



Cite this: *J. Mater. Chem. A*, 2026, 14, 22751

Mechanistic insights into the formation of N-vacancies at sp^2 -hybridized sites in non-metal doped g- C_3N_4 for solar-to- H_2 conversion and environmental remediation reactions

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Designing and constructing an efficient photocatalyst based on graphitic carbon nitride (g- C_3N_4) nanosheets is vital for solar-to-fuel and pollutant degradation reactions. Particularly, defect engineering can effectively modify the electronic band structures, serve as active sites and promote charge separation, leading to enhanced photocatalytic activity. Herein, we report dual non-metal doped g- C_3N_4 (C- and O-doped g- C_3N_4) with N-vacancies for photoredox reactions. Benefitting from dual doping, N-defects and a porous nature, the optimized g- C_3N_4 photocatalyst displays extended visible-light harvesting, a higher specific surface area, and efficient photoinduced charge separation. Consequently, the as-designed g- C_3N_4 exhibits a higher visible-light-driven photocatalytic H_2 evolution activity of approximately $1850 \mu\text{mol g}^{-1} \text{h}^{-1}$, along with stable performance over 24 hours. In addition, the defect-engineered g- C_3N_4 photocatalyst delivers a high tetracycline degradation efficiency of 82%. The enhanced activity can be attributed to the synergistic effects of midgap states induced by doping and N-defects, along with improved charge-carrier separation. Furthermore, the physical mechanism governing carrier dynamics is systematically investigated. Our work offers useful guidance for the design of two-dimensional (2D) porous nanosheets for photocatalytic systems and optoelectronic device applications.

Received 2nd July 2025
Accepted 22nd April 2026

DOI: 10.1039/d5ta05329c

rsc.li/materials-a

1. Introduction

The need to replace a society based on fossil fuels with clean renewable energy has been widely recognized. As a clean energy source with ultra-high energy density, hydrogen (H_2) is being swiftly industrialized in the context of carbon neutrality. Therefore, the semiconductor-based photocatalytic H_2 evolution reaction, which utilizes abundant solar light and water, offers a promising route to meet this demand.^{1–3} Graphitic carbon nitride (g- C_3N_4 or GCN) is a robust organic metal-free semiconductor photocatalyst that has attracted great attention for the H_2 evolution reaction (HER) due to its distinctive properties, such as tunable band structures, visible-light absorption, environmentally benign nature, abundance, and thermal and chemical stability.^{4–6} However, the solar-to- H_2 conversion efficiency of GCN is hindered by insufficient light absorption in the visible-light

region (bandgap; $E_g = 2.7 \text{ eV}$), a lower surface area and a quick charge recombination rate.⁷ Therefore, designing GCN with enhanced broad-spectrum light-harvesting properties is one of the most effective routes for improving the solar-to-hydrogen conversion reaction. To improve the photocatalytic activity of GCN, various strategies have been used, such as doping,^{8–10} loading of metal nanoparticles,^{11–13} nanostructure modulation,^{14–16} and fabrication of heterojunctions.^{17–19} The doping of GCN causes lattice distortion, better electrical conductivity, enhanced light absorption, and the spatial twisting of layers, which result in improved photocatalytic H_2 evolution activity. The loading of metal NPs onto GCN could form a Schottky barrier that facilitates the rapid transfer of electrons from GCN, thereby considerably improving charge separation properties. Besides, precious metals, like gold (Au) or silver (Ag), exhibit a localized surface plasmon resonance (LSPR) effect, which effectively boosts light harvesting and thereby promotes photoreduction reactions. Particularly, GCN nanostructures, compared with bulk GCN, offer large specific surface areas, more abundant edge and active sites, enhanced in-plane electron mobility and improved delocalization of charge carriers under photoexcitation, thereby increasing photocatalytic activity. Several GCN-based heterostructured photocatalysts were designed to restrict the electron-hole recombination rate and further boost the interfacial charge transfer *via* type-I, type-II, Z-

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scheme, or S-scheme mechanisms, thereby achieving excellent photocatalytic H₂ evolution activity. Although these strategies assisted in improving the HER performance of GCN photocatalysts, the design and evaluation of charge generation and transfer properties are quite complex. These approaches also involve the use of precious metals, and the synthetic routes are time-consuming.

Bulk GCNs are commonly obtained *via* thermal polymerization of nitrogen-containing precursors (such as melamine, urea and dicyandiamide), but have a weakness of producing GCN sheets with poorly ordered domains and lower surface area, which results in poor charge migration and fewer active sites for photochemical reactions. This problem was addressed by an alternative synthetic approach to preparing GCN nanostructures *via* precursor modification strategies. In this approach, the thermal condensation of pretreated melamine results in GCN nanostructures with well-exposed sites and improved charge generation and transfer properties. At the same time, this approach involves modification of the GCN surface with different functional groups, thus altering the C/N ratio, and extending light harvesting to the near-infrared regions (NIR). Therefore, most studies involve the pretreatment of precursors with external organic compounds or embedding templates into the precursors; subsequent thermal polymerization at high temperatures produces excellent GCN photocatalysts. For example, the introduction of ammonium persulfate ((NH₄)₂S₂O₈)²⁰ or ammonium chloride (NH₄Cl)²¹ into melamine, followed by calcination, yields porous GCN with a better morphology and higher specific surface area, thereby enhancing the photocatalytic HER. During the thermal polymerization reaction, these ammonium-based components release NH₃ gas, which imparts the porous nature and exfoliates the bulk GCN into nanosheets. Carbonate-based compounds, such as MgCO₃ and NaHCO₃, were also mixed with melamine, and during thermal polymerization, the released CO₂ gas impacted the s-triazine rings, resulting in highly ordered porous GCN with excellent photocatalytic activity.^{22,23} More recently, O-doped porous g-C₃N₄ (OCN) was obtained by mixing oxalic acid with melamine, followed by a thermal polymerization reaction. This approach leverages the elemental doping and porous structure, significantly improving the photocatalytic activity.²⁴ Next, carbon-doped GCN was synthesized using chitosan *via* a self-assembly approach. Experimental results specify that C-atoms have been incorporated into the GCN lattice by replacing the bridged N atoms, causing the delocalized π -bond formation. Consequently, improved visible light absorption and the charge separation in the GCN photocatalyst were observed.^{2,25} Sun *et al.* proposed a method to introduce π -electrons into the O-doped carbon nitride for a photocatalytic H₂ evolution reaction; they mixed urea with 4-iodobenzaldehyde, followed by thermal condensation. Interestingly, aromatic π -electrons and oxygen dopants were instantaneously introduced into the carbon nitride network, and the optimized GCN sample exhibited remarkable photocatalytic hydrogen production activity.²⁶ In this context, synthesizing GCN nanostructures possessing uniform morphology with greater surface area and enhanced charge transfer mechanisms presents a challenging

but promising approach for designing highly active and stable photocatalysts for H₂ evolution from water-splitting reactions.

Motivated by the above demonstrations on nonmetal doping, porous structure, and nanostructure engineering of GCN-based efficient photocatalysts for photoredox reactions, a high photocatalytic activity for H₂ evolution could be anticipated with the pretreated melamine-derived GCN. Herein, carbon and oxygen-doped porous GCN nanosheets were synthesized from a tannic acid-treated melamine precursor. The obtained GCN samples displayed excellent photocatalytic H₂ evolution activity of 1850 $\mu\text{mol g}^{-1} \text{h}^{-1}$ with an apparent quantum yield of 2.7%. Evidently, the doping of C and O-atoms into the GCN lattice extended the light absorption properties to the IR region. Moreover, the boosted charge transfer efficiency by the defects and dual doping, and the porous structure of GCN nanostructures could enhance the mass transport of reactants and products. The strategy of precursor modification and thermal polymerization provides an opportunity to regulate the molecular structure of GCN *via* external non-metal atom doping.

2. Experimental section

2.1. Preparation of g-C₃N₄ samples

The bulk g-C₃N₄ sample was obtained by calcining the melamine (MA) precursor without any modification at a higher temperature. Briefly, 4 g of melamine was taken in a crucible, covered with a lid, and then thermal polymerization was carried out at 550 °C for three hours at a ramping rate of two degrees per minute under an air atmosphere. The resultant yellow substance was gradually cooled to room temperature and then ground in a mortar for several minutes to obtain a fine powder of bulk g-C₃N₄ sample, defined as BCN.

Next, g-C₃N₄ nanostructures were prepared from the tannic acid-modified melamine precursors. Initially, 10 mg of tannic acid (TA) was mixed with 4 g of melamine in an agate mortar and mixed for 15 min. The resultant mixture was taken into a 50 mL crucible enclosed with a lid and heated to 550 °C for 3 hours at a ramping rate of 2 °C min⁻¹ under an air atmosphere. After cooling, the grey powder was ground in a mortar and the obtained sample was defined as CNTA-10, where 10 refers to the content of TA mixed with the melamine precursor. The other GCN samples were prepared under identical conditions by adding 25, 50, 100 and 200 mg of TA to the melamine precursor, and the obtained samples were denoted as CNTA-25, CNTA-50, CNTA-100 and CNTA-200, respectively.

2.2. Characterization details

The morphologies of the prepared samples were investigated using field-emission scanning electron microscopy (FE-SEM; Hitachi S-4800) and transmission electron microscopy (TEM; Hitachi H-7600). High-resolution TEM images and elemental mapping profiles were recorded on the FEI Titan G2 FE-TEM instrument operating at a voltage of 200 kV. UV-vis absorption properties of GCN photocatalysts were investigated using a SCINCO spectrophotometer in the wavelength range of 300–900 nm. The elements present and their characteristics were

determined *via* X-ray photoelectron spectroscopy (XPS) using a Thermo Scientific K-alpha instrument. The XPS atomic percentages provided in the manuscript are within $\sim 1\%$ error, whereas the peak positions of the C-, N- and O-elements are within ± 0.05 eV error. The room-temperature photoluminescence spectra were recorded on a SCINCO spectrofluorometer at an excitation wavelength of 325 nm. Specific surface area and pore-structure details were investigated *via* N_2 sorption measurements (BELSORP Mini II, Japan) at a liquid N_2 temperature of 77 K. Before obtaining the isotherms, the samples were degassed at 150 °C for 6 hours. The functional groups were determined *via* FT-IR spectra (Jasco FT-IR-6100, Japan) using a standard KBr pellet method. The solid-state electron paramagnetic resonance (EPR) measurements were carried out at X-band frequency on a Bruker EMX PremiumX spectrometer. EPR signals were measured for three different batches of catalysts under identical conditions. The relative intensities of the Lorentzian lines ($g = 2.003$) were found to be consistent within a 5% margin of error. The trapping experiments were performed with 5,5-dimethyl-1-pyrroline N-oxide (DMPO) as a radical capture agent. Typically, the photocatalyst sample (10 mg) was added to a methanol solution (for $\cdot O_2^-$ signal) or DI water (for $\cdot OH$ signal) in a container. After deoxidizing, the mixture was photoirradiated for a specified time and the solution was analyzed using an EPR instrument. For comparison, the solution was also analyzed before being irradiated with light.

2.3. Photocatalytic H_2 evolution measurements

The photocatalytic H_2 evolution reaction measurements of the prepared samples were conducted in a quartz reactor in which 50 mg of the catalyst sample was dispersed in 50 mL aqueous solution containing 10 vol% triethanolamine (TEA) as the sacrificial electron donor and 1 wt% Pt as the co-catalyst. The reactor was tightly closed with a rubber septum and then purged with Ar gas to completely remove air before irradiating the reactor using a 150 W Xe lamp provided with a 420 nm cutoff filter. The evolved gases were quantified by a gas chromatograph with a thermal conductive detector (TCD) and a 5A molecular sieve column, using argon as the carrier gas. All photocatalytic tests were performed in triplicate to ensure the reproducibility and nature of the photocatalyst. The irradiation wavelength-dependent H_2 evolution activity tests were performed similarly, as outlined above, only changing the cut-off filters. The apparent quantum yield (AQY) for the H_2 evolution was determined at 420 nm wavelength using the following formula:

$$\begin{aligned} \text{AQY (\%)} &= \frac{\text{no. of evolved } H_2 \text{ gas molecules}}{\text{no. of incident photons}} = \frac{N_e}{N_p} \times 100\% \\ &= \frac{2Mnhc}{SPt\lambda} \times 100\% \end{aligned} \quad (1)$$

where M is the number of H_2 moles released, N is Avogadro's constant, h is Planck's constant, c is the speed of light, P is the

intensity of the irradiation light, S is the irradiation area, and λ is the wavelength of the incident light.

2.4. Photocatalytic tetracycline degradation tests

The photocatalytic tetracycline (TC) degradation measurements were performed in a reactor using a 150 W xenon lamp fitted with a filter that only allows visible light above 400 nm. Here, 50 mg of BCN or CNTA samples were added to 100 mL of tetracycline solution (TC: 20 mg L^{-1}) under dark conditions and stirred for around 30 min until the adsorption-desorption equilibrium was accomplished. Every 20 minutes, 5 mL of the solution was taken out and centrifuged. The supernatant solution was tested to monitor the TC absorption peak around 358 nm by using a UV-vis spectrophotometer.

3. Results and discussion

3.1. Synthesis, structural and morphological studies

In a typical synthesis method, melamine was directly taken into a crucible and heated to 550 °C for 3 hours, resulting in the bulk $g\text{-}C_3N_4$ (BCN). Next, various contents of tannic acid were mixed with the melamine precursor and then calcined at the same temperature to obtain C- and O-doped $g\text{-}C_3N_4$ (CNTA) samples. During the thermal polymerization reaction, tannic acid decomposes and infuses into the GCN network, resulting in C- and O-doped GCN. The detailed procedure for the preparation of BCN and CNTA samples is given in Fig. 1a. The phase purity and crystallinity of BCN and CNTA samples were investigated *via* powder XRD patterns. As seen from Fig. 1b, the BCN sample displayed two peaks around 13.0° and 27.4°, corresponding to diffraction planes (100) and (002), respectively. The (100) plane is ascribed to the in-plane trigonal nitrogen linkage of tri-s-triazine motifs, whereas the (002) plane resulted from the periodic stacking of layers of conjugated aromatic systems.^{27,28} The reduced intensity and broadening of peaks mainly resulted from the shortened length of interlayer periodicity (disorder) and decreased spacing between the layers of CNTA nanosheets.^{29–31} The insertion of TA into melamine and the subsequent calcination causes the structural distortion of GCN and weakens the aggregation of the formed sheets. The intensity of the (100) peak in CNTA samples gradually decreased and almost disappeared, which suggests that the tannic acid template could react with the melamine intermediates during the high-temperature thermal polymerization reaction and destroy the ordered arrangement of in-plane tri-s-triazine rings. Next, the (002) peak intensity also decreased and the peak position shifted from 27.4° (for BCN) to 27.5° (CNTA samples), demonstrating that the interlayer stacking distance decreased,³² which was confirmed by the calculations of the d -spacings of BCN ($d = 0.3250$ nm) and CNTA-100 (0.3244 nm). The molecular structure and the presence of various functional groups in BCN and CNTA were analyzed by FT-IR measurements (Fig. 1c) and the FT-IR spectra were almost identical to that of pristine BCN, where all the characteristic peaks of $g\text{-}C_3N_4$ at 810, 1200–1600 and 3000–3700 cm^{-1} , corresponding to the s-triazine ring, C–N heterocycles and stretching vibration for $-NH/OH$, respectively,

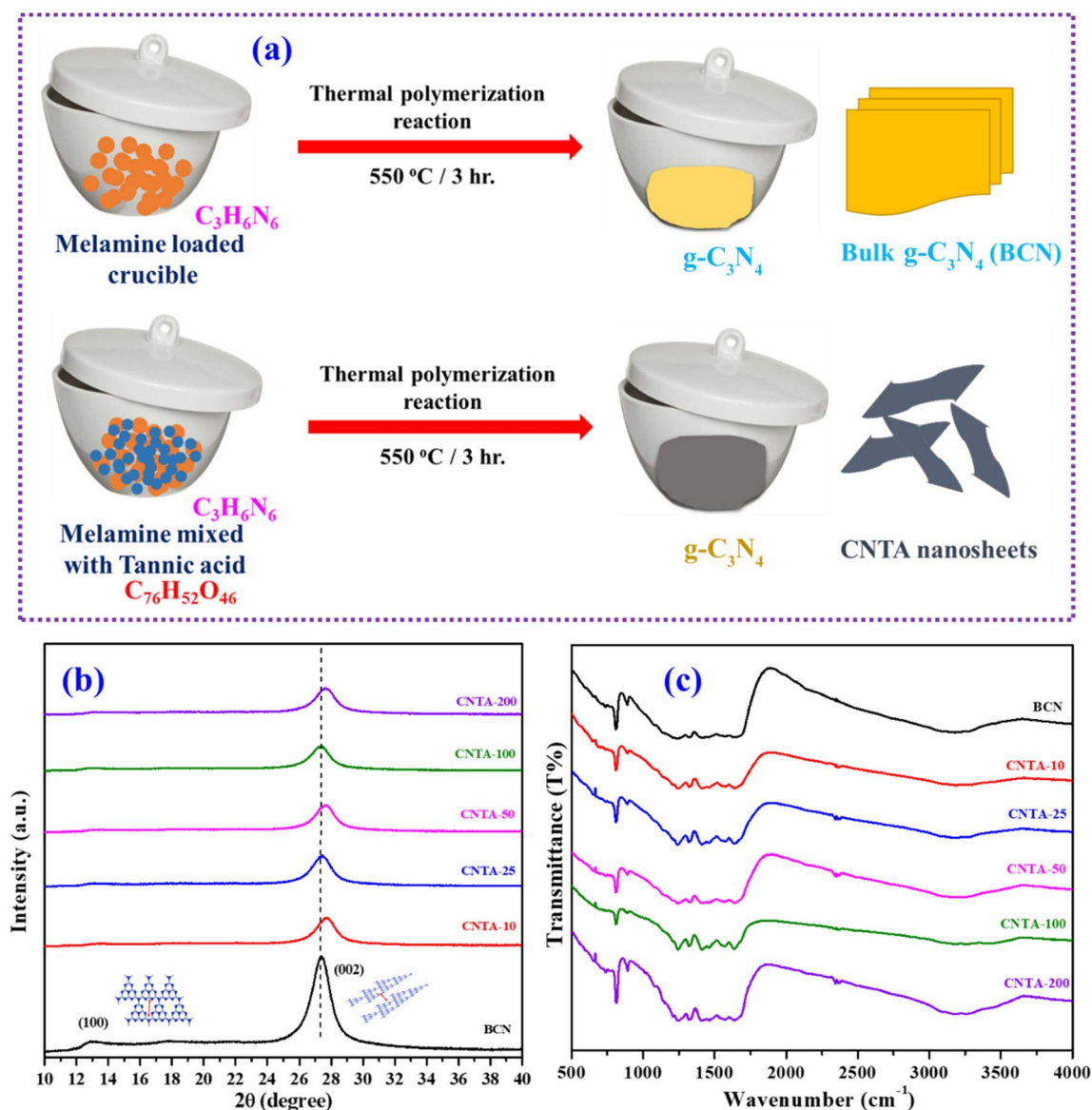


Fig. 1 (a) Schematic of the preparation, (b) powder X-ray diffraction patterns and (c) FT-IR spectra of BCN and CNTA nanosheets.

were clearly observed. Interestingly, the intensity of the 810 cm^{-1} peak was significantly weakened in all CNTA samples (except CNTA-200), confirming the structural imperfections, destruction of triazine rings, and N-defects, consistent with the XRD results.^{33,34} These results further endorse that the prepared CNTA samples are indeed $g-C_3N_4$, which were derived from the tannic acid-treated melamine precursors.^{25,35}

X-ray photoelectron spectroscopy was used to investigate the surface chemical states, bonding information, the nature of dopants, and the defects produced in the obtained GCN samples. As shown in Fig. S1, the XPS survey scan spectra of GCN samples exhibited mainly C-1s, N-1s and O-1s signals with slight signal intensity changes. The high-resolution XPS spectrum of C-1s (Fig. 2a) showed three binding energy peaks around 284.40, 286.55 and 288.00 eV, which are characteristic of graphitic carbon in C-C or C=C sites, C-N/C-N, and sp^2 -

hybridized C (N-C=N) in the aromatic rings of the $g-C_3N_4$ heterocycles, respectively.^{36,37} Another low-intensity peak around 289.45 eV corresponds to O-C=O bonding, indicating that the O-atom is directly bonded to the C atom through substituting for N-atoms in the N-C=N bond.^{38,39} Meanwhile, the N-1s XPS spectrum (Fig. 2b) in the CNTA-100 sample displayed a small peak around 403.00 eV, related to the charge localization/ π -excitation effect in heterocycles.^{35,38} Another strong and intense peak starting from 395.0 to 401.5 eV could be deconvoluted into three peaks, 397.55 eV for sp^2 -hybridized nitrogen in triazine rings (C-N=C; N1-site), 399.25 eV for tertiary N (N-(C)₃; N2-site), and 400.20 eV for sp^3 primary nitrogen atoms (N-H/NH₂; N3-site).^{11,40} Notably, no binding energy peak related to N-O bonding was observed, demonstrating that O-atoms replace nitrogen atoms rather than carbon atoms. Next, to elucidate the doping of the O-element in

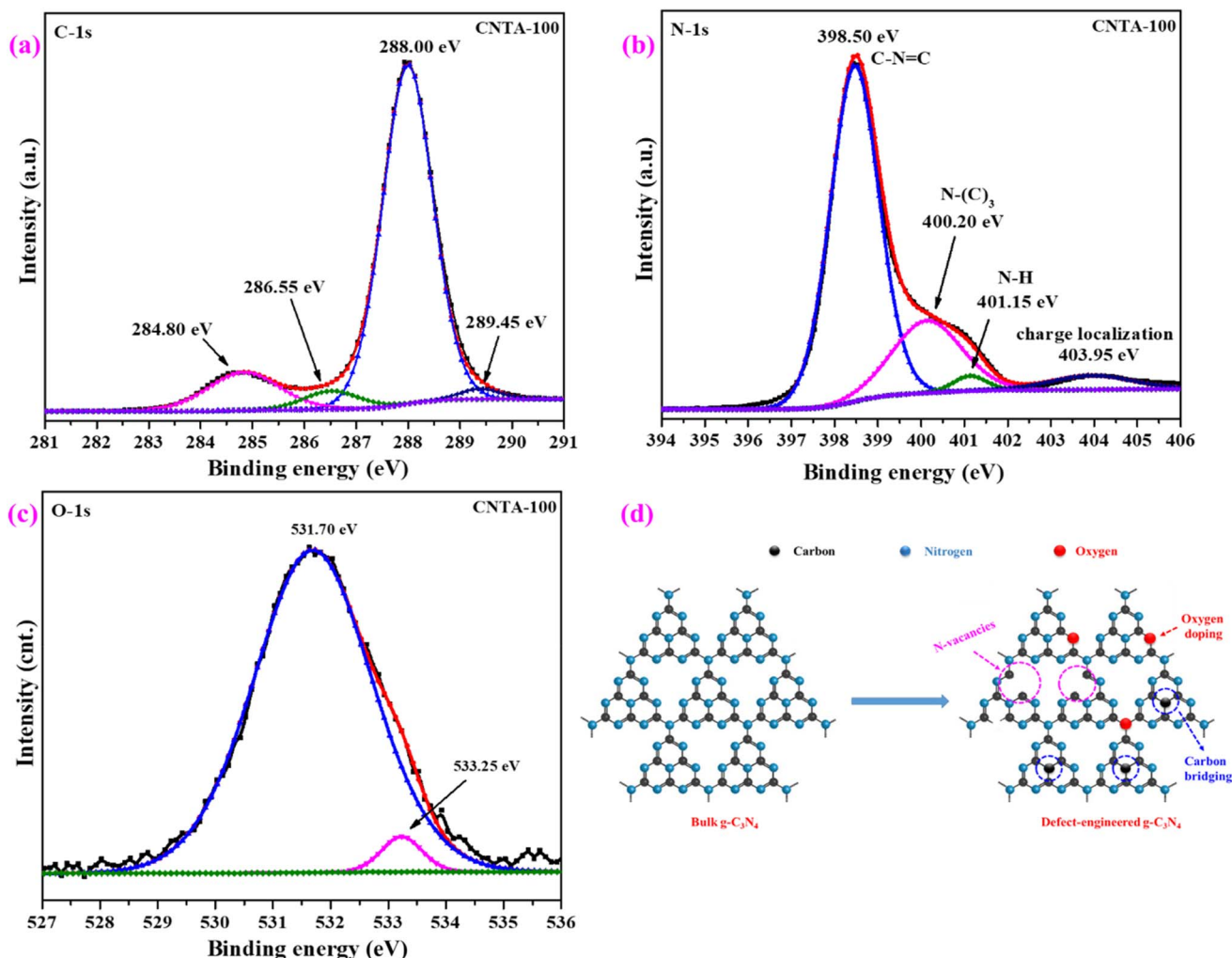


Fig. 2 High-resolution XPS spectra of (a) C-1s, (b) N-1s and (c) O-1s elements. (d) Illustration of the formation of defects and doping in the $g\text{-C}_3\text{N}_4$ network of the CNTA-100 sample.

the $g\text{-C}_3\text{N}_4$ matrix, the high-resolution XPS spectrum of the O-1s element in the CNTA-100 sample was recorded and displayed in Fig. 2c. According to Fig. 2c, the O-1s spectrum can be deconvoluted into two peaks around 531.70 and 533.25 eV, corresponding to C-OH and C-O-C, respectively.⁴¹ These peaks indicate the successful incorporation of oxygen atoms into the $g\text{-C}_3\text{N}_4$ structure.^{2,24} Concerning the BCN sample and to examine the effect of TA on the melamine precursor to obtain CNTA samples, the C-1s and N-1s spectra of BCN were also recorded and provided in Fig. S2. As seen from Fig. S2, 2a and b, the C-1s and N-1s elements in the CNTA-100 sample exhibited a similar set of peak positions with a slight shift toward lower binding energy values, representing the effects of C- and O-dopants in the $g\text{-C}_3\text{N}_4$ network. Further, Table S1 lists the atomic percentage details of C-1s, N-1s and O-1s elements in the prepared bulk $g\text{-C}_3\text{N}_4$ and CNTA samples. As seen from Table S1, the carbon content in the CNTA samples increased, while the N content decreased. All CNTA samples consist of O-content around 3 at%. Here, the proposed tannic acid treatment

facilitated the loss of N-atoms (causing the N-defects), which were occupied by O-atoms *via* C-O or C=O bonding.

The peak intensity ratio of C=N-C/C-(N)₃ in the CNTA-100 sample (Fig. 2b) decreased to 3.410 from 4.200 for BCN, specifying that the N-vacancies in the CNTA-100 sample arise at the position of the sp^2 -hybridized nitrogen (C=N-C) in the heptazine ring.⁴² Interestingly, the peak intensity ratios of N-C=N/C-C (Fig. 2a, C-1s XPS) were also estimated to be 12.715 for BCN and 8.029 for the CNTA-100 sample, also verifying the existence of N-vacancies in the CNTA samples. The detailed analysis of chemical bonding from XPS N-1s spectra is summarized in Table S2. The percentage of sp^2 -hybridized N (in C=N-C) decreased from 63.8% for BCN to 48.5% for the CNTA-100 sample, indicating that N-defects could be introduced in sp^2 -hybridized N-sites. The formation of N-vacancies in the CNTA samples might be due to the release of higher amounts of CO_2 and NH_3 gases during the thermal polymerization reaction. At high temperatures, the released NH_3 gas can decompose into $\text{NH}_2^\cdot$, $\text{NH}^\cdot$ radicals, which can etch some of the sp^2 -hybridized N of the C=N-C lattice positions in the $g\text{-C}_3\text{N}_4$

network. This process led to the escape of N-atoms, resulting in the creation of N-vacancies.^{43,44} Finally, the CNTA samples obtained *via* the treatment of melamine with tannic acid possess dual defects, such as doping (C- and O-) and N-defects in the g-C₃N₄ structure (depicted in Fig. 2d). The defect engineering of g-C₃N₄ nanosheets *via* C-doping or N-vacancies yields C-rich carbon nitrides that exhibit enhanced activity in photocatalytic H₂ evolution and organic contaminant degradation reactions. Previous studies also confirmed that non-metal doping and vacancies can modify the electron structure, improving the visible light-harvesting properties and charge separation rate, thereby promoting photocatalytic activity.^{45–47} The presence of N-defects in CNTA samples was characterized by EPR measurements. As seen in Fig. S3, all samples (BCN, CNTA-25, CNTA-50, CNTA-100 and CNTA-200) displayed a characteristic Lorentzian peak, corresponding to unpaired electron signals in sp²-carbon atoms within heptazine-based g-C₃N₄.⁴⁸ The intensity of the Lorentzian line of CNTA samples increased with the tannic acid content from 25 to 200 mg; among them, the CNTA-100 sample exhibited the highest EPR signal intensity. The changes in EPR intensity for CNTA samples revealed the formation of nitrogen defects in the GCN network, which could open the heptazine units and thus donate a lone pair of electrons to the adjacent sp²-carbon atoms.⁴⁹ Particularly, the higher EPR intensity signal specifies a higher unpaired electron density, suggesting that mixing tannic acid with the melamine and the subsequent thermal polymerization reaction could increase the amount of nitrogen defects.⁵⁰

Next, the microstructures and surface morphology of the prepared bulk g-C₃N₄ and defect-engineered g-C₃N₄ nanostructures were examined using FE-SEM and TEM images. As seen from Fig. 3, the FE-SEM images of the BCN sample displayed the typical bulk morphology, whereas the CNTA samples exhibited exfoliated nanosheet-type morphology. The TEM images of all the prepared g-C₃N₄ samples are also provided in Fig. 3 and reveal that the CNTA samples derived from tannic acid-treated melamine precursors have a unique morphology, depicting a certain degree of exfoliation of aggregated bulk sheets into thin nanosheets, which is consistent with the decreased (002) peak in the X-ray diffraction patterns (Fig. 1b). By comparing with the TEM image of BCN, the morphology/nanosheets of CNTA samples are thinner, and the edge folding specifies that the CNTA samples were flexible due to lowered thickness. As the amount of tannic acid increased in the melamine precursor, the CNTA samples changed from bulk sheets to nanosheets and then to edge-folded nanosheets. As shown in Fig. S4, tannic acid treatment also revealed that the obtained CNTA samples are composed of pores that originated from etching and defects. During the thermal polymerization reaction, the gases produced could act as bubble templating agents, causing the formation of pore structures.²⁵ The porous nature improves the g-C₃N₄ nanosheets' surface area, thereby offering abundant reactive sites and increasing the mass transfer.⁵¹ Further, the inspection of the CNTA-100 photocatalyst sample by HR-TEM images (Fig. 4a and b) confirmed the formation of edge-folding and the curly nature of the nanosheets. Meanwhile, the absence of lattice spacing in Fig. 4c

and the SAED pattern (Fig. 4d) indicates an amorphous nature, which is consistent with the powder X-ray diffraction pattern results. Fig. 4e–h and i demonstrate the elemental mapping profiles that were obtained from HAADF-STEM and STEM-EDAX analyses, respectively. In Fig. 4e and f, the elemental mapping of the CNTA-100 sample demonstrates the uniform distribution of C, N and O elements.

The BET specific surface area and pore-size details were investigated *via* the nitrogen adsorption–desorption isotherms. Fig. S5a and b display the N₂ adsorption–desorption isotherms and their corresponding pore-size distribution profiles for BCN and CNTA-100 photocatalyst samples. As seen from Fig. S5a, the adsorption isotherms of both BCN and CNTA-100 samples are ascribed to type IV behaviour, with H3-type hysteresis loops. From the adsorption–desorption isotherms, the specific surface areas of BCN, CNTA-10, CNTA-25, CNTA-50, CNTA-100 and CNTA-200 samples were estimated as 10.41, 10.51, 17.63, 19.98, 23.80, and 17.86 m² g^{−1}, respectively (Table S3). These values indicate that the specific surface area of the CNTA-100 sample is 2.3 times higher than that of the bulk graphitic carbon nitride (BCN) sample; as a result, the CNTA-100 sample offers more catalytically active sites, which directly improves the photocatalytic activity. In addition, Fig. S5b shows that the pore-size distribution curves derived from the BJH method are from mesoporous-type materials. This porous structure effectively assists in the mass transfer, reduces the photoexcited electron transfer path, and thereby decreases the electron–hole recombination rate, henceforth improving photocatalytic activity.^{52,53}

3.2. Light harvesting, optical bandgap and band structure studies

The g-C₃N₄ samples resulting from tannic acid-treated melamine are expected to show improved visible light absorption and electronic band structure properties. Consequently, the extended light absorption properties of the GCN photocatalyst samples could increase the number of photoexcited charge carriers available for photochemical reactions. The CNTA samples showed enhanced visible-light harvesting properties ranging from 460 to 900 nm; meanwhile, BCN displayed an absorption below ~460 nm. As shown in Fig. 5a, a progressive redshift in the absorption edge was observed as the amount of TA increased, along with the sample color changing from light yellow to grey. The mixing of tannic acid in the melamine precursor caused elemental doping, which can affect the optical absorption of photocatalytic materials; this redshift phenomenon is further evidence of the incorporation of C- and O-atoms into the g-C₃N₄ network. Besides, the CNTA samples showed extended absorption tails in the visible and NIR regions, *i.e.*, the Urbach band tail, signifying that dopant-related midgap states were created and altered the band structure of g-C₃N₄.^{54,55} The formation of intermediate bandgap states considerably facilitates the absorption of photons with energies even smaller than the value of the forbidden bandgap. Hence, associated with incorporating C- and O-atoms into the g-C₃N₄ network, the CNTA samples displayed a noticeably improved optical absorption across the ultraviolet, visible, and near-infrared

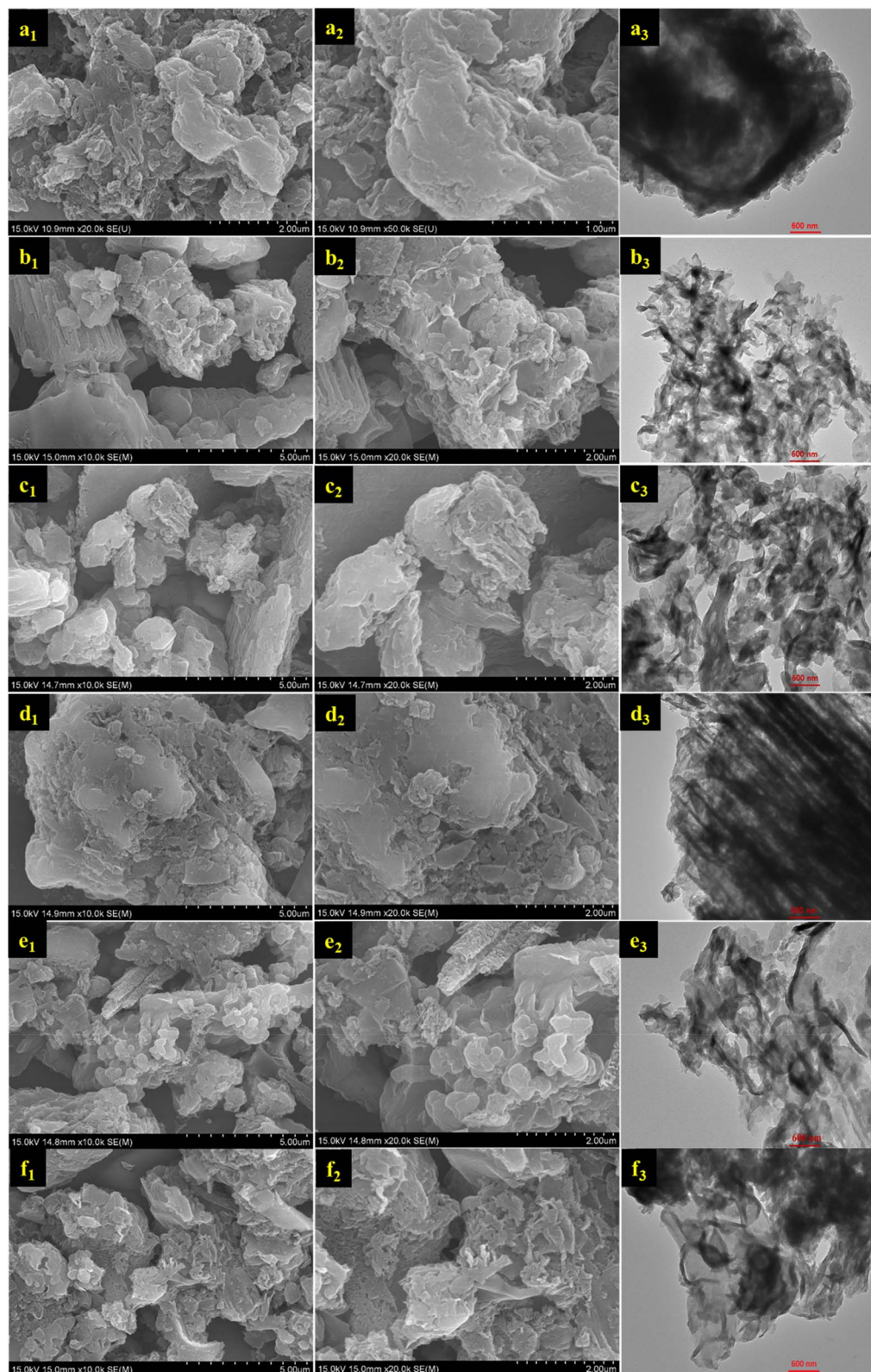


Fig. 3 FE-SEM and TEM images of the BCN (a₁, a₂ and a₃), CNTA-10 (b₁, b₂ and b₃), CNTA-25 (c₁, c₂ and c₃), CNTA-50 (d₁, d₂ and d₃), CNTA-100 (e₁, e₂ and e₃) and CNTA-200 (f₁, f₂ and f₃) photocatalyst samples. Scale bar for TEM images is 600 nm.

regions, as well as improved absorption intensity.^{2,24} The enhanced light harvesting properties of the GCN samples were also confirmed by estimating the bandgap energies from the

Tauc plots, and are given in Fig. 5b. The Tauc plots show that the calculated bandgap energies are quite different from BCN and were determined as 2.75, 2.67, 2.71, 2.63, 2.60 and 2.68 for

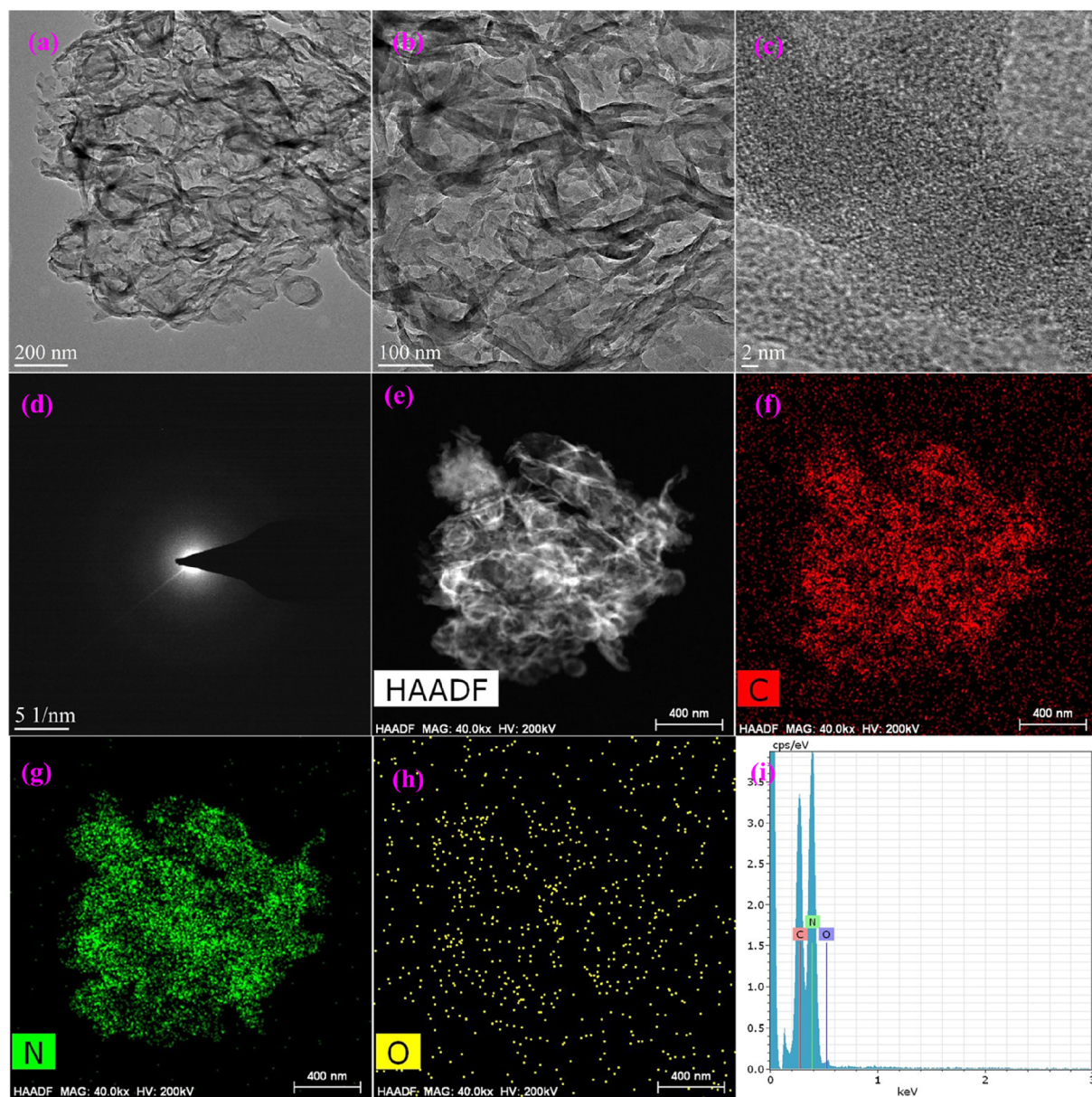


Fig. 4 (a–c) High-resolution TEM images, (d) SAED pattern, (e–h) HAADF-STEM EDS elemental mapping profiles and (i) STEM-EDX spectrum of the CNTA-100 sample.

BCN, CNTA-10, CNTA-25, CNTA-50, CNTA-100 and CNTA-200, respectively. Certainly, doping has an important effect on the optical bandgap of CNTA samples. Next, the valence band maximum edge potentials (E_{VB}) of BCN and CNTA samples were measured from the valence band XPS (Fig. 5c); the E_{VB} values increased from 1.5 eV for BCN to 2.00 eV for CNTA samples, depending on the tannic acid content. Together with the estimated bandgap values, the conduction band edge potentials ($E_{CB} = E_{VB} - E_g$) were determined, and the detailed band structures of all the photocatalyst samples are provided in Fig. 5d. It is evident that both CB and VB positions were continuously adjusted and the band structures could be exceptionally tuned for the effective visible light harvesting, which is a driving force for the H_2 evolution reaction.

3.3. Photocatalytic H_2 evolution and tetracycline degradation studies

The photocatalytic activity of the prepared carbon nitride samples was evaluated *via* a visible-light ($\lambda > 420$ nm)-driven water-splitting reaction. As seen from Fig. 6a and b, the bulk sample BCN exhibited a poor hydrogen evolution rate of $212.53 \mu\text{mol g}^{-1} \text{h}^{-1}$, which was lower than that of the CNTA samples that were obtained from the precursors of tannic acid-mixed melamine. The CNTA samples with better light-harvesting properties and surface area showed higher photocatalytic activity. All the CNTA samples exhibited an enhancement in the visible photocatalytic H_2 evolution activity compared to bulk carbon nitride. The optimized sample CNTA-100 displayed the highest H_2 evolution rate of $1850.61 \mu\text{mol g}^{-1} \text{h}^{-1}$, which is 8.7

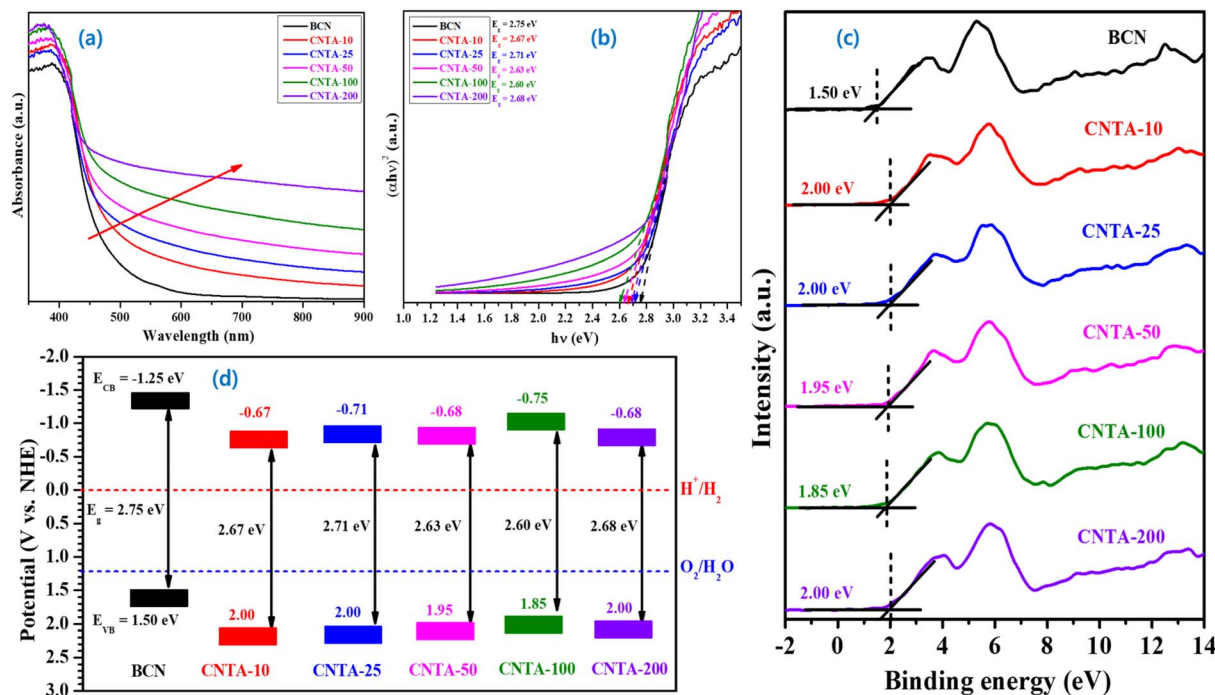


Fig. 5 (a) UV-vis DRS spectra, (b) optical bandgap measurements, (c) valence band XPS and (d) band structure analysis of BCN and CNTA photocatalyst samples.

times that of the BCN sample. It was also clear that the mixing of tannic acid with melamine and the subsequent calcination, resulting in the C- and O-doped GCN, provided higher photocatalytic H_2 evolution activity. This superior activity is not only caused by a higher specific surface area, but is also ascribed to enhanced light harvesting. During the photochemical reactions, CNTA samples could harvest a wide range of visible light to produce more electrons and eventually accelerate the charge separation to initiate the H_2 evolution reaction. The catalytic stability of the CNTA-100 photocatalyst sample was assessed by five consecutive operations (Fig. 6c). After 20 h, $\sim 9384.24 \mu\text{mol g}^{-1}$ was generated without noticeable deactivation, demonstrating good stability for long-run reactions. To further validate the structural stability of the optimized photocatalyst, XRD patterns of the CNTA-100 sample were obtained before and after the H_2 evolution reaction. As displayed in Fig. 6d, the phase structure of the photocatalyst remained the same after repeated tests. Next, hydrogen evolution measurements were carried out to determine the effects of various sacrificial agents such as triethanolamine (TEA), ethanol (EOH), methanol (MeOH), $\text{Na}_2\text{S} + \text{NaSO}_3$ (NS) and lactic acid (LA) during the water-splitting reaction. As shown in Fig. 6e, CNTA-100 had the highest H_2 evolution rate of $1850.60 \mu\text{mol g}^{-1} \text{h}^{-1}$ for TEA among the other sacrificial agents, and the order of the H_2 evolution rates for CNTA-100 is $\text{TEA} > \text{MeOH} > \text{LA} > \text{NS} > \text{EOH}$. Since the optimized sacrificial agent TEA is more viscous, we further optimized the concentration of TEA in the H_2 evolution reaction experiments. According to Fig. 6f, the H_2 evolution rate increased with the concentration of TEA up to 10 vol%, and decreased thereafter, as the higher viscosity and the number of TEA molecules in the

reaction solution could decrease the light absorption properties of the CNTA-100 photocatalyst sample. Excessive concentrations can lead to adsorption onto the photocatalyst surface, eventually blocking the reactive sites and inhibiting the H_2 evolution reaction. The wavelength-dependent H_2 evolution activity was also investigated for CNTA-100 (Fig. 6g). The trend of H_2 production data aligns well with the absorption features of the optimized sample, suggesting that the H_2 generation reaction is mainly driven by light-induced electrons in the graphitic carbon nitride catalyst. H_2 evolution tests were further conducted to optimize the catalyst loading in the photochemical reaction. As shown in Fig. 6h, the CNTA-100 sample with a loading of 50 mg in the reaction experiment exhibited the highest activity. The changing trends with the catalyst loading amounts are initiated from the severe light scattering and reduced light penetration depth, which may decrease the light-harvesting properties in the reaction system. The photocatalytic performance of CNTA-100 was compared with that of other reported non-metal doped and defect-engineered $g\text{-C}_3\text{N}_4$ photocatalysts (Table S4). Apparently, CNTA-100 exhibits a comparable photocatalytic performance and even surpasses most non-metal doped and N-defective $g\text{-C}_3\text{N}_4$ photocatalysts. Therefore, the present work highlights the importance of non-metal doping and defects in enhancing the photocatalytic H_2 evolution activity of $g\text{-C}_3\text{N}_4$.

To understand the effect of a single dopant and the templating approach, other GCN photocatalysts were also prepared. The new $g\text{-C}_3\text{N}_4$ photocatalyst was derived from the direct calcination of the urea precursor. The relevant characterizations, such as powder XRD patterns, SEM and TEM images

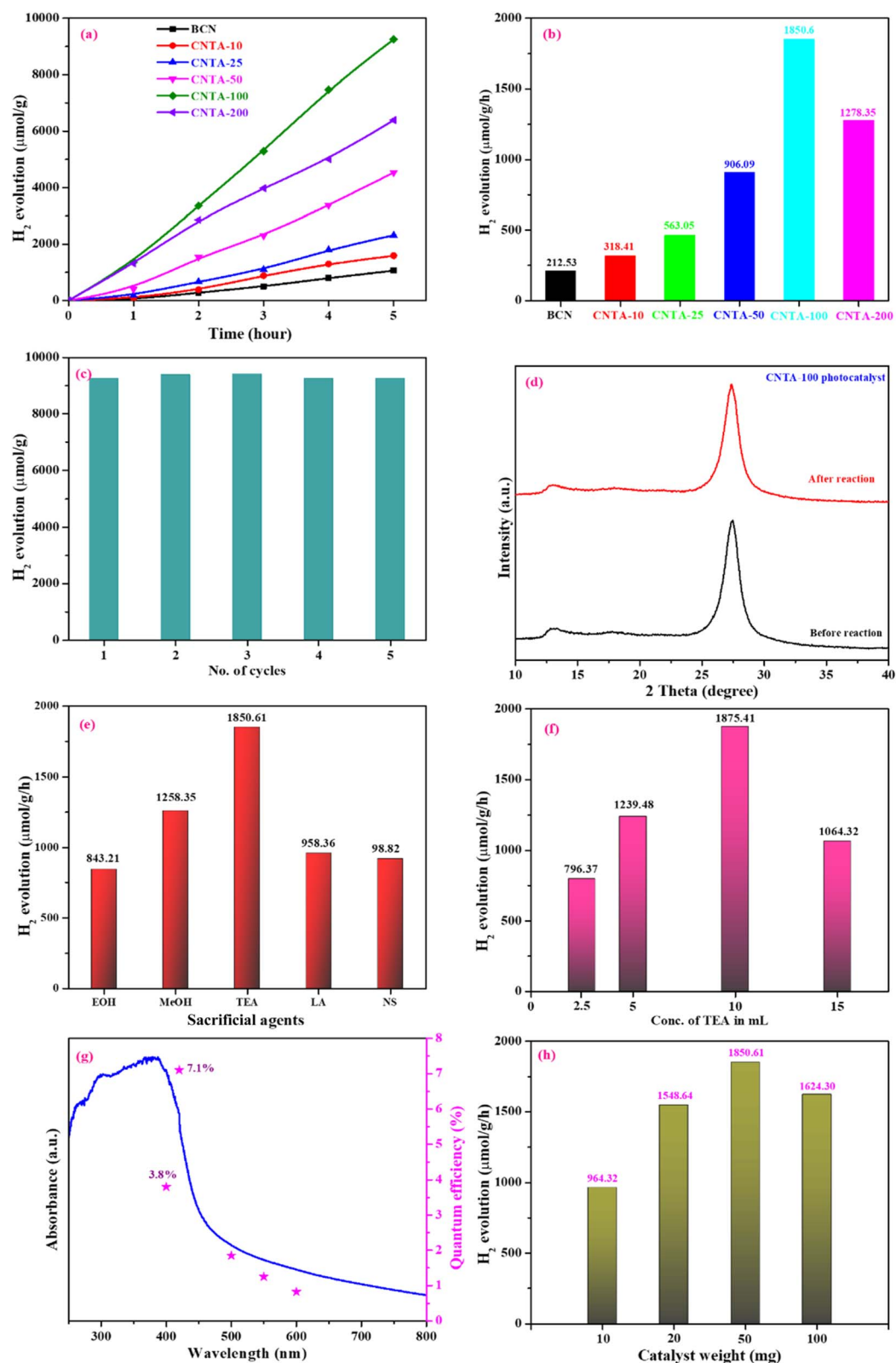


Fig. 6 Visible light-driven photocatalytic H_2 evolution measurements: (a) time-course H_2 evolution and (b) H_2 evolution rates of BCN and CNTA photocatalyst samples. H_2 evolution measurements to optimize several parameters of the CNTA-100 sample: (c) cycling tests to determine stability, (d) XRD patterns before and after cycling tests, (e) sacrificial agents, (f) concentration of TEA, (g) apparent quantum yield (AQY) measurements and (h) catalyst loading.

(Fig. S6–S8), revealed that the direct calcination of urea at 550 °C for 3 hours resulted in the formation of g-C₃N₄ (CN–U). Therefore, the relevant photocatalytic H₂ evolution tests were conducted on BCN (derived from the melamine precursor), CN–U (derived from urea), and CNTA samples, which were prepared from tannic acid mixed with melamine precursors. Another

sample was also prepared by considering the post-doping strategy, in which tannic acid is mixed with BCN (bulk g-C₃N₄ derived from calcination of melamine) to realize single doping into the g-C₃N₄ network as C-doped g-C₃N₄ (CCN). Next, the photocatalytic performances of all samples were compared and shown in Fig. S9, where it can be seen that the g-C₃N₄ derived

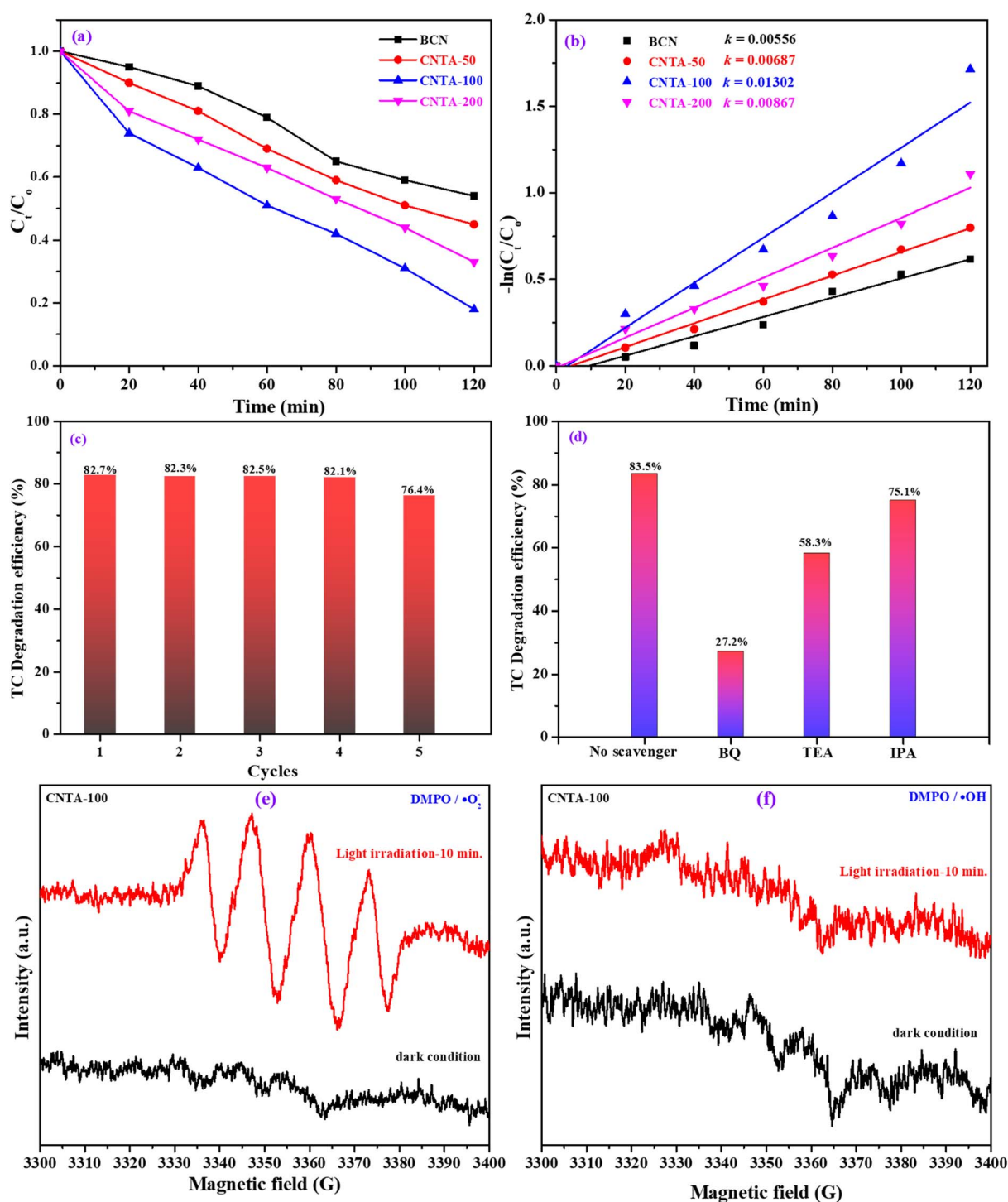


Fig. 7 (a) Photocatalytic tetracycline degradation efficiency curves, (b) corresponding first-order kinetics plots, (c) cycling experiments to determine stability, (d) TC degradation activity under various quenching agents, and (e) EPR spectral analysis for $\cdot\text{O}_2^-$ radicals and (f) $\cdot\text{OH}$ radicals using DMPO as a trapping agent with the CNTA-100 photocatalyst sample.

from urea shows higher activity than that of BCN due to its slightly higher surface area, according to our previous experimental results. Meanwhile, C-doped $g\text{-C}_3\text{N}_4$ (CCN) displayed a photocatalytic H_2 evolution rate of $410.24 \mu\text{mol g}^{-1} \text{h}^{-1}$, which is higher than the undoped $g\text{-C}_3\text{N}_4$ and lower than the C,O-doped $g\text{-C}_3\text{N}_4$. Hence, these results indicate that the mixing of tannic acid with melamine and the subsequent calcination, which resulted in the C- and O-doped GCN, offered higher photocatalytic H_2 evolution activity. The comparison shows that the dual C- and O-incorporation creates a synergistic effect, which is superior to the single C-doping and bare samples.

Additionally, to understand the photocatalytic performance of GCN samples, the dye degradation tests were conducted by degrading a 20 mg L^{-1} aqueous solution of tetracycline (TC) under a 150 W Xe lamp. Fig. 7a demonstrates the photocatalytic tetracycline degradation activity of BCN and CNTA samples over a 120-minute reaction period. The bulk $g\text{-C}_3\text{N}_4$ derived from the direct calcination of melamine precursor exhibited a lower degradation efficiency of around 46.0%, attributed to its poor visible light absorption and higher photoinduced charge recombination rate. Meanwhile, the photocatalyst samples obtained from the thermal polymerization of tannic acid-treated melamine precursors, *i.e.*, C- and O-doped $g\text{-C}_3\text{N}_4$ samples (CNTA), displayed enhanced photocatalytic TC degradation. As seen from Fig. 7a, the CNTA-50, CNTA-100 and CNTA-200 photocatalyst samples degraded the tetracycline with efficiencies of 55.0%, 82.0%, and 67.8%, respectively. It is obvious that the C- and O-doping into $g\text{-C}_3\text{N}_4$ nanosheets has a strong impact on improving the photocatalytic activity. As the amount of tannic acid with melamine increased to obtain CNTA samples, the TC degradation efficiency increased, and among the samples, CNTA-100 displayed the maximum photocatalytic TC degradation activity over 120 min. The highest TC degradation efficiency of 82.0% for the CNTA-100 sample supplements the H_2 evolution activity measurements, owing to its improved light harvesting and specific surface area. The suitable C- and O-doping content not only extends the light absorption range but also adjusts the band structures. Next, the degradation of TC was verified by the Langmuir–Hinshelwood quasi-level kinetic equation,⁵⁶

$$\ln(C_i/C_0) = -kt, \quad (2)$$

where k (min^{-1}) denotes the rate constant, and C_0 and C_t are the initial and final concentrations at a time t . According to Fig. 7b, the rate constants of BCN, CNTA-50, CNTA-100, and CNTA-200 were determined as 0.00556, 0.00687, 0.01302, and 0.00867 min^{-1} , respectively. From these results, the rate constant of the CNTA-100 sample was 2.3 times higher than that of BCN, suggesting that CNTA-100 has greater degradation efficiency. Therefore, controlling the C-, O-doping and N-defects in GCN can improve its electronic properties and overall photocatalytic TC degradation performance. After the degradation experiments, the used CNTA-100 photocatalyst sample was washed with distilled water and dried at a temperature of 60°C for the next cycle of degradation experiments. After performing cyclic experiments to assess the stability of the CNTA-100 sample in photocatalytic TC degradation, it was detected that following 5 cycles, the

degradation efficiency decreased from 82.7% to 76.4%, indicating a reduction of 7.6% compared to the initial value (Fig. 7c). The decrement in degradation efficiency was attributed to the slight photocatalyst loss during the recovery washing procedure, causing a reduction in TC degradation activity. To highlight the stability of the CNTA-100 photocatalyst sample, the powder XRD pattern and TEM images were recorded and are presented in Fig. S10. The results indicate that no significant changes were observed in the sample structure or morphology after the cycling experiments. These recycling experiments demonstrated that CNTA-100 exhibited considerable stability and maintained high activity even after repetitive use, indicating its potential for practical applications as an immobilized catalyst.

The identification of reactive species in the photocatalytic TC degradation reaction was investigated by using several trapping experiments. In this work, the various scavengers such as *p*-benzoquinone (BQ), triethanolamine (TEA), and isopropyl alcohol (IPA) were separately added to inhibit the activities of $\cdot\text{O}_2^-$, h^+ , and $\cdot\text{OH}$ radicals, respectively, during the photocatalytic TC degradation reaction. According to Fig. 7d, it was evident that the CNTA-100 photocatalyst sample attained a photodegradation efficiency of 83.5% for TC under quenching agent-free conditions. The introduction of IPA did not exert a significant impact on the photodegradation efficiency (79.1%). However, by using TEA and BQ, the removal rates decreased to 58.3% and 26.7%, respectively. Hence, it can be inferred that h^+ and $\cdot\text{O}_2^-$ play crucial roles in the TC photodegradation reaction. Next, the free radicals produced during the photocatalytic TC degradation reaction were determined by the EPR measurements. As shown in Fig. 7e and f, $\cdot\text{O}_2^-$ and $\cdot\text{OH}$ radicals were not produced or had less intense signals in the absence of light irradiation. However, after 10 min of light irradiation, the characteristic peaks of $\cdot\text{O}_2^-$ were observed. Meanwhile, the distinct peaks related to $\cdot\text{OH}$ radicals were not observed in the EPR spectra of the CNTA-100 sample (Fig. 7f). This phenomenon is consistent with the previous quenching experiment results, confirming that $\cdot\text{O}_2^-$ radicals are the main reactive species responsible for the photocatalytic TC degradation.

3.4. The investigation of charge carrier separation/transfer behaviors

The charge-carrier generation, transfer, and recombination details of the prepared GCN-based photocatalysts were investigated by steady-state photoluminescence (PL), time-resolved photoluminescence (TR-PL), transient-photocurrent density, and electrochemical impedance spectroscopy measurements. At first, the electron–hole recombination rate of the catalysts was determined by room-temperature PL spectra. As shown in Fig. 8a, the major emission wavelength of BCN is $\sim 465 \text{ nm}$ upon excitation at 320 nm . This broad emission peak around 465 nm is ascribed to the band–band PL phenomenon with the energy of light, which is nearly equal to the optical bandgap of bulk CN. The PL spectra of CNTA samples are also provided in Fig. 8a and were compared with that of BCN, exhibiting the decreased PL intensity for all CNTA samples. It is generally acknowledged that the PL intensity is directly related to the electron–hole recombination rate; the higher PL intensity represents a rapid charge recombination rate,

whereas the lower intensity characterizes the efficient charge separation process. As shown in Fig. 8a, the PL intensity of CNTA samples remarkably decreased, and the CNTA-100 sample displayed the lowest PL intensity, indicating that the simultaneous C- and O-doping could significantly lessen the photoexcited electron-hole recombination rate and enhance the charge separation efficiency toward higher photocatalytic activity. To obtain more evidence about this optical phenomenon, the TR-PL decay curves of the CNTA-100 sample were compared with those of the BCN photocatalyst sample. As seen in Fig. 8b, the PL decay curves of the photocatalyst samples can be mathematically described using the following biexponential function (eqn (3)), and the average carrier lifetime (τ_a) can be calculated from eqn (4):^{57,58}

$$f(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) \quad (3)$$

$$\tau_a = (A_1\tau_1^2 + A_2\tau_2^2)/(A_1\tau_1 + A_2\tau_2) \quad (4)$$

where τ_1 and τ_2 are the fluorescence lifetimes and A_1 and A_2 are their corresponding amplitudes. The average PL lifetime of the CNTA-100 photocatalyst sample is 16 ns, which is lower than the PL lifetime of the BCN photocatalyst (18 ns), again confirming the improved charge separation/exciton dissociation in CNTA-

100 compared to that of BCN. The TR-PL decay curves of both BCN and CNTA-100 samples were fitted according to the biexponential kinetics function, and their corresponding decay components of τ_1 and τ_2 are provided in Table S5. As mentioned in eqn (4), the shorter lifetime component (τ_1) indicates the nonradiative quenching, while the longer component τ_2 originates from the recombination of free excitons in the materials. As seen from Table S5, for CNTA-100, the emission lifetimes of both τ_1 and τ_2 values are 3.6 ns and 91 ns, respectively, which are shorter than those of BCN ($\tau_1 = 3.9$ ns and $\tau_2 = 94$). The decreased lifetimes indicate that the C- and O-doped GCN with N-vacancies sample (CNTA-100) promoted photogenerated charge carrier separation toward enhanced photocatalytic activity.^{59,60} The investigation of charge separation efficiency was also conducted *via* photocurrent density ($j-t$) measurements. As shown in Fig. 8c, the photocurrent response of CNTA-100 was higher than that of the BCN sample. The higher photocurrent response during light-on and light-off cycles is initiated by the swift charge transfer due to C- and O-doping into g-C₃N₄, while inhibiting the charge recombination. As a result, a higher number of charge carriers participated in the photochemical reaction toward enhanced photocatalytic

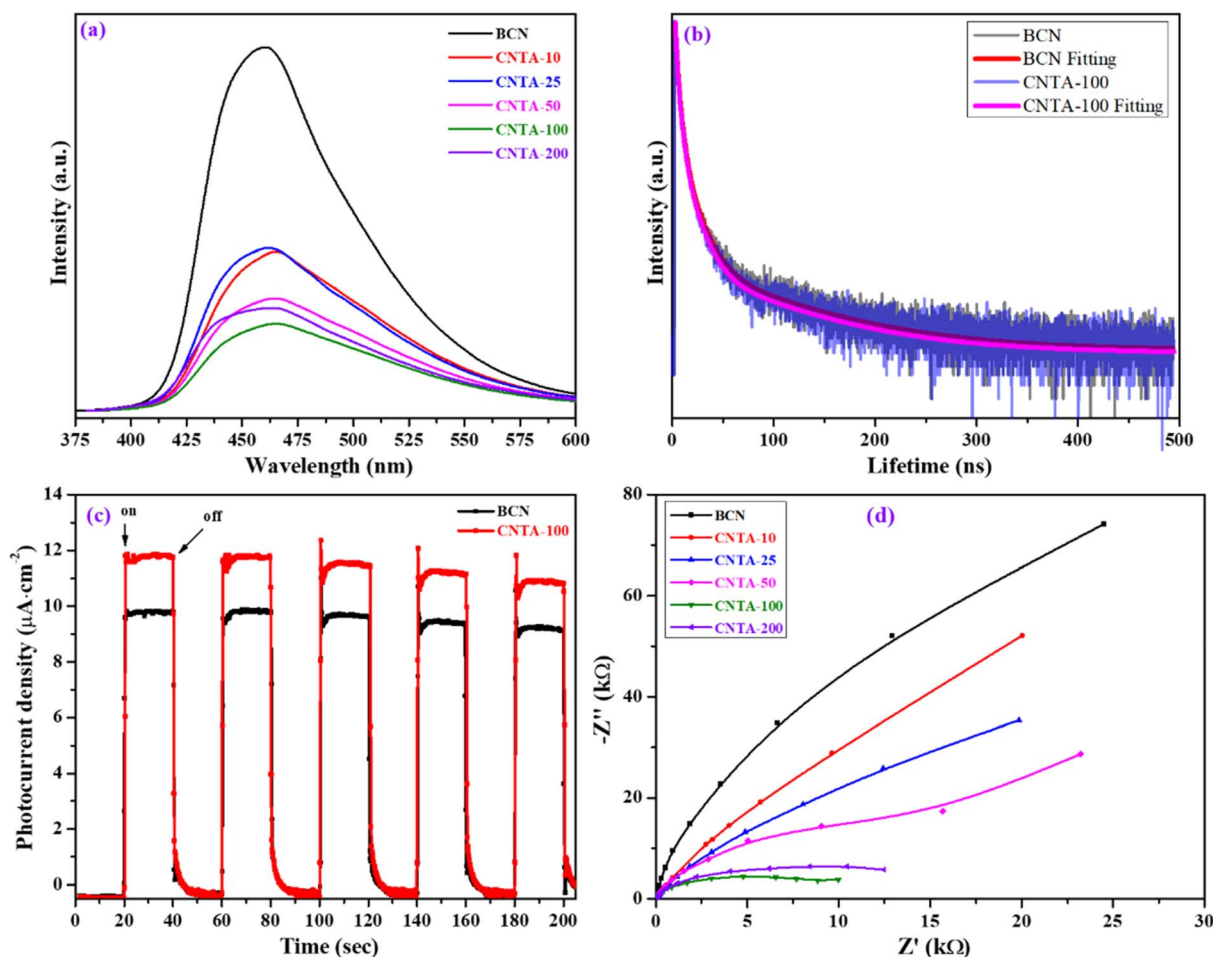


Fig. 8 Charge generation and separation studies: (a) steady state photoluminescence (PL) and (b) time-resolved photoluminescence (TR-PL) spectra. (c) Transient photocurrent and (d) electrochemical impedance spectroscopy (EIS) measurements.

activity. Fig. 8d demonstrates that the Nyquist plot with the smallest semicircle was induced by less resistance to charge transfer inside the defect-engineered g-C₃N₄ sample (CNTA-100). The BCN sample showed a large arc radius, revealing that the BCN sample suffered a greater hindrance to the charge transport.^{61,62} These results indicate that the defects in the CNTA-100 sample significantly improved the photoexcited charge carrier separation, resulting in enhanced photocatalytic activity consistent with the H₂ evolution and tetracycline degradation tests.

Considering the structural and photocatalytic studies of BCN and CNTA samples, we affirm that the following features were responsible for the much higher photocatalytic activity of the CNTA-100 photocatalyst sample. Firstly, the increased specific surface area offers abundant catalytically active sites for photoredox reactions. A porous structure is also beneficial for the prompt diffusion of mass transfer and inhibiting the charge recombination, which dramatically accelerates the photocatalytic reactions. Second, based on the collective analysis of UV-vis DRS and band structure analysis, the CNTA-100 sample could absorb more visible light and has a lower flat potential and higher donor density, thermodynamically improving the photocatalytic reaction. Third, the CNTA-100 photocatalyst sample demonstrated a significantly enhanced photoinduced charge carrier generation and transfer properties and, consequently, higher photocatalytic activity. Lastly, the introduction of C- and O-doping, and N-vacancies in the g-C₃N₄ framework could modify the band structure by creating an additional energy level in the band gap (midgap states) and act as trapping sites to avoid the photoinduced charge carrier recombination.⁶³ Further, unsaturated coordination electrons resulting from the defects enhanced the electronic interactions with the adsorbed molecules, thus boosting the photocatalytic activity.

3.5. Density functional theory (DFT) predictions

First-principles calculations were conducted using density functional theory (DFT). Structural optimization, defect formation energy estimates, electronic structure (density of states), and charge density difference analyses were conducted utilizing the OpenMX software, which employs the linear combination of pseudoatomic orbitals (LCPAO) approach.⁶⁴ The generalized gradient approximation utilizing the Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional was applied, in conjunction with norm-conserving pseudopotentials. A suitably large g-C₃N₄ supercell was created to simulate three possible nitrogen vacancies N1, N2, and N3, in g-C₃N₄, along with their oxygen-stabilized forms, therefore minimizing defect–defect interactions. All atomic positions were completely optimized until the residual forces fell below 0.01 eV Å^{−1}, and the total energy convergence criterion was established at 10^{−6} eV.^{65,66} Vacancy formation energies were assessed using suitable chemical potentials to determine thermodynamic viability. Calculations of optical characteristics and work function were conducted with the CASTEP code within a plane-wave pseudopotential framework. Ultrasoft pseudopotentials and the PBE functional were utilized, including Grimme's D3 dispersion

correction for including the van der Waals interactions, with a plane-wave energy cutoff set at 400 eV. Brillouin zone sampling was performed using a 3 × 3 × 1 Monkhorst–Pack *k*-point grid, appropriate for the two-dimensional supercell model.⁶⁷ The frequency-dependent complex dielectric function was computed to examine optical responses from the ultraviolet to the near-infrared spectrum. The work function was derived from the planar-averaged electrostatic potential by determining the energy difference between the vacuum level and the Fermi level. A vacuum thickness of no less than 15 was implemented along the surface normal direction to prevent interactions between periodic pictures. $E_f = E_{\text{defect}} - E_{\text{pristine}} + n\mu_N - m\mu_O$; where E_{defect} and E_{pristine} are the total energies of the defective and pristine g-C₃N₄ supercells, respectively. n is the number of removed nitrogen atoms, and μ_N is the chemical potential of nitrogen.⁶⁸ For the N vacancy formation energy calculation, we simplified the aforementioned formula as follows: $E_f = E_{\text{defect}} - E_{\text{pristine}} + n\mu_N$.

Density functional theory (DFT) studies elucidated the site-selective creation and stabilization of nitrogen vacancies in g-C₃N₄ by correlating formation energy, local structural flexibility, and chemical stabilization through oxygen. In pristine defective structures, the N2 vacancy is thermodynamically favored, demonstrating the lowest formation energy ($E_f = 1.499$ eV) in comparison to the N3 ($E_f = 2.251$ eV) and N1 vacancies ($E_f = 5.435$ eV) (Fig. 9a and S11). The energetic hierarchy suggests that the N2 site has a local coordination environment that facilitates lattice relaxation more efficiently following the nitrogen removal, while the N1 site is structurally rigid and energetically resistant to vacancy formation.⁵ Structural relaxation demonstrates this interpretation. The creation of an N2 vacancy causes significant bond-length redistribution, with adjacent bonds measuring 1.338–1.518 Å, indicating the disruption of local π -conjugation and the formation of unsaturated carbon centers (Fig. 9a and S11). This significant distortion, although energetically expensive in the perfect lattice, generates chemically active regions that are highly susceptible to heteroatom integration. The inclusion of oxygen significantly alters the energy landscape. All vacancy configurations are thermodynamically viable, as evidenced by negative formation energies, indicating spontaneous stabilization. The O-doped N2 vacancy demonstrated the lowest formation energy ($E_f = -1.838$ eV), rendering it the most stable and viable defect configuration, exceeding both O-doped N3 ($E_f = -1.714$ eV) and O-doped N1 ($E_f = -1.184$ eV) (Fig. 9a and S11). The inclusion of oxygen constricts the local bond-length distribution at the N2 site to 1.336–1.369 Å, indicating that oxygen not only provides energy stabilization to the defect but also alleviates excessive lattice strain *via* advantageous C–O bonding.

The electronic redistribution caused by nitrogen vacancies and oxygen incorporation in g-C₃N₄ was visualized using charge-density difference (CDD) analysis, where cyan regions show charge depletion and yellow regions display charge accumulation (Fig. 9b).⁶⁹ In the defective structure, notable charge depletion (cyan) is evident around the nitrogen framework adjacent to the vacancy, while substantial charge accumulation (yellow) is present on the neighboring carbon atoms,

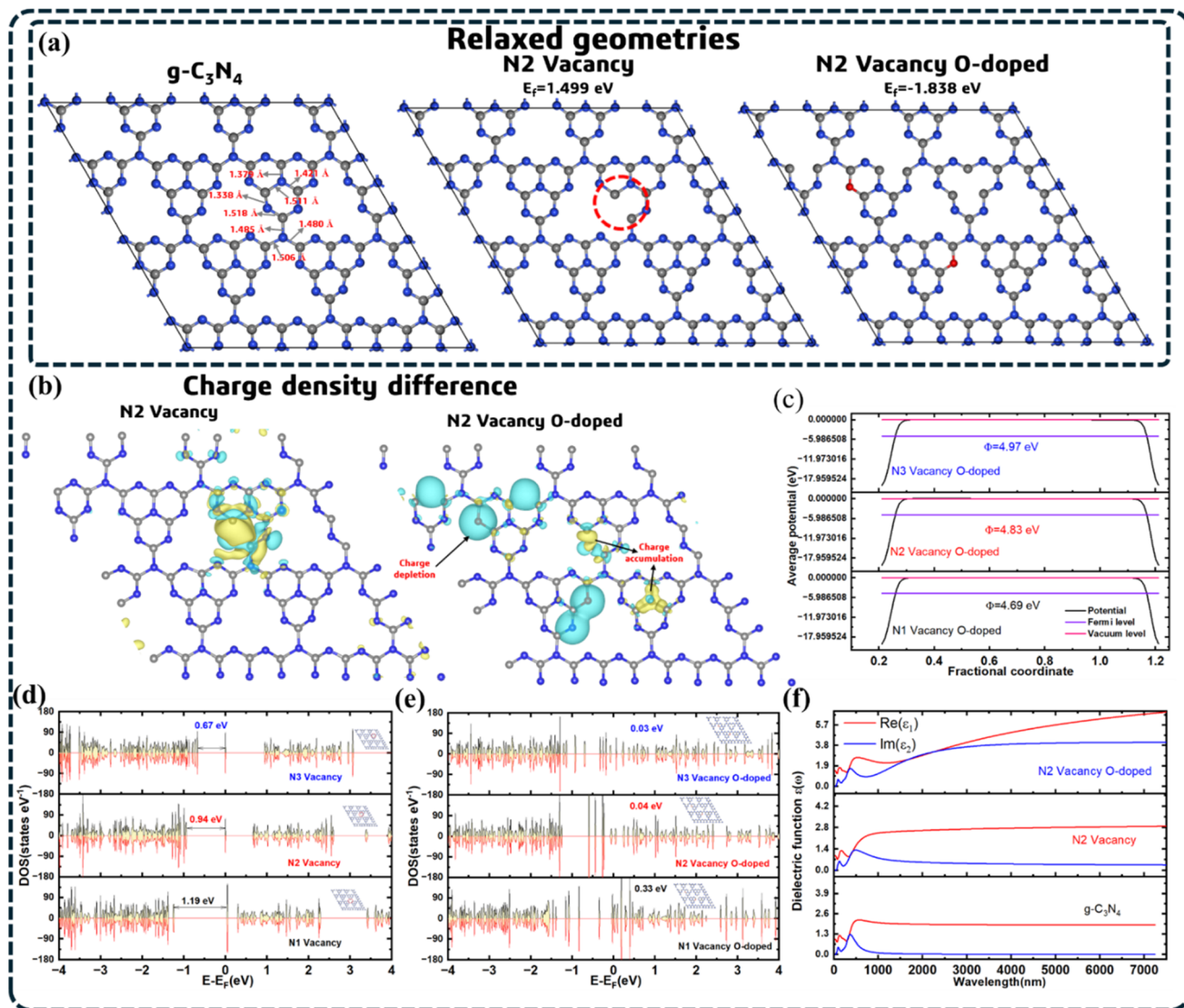


Fig. 9 Density functional theory (DFT) analysis of nitrogen vacancy formation, oxygen stabilization, and the resulting electronic and optical properties of g-C₃N₄. (a) Optimized, pristine g-C₃N₄ structure with representative bond lengths and optimized N2 defective site containing C₃N₄ (highlighted by dashed circles). (b) Charge density difference (CDD) maps of O-stabilized N2 vacancy configurations, where yellow and cyan isosurfaces denote charge accumulation and charge depletion, respectively. (c) Planar-averaged electrostatic potential profiles used to evaluate the work functions of O-doped N1, N2, and N3 vacancy structures. (d and e) Total density of states (TDOS) of g-C₃N₄ with N1, N2, and N3 vacancies before and after oxygen incorporation, showing defect-induced bandgap modulation. (f) Wavelength-dependent real [Re(ϵ_1)] and imaginary [Im(ϵ_2)] parts of the dielectric function for pristine g-C₃N₄, N2 vacancy and O-stabilized N2 vacancy structures, illustrating enhanced light-matter interaction upon defect engineering.

corroborating the emergence of electron-rich unsaturated carbon centers resulting from nitrogen removal. Following the incorporation of oxygen at the vacancy site, the CDD maps indicate increased charge accumulation (yellow) localized around the oxygen-coordinated carbon atoms, alongside charge depletion (cyan) in the adjacent lattice. This redistribution demonstrates robust C–O bonding and efficient correction for the charge imbalance caused by vacancies. The charge accumulation is spatially localized, suggesting that O-stabilized N2 vacancies serve as electronically active sites instead of recombination centers.

The planar-averaged electrostatic potential profiles were computed to assess the influence of nitrogen vacancies and oxygen incorporation on the surface electronic characteristics of g-C₃N₄. Pristine g-C₃N₄ displays a work function (Φ) of 4.69 eV, acting as the reference state (Fig. S12a). The introduction of nitrogen vacancies results in a significant rise in Φ , signifying improved surface electron binding. The N2 vacancy, recognized as the most thermodynamically favourable defect, demonstrates a work function of 5.20 eV, whilst the N3 and N1 vacancies have Φ values of 5.39 eV and 4.91 eV, respectively (Fig. S12b). The elevation in work function indicates electron depletion at the surface due to vacancy-induced lattice

deformation and charge redistribution. The introduction of oxygen results in a reduction of work functions across all faulty structures, signifying good electronic stabilization. The O-doped N2 vacancy demonstrates a decreased work function of 4.83 eV (Fig. 9c), nearing that of pristine g-C₃N₄, although staying inferior to the N2-vacancy-only arrangement (5.20 eV). This reduction indicates that oxygen incorporation mitigates the charge imbalance caused by vacancies and enhances surface electron transport efficiency.

The total density of states (TDOS) analysis demonstrates that nitrogen vacancies and oxygen incorporation significantly alter the electronic properties of g-C₃N₄. Unmodified g-C₃N₄ displays a semiconducting nature with a bandgap of 2.73 eV, which explains its restricted visible-light absorption and moderate charge-transport capabilities (Fig. S13).⁷⁰ The introduction of nitrogen vacancies creates defect-related states adjacent to the Fermi level, resulting in a notable bandgap reduction to 0.67 eV (N3), 0.94 eV (N2), and 1.19 eV (N1) (Fig. 9d).⁶⁸ This phenomenon enhances carrier availability and electronic conductivity, with the N2 vacancy exhibiting a particularly pronounced increase in the total density of states near the Fermi level. The incorporation of oxygen alters the electronic structure, resulting in O-doped vacancy systems that display almost continuous states near the Fermi level, with minimal effective gaps of 0.03 eV (N3-O), 0.04 eV (N2-O), and 0.33 eV (N1-O) (Fig. 9e). This suggests that oxygen stabilizes vacancy-induced states while preserving electronic accessibility, rather than creating deep trap centers. The observed discrepancy between the significantly diminished electronic bandgap derived from total density of states (TDOS) and the greater optical bandgap measured experimentally can be determined by the Moss-Burstein effect, wherein defect-induced carriers occupy low-energy conduction states, thereby elevating the optical absorption threshold to higher energies.⁷¹ The TDOS results indicate that oxygen-stabilized N2 vacancies achieve an ideal equilibrium of elevated carrier density and electronic stability, hence directly facilitating the improved charge separation and photocatalytic efficacy demonstrated in experiments.

The wavelength-dependent dielectric function provides quantitative insight into how N2 vacancies and oxygen incorporation enhance the optical response of g-C₃N₄ across the UV-visible-NIR spectrum, aligning precisely with experimental findings. Pristine g-C₃N₄ exhibits a constrained dielectric response, with the real component $\text{Re}(\epsilon_1)$ swiftly reaching saturation at around 1.5–1.7 beyond ~800 nm, while the imaginary component $\text{Im}(\epsilon_2)$, indicative of optical absorption, is predominantly restricted to the UV spectrum below ~450 nm and diminishes significantly at longer wavelengths (Fig. 9f).⁷² This behavior aligns with the experimentally observed abrupt absorption edge and limited visible-light utilization. Conversely, the N2 vacancy system demonstrates an augmented dielectric response, with $\text{Re}(\epsilon_1)$ rising to approximately 2.6–2.8 and $\text{Im}(\epsilon_2)$ maintaining a finite value in the visible spectrum up to around 700–800 nm, signifying the occurrence of defect-induced optical transitions and prolonged light absorption, consistent with the red-shifted UV-vis absorption and diminished PL intensity. The O-doped N2 vacancy exhibits the most

pronounced optical enhancement, characterized by a continuous increase in $\text{Re}(\epsilon_1)$ with wavelength, exceeding approximately 5.5–5.8 in the near-infrared region (>2000 nm), while $\text{Im}(\epsilon_2)$ remains notably high (~1.8–2.0) across an extensive spectral range from the visible (400–700 nm) to deep into the NIR (>3000 nm). The persistent dielectric and absorptive response at long wavelengths signifies robust light-matter interaction, heightened polarization, and diminished excitonic binding, which elucidates the experimentally observed extensive visible-to-NIR light harvesting and exceptional photocatalytic H₂ evolution and pollutant degradation efficacy. The investigation of the dielectric function verifies that oxygen-stabilized N2 vacancies significantly enhance the optical responsiveness of g-C₃N₄ throughout the entire solar spectrum.

The structural adaptation of the N2 site, along with robust chemical stabilization by oxygen, accounts for the experimentally observed prevalence of N2 vacancies in g-C₃N₄. Oxygen-stabilized N2 defects exhibit significant thermodynamic viability and diminished lattice distortion, which result in electrically asymmetric yet structurally stable sites that enhance charge-carrier localization, inhibit recombination, and facilitate photocatalytic performance.

3.6. Photocatalytic activity mechanism

Based on structural characterization, DFT modelling studies, and photocatalytic activity measurements, at first, the higher photocatalytic H₂ evolution activity of the CNTA-100 photocatalyst sample is presented in Fig. 10. The C- and O-doped porous g-C₃N₄ photocatalyst sample with N-vacancies efficiently separated the photoexcited charge carriers and improved the photocatalytic H₂ evolution activity. Upon visible light irradiation of the CNTA-100 sample, the VB electrons are photoexcited to the CB energy level and participate in the photoredox reaction, causing the HER, while the leftover holes in the VB oxidize the sacrificial agent TEA. Moreover, benefiting from the C- and O-doping and N-vacancies, which could easily induce the midgap states between CB and VB positions, the photoinduced electrons easily shift to midgap states. These midgap states could act as separation centers to extract electrons from the CB and thus greatly reduce the recombination rate between electrons and holes. Since the CB potential of the CNTA-100 sample is −0.75 eV, which is more negative than the required potential to convert 2H⁺ to H₂ molecules, a higher photocatalytic H₂ evolution activity was attained. The obtained CNTA-100 photocatalyst sample with a higher specific area and porous nature offers more abundant accessible sites and assists in deeply infiltrating the adsorbed molecules; consequently, a prominent enhancement in the H₂ evolution rate for the CNTA-100 sample is achieved. The created N-vacancies in the CNTA-100 sample act as carrier traps and retard the recombination of photogenerated charge carriers, which assists in improving the charge carrier separation efficiency towards higher H₂ evolution activity. In addition, after removing the N-atoms at the C–N=C sites, the residual unsaturated C-atoms around the C-sites are favorable for adsorbing more reactant and water molecules, and then activating them with the

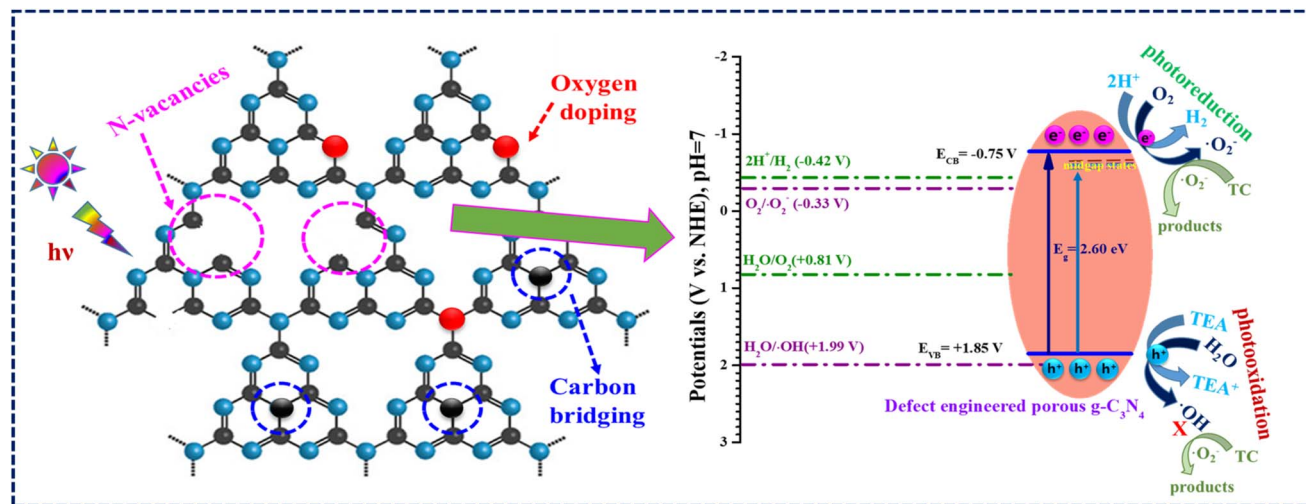


Fig. 10 Photocatalytic H_2 evolution and tetracycline degradation reaction mechanisms on the surface of the CNTA-100 photocatalyst sample.

accumulated electrons, further promoting the generation of H_2 molecules *via* the accepted electrons.^{73,74}

Thus, based on these measurements, the reasonable photocatalytic TC degradation mechanism over the CNTA-100 photocatalyst sample is discussed as follows. First, when a photocatalyst sample is irradiated with visible light, the electron-hole pairs are generated. It is worth noting that the conduction band (CB) position of the CNTA-100 sample is -0.75 eV, which is more negative than the reduction potential of $\text{O}_2/\text{O}_2^{\cdot-}$ (-0.33 V vs. NHE),³² which expedites the reduction of adsorbed O_2 on the catalyst surface to form $\text{O}_2^{\cdot-}$ radicals *via* electrons. These $\text{O}_2^{\cdot-}$ species can directly oxidize the TC into smaller molecules, thereby stimulating its degradation. Next, the valence band with a potential of 1.85 eV is less positive than the oxidation potential of $\text{OH}/\text{OH}^{\cdot}$ (2.38 V vs. NHE), representing the inability to generate a significant amount of $\text{OH}^{\cdot}$ radicals in the photocatalytic degradation reaction. Therefore, in the case of the CNTA-100 photocatalytic system, the primary active species accountable for the efficient photodegradation of TC are $\text{O}_2^{\cdot-}$ and h^+ , consistent with the results obtained from the active species trapping experiments.⁷⁵ The photoinduced electrons react with the dissolved oxygen molecules to produce $\text{O}_2^{\cdot-}$, which, together with the holes left in the valence band are highly efficient in attacking tetracycline during the photocatalytic degradation reaction.

4. Conclusions

To summarize, a highly efficient $\text{g-C}_3\text{N}_4$ photocatalyst has been successfully derived from the thermal polymerization of tannic acid-modified melamine precursors. Experimental and DFT theoretical predictions demonstrate that the infusion of tannic acid into the melamine and subsequent thermal polymerization can release gases such as CO_2 and NH_3 from tannic acid, allowing C- and O-doping and removing N-atoms from sp^2 -hybridized sites in the $\text{g-C}_3\text{N}_4$ framework. The resulting C- and O-doped $\text{g-C}_3\text{N}_4$ featuring N-vacancies can synergistically enhance visible light absorption and photogenerated charge

separation by introducing midgap states, thereby improving photocatalytic H_2 evolution and tetracycline degradation activity. As a result, the optimized photocatalyst demonstrated a remarkable H_2 evolution rate of $1850.61 \mu\text{mol g}^{-1} \text{h}^{-1}$ (~ 9 times higher than BCN) and TC pollutant degradation of 82%. The superior photocatalytic H_2 evolution rate is credited to the higher specific surface area, electronic band structure with higher photoredox power, and the promotional effects of N-vacancies *via* adsorption and activation of reactant molecules, thus becoming highly efficient active sites for photochemical reactions. This study delivers novel insight into the fabrication of nitrogen-deficient visible-light-responsive $\text{g-C}_3\text{N}_4$ photocatalysts for efficient solar energy conversion and in water pollutant remediation reactions.

Author contributions

Rama Krishna Chava: conceptualization, methodology, validation, formal analysis, investigation, data curation, writing – original draft, writing – review and editing. Annamalai Raja: investigation, resources. Sathish Panneer Selvam: software, formal analysis, resources. Shanmugasundaram Kamalakannan: software, formal analysis, resources. Misook Kang: writing – review and editing, supervision, funding acquisition.

Conflicts of interest

All authors declare that they have no conflicts of interest.

Data availability

The data supporting this article have been included as part of the supplementary information (SI). Supplementary information is available. See DOI: <https://doi.org/10.1039/d5ta05329c>.

Acknowledgements

This study was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIT) (no. 2022R1A2C2008313) for which the authors are grateful.

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