Enhancing Visible Light Catalytic Efficiency through Modulating Electron Cloud Density via Structure-Function Relationship

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Abstract

Structural modulation of pristine graphitic carbon nitride presents a significant challenge in the rational design of catalysts for efficient degradation of small organic pollutants under visible light. In this study, we combining first-principles calculations and structure-function relationship to predict a high-performance catalyst. The results indicate that CN-8 exhibits a significant degree of separation between electrons and holes, the CN-8 exhibits exceptional degradation efficiency towards rhodamine B, tetracycline and bisphenol A under visible light irradiation. The degradation rate constants are 0.6436 min-1, 0.2432 min-1, and 0.1394 min-1 higher than that of bulk g-C3N4 (0.0561 min-1, 0.0648 min-1, 0.0232 min-1), respectively. Density functional theory calculations, and structure-function relationship investigations confirm that the superior catalytic activity of CN-8, modifying the amino position changes the electron cloud distribution, promoting efficient separation of photo-generated electron-hole pairs. This study offers valuable insights for developing eco-friendly and efficient photocatalysts for environmental remediation.

Enhancing Visible Light Catalytic Efficiency through Modulating Electron 1 **Cloud Density via Structure-Function Relationship** 2 3 Hong Tu, Yao Tang, Renjiang Guo, Yin Xu, Shengxin Guo, Shunhong Chen, Ya Wang, Yaming Liu, Jian Wu* 4 5 National Key Laboratory of Green Pesticide, Key Laboratory of Green Pesticide and Agricultural Bioengineering, Ministry of 6 Education, Guizhou University, Huaxi District, Guivang 550025, China 7 Email Address: jwu6@gzu.edu.cn 8 9 **Keywords**: g-C₃N₄, DFT, photo-degradation Structural modulation of pristine graphitic carbon nitride presents a significant challenge in the 10 rational design of catalysts for efficient degradation of small organic pollutants under visible light. 11 12 In this study, we combining first-principles calculations and structure-function relationship to predict a high-performance catalyst. The results indicate that CN-8 exhibits a significant degree of 13 separation between electrons and holes, the CN-8 exhibits exceptional degradation efficiency 14 15 towards rhodamine B, tetracycline and bisphenol A under visible light irradiation. The degradation rate constants are 0.6436 min⁻¹, 0.2432 min⁻¹, and 0.1394 min⁻¹ higher than that of bulk g-C₃N₄ 16 (0.0561 min⁻¹, 0.0648 min⁻¹, 0.0232 min⁻¹), respectively. Density functional theory calculations, and 17 structure-function relationship investigations confirm that the superior catalytic activity of CN-8, 18 modifying the amino position changes the electron cloud distribution, promoting efficient 19 20 separation of photo-generated electron-hole pairs. This study offers valuable insights for developing eco-friendly and efficient photocatalysts for environmental remediation. 21 22

23 **1. Introduction**

Currently, the escalating issue of water pollution is primarily attributed to industrial sewage discharge, the widespread use of antiviral drugs in the medical field, and agricultural drug use.^[1] The presence of emerging pollutants such as pharmaceutical products (tetracycline (TC)), industrial raw materials (bisphenol A (BPA)), pesticides, and dyes (rhodamine B (RhB), methylene blue (MB)) in water systems poses a severe threat to the environment and living organisms.^[2-4] Pharmaceutical products, including TC, are commonly used in human and veterinary medicine.^[5] When these

pharmaceuticals are excreted or improperly disposed of, they can enter water systems through 30 wastewater treatment plants or runoff from agricultural fields. TC is known to have antimicrobial 31 properties, which can lead to the development of antibiotic-resistant bacteria in the environment. 32 33 Additionally, TC can disrupt the natural microbial balance in ecosystems, affecting nutrient cycling and overall ecosystem health^[6]. Industrial raw materials such as BPA are widely used in the 34 production of plastics and epoxy resins.^[7] BPA can leach into water sources from plastic containers, 35 bottles, and cans. It is considered an endocrine-disrupting chemical, meaning it can interfere with 36 37 hormonal systems in both humans and wildlife. BPA has been linked to various health issues, including reproductive disorders, developmental abnormalities, and certain types of cancers. 38 Insecticide, such as fluralaner (FLLN), are used to control pests agriculture and public health. These 39 chemicals can enter water systems through runoff and leaching from treated fields.^[8] FLLN is a 40 41 broad-spectrum insecticide that targets parasites in animals. However, its presence in water bodies can have detrimental effects on non-target organisms, including aquatic insects, honeybee, and 42 amphibians.^[9] Pesticides can disrupt the balance of ecosystems and harm sensitive species, leading 43 to declines in biodiversity. Dyes, such as RhB and MB, are commonly used in industries such as 44 45 textiles, printing, and paper manufacturing. Discharge of dye-containing wastewater into water systems can result in the contamination of aquatic environments. Dyes can reduce light penetration 46 in water bodies, affecting photosynthesis and disrupting the growth and development of aquatic 47 plants^[10]. They can also be toxic to aquatic organisms, causing adverse effects on their survival, 48 49 reproduction, and overall ecological balance.

Overall, the presence of these emerging pollutants in water systems can have wide-ranging 50 impacts on the environment, including the disruption of ecosystems, harm to living organisms, and 51 potential risks to human health.^[11] It is crucial to develop effective methods for their removal and 52 remediation to ensure the protection and sustainability of our water resources. To address this 53 critical challenge, photocatalysis has emerged as a promising strategy for pollutant degradation. 54 However, the low utilization efficiency of sunlight and the high recombination rate of photoinduced 55 charge carriers significantly hinder the overall quantum efficiency and practical applications of 56 photocatalysis.^[12] Moreover, there is an urgent need for green and sustainable technologies and 57 policies to effectively mitigate or eliminate the presence of antibiotic residues and dyes in water 58 systems. These stable and nonbiodegradable chemical species, such as RhB, MB, TC, FLLN, and 59

60 BPA, have the potential to bioaccumulate and cause adverse effects like endocrine disruption, 61 reproductive anomalies, and eco-toxicity, even in trace amounts in water. Given the demand and 62 stress for clean and potable water, several projects on water reclamation, recycling, and reuse are 63 emerging worldwide.

Semiconductor photocatalysis has shown great potential in degrading aqueous pollutants. 64 Among various semiconductors, graphitic carbon nitride (g-C₃N₄) stands out as a promising 65 inorganic nonmetal conjugated semiconductor. The photocatalytic activity of g-C₃N₄ can be 66 67 enhanced through various strategies, including doping, functionalization, and structural optimization.^[13-14] These approaches aim to modify the electronic structure, surface properties, and 68 structural characteristics of g-C₃N₄, ultimately improving its ability to absorb visible light and 69 facilitate efficient charge separation and transfer. These advancements hold great potential for the 70 71 development of highly efficient g-C₃N₄-based photocatalysts for environmental applications in pollutant removal from water systems.^[15-16] It features a layered graphite-like structure with triazine 72 or heptazine as its basic unit. In recent years, g-C₃N₄ has gained significant attention in the field of 73 photocatalysis due to its excellent physicochemical stability, large surface area, and non-toxicity. 74 75 Importantly, g-C₃N₄ has a conduction band positioned at -1.4 V and a valence band positioned at 1.3 V, making it highly efficient in absorbing visible light. These unique electronic properties 76 enable g-C₃N₄ to effectively utilize visible light for photocatalytic reactions.^[17] Therefore, g-C₃N₄ 77 materials hold great promise for environmental applications in removing pollutants from water. 78

79 In this study, we proposed a method to modify the electronic cloud density distribution of the organic conjugated framework through amino modification, which promotes the separation of 80 photo-generated charge carriers. By introducing organic small molecules containing benzaldehyde 81 to pristine g-C₃N₄, the resulting imide structure exhibited an expanded shift in electron cloud 82 density. Previous research has successfully modified the amino group to enhance photocatalytic 83 activity.^[18-19] Based on theoretical analysis and literature precedents, we investigated the influence 84 of substituents on the electron cloud density above the benzene ring. Introducing a strong 85 electron-withdrawing group onto the benzene ring enhanced the effective separation of electrons 86 and holes. Our team utilized Density Functional Theory (DFT) to compute the first excited state (S1) 87 electron-holes distribution patterns of twelve unique functional groups and S1~S5(first excited state 88 to fifth excited state) electron-holes distribution of CN-8 and g-C₃N₄ supercell (Figure 1).^[20] This 89

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method effectively enhances the conjugation of pi-pi bonds and increases the separation distance of
electron-hole pairs, leading to significantly enhanced photocatalytic activity. This study proposes,
for the first time, the reliable verification of the structure-function relationship by using DFT to
calculate electron-holes.^[21]

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Figure 1. The electron-holes distribution of the first to fifth excited states in $g-C_3N_4$ and CN-8 calculated by DFT calculations.

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117 2. Results and Discussion

118 **2.1 Preparation and characterization of photocatalysts**

To prepare a highly active CN-8 catalyst with enhanced light absorption, a temperature 119 gradient selection approach was employed during the synthesis of g-C₃N₄. It was found that 120 temperatures below 520 °C resulted in insufficient urea polymerization, while higher temperatures 121 (590, 600, 610 °C) led to low yields.^[22-23] Therefore, g-C₃N₄ precursor materials were prepared at 122 520, 550, and 580 °C. Infrared spectroscopy revealed an increase in -C=N (1660-1680 cm⁻¹) bonds 123 with increasing temperature (Figure 2i). Among the synthesized materials, CN580 exhibited the 124 best degradation activity towards RhB under visible light at 450 nm. CN580 was further modified 125 126 using 12 different benzaldehyde derivatives connected to the phenyl ring, resulting in the synthesis of CN-1 to CN-12.^[24] After modifying CN580 with p-nitrobenzaldehyde to obtain CN-8, the 127 infrared spectra showed the disappearance of hydrogen bonds formed by amino groups absorption 128 peak (3620-3680 cm⁻¹).^[25] Density functional theory (DFT) calculations, combined with 129 experimental screening, identified CN-8 as the most suitable catalyst. The SEM images shown in 130 Figure S1(Supporting Information) indicate that CN520, CN550, CN580, and CN-8 have a 2D 131 plate structure due to strong π - π stacking, while HRTEM images (Figure 2) show that they have a 132 transparent sheet-like morphology. However, the selected area electron diffraction (SAED) pattern 133 (Figure 2c, inset) does not show any lattice fringes, suggesting that CN-8 is amorphous.^[26] 134

To analyze the crystal structure of CN520, CN550, CN580, and CN-8, we examined their 135 X-ray powder diffraction (XRD) patterns (Figure 2j). These patterns revealed two distinct 136 diffraction peaks at 13.1° and 27.3°, corresponding to the (100) in-plane long-range atomic order 137 and (002) interlayer-stacking motif, respectively.^[27] As the calcination temperature of g-C₃N₄ 138 increased, we observed an increase in the intensity of the (002) peak, indicating an improvement in 139 the stacking order of the interlayers. This suggests that higher calcination temperatures promote the 140 formation of a more ordered crystal structure. Furthermore, when comparing the modified sample 141 (CN550-8) to CN550, we observed a significant increase in peak intensity.^[28] This indicates that the 142 modification with electron-donating groups at the amino position (CN-8) enhances the crystallinity 143 of the material, leading to a more organized and stable structure. This enhancement in crystal 144 structure may contribute to the improved photocatalytic performance observed in the degradation 145 experiments. Overall, these XRD results provide strong evidence for the structural changes induced 146 147 by the modification of g-C₃N₄ and highlight the potential of these modified materials for various applications. 148

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Figure 2. (a-b) SEM and (c-e) TEM images of CN-8, (f-h) the corresponding elemental mapping on C, N, and O.
(i) FT-IR for CN520, CN550, CN580, and CN-8. (j) XRD for CN520, CN550, CN550-8, and CN-8.

To verify the structural change in CN520, CN550, CN550-8, and CN-8, Fourier transform 171 infrared (FTIR) spectroscopy was performed. The absorption peak of the -C=N bond (1620-1680 172 cm^{-1}) increases with the increase of the calcination temperature of g-C₃N₄, as shown in the Figure 173 2i. The -NH₂ stretching vibration peak of the N-H bond and hydrogen bonds between molecules 174 are located at 3620-3680 cm⁻¹ for CN520, CN550, and CN580. The disappearance of this 175 absorption peak in the CN-8 sample indicates successful modification of the amino group. These 176 peaks demonstrate that benzaldehyde-type compounds have been successfully introduced into the 177 framework of g-C₃N₄. 178

To better understand the structure and surface chemical properties of CN-8, we conducted X-ray photoelectron spectroscopy (XPS) characterizations. Both XPS survey spectrum and O 1s spectrum with binding energy at 532.6 eV indicate the introduction of p-nitrobenzaldehyde (**Figure 3**c).^[29] As shown in **Figure 3**d-i and Supplementary Table 4, the C 1s and N 1s spectra exhibit



Figure 3. (a) XPS survey for ,CN550, CN550-8, and CN-8. (b) XPS valence for CN550, CN550-8, and CN-8. (c-i)
XPS of O 1s (c), C 1s (d-f) , and N 1s (g-i).

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characteristic peaks of C and N heterocycle frameworks. Specifically, the N=C–N, N–(C)₂, and N–(C)₃ peaks are observed at 288.1, 398.4, and 400.6 eV, respectively.For CN-8, the higher binding energies of the C 1s, N 1s, and O 1s are associated with the structural change modified by the p-nitrobenzaldehyde. It is notable that the integrated peak area ratio N-(C)₂ in N 1s is significantly increased from 13.03 % (CN550) to 22.45 % (CN-8)(Table S4).^[30]



Figure 4. The XPS analysis of CN-8 was performed under an N₂:O₂ atmosphere ratio of 8:2, including measurements under dark and 5-minute light conditions.

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From **Figure 4**, it is evident that the surface elemental bands of CN-8 undergo significant changes under dark and light conditions. In the C 1s spectrum, the C-C peak at 284 eV increases from 56.4% to 62.5%, while the N-C=C content decreases from 12.3% to 1.8%. In the N 1s spectrum, the N-(C)₂ peak increases from 10% to 16.2%, and N-(C)3 increases from 4.2% to 5.5%. The O 1s spectrum shows a decrease in -NO₂ content from 15.7% to 12.6%. Additionally, the valence band decreases from 1.06 eV under dark conditions to 0.62 eV. These findings suggest

significant surface modifications and potential enhancements in the photocatalytic performance of
 CN-8.^[31]



Figure 5. (a) Band structure alignments. (b-c) Mott-Schottky plots of CN550 and CN-8. The potential values in these figures can be converted to potential relative to the standard hydrogen electrode (NHE) using the formula: E (NHE) = E (Ag/AgCl) + 0.197 V. (d) Nyquist plots periodic of CN550 and CN-8 from Electrochemical impedance spectroscopy. (e) ON/OFF photocurrent response. (f) The BJH pore size distributions and (i) N₂ adsorption isotherms of CN550 and CN-8. (g-h) Raman spectrum of CN550 and CN-8.

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The amino modification and variation in calcination temperature significantly impact the optical properties and light absorption capabilities. From UV-vis DRS shows that CN-8 demonstrates a stronger and red-shifted absorption capacity compared to CN550 (**Figure S2**a). The calculated Kubelka-Munk function reveals a progressively narrowed, direct bandgap from 2.49 eV in CN550 to 2.05 eV in CN-8 (**Figure S2**b). The flat band potentials estimated from the measured Mott-Schottky plots are directly employed as the conduction band (CB) edge potentials (**Figure 5**b-c, **Figure S3**). From XPS valence band (VB) edge potentials of CN550 and CN-8 are estimated as 2.11 and 1.78 eV, respectively(**Figure 3**b), establishing the band structure alignments in **Figure 5**a. Charge transfer and separation in CN-8 are further elucidated through steady-state and time-dependent photoluminescence (PL) measurements. The PL spectra (**Figure 6**b) confirm a red-shift in CN-8, indicating a reduced bandgap.

By fitting a double exponential equation (Figure 6a; Table S5), it was found that the 286 287 electron/hole recombination lifetimes of CN520 were relatively short, but after high-temperature calcination and modification with dinitrobenzaldehyde at the amino sites, the electron/hole 288 recombination lifetimes of the material were significantly improved. Considering the longer PL 289 lifetime, CN-8 was considered the optimal choice. The photocatalytic performances of CN550 and 290 291 CN-8 were investigated using electrochemical impedance spectroscopy (EIS) (Figure 5d). By comparing CN-8 to CN550 (Figure 5e), indicating its weak electron transfer ability and efficient 292 separation of photogenerated carriers for photocatalysis. It can be observed from the graph that the 293 differences in amino modification and calcination temperature resulted in changes in the electron 294 transfer pathways, thereby affecting the intensity of the photoresponse signal. As shown in Figure 295 5i and Table S5, CN550 and CN-8 exhibit type IV isotherms owing to the presence of abundant 296 mesopores. The CN-8 catalysts exhibit much higher specific surface areas and porosities than 297 CN550 up to 92.07 m²g⁻¹and 0.2785 cm³g⁻¹, which is beneficial for facilitated mass diffusion 298 299 kinetics during catalysis. The Raman spectroscopy test reveals that CN-8 exhibits a broader peak width and relatively lower peak position, indicating the presence of lattice defects and distortions in 300 its structure. In contrast, CN550 demonstrates higher peak positions and narrower peak widths, 301 suggesting a more intact and stable lattice structure (Figure 5g-h).^[32] 302

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Figure 6. (a) Time-resolved photoluminescence spectra of CN520, CN550, CN550-8, and CN-8. (b) Steady-state PL spectra of CN520,CN550, CN580, CN550-8. (c) XRD comparison between original CN-8 and CN-8 after 5 cycles. (d-f) EPR of $\cdot O^{2-} \cdot OH$, and e⁻ under dark and light conditions.

327 2.2 DFT calculation

To gain a deeper understanding of the relationship between amino modification and the 328 distribution of electrons and holes, we conducted first-principle density functional theory (DFT) 329 calculations. After optimizing the structure and performing single-point energy calculations, we 330 analyzed the energy of the first excited state. By plotting the distribution of electrons and holes in 331 the first excited state and comparing it with the experimental rates of RhB photocatalytic 332 degradation (Figure 7a-c; Table S3), we observed that higher proportions of electrons and holes on 333 the modified fragments corresponded to higher catalytic rates. Among them, CN-8 and CN-9 334 exhibited the highest proportion of electron holes. We further investigated the bond lengths between 335 N and O in the modified fragments (Figure S4) and found that CN-8 had longer bonds, facilitating 336 better separation of electrons and holes (Figure 8). 337

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Figure 7. (a) The chemical structures and S1 electron-holes distribution hot-maps of CN-1~CN12. (b) Steady-state PL spectra of CN-1~CN12. (c) Time curves of degradation of RhB by CN-1~CN-12 under the irradiation of a 6 W LED lamp at $\lambda = 450$ nm.

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Figure 8. Visualization of the First Excited State electron-holes in CN-1~CN-12.

393 **2.3 Degradation mechanism**

A reasonable reaction mechanism has been proposed in **Figure 10**a, taking into account the aforementioned studies. In neutral conditions (pH 7), electrons and holes are generated on the CN-8 surface through efficient absorption of visible light, leading to charge separation. Oxygen molecules are activated by nearby electrons, resulting in the generation of a significant quantity of $\cdot O_2^-$ anion radicals through the one-electron reduction of oxygen (E($O_2/\cdot O_2^-$) = -0.33 V vs. NHE, as represented by **Text S1** Equation (1), Supporting Information).^[33]

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432 (the redox potential of $\cdot O_2^{-/}H_2O_2$ is 0.94 V vs NHE, Text S1 Equation (3), Supporting

Information).^[34] Subsequent one-electron reduction of H₂O₂ leads to the generation of ·OH radicals 433 indirectly (the redox potential of H₂O₂/·OH is 0.32 V vs NHE, Text S1 Equation (4), Supporting 434 Information). From the comparison in band structure alignment between CN-8 and CN550, we 435 conclude that the separation of electrons and holes caused by modification of the amino site are 436 esential for such direct and indirect generation of reactive species(Text S1 Equation (1-9), 437 Supporting Information). After LC-MS analysis, the possible degradation pathway of FLLN is 438 illustrated in Figure 9 (FLLN LC-MS analysis, Supporting Information). We conducted 439 440 bio-toxicity tests before and after FLLN degradation, and the results revealed a reduction in toxicity by over 95% following degradation (Figure S13). The mineralization rates of organic pollutants 441 RhB, MB, TC, BPA, and FLLN, under 12 W LED λ = 450 nm illumination for 60 minutes, were 442 found to be 85.07%, 34.68%, 90.95%, 89.13%, and 46.06%, respectively. These results highlight 443 the remarkable efficacy of our approach in degrading these small molecular pollutants (Figure S6). 444

Contribution of h^+ , $\cdot O_2^-$, $\cdot OH$, and 1O_2 to RhB degradation. The decreased degradation kinetics 445 by CN-8 after adding Na₂C₂O₄, DMPO, BQ, and DMSO into reaction system suggested that 446 h⁺, $\cdot O_2^-$, $\cdot OH$, and 1O_2 had contribution to RhB degradation where α and β are the decreased 447 448 degradation kinetic efficiencies and relative contribution of different reactive species to RhB degradation, respectively. k_0 is the pseudo-first-order constant for RhB degradation without 449 scavenger as control, $k_{Na_2C_2O_4}$, k_{BQ} , k_{DMPO} , and k_{DMSO} are the pseudo-first-order constants for 450 RhB degradation when Na₂C₂O₄, BQ, DMPO, and DMSO were added into the suspension, 451 respectively(Text S2 Equation (10-17), Supporting Information).^[35] 452

Fundamentally, Photochemical oxidation may involve different reactive species like hole (h⁺), 453 superoxide radical ($\cdot O^{2-}$), hydroxyl radical ($\cdot OH$), and singlet oxygen ($^{1}O_{2}$). Supplementary Fig. 4a 454 depicts the ESR spectra using 2,2,6,6-Tetramethylpiperidine 1-oxyl (TEMPOL) as spin-labeling 455 agent. After 5 minutes of illumination, the ESR intensity of TEMPOL did not change, indicating 456 that CN-8 generate photoinduced electrons under light exposure did not captured by TEMPOL. 457 Figure 6d-f demonstrates that spin trapping experiments using 5,5-dimethyl-1-pyrroline N-oxide 458 (DMPO) provide direct evidence of the formation of DMPO- O^{2-} adducts (quartet, 1:1:1) and 459 DMPO-OH adducts (quartet, 1:2:2:1).^[35] No EPR signal is observed when there is no DMPO or in 460 the dark. The influence of such reactive species was validated by the use of corresponding 461 scavengers with other identical conditions, namely, sodium oxalate (NaC₂O₄, h⁺ scavenger), 462

benzoquinone (BQ, $\cdot O^{2-}$ scavenger), dimethylsulfoxide (DMSO, ${}^{1}O_{2}$ scavenger) and dimethylpyridine nitrogen oxide (DMPO, $\cdot OH$ and $\cdot O^{2-}$ scavenger) were added to reaction system in separate runs. Fig 5b and Equation (13-16) show that $\beta(h^{+}) = 16.36$ %, $\beta(\cdot O_{2}^{-}) = 19.59$ %, $\beta(\cdot OH) = 31.67$ %, and $\beta({}^{1}O_{2}) = 32.38$ % are the decreased degradation kinetic efficiencies and relative contribution of different reactive species to RhB degradation, respectively.





In addition, the degradation of RhB remain nearly identical after five cycles, implying our CN-8 catalyst is highly stable and recyclable (**Figure S7**). The XRD (**Figure 6**c), FT-IR (**Figure S5**) and SEM (**Figure S9**) comparisons between the original CN-8 and CN-8 after 5 cycles reveal that its corresponding structure remains intact, indicating no structural degradation of CN-8 after 5

494 cycles. We have further extended the reaction scope to other organic pollutants including MB, TC,495 BPA and FLLN.



515 Figure 11. Degradation of MB, TC, BPA and FLLN under the irradiation of a 12 W LED lamp at $\lambda = 450$ nm.

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2.4 Photocatalytic degradation test

We conducted photocatalytic degradation tests of CN-8-EDTA on RhB, MB, TC, and BPA using a catalyst concentration of 0.5 g/L. The optimal amount of EDTA was determined by screening the degradation rate of RhB, and it was found that adding more than 600 μ L did not significantly enhance the degradation rate. Therefore, we chose to use 600 μ L of EDTA.

Before the addition of EDTA, the first-order rate constants (k) of CN-8 for RhB, MB, TC, BPA and FLLN were 0.2109 min⁻¹, 0.0844 min⁻¹, 0.1528 min⁻¹, 0.0731 min⁻¹ and 0.0208 min⁻¹, respectively. After adding 600 µL of EDTA, the degradation rates of RhB, TC, BPA and FLLN

increased significantly, with k values of 0.6436 min⁻¹, 0.2432 min⁻¹, 0.1394 min⁻¹ and 0.1557 min⁻¹, 525 respectively. However, the degradation rate of MB decreased, with a k value of 0.0658 min⁻¹. The 526 addition of EDTA facilitated O^2 reduction through H-bonding, promoting the generation of O^2 527 and ¹O², thereby increasing the degradation efficiency. EDTA also acted as a scavenger for 528 529 hydroxyl radicals, further enhancing the degradation process. However, in the case of MB, the reaction rate actually decreased, indicating that ·OH is the main active radical for its degradation. 530 To further analyze the degradation of TC, BPA and FLLN, we plotted in situ trace UV-visible 531 532 absorption spectra (Figure S10-12, Supporting Information). We conducted a comparative study with similar catalysts and found that the photocatalytic performance of CN-8 is at the cutting edge 533 level (Table S6-9, Supporting Information). 534

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536 **3. Conclusion**

In summary, we present a novel approach for modifying g-C₃N₄ using benzaldehyde 537 compounds with various electron-donating and electron-withdrawing groups at the amino position. 538 Through DFT calculations and experimental validation, we identified CN-8 as the most efficient 539 540 compound for degradation, with a rate of 0.0844 min⁻¹ towards MB. By adding EDTA, the degradation rates of RhB, TC, BPA and FLLN were significantly improved to 0.6436 min⁻¹, 0.2432 541 min⁻¹, 0.1394 min⁻¹ and 0.1557 min⁻¹, respectively. Mechanistic studies confirmed that the 542 introduction of strong electron-donating functional groups at the amino position of g-C₃N₄ enhances 543 544 the separation of photogenerated charge carriers. This enhancement enables CN-8, in the presence of EDTA, to generate superoxide radicals more effectively under light conditions, thereby 545 promoting the degradation reaction. This work provides a promising strategy for designing efficient 546 photocatalysts for water pollutant decontamination. 547

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549 **4. Experimental Section**

550 4.1 Materials and reagents

551 Urea, absolute ethyl alcohol, glacial acetic acid, Na₂C₂O₄, DMSO, DMPO, BQ, TEMPOL,

- 552 RhB, MB, TC, and BPA were purchased from Macklin. 4-fluorobenzaldehyde (CN-1),
- 553 2,3-dimethylbenzaldehyde (CN-2), 3-nitrobenzaldehyde (CN-3), 4-bromobenzaldehyde (CN-4),

- terephthalaldehyde (CN-5), 2-nitrobenzaldehyde (CN-6), 2-bromo-6-nitrobenzaldehyde (CN-7),
- 4-nitrobenzaldehyde (CN-8), 2,4-dinitrobenzaldehyde (CN-9), 3-fluoro-4-nitrobenzaldehyde
- 556 (CN-10), 3-methyl-4-nitrobenzaldehyde (CN-11), and 2,6-difluorobenzaldehyde (CN-12) were

557 purchased from Aladdin.

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559 4.2 Synthesis of pristine g-C₃N₄(CN550) and CN580

The CN550 were fabricated by a typical synthesis route. In brief, urea (10.0 g) in a silica boat was heated at 550 °C for 3 h using a heating rate of 10 °C min⁻¹in a muffle furnace in an air atmosphere. The resulting yellow product was pulverized using an agate mortar for further utilization. The synthesis of CN580 is similar to CN550, with the only difference being its calcination temperature at 580 °C.

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566 **4.3 Synthesis of CN-1~CN-12**

Place 0.5 g of CN580 into a 100 mL round bottom flask and add 50 mL of anhydrous ethanol. Stir the mixture evenly and then add 0.1g of 4-nitrobenzaldehyde (CN-8). Reflux the solution at 80 °C for 12 hours. Once the reaction is complete, pour the mixture into 200 mL of ice water and stir for 10 minutes. Then, filter it, rinse it three times with distilled water, followed by three rinses with anhydrous ethanol.^[31] Dry the product in an 80 °C oven for 2 hours and grind it into powder using an agate mortar. CN-1 to CN-12 are all prepared using this method with different benzaldehyde compounds.

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575 4.4 Material characterizations

The morphology and structure of the samples were characterized by SEM(FEI Nova 576 NanoSEM450), TEM (FEI Talos F200C), and HRTEM. X-ray diffraction (XRD) (Japan Rikagu 577 Ultima IV). X-ray photoelectron spectroscopy was performed using a Thermo SCIENTIFIC 578 ESCALAB 250Xi system . All binding energies were calibrated by using the contaminant carbon 579 (C 1 s = 284.8 eV) as a reference. Fourier transform infrared (FTIR) spectra were obtained on 580 Thermo Fisher iS5. The Bruker EMXPlus used for ESR testing. The full pore was tested using the 581 Micromeritics ASAP2460 from the United States. Diffuse reflectance absorption testing was 582 conducted using the UH4150 instrument. Photocurrent correlation testing was performed using the 583

584 CHI660e instrument from China-Shanghai Chenhua. PL testing was conducted using the Hitachi 585 F-4700. The electronic transient lifetime was measured using the Horiba Fluorolog-QM steady-state 586 and transient fluorescence phosphorescence spectrometer. The Raman spectroscopy tests using the 587 Thermo DXR2xi instrument from the renowned American company, Thermo Fisher Scientific. The 588 LC-MS tested by the U3000 system from the renowned American company, Thermo Fisher 589 Scientific. The TOC (Total Organic Carbon) testing using the varioTOC select instrument from the 590 renowned German company, Elementar.

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592 **4.5 Computational methods**

All DFT calculations were performed using Gaussian 09 software. The method chosen for structure optimization was DFT-(B3LYP) with a basis set of 6-31G. The single-point energy calculations were performed using TD-DFT-(CAM-B3LYP) with a basis set of 6-31G' d. The data obtained from DFT calculations were processed using Multiwfn software.

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598 **4.6 Photocatalytic degradation experiment**

599 The photocatalytic degradation experiments were conducted using the PL-SX100A multi-channel photocatalytic reaction instrument. Visible light with a wavelength of $\lambda = 450$ nm 600 was selected, and the volume of the degradation solution was 10 mL. The catalyst dosage was 0.5 601 g/L, and the experiments were conducted in parallel in 3 groups, with the average values taken. For 602 testing RhB, the LED light intensity selected was 6 W, while for testing MB, TC, and BPA, the 603 LED light intensity selected was 12 W. The absorbance values of RhB and MB were measured 604 using the BioTek uQuant full-wavelength microplate reader. The TC and BPA were measured using 605 the Thermo Fisher NanoDrop One microvolume UV-Vis spectrophotometer. 606

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608 4.7 Regression analysis

609 We used Origin Pro 2022 software to analyze the measured results. The iterations were 610 conducted until a Chi-square tolerance of 1×10^{-9} was reached, and the fits were iterated until at 611 least 95% of the data matched the model ($R^2 > 0.95$).

612

613 Supporting Information

614	Supp	orting Information is available from the Wiley Online Library or from the author.	
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618	Ack	nowledgements	
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625	Author contributions		
626	Hong Tu designed and performed the experiments, collected and analyzed the data, and wrote		
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632	Competing interests		
633	The authors declare that they have no competing interests.		
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635	References		
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697 (a) Urea was calcined and (b) then the CN series was synthesized by condensing amino groups with different

698 benzaldehyde compounds. (c) DFT calculations determined the single-point energy and revealed the electron hole

699 distribution in the first excited state. The CN series exhibited degradation activity under visible light with water as

700 the solvent for RhB, MB, TC, BPA and FLLN.