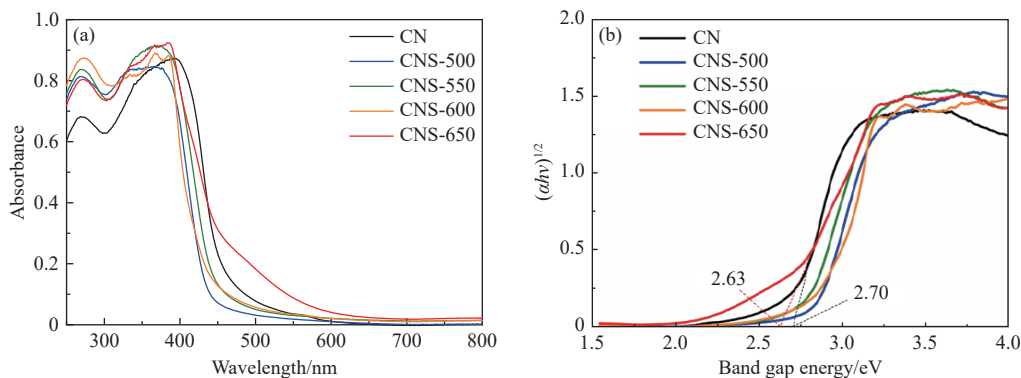


Fig. 7 (a) The UV-vis DRS spectra; (b) Plots of energy bandgap spectra of all samples

Figure 8 presents the PL emission spectra of the samples excited at 360 nm. In general, a weaker PL signal suggests a lower recombination rate of photoinduced charge carriers^[40–41]. As illustrated in Figure 8, the emission intensity of the CNS series gradually decreases with increasing calcination temperature compared to the pristine CN sample, with a particularly notable reduction observed for CNS-600 and CNS-650. Among them, CNS-650 exhibits the weakest emission signal, appearing nearly as a flat line, suggesting the lowest recombination rate of photogenerated electron-hole pairs and, consequently, the most efficient charge separation.

2.4 Evaluation of the catalytic performance

The photocatalytic performance of the CNS catalysts were assessed by monitoring dye degradation under visible-light irradiation at different wavelengths ($\lambda = 420, 575$ and 660 nm). As shown in Figure 9(a), under red light (660 nm) irradiation, the reference CN sample exhibited negligible degradation of RhB within 240 min. In contrast, upon reaching adsorption-desorption equilibrium, all CNS samples showed a significant decline in RhB concentration upon light exposure. The apparent reaction rate constants for CN, CNS-500, CNS-550, CNS-600 and CNS-650 were calculated to be 0.0005 , 0.0009 , 0.0029 , 0.0034 and 0.0037 min^{-1} , respectively. As illustrated in Figure 9(b) and 9(c), the red-light-driven photocatalytic degradation rate of CNS-650 is approximately 7.4 times higher than that of pristine CN, highlighting its superior visible-light responsiveness.

Under light irradiation at 420 and 575 nm, as shown in Figure 9(d) and 9(e), the RhB solution was rapidly degraded by the CNS series catalysts. Notably, CNS-650 achieved complete degradation within just 30 min. The degradation rate followed the order: CNS-650 > CNS-600 > CNS-550 > CNS-500, consistent with the trend observed under 660 nm red light. Furthermore, as illustrated in Figure 9(f), the CNS catalysts also exhibited good photocatalytic activities for the degradation of Methylene Blue (MB) and Methyl Orange (MO), confirming their broad-spectrum activity under visible-light irradiation.

2.5 Photoelectric performance test

To investigate the charge behavior of the semiconductor catalyst before and after illumination, transient photocurrent responses of pristine CN and the CNS-650 catalyst were measured.

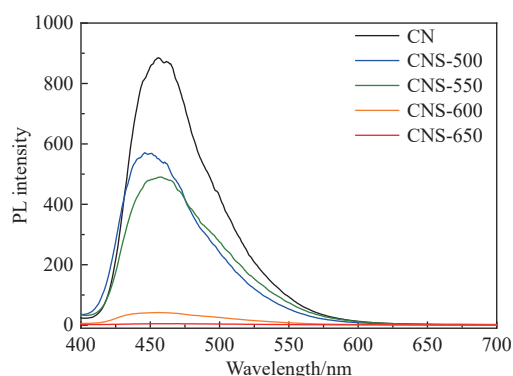


Fig. 8 PL spectra of CN and CNS samples

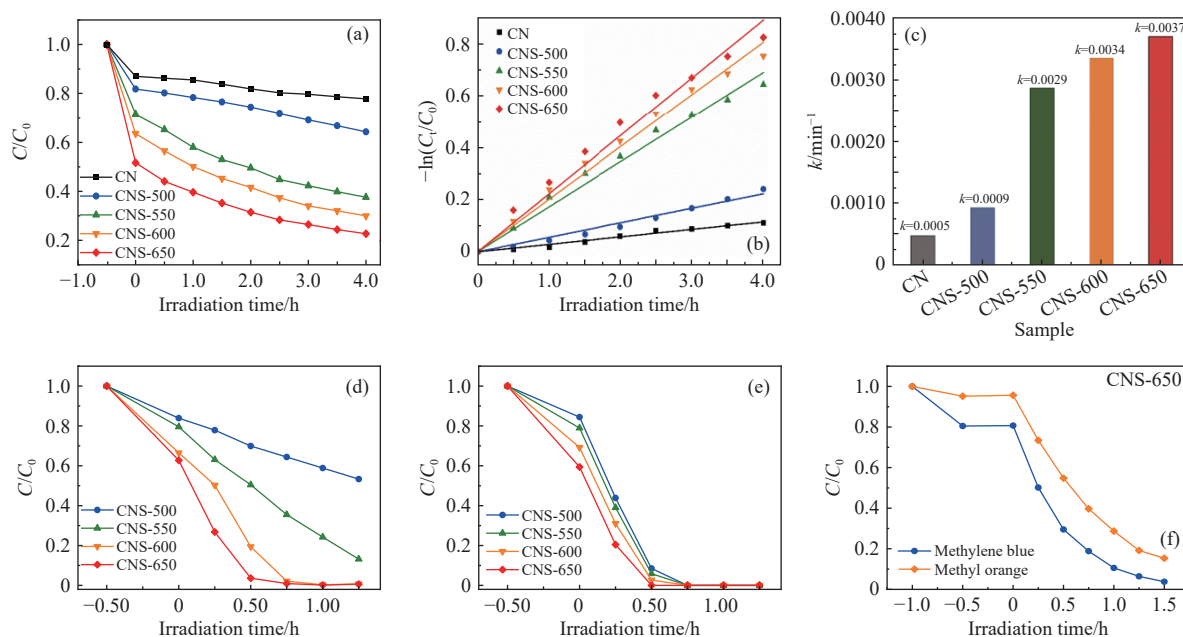


Fig. 9 (a) Comparison of the performance of photocatalysts on the RhB degradation under 660 nm LED irradiation; (b) and (c) The corresponding first-order kinetics plots; (d) and (e) Comparison of the performance of photocatalysts on the RhB degradation under 575 and 420 nm LED irradiation; (f) Comparison of the performance of photocatalysts on the MB and MO degradation under 420 nm LED irradiation (C_t : concentration, C_0 : initial concentration)

As shown in Figure 10(a), the photocurrent-time ($i-t$) curves were recorded under periodic light on/off cycles. Upon illumination, the photocurrent increased sharply and decreased rapidly when the light was turned off. Notably, CNS-650 exhibited a photocurrent density nearly four times greater than that of bulk CN. This enhancement is attributed to the unique brush-like 3D structure, which facilitates more efficient charge separation, transfer, and photocatalytic degradation^[42]. LSV curves of the catalysts are shown in Figure 10(b). Compared with pristine CN, CNS-650 exhibits a lower overpotential, suggesting a reduced energy barrier for initiating photocatalytic reactions^[43], specifically, at a current density of -0.025 mA/cm^2 , the overpotential of CNS-650 is 0.34 V, which is significantly lower than that of CN (0.63 V). EIS was conducted to evaluate the interfacial charge transfer resistance of the catalysts. As shown in Figure 10(c), semicircular Nyquist plots were obtained by fitting the EIS data. The radius of the Nyquist semicircle reflects the resistance to interfacial charge transfer^[44]. Compared with bulk CN, CNS-650 exhibits a smaller semicircular radius, indicating lower interfacial resistance and more efficient transport of photogenerated charge carriers. These electrochemical results are consistent with the observed photocatalytic degradation performance, further confirming that morphology engineering of carbon nitride effectively modulates the migration behavior of photogenerated carriers, thereby enhancing overall photocatalytic efficiency.

To evaluate the electrochemically active surface area, cyclic voltammetry measurements were performed at

various scan rates, as shown in Figure 11(a), (b). electrochemically active surface area is proportional to the double-layer capacitance (C_{dl}) extracted from the CV curves, with a higher C_{dl} value indicating a greater density of electrochemically active sites. The C_{dl} of CNS-650 ($32.67 \mu\text{F/cm}^2$) is notably higher than that of pristine CN ($18.75 \mu\text{F/cm}^2$), indicating a substantially greater number of exposed catalytic active sites (Figure 11(c))^[45]. These findings confirm that morphology engineering—particularly the construction of a brush-like three-dimensional architecture—promotes the exposure of a larger number of catalytic active sites on the CN surface.

The catalyst's band structure was examined using Mott-Schottky measurements. The Fermi levels were estimated from the Mott-Schottky plots by extrapolating the linear regions to the x -intercepts at 1000 and 2000 Hz. As shown in Figure 12, the positive slopes of the Mott-Schottky plots for CN and CNS-650 confirm that both materials are n -type semiconductors. Additionally, the Fermi levels of CN and CNS-650 were determined to be -0.92 and -0.90 V vs. NHE , respectively. According to previous studies, the conduction band (E_{CB}) of an n -type semiconductor generally lies $0.1\text{--}0.3 \text{ eV}$ below its Fermi level in terms of potential^[46]. Accordingly, the E_{CB} values of CN and CNS-650 were estimated to be -1.02 and -1.00 eV , respectively. Correspondingly, the valence band positions (E_{VB}) were determined to be $+1.68$ and $+1.63 \text{ eV}$, respectively, using the equation $E_{VB} = E_{CB} + E_g$, based on the $(\alpha h\nu)^{1/2}$ vs. $h\nu$ plots^[47–48].

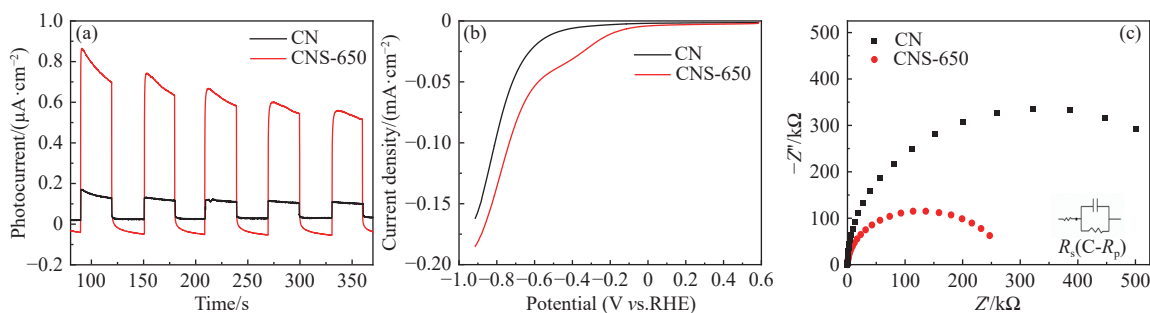


Fig. 10 $I-t$ curves (a), LSV curves (b), Nyquist plot (c) of CN and CNS-650 samples

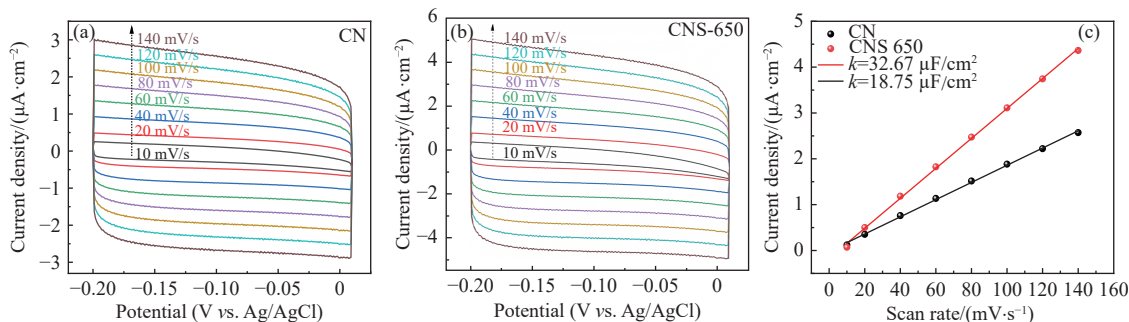


Fig. 11 The CV curves at different scanning rates of (a) CN and (b) CNS-650; (c) The fitting curves between the capacitances and scanning rates

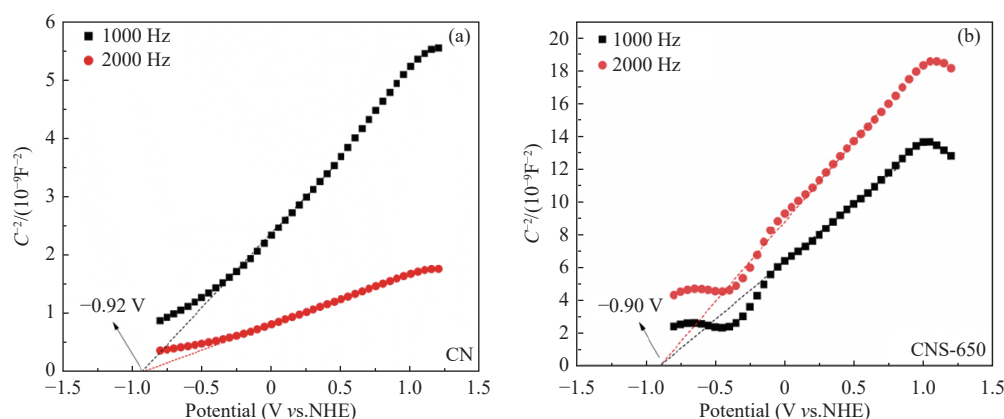


Fig. 12 Mott-Schottky plots of (a) CN and (b) CNS-650

2.6 Photocatalytic mechanism

To elucidate the underlying reaction mechanism, radical/hole trapping experiments were additionally conducted, as illustrated in Figure 13. The benzoquinone (BQ), disodium ethylenediamine tetraacetate (EDTA-2Na) and tert-butanol (*t*-BuOH) were selected as the trapping agents for the superoxide radical ($O_2^{\cdot-}$), holes (h^+) and hydroxyl radicals ($\cdot OH$), respectively^[49]. As shown in Figure 13, the addition of EDTA-2Na to the RhB solution had little effect on the degradation efficiency of CNS-660. This result suggests that holes (h^+) played a negligible role in the degradation process. In contrast, the presence of *t*-BuOH reduced the RhB degradation rate, whereas the addition of BQ markedly suppressed it.

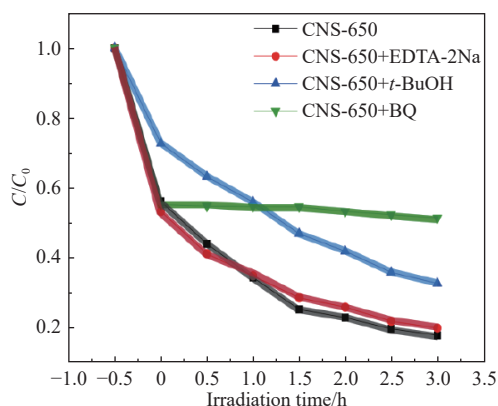
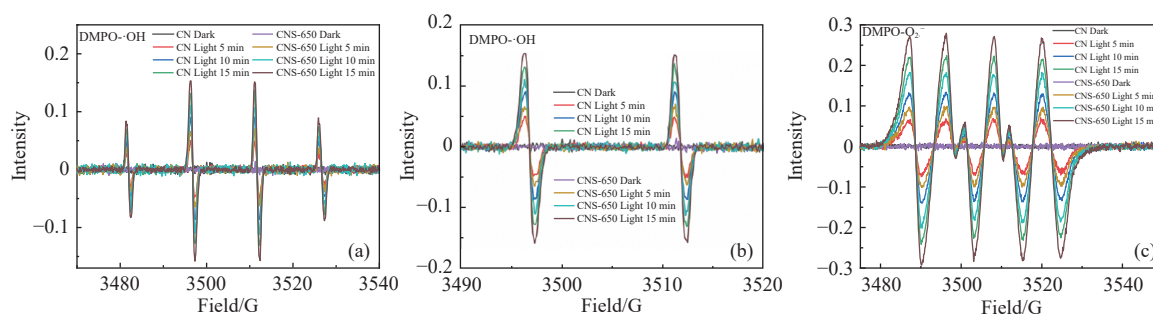


Fig. 13 Photocatalytic activity of CNS-650 for RhB degradation with various scavengers under 660 nm LED irradiation

These results demonstrate that the superoxide radical ($O_2^{\cdot-}$) was the primary reactive oxygen species, while the hydroxyl radical ($\cdot OH$) functioned as the secondary species in RhB degradation under red-light irradiation.

Furthermore, to elucidate the role of reactive species during the photocatalytic process, electron spin resonance (ESR) spectroscopy was utilized with 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) serving as the spin-trap. This technique enabled the identification of radical intermediates generated *in situ* under visible-light exposure in both CN and CNS-650 samples^[50–51]. ESR measurements provided direct evidence that the reactive oxygen species ($O_2^{\cdot-}$ and $\cdot OH$) are primarily responsible for the photodegradation observed in CN and CNS-650, strongly indicating that the photocatalytic oxidation of organic compounds on the brush-like CN proceeds *via* surface-mediated oxygen reduction pathways. As shown in Figure 14, characteristic ESR signals corresponding to $O_2^{\cdot-}$ and $\cdot OH$ radicals were observed under light irradiation, and their intensities increased progressively with extended irradiation time. CNS-650 exhibited significantly stronger ESR signals for $O_2^{\cdot-}$ and $\cdot OH$ radicals compared to CN, indicating its superior ability to generate or convert reactive oxygen species during the photocatalytic process. This result reveals that the brush-like CN structure facilitates the generation of more photoexcited electron-hole pairs, subsequently promoting the formation and transformation of abundant redox-active species, thereby enhancing the photocatalytic degradation reaction.

Based on the above findings, the photocatalytic mechanism of the brush-like CNS-650 is illustrated in Figure 15.

Fig. 14 ESR spectra of (a), (b) DMPO- $\cdot OH$ and (c) DMPO- $O_2^{\cdot-}$ in dark and under light irradiation

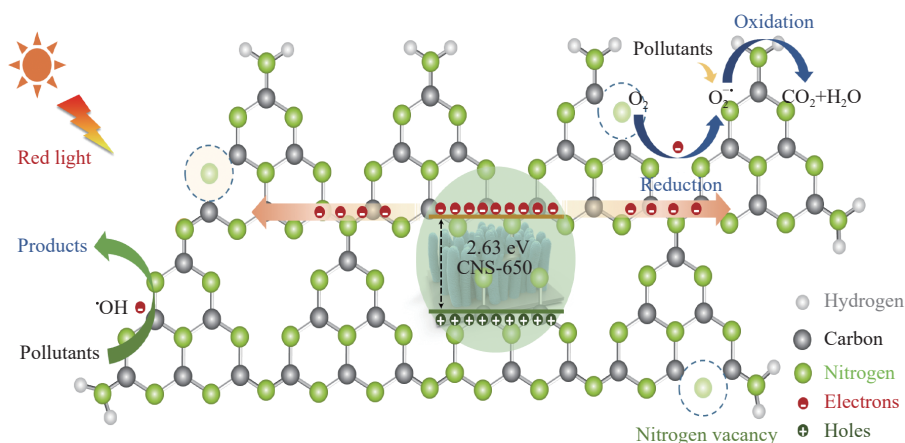
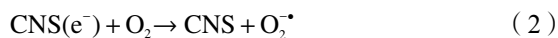


Fig. 15 The plausible mechanism of the photocatalytic performance of CNS-650

CNS-650, characterized by a narrow band gap and enriched with nitrogen defects, can be efficiently excited under red-light irradiation, leading to the generation of electron-hole pairs. In traditional $g\text{-C}_3\text{N}_4$ materials, the majority of photogenerated charge carriers recombine swiftly, leaving only a limited number of electrons available to engage in photocatalytic processes. However, the unique brush-like 3D architecture of CNS-650 enables more efficient transport of photogenerated electrons along the “bristle-like” pathways, promoting their migration to the catalyst surface, where they generate reactive oxygen species. Consequently, the recombination of photogenerated electrons and holes on the CNS-650 surface is effectively suppressed. The photogenerated electrons are likely to react with dissolved O_2 to produce superoxide radicals ($\text{O}_2^{\bullet-}$), which can further generate hydroxyl radicals ($\bullet\text{OH}$) through a secondary reaction with additional electrons. In contrast, the valence band (VB) potential of CNS-650 is less positive than the standard redox potential of $\bullet\text{OH}/\text{OH}^-$, indicating that the photogenerated holes in CNS-650 lack sufficient oxidative power to convert OH^- into $\bullet\text{OH}$ ^[52]. Drawing on the preceding analysis, a reasonable photocatalytic reaction pathway is outlined as follows^[53]:



The CNS sample is excited under red-light irradiation, leading to the generation of electrons and holes (Eq. (1)). On the brush-like 3D skeleton, the photogenerated electrons are captured by adsorbed molecular oxygen to produce superoxide radicals, which play a key role in dye degradation (Eq. (2)). Alternatively, the superoxide radicals can further react with protons and electrons to generate hydroxyl radicals, which act as stronger oxidizing agents (Eq. (3)).

Therefore, the remarkable enhancement in the photocatalytic activity of CNS-650 can be ascribed to the

synergistic effects of its optimized morphology and tailored molecular structure:

(1) The brush-like 3D architecture of CNS-650 maximizes visible-light harvesting through a multiple-reflection effect. Moreover, this unique structure facilitates the formation of nitrogen defects on the catalyst surface, thereby significantly enhancing its red-light absorption capacity.

(2) The incorporation of the brush-like architecture modulates the electronic structure of pristine CN, resulting in the generation of additional catalytic active sites. Such structural tuning extends the range of visible-light absorption, enhances charge transport properties, and promotes effective separation of photoinduced electron-hole pairs.

(3) The superoxide radical ($\text{O}_2^{\bullet-}$) is identified as the dominant reactive species in visible-light-driven photocatalysis, while hydroxyl radicals ($\bullet\text{OH}$) serve as secondary contributors that assist in the degradation process.

3 Conclusion

In this study, a supramolecular precursor was employed to synthesize a brush-like three-dimensional carbon nitride with a nitrogen-vacancy-rich surface, which significantly enhanced red-light absorption. Compared with bulk $g\text{-C}_3\text{N}_4$, the brush-like architecture offers a higher density of catalytic active sites and promotes both charge-carrier migration and mass transport. This markedly improves the separation efficiency of photogenerated charge carriers, thereby enabling the generation of larger quantities of key reactive species ($\text{O}_2^{\bullet-}$ and $\bullet\text{OH}$) for enhanced photocatalytic performance. The synergistic effects of morphological optimization and nitrogen vacancies significantly enhanced the photocatalytic degradation activity, with the brush-like 3D $g\text{-C}_3\text{N}_4$ exhibiting a red-light-driven degradation rate 7.4 times higher than that of bulk $g\text{-C}_3\text{N}_4$. Furthermore, we propose that the red-light photocatalytic efficiency of CNS materials can be further improved through rational modulation of their surface properties and electronic

structures.

Declaration of Competing Interest

The authors declare no conflict of interest.

References

- [1] YAN Z, YIN K, XU M, et al. Photocatalysis for synergistic water remediation and H₂ production: A review[J]. *Chem Eng J*, 2023, 472: 145066.
- [2] TAO X, ZHAO Y, WANG S, et al. Correction: Recent advances and perspectives for solar-driven water splitting using particulate photocatalysts[J]. *Chem Soc Rev*, 2022, 51: 3561–3608.
- [3] WANG X, MAEDA K, THOMAS A, et al. A metal-free polymeric photocatalyst for hydrogen production from water under visible light[J]. *Nat Mater*, 2009, 8: 76–80.
- [4] ZHUZHANG H, LIANG X, LI J, et al. Precise manipulation on the structural defects of poly (Triazine imide) single crystals for efficient photocatalytic overall water splitting[J]. *Angew Chem Int Ed*, 2025, 137(11): e202421861.
- [5] YANG M, LIAN R, ZHANG X, et al. Photocatalytic cyclization of nitrogen-centered radicals with carbon nitride through promoting substrate/catalyst interaction[J]. *Nat Commun*, 2022, 13: 4900.
- [6] CHEN Y, CHENG M, LAI C, et al. The collision between g-C₃N₄ and QDs in the fields of energy and environment: Synergistic effects for efficient photocatalysis[J]. *Small*, 2023, 19(14): 2205902.
- [7] CHENG J, HOU Y, LIAN K, et al. Metalized carbon nitrides for efficient catalytic of Functionalization of CO₂[J]. *ACS Catal*, 2022, 12(3): 1797–1808.
- [8] LIU Y, GUO X, CHEN Z, et al. Microwave-synthesis of g-C₃N₄ nanoribbons assembled seaweed-like architecture with enhanced photocatalytic property[J]. *Appl Catal B: Environ*, 2020, 266: 118624.
- [9] WANG S, ZHANG J, LI B, et al. Morphology-dependent photocatalysis of graphitic carbon nitride for sustainable remediation of aqueous pollutants: A mini review[J]. *J Environ Chem Eng*, 2022, 10(3): 107438.
- [10] CHEN W, LIU M, LI X, et al. Synthesis of 3D mesoporous g-C₃N₄ for efficient overall water splitting under a Z-scheme photocatalytic system[J]. *Appl Surf Sci*, 2020, 512: 145782.
- [11] AHMED M, MAHMOUD S, MOHAMED A, et al. Unveiling the photocatalytic potential of graphitic carbon nitride (g-C₃N₄): A state-of-the-art review[J]. *RSC Adv*, 2024, 14(35): 25629–25662.
- [12] LAU V, LOTSCH B. A tour-guide through carbon nitride-land: Structure-and dimensionality-dependent properties for photo(electro)chemical energy conversion and storage[J]. *Adv Energy Mater*, 2022, 12(4): 2101078.
- [13] ZHANG Q, HUANG S, DENG J, et al. Ice-assisted synthesis of black phosphorus nanosheets as a metal-free photocatalyst: 2D/2D heterostructure for broadband H₂ evolution[J]. *Adv Funct Mater*, 2019, 29(28): 1902486.
- [14] ZHANG Q, YANG F, ZHOU S, et al. Broadband photocatalysts enabled by 0D/2D heterojunctions of near-infrared quantum dots/graphitic carbon nitride nanosheets[J]. *Appl Catal B: Environ*, 2020, 270: 118879.
- [15] MAJDOUB M, SENGOTTUVELU D, NOURANIAN S, et al. Graphitic carbon nitride quantum dots (g-C₃N₄ QDs): From chemistry to applications[J]. *ChemSusChem*, 2024, 17(13): e202301462.
- [16] JING X, ZHANG Y, CHANG H, et al. When 2D g-C₃N₄ meets 0D CNQDs and 1D CNTs: A strategy for photocatalytic hydrogen production over a ternary non-metallic catalyst[J]. *Sep Purif Technol*, 2024, 343: 127161.
- [17] ZHAO B, ZHONG W, CHEN F, et al. High-crystalline g-C₃N₄ photocatalysts: Synthesis, structure modulation, and H₂-evolution application[J]. *Chin J Catal*, 2023, 52: 127–143.
- [18] CHEN L, MAIGBAY M, LI M, et al. Synthesis and modification strategies of g-C₃N₄ nanosheets for photocatalytic applications[J]. *Adv Powder Mater*, 2024, 3(1): 100150.
- [19] CHEN Y, TAN L, ZHANG H, et al. Metal-free in situ carbon-nanotube-modified mesoporous graphitic carbon nitride nanocomposite with enhanced visible light photocatalytic performance[J]. *Res Chem Intermed*, 2021, 47: 3349–3362.
- [20] ANUS A, PARK S. The synthesis and key features of 3D carbon nitrides (C₃N₄) used for CO₂ photoreduction[J]. *Chem Eng J*, 2024, 486: 150213.
- [21] WANG J, WANG S. A critical review on graphitic carbon nitride (g-C₃N₄)-based materials: Preparation, modification and environmental application[J]. *Coordin Chem Rev*, 2022, 453: 214338.
- [22] ALLAM T, BALDERSTON D E, CHAHAL M K, et al. Tools to enable the study and translation of supramolecular amphiphiles[J]. *Chem Soc Rev*, 2023, 52: 6892–6917.
- [23] DHARMARAJAN N P, VIDYASAGAR D, YANG J H, et al. Bio-inspired supramolecular self-assembled carbon nitride nanostructures for photocatalytic water splitting[J]. *Adv Mater*, 2024, 36(2): 2306895.
- [24] BARRIO J, LI J, SHALOM M. Carbon nitrides from supramolecular crystals: From single atoms to heterojunctions and advanced photoelectrodes[J]. *Chem Eur J*, 2023, 29(62): e202302377.
- [25] TIAN S, YIN Y, LIU M, et al. Atomically dispersed Cu-N₃ on hollow spherical carbon nitride for acetaminophen degradation: Generation of ¹O₂ from H₂O₂[J]. *Sep Purif Technol*, 2023, 318: 124016.
- [26] XUE X, CHEN H, XIONG Y, et al. Near-infrared-responsive photo-driven nitrogen fixation enabled by oxygen vacancies and sulfur doping in black TiO_{2-x}S_y nanoplatelets[J]. *ACS Appl Mater Interfaces*, 2021, 13(4): 4975–4983.
- [27] LI J, PAN W, LIU Q, et al. Interfacial engineering of Bi₁₉Br₃S₂₇ nanowires promotes metallic photocatalytic CO₂ reduction activity under near-infrared light irradiation[J]. *J Am Chem Soc*, 2021, 143(17): 6551–6559.
- [28] YANG P, WANG R, ZHOU M, et al. Photochemical construction of carbonitride structures for red-light redox catalysis[J]. *Angew Chem Int Edit*, 2018, 130(28): 127161.

- 8810–8813.
- [29] ZHENG Y, LIU Y, GUO X, et al. In-situ construction of morphology-controllable OD/1D g-C₃N₄ homojunction with enhanced photocatalytic activity[J]. Appl Surf Sci, 2021, 563: 150317.
- [30] LI J, ZHANG H, LI Y, et al. Asymmetrical intra-molecular junction enables redox active sites on bio-decorated carbon nitride toward H₂O₂ photosynthesis[J]. Chem Eng J, 2025, 519: 165018.
- [31] WANG P, WEI S, SUN K, et al. Study on the synergistic catalysis of CeO₂ regulated Co⁰–Co^{δ+} dual sites for direct synthesis of higher alcohols from syngas[J]. Ind Eng Chem Res, 2022, 61(11): 3900–3909.
- [32] WANG P, TIAN L, GAO X, et al. Two - photon absorption in a defect - engineered carbon nitride polymer drives red - light photocatalysis[J]. ChemCatChem, 2020, 12(16): 4185–4197.
- [33] LIU Y, CHEN X, KAMALI M, et al. Unraveling the presence and positions of nitrogen defects in carbon nitride[J]. Adv Funct Mater, 2024, 34(40): 2405741.
- [34] WANG P, WEI S, HAN Y, et al. Metal-free C₆₀-doped mesoporous carbon nitride drives red-light photocatalysis[J]. Langmuir, 2024, 40(27): 14045–14056.
- [35] LIU Y, ZHENG Y, ZHANG W, et al. Template-free preparation of non-metal (B, P, S) doped g-C₃N₄ tubes with enhanced photocatalytic H₂O₂ generation[J]. J Mater Sci Technol, 2021, 95: 127–135.
- [36] NGUYEN P A, DAO Q D, DANG T T, et al. Highly dispersed PtO over g-C₃N₄ by specific metal-support interactions and optimally distributed Pt species to enhance hydrogen evolution rate of Pt/g-C₃N₄ photocatalysts[J]. Chem Eng J, 2023, 464: 142765.
- [37] ZANDIPAK R, BAHRAMIFAR N, TORABI M, et al. Synergistic effect of graphitic-like carbon nitride and sulfur-based thiazole-linked organic polymer heterostructures for boosting the photocatalytic degradation of pharmaceuticals in water[J]. Chem Eng J, 2024, 494: 152843.
- [38] XIE Z K, JIA Y J, HUANG Y Y, et al. Near-infrared light-driven photocatalytic reforming lignocellulose into H₂ and chemicals over heterogeneous carbon nitride[J]. ACS Catal, 2023, 13(20): 13768–13776.
- [39] HUANG J, KLAHN M, TIAN X, et al. Exfoliated polymeric carbon nitride nanosheets for photocatalytic applications[J]. ACS Appl Nano Mater, 2024, 7(7): 7442–7452.
- [40] YANG R, SHI H, ZHAO J, et al. Novel asymmetric aggregation strategy to boost charge separation in carbon nitride polymers for high-performance hydrogen photosynthesis[J]. ACS Catal, 2024, 14(12): 9607–9617.
- [41] DU W, SHI H, ZHANG H, et al. Controlled asymmetric aggregation advances $n \rightarrow \pi^*$ electronic transition and charge separation for enhanced photocatalytic hydrogen synthesis[J]. J Catal, 2024, 432: 115453.
- [42] LI X, WAN J, MA Y, et al. Mesopores octahedron GCNOX/Cu₂O@C inhibited photo-corrosion as an efficient visible-light catalyst derived from oxidized g-C₃N₄/HKUST-1 composite structure[J]. Appl Surf Sci, 2020, 510: 145459.
- [43] ZHANG L, HAO X, LI J, et al. Unique synergistic effects of ZIF-9(Co)-derived cobalt phosphide and CeVO₄ heterojunction for efficient hydrogen evolution[J]. Chinese J Catal, 2020, 41: 82–94.
- [44] HAN Z, YANG Z, XIE Y, et al. Photothermalcatalytic hydrogen production by continuous gaseous water splitting over Ni₃N/g-C₃N₄[J]. ChemCatChem, 2025, 17(8): e202500128.
- [45] HAN Y, HE J, HU L, et al. In-situ growth 2D Fe₂P nanosheets on the surface of 1D Cd_{0.9}Zn_{0.1}S nanorods for remarkably improved photocatalytic H₂ evolution[J]. Appl Catal A: Gen, 2024, 677: 119661.
- [46] XIE Z, FENG Y, WANG F, et al. Construction of carbon dots modified MoO₃/g-C₃N₄ Z-scheme photocatalyst with enhanced visiblelight photocatalytic activity for the degradation of tetracycline[J]. Appl Catal B: Environ, 2018, 229: 96–104.
- [47] LIU Q, YU Z, LIANG D, et al. Elemental imprinting-induced interfacial growth strategy to bridge g-C₃N₄ and Bi₂MoO₆ with engineering rapid electron transfer pathway for efficient visible light-driven photocatalysis[J]. Chem Eng J, 2024, 496: 154057.
- [48] LUO H, SHAN T, ZHOU J, et al. Controlled synthesis of hollow carbon ring incorporated g-C₃N₄ tubes for boosting photocatalytic H₂O₂ production[J]. Appl Catal B: Environ, 2023, 337: 122933.
- [49] ZHANG Q, DENG J, XU Z, et al. High-efficiency broadband C₃N₄ photocatalysts: Synergistic effects from upconversion and plasmons[J]. ACS Catal, 2017, 7(9): 6225–6234.
- [50] LIU W, WANG Y, HUANG H, et al. Spatial decoupling of redox chemistry for efficient and highly selective amine photoconversion to imines[J]. J Am Chem Soc, 2023, 145(13): 7181–7189.
- [51] LU X, CHEN Z, HU Z, et al. Boosted charge transfer for highly efficient photosynthesis of H₂O₂ over Z-scheme Γ/K⁺ Co-doped g-C₃N₄/metal–organic-frameworks in pure water under visible light[J]. Adv Energy Mater, 2024, 14(38): 2401873.
- [52] HASSANI A, KRISHNAN S, SCARIA J, et al. Z-scheme photocatalysts for visible-light-driven pollutants degradation: A review on recent advancements[J]. Curr Opin Solid St M, 2021, 25(5): 100941.
- [53] MAMBA G, MISHRA A K. Graphitic carbon nitride (g-C₃N₄) nanocomposites: A new and exciting generation of visible light driven photocatalysts for environmental pollution remediation[J]. Appl Catal B: Environ, 2016, 198: 347–377.

非金属刷状三维氮化碳驱动高效红光光催化

王 鹏¹, 韩燕玲¹, 刘园园^{1,*}, 芦鹏飞², 李 晓^{2,*}

(1. 徐州工程学院 材料与化学工程学院, 江苏 徐州 221018; 2. 中国矿业大学 化工学院, 江苏 徐州 221116)

摘 要: 本研究以三聚氰胺和三聚氰酸为前驱体, 通过水热法在氢键驱动下自组装形成超分子晶体, 再经高温热聚合构筑具有独特“毛刷状”形貌的三维氮化碳材料。研究发现, 此种刷状三维结构能够暴露更多活性位点, 显著促进电子传输, 并有效抑制光生电子-空穴对的复合。机理研究表明, 光催化过程中起主导作用的活性物种为超氧自由基($\text{O}_2^{\bullet-}$)与羟基自由基($\bullet\text{OH}$)。此外, 刷状结构表面富含氮空位, 进一步增强了催化剂对可见光的吸收能力。在以罗丹明 B 为模型污染物的光催化降解实验中, 刷状氮化碳(CNS-650)在 660 nm 红光照射下的降解速率达到传统块状氮化碳的 7.4 倍。本研究为开发高效非金属三维光催化剂提供了新思路。

关键词: 光催化; 氮化碳; 三维结构; 红光

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作者简介:



王鹏(1986), 博士, 副教授, 研究方向为 C1 化学与化工, wangp@xzit.edu.cn。



李晓(1989), 博士, 副教授, 研究方向为 C1 化学与化工、煤炭清洁转化及固废资源化利用, lixiao@cumt.edu.cn。



刘园园, 博士, 讲师, 研究方向为光催化, liuyuanyuan@xzit.edu.cn。