Efficient visible light driven degradation of sulfamethazine and tetracycline by salicylic acid modified polymeric carbon nitride via charge transfer

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Abstract

Photocatalysis has been widely studied as a promising technique for removal of organic pollutants in wastewater. A modified carbon nitride has been designed for this purpose. In this study, a facile method to synthesize distorted carbon nitride by simply copolymerizing urea and salicylic acid has been explored. The incorporation of SA induced the structural change from planar structural to distorted curls structural. Compared to pristine CN, the CN-SA shows wide light absorption, which is attributed to the $n \rightarrow \pi^*$ transition at the nitrogen atoms with lone pair electrons of heptazine units. The photoelectrode of CN-SA exhibited higher photoeur and lower charge resistance than that of pristine CN electrode, indicating that the ph ted charge carriers of CN-SA are more efficiently separated. As a result, the optimized CN-SA shows 2-fold enhancement in degradation of tetracycline (TC) as compared to N. Furthermore, we found that the degradation rate of sulfamethazine (SMZ)_was 0823 min⁻¹ using the CN-SA photocatalyst, CN (0.0293 min⁻¹). In addition, the CN-SA shows which is three times higher than that good stability without structur charge or loss of photocatalytic performance after four cycles. According to the ra trapping experiments and electron spin resonance analyses, •O₂⁻ and h⁺ were the main active species involved in the degradation of organic pollutants. The developed strategy provides a novel approach to design the tunable band structure of organic semiconductor materials for various applications.

Keywords: Carbon nitride; Salicylic acid; Antibiotics; photocatalysis degradation; Charge separation.

1. Introduction

In the past decades, the increasing problem of environmental deterioration has strengthened interest in related research [1-6]. As the main source of environmental pollution, the water pollution caused by organic compounds is considered as one of the most challenging issues in environment. For instance, the total amount of tetracyclines and sulfonamides used in China in 2013 was estimated to be 12,000 tons and 7920 tons, respectively [7 addition, they have not only been found in water and sediment, but also in edatope, es tetracycline [13-17]. It is necessary to remove these contaminants from the polluted environment due to the sunlight driven photocatalysis for bioaccumulation and persistence [18, 19]. Semicond cto contaminant removal has attracted much atter The catalyst design is crucial for the on. nomy and stable catalyst is urgent. Recently, photodegradation reaction, and dev compared with traditional pho the conjugated organic polymers photocatalysts have been extensively st

In recent years, metal-free organic semiconductor polymeric carbon nitride (PCN) has attracted significant interest of researches due to their chemical stability and simple synthesis methods [24-26]. PCN has turned out to be a fascinating photocatalyst for environmental remediation, water splitting, CO₂ reduction, and synthetic organic chemistry [27-30]. Various strategies were explored to overcome its weakness such as low surface area, inadequate optical absorption, and fast charge recombination [31, 32]. Our group has demonstrated that heterojunction formed by PCN with other semiconductors (eg. Bi₁₂O₁₇Cl₂ Bi₂WO₆) was beneficial to charge carriers separation [33]. The introduction of heteroatoms is proved to be effective for band structure manipulation and charge carrier separation of PCN [34]. Besides heteroatoms, the homoatoms (C and N atom) also played an important role in the photocatalytic activity of PCN [35, 36]. The introduction of homoatoms could be obtained by copolymerization of another similar aromatic structure with the PCN precursor [37].

Various organic molecules with cyano and amino groups have been introduced into the carbon nitride networks by copolymerization [38, 39]. Wang et al first demonstrated that copolymerizing barbituric acid with urea could significantly enhanced e optio l absorption and thus improve the photocatalytic activity [40]. Since then, benzene based monomers like phenylurea, benzoic acid, m-trihydroxybenzene were repo ted to opolymerize with the precursors (i.e. melamine, dicyandiamide and urea) [41, acture of aromatic ring was similar to that of triazine. Anchoring aromatic strug the surface of PCN would expand the π electrons ire d arge pair separation [43-46]. The benzene-based of the PCN aromatic system an hic structure to manipulate the band gap of PCN. Previous monomers could improv jonship between charge carriers separation and photocatalytic activity works revealed that efficiency [32]. However, the relationship between photocatalytic activity and exciton dissociation was not clear. It is highly desired to explain the exciton dissociation in the aromatic-based carbon nitride and explore the potential environment applications.

In this work, we reported a strategy of surface engineering on PCN, where salicylic acid (SA) was chosen as the co-monomer to react with urea and obtained the resulting product. SA is a common benzene ring-containing acid with a carboxyl group and a phenolic hydroxyl group,

which is often used in the pharmaceutical industry. Through thermal copolymerization strategy, aromatic rings can be doped into carbon nitride structures, leading to a wide range of visible light absorption and high efficiency of charge carrier separation, thus obtained a better photocatalytic activity. The incorporation of SA into the PCN induced a structural distortion and the non-metal group doping, which was beneficial to the separation of charge carriers. As a result, the modified PCN exhibited enhanced photocatalytic activity in removal of TC or SMZ under visible light irradiation.

2. Experimental section

2.1 Materials synthesis



Urea and salicylic acid were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). MilliQ ultra-pure water who a resistivity higher than 18.2 M Ω ·cm was used in whole experiments. The traditional province carbon nitride (PCN) samples were synthesized from urea [47]. 10 g of untrawar provinto an alumina crucible with a cover, heated at a rate of 15 °C min⁻¹ and kepter 10 °C for 2 h in a muffle furnace, and then cooled down naturally.

The modified PCN composites were synthesized from urea and salicylic acid with different mass ratios. Typically, 10 g urea and a varied amount (i.e. 0.02, 0.05, or 0.1 g) of salicylic acid (SA) were first dissolved in 10 mL mixed solution which containing 8 mL of water and 2 mL of ethanol. The suspension was stirred at ambient temperature for 2 h and followed by ultrasonication for another 1 h. Then the suspension was dried at 90 °C. Finally, the obtained dried products were further transferred into a ceramic crucible with a cover and heated at a rate of 15 °C min⁻¹ and kept at 550 °C for 2 h in a muffle furnace. The products were labeled as CN-SA-x, and x

(g) was represented the amount of SA.

2.2 Characterizations

The crystal phase of photocatalysts was collected by powder X-ray diffraction (XRD) patterns on Rigaku D/max-2500 instrument in the region of 5 ° to 80 °. The spectra of Fourier transform infrared (FT-IR) were characterized by BioRad FTS-600 spectrometer. Scanning electron microscopy (SEM, Helios NanoLab 600i) and transmission electron microscopy (TEM FEI, Tecnai G2F20) were used to characterize the morphology of CN samples. The specific surface area, pore volume and pore size of CN samples were collected by the Runnauer Emmett-Teller at 77 k. The elements binding states of CN samples were investigated on X-ray photoelectron spectra (XPS, ESCALAB 250Xi). The range of light absorption has detected by UV-vis diffuse reflectance spectra (DRS, Cary 300). Photologianes and (PL) spectra were collected using a Perkin Elmer Luminesence Spectrometers (S 5 B) with excitation wavelength of 368 nm.

2.3 Photocatalytic activity test

Tetracycline (TT) of sulfamethazine (SMZ) were used as probe contaminants in photocatalytic activity studies. The simulated visible light source was obtained by a 300 W xenon lamp with a 420 nm filter. The average intensity of the irradiation at above 420 nm was about 62 mW cm⁻². The prepared sample was dispersed in distilled water (0.5 g L⁻¹) by sonication. The sample was mixed in stock solution (100 μ M of TC, SMZ) under continuous stirring until the adsorption equilibrium between the pollutant and the catalyst. After turning on the light in interval time, 2 mL of suspension was taken out and then centrifuged. The concentration TC and SMZ

were measured with UV-vis spectrophotometer and HPLC-UV (Detailed analytic methods were presented in Text S1).

2.4 Photoelectrochemical measurements

Photoelectrochemical measurements were conducted in the quartz cells and the data were collected by CHI 760E workstation. The three-electrode system involved an Ag/AgCl (3 M KCl) as the reference electrode, a Pt plate as the counter electrodes and the samples dispersed on a FTO glass as the working electrode. The system was carried out in 0.2 M Na₂SO₄ aqueous solution under visible light irradiation (300 W Xe arc lamp, $\lambda > 420$ nm. The working electrode was fabricated as following process: 5 mg catalyst was dispersed in 1 mL of N, N-Dimethylformamide by sonication to obtain a slurry solution. Then, the suffrequence of a cleaned FTO glass and then calcined at 120 °C for 2 h.

- 3. Results and discussion
- 3.1 Structures and composition of the as-prepared sample

The CN-SA sample was predured with urea and salicylic acid via polymerization as shown in Scheme S1. The final products were denoted as CN-SA-x, where x is the amount of SA. The crystal structure and phase of the as-prepared samples were obtained by XRD. The XRD patterns of the PCN and CN-SA-x are depicted in Fig. 1a. All samples are revealed typical graphic layered structures. The characteristic peak located at 20 of 27° is attributed to (002) plane of PCN, while the other peak at 13° is ascribed to (100) plane of PCN [34, 48]. After incorporated with SA, the peak intensity of (002) was broadened. The chemical structure of fabricated samples was collected by FT-IR spectra presented in Fig. 1b-d. From the 400-4000 cm⁻¹ (Fig. 1b), the structures of

CN-SA samples were almost identical to that of PCN. In the spectra of 800-1400 cm⁻¹ (Fig. 1c), the weak peak at 950-1200 cm⁻¹ was attributed to the skeleton vibration mode of benzene ring in the CN-SA. As shown in Fig. 1d, the weak peak at 1445 and 1500 cm⁻¹ were found in CN-SA, which come from the stretching vibration of the C=C aromatic skeleton of SA [49]. These results could confirm the SA was doping in the PCN framework successfully [50-52].

The detailed surface chemical composition of PCN and CN-SA-0.05 were further studied by XPS. In Fig. 2a, the C, N, O elements are observed in the survey spectrum. CN-SA-0.05 shows the similar chemical structure with the PCN (Fig. S1). The C 1s spectrum i ed into two peaks at 288.1 and 284.6 eV, corresponding to N-C=N bonds and graphi espectively (Fig. 2b) [53]. In the analysis for N 1s, peaks located at 398.4, 399 0.8, and 404.6 eV are belonging to the binding energy of C-N=C, N-C₃, C-NH group te charging effects of π -excitations, separately (Fig. 2c). For O 1s, two peaks for O 1s inding energy at 532.6 eV and 531.8 eV were hydroxyl groups and N-C-O species, respectively observed, which were corresponded tios and the area ratios of C-N=C/N-C₃ were calculated from XPS (Fig. 2d) [54]. The C/N molar r spectra in Table 1.1 ncorporation, the C/N ratio of CN-SA-0.05 increased. The area ratio of C-N=C/N-C₃ was calculated as 1.19 for PCN and 1.09 for CN-SA-0.05, which indicated that C-N=C would transform to N-C₃. In addition, the element analysis was used to further investigate the C/N ratios of PCN and CN-SA samples in Table S1, the C/N molar ratio increases from 0.66 for the PCN to 0.68 and 0.71 for CN-SA-0.05 and CN-SA-0.1, respectively. Therefore, SA was incorporated into the heptazine units successfully.

The morphology of PCN and CN-SA-0.05 were characterized by SEM and TEM. In Fig. 3a and 3b, PCN showed the typical graphical packed layer structure [55, 56]. When SA was added,

the nanosheets were broken into small sheets and they tended to be curved. As shown in Fig. S2, SEM elemental mapping confirms the homogenous distribution of C, N, and O elements in CN-SA-0.05, indicating the successful fabrication of CN material. The morphology of samples was further examined by TEM (Fig. 3c-d). The TEM image of CN-SA-0.05 presents a large scale of lamellar structure, which contains the nanosized pores with diameters ranging from 40 nm to 100 nm. It means that the holely thin nanosheets were synthesized with the incorporation of SA. N₂ adsorption tests were utilized to examine the surface and porous properties. In Fig. S3, both CN and CN-SA samples presented type IV sorption isotherms with an H1 rate hysteresis loop, suggesting to the porous features of the as-prepared samples [57]. A buowain Table S3, it can be seen that the specific surface area showed no big difference from PCN to CN-SA, revealing that the enhanced activity was may not ascribed to the surface area.

3.2 Optical properties of prepared samples

Optical absorption of PCN and QCCA-Second plane are tested by DRS. All the samples showed the visible light absorption properties in Fig. 4a. The absorption edge of PCN was around 460 nm, which was mainly visible to the $\pi \rightarrow \pi^*$ transition. With the increased amount of SA, CN-SA shows a red-shift in the optical absorption, which was attributed to $n \rightarrow \pi^*$ transition involving the lone pairs of the edge nitrogen atoms in heptazine units [58]. Also, the color of CN-SA-x samples changed from white-yellow to dark yellow, which indicated that the incorporation of SA into the CN networks will narrow the band gap of PCN (Fig. S4). This change was beneficial to the visible light absorption and to improve the photocatalytic activity of PCN. As shown in Fig. 4b, the band gap of PCN is about 2.56 eV determined from the tauc plot. The band gap was decreased from 2.48 eV (CN-SA-0.02) to 2.32 eV (CN-SA-0.1). This behavior was also found in other studies of the copolymerization of PCN with barbituric acid and 2-amino benzonitrile [40].

Mott-Schottky plots and valence band X-ray photoelectron spectroscopy (VB-XPS) were used to measure the band edge positions of PCN and CN-SA-0.05 [59]. As shown in Fig. 4c, the flat band potentials of PCN and CN-SA-0.05 obtained from Mott-schottky plots are -1.13 and -0.95 V versus the Ag/AgCl electrode, which corresponding to -0.91 and -0.73 V versus NHE, respectively. Besides, Fig. 4d showed the VB-XPS spectra of PCN and CN-SA-0.05. It can be seen that the gap between VB and Fermi level was 2.16 eV for the PCN, and it was 2.37 eV for CN-SA-0.05. The flat potential is almost equal to that of the Fermi level [62–61]. Thus, the VB positions of PCN and CN-SA-0.05 were equal to 1.25 and 1.64 eV. Schule 3 and VB positions of PCN are located at -1.31 and 1.25 eV, respectively. Meanthile, the CB and VB positions of CN-SA-0.05 located at -0.76 and 1.64 eV.

3.3 Enhancement of photocatalytic activity

As a widely used antibiotic, TC has been deen sively used in many areas and the residues have becoming an issue. The photoettalyth activities of PCN and CN-SA samples were examined by degradation of TC trequerus solution. The adsorption capacity of all samples for TC in the dark was negligible (Fig. S5) Control experimental results revealed that the self-degradation of TC was negligible either without photocatalyst or in the presence of photocatalyst in the dark. The photocatalytic activity of PCN, CN-SA-0.02, CN-SA-0.05, and CN-SA-0.1 samples was presented in Fig. 5a. CN-SA-0.05 showed the highest photocatalytic activity for TC compared to that of other test samples. TC was effectively removed in the presence of CN-SA-0.05 with a removal efficiency of above 86% obtained in 60 min. PCN had the lowest reactivity, only 62% of TC was decomposed within 60 min of light illumination. TC removal curves obeyed the first-order kinetic equation (Fig. 5b), the apparent TC removal rate constants of CN-SA-0.05 (0.0327 min⁻¹) was almost two times that of the PCN (0.0162 min⁻¹). The above results suggest that an optimal amount of salicylic acid doping can improve the photocatalytic efficiency of PCN. It is worth noting that CN-SA-0.05 not only shows higher reactivity for removal of organic contaminants but also for the mineralization of TC than PCN in TOC removal (Fig. S6). The degradation products have been identified by HPLC-MS (Fig. S7, Table S3).

The pollutants concentration varies widely in the natural environment. The influence of the initial concentration on the photocatalytic activity was significant. Dif itial concentration of TC (varying from 5 to 40 mg L⁻¹) was utilized to test the active N-SA-0.05, and the results were depicted in Fig. 5c. With the concentration reasing from 5 to 40 mg L⁻¹, the removal efficiency dropped from 92% to 70% for CM 05 in 1h irradiation. This phenomenon could be explained that a certain amount of CN -0.05 can generate the same active species to vere produced from the high concentration of TC react with TC. In addition, more int f cata yst dosage on the removal of contaminant, the optimized [62]. To determine the effect 0.2 to 2.0 g L^{-1} . The initial concentration of TC was 10 mg L^{-1} . catalyst dosage was rom rieč The photocatalytic degradation efficiency for TC at different dosage of catalyst is displayed in Fig. 5d. When the catalyst dosage increased from 0.2 to 1.0 g L^{-1} , the degradation efficiencies of TC increased from 40% to 80%. However, when the dosage of CN-SA-0.05 exceeded 1.0 g L^{-1} , the removal rate changed into decrease. Therefore, the optimum dosage for CN-SA-0.05 is 1.0 g L^{-1} in the following study.

To evaluate the practical application, TC degradation was explored on CN-SA-0.05 sample over four repeated cycles. As shown in Fig. 6a, the CN-SA-0.05 showed a good catalytic stability and negligible decrease of activity after four cycles in TC aqueous solution. In addition, the composition of the recycled CN-SA-0.05 sample was also examined by FT-IR (Fig. 6b). As shown in Fig. S8, the crystal structure and the composition of used CN-SA-0.05 were kept well by XPS and XRD. Furthermore, the stability of the CN-SA-0.05 was confirmed by SEM after the cycle runs in Fig. 6c-d. Hence, the CN-SA-0.05 is a stable and efficient photocatalyst, which is benefit for applied in practical application in future.

In order to reveal the photodegradation selectivity of CN-SA samples, sulfamethazine (SMZ) was also employed to be the probing reactant. SMZ was listed as a pr brit k group due to its high toxicity to bacteria even at low concentrations [63]. The adso pacity of SMZ in the dark was negligible for all samples (Fig. S9). Without yst, only 5% of SMZ in aqueous solution has been degraded in 1 h under visible light rra on. As shown in Fig. 7a, about 80% of SMZ was degraded by PCN. With regard to the **CN**-SA samples, all of them showed improved N. The degradation efficiency of SMZ was 97%, degradation activity in comparison 99%, and 95% for CN-SA-0.0 CNSA-0.05, and CN-SA-0.1, respectively. As revealed by the he samples (Fig. 7b), the apparent rate constants of PCN, pseudo-first-order CN-SA-0.02, CN-SA-0.05 and CN-SA-0.1 are 0.0293 min⁻¹, 0.0493 min⁻¹, 0.0823 min⁻¹ and 0.0633 min⁻¹, respectively. Among these catalysts, the CN-SA-0.05 has displayed the optimum photocatalytic activity, which is about 3 times than that of PCN. This result indicates that the CN-SA samples possess excellent photo-oxidation activity, which could be employed to removal of the various organic contaminants. The TOC removal efficiency of SMZ for PCN and CN-SA-0.05 after 2 h visible light illumination was presented in Fig. S10. The degradation products have been identified by HPLC-MS (Fig. S11, Table S4). It can be seen that the degradation rate of SMZ was higher than TC, which was due to the SMZ has the -SO₂-NHchemical bonds. The -SO₂-NH- chemical bonds in SMZ was easier to be destroyed than benzene group in TC for CN-SA sample.

3.4 Photocatalytic activity enhancement mechanism

The separation efficiency of charge carriers in PCN and CN-SA sample was investigated by photoluminescence (PL). As shown in Fig. 8a, PCN exhibits a strong and wide emission peak centered at 462 nm. The PL peak of CN-SA sample also showed a red shift compared to that of PCN, which is in good agreement with DRS result. The PL intensi N-SA sample was significantly lower than that of PCN, which indicates that the combination may be inhibited. Time-resolved fluorescence decay spectra of N and CN-SA-0.05 confirmed the improvement of charge separation (Fig. 8b). The fi me of the PCN and CN-SA-0.05 are ted presented in Table 2. The calculated average lifetime decreased from 7.79 ns for PCN to 6.52 ns for CN-SA-0.05. The average life red by TRPL was singlet exciton lifetime. This gests the exciton dissociation was enhanced by the distorted decreased singlet lifetime su distorted structural of CN-SA promoting the singlet exciton to structural of CN dissociate, then also chances the fast charge carrier transfer from bulk to intersurface without recombination [65].

The mechanism of improved charges separation efficiency of CN-SA sample has been examined by photoelectrochemical response. The transient photocurrent density of PCN and CN-SA sample showed a rapid and stable photocurrent in Fig. 8c. The photocurrent of CN-SA-0.05 (0.4 μ A cm⁻²) was nearly 8 times higher than the PCN (0.05 μ A cm⁻²), indicating that the SA modification can improve the charge transfer efficiency. It is known that the arc radius on the EIS Nyquist plot reflects the interfacial charge transfer and separation efficiency [41]. As shown in Fig. 8d, the diameters of arc radius for CN-SA-0.05 sample are smaller than PCN, suggesting that the separation and transfer of charges on the surface of CN-SA-0.05 were improved. Furthermore, the positive slope of Mott-Schottky plots indicated that electrons served as the majority charges in PCN and CN-SA samples. The slope of CN-SA-0.05 electrode is lower than that of the PCN electrode (Fig. 4c), indicating increased donor density was obtained by CN-SA-0.05. The increased donor density was also indicated improved charges separation and transfer efficiency [49]. These above results are in according in the enhanced photocatalytic activity of CN-SA samples.

To further elucidate the mechanism of the CN-SA 5 on the degradation of TC under visible light irradiation, the active species trapping in was proceeded by using isopropyl 4-hydroxy-2,2,6,6-tetrame hylpiperidineN-oxyl alcohol (IPA), (TEMPOL) and -2Na), which acted as effective $\bullet OH$, $\bullet O_2^-$, and ethylenediaminetetraacetic acid dise ly. At shown in Fig. 9, the degradation of TC was decreased from holes (h⁺) scavengers, respectiv EMPOL. The EDTA-2Na was also affects the degradation of TC, 79% to 26% after a which means that the h are one of the main active species. The addition of 1mM IPA had slightly suppression on the removal efficiency of TC, indicating that •OH may not play an important role as indispensable as other species in the process of TC degradation. It can be seen that the photogenerated $\bullet O_2^-$ and holes were the main oxidant in the process of photocatalysis reaction. The ESR spin-trap technique was further employed to detect the reactive species of CN-SA-0.05 in the photocatalytic reaction system. Fig. 10 shows the signal response of the $\bullet O_2^-$ (a) and $\bullet OH$ (b) detected by ESR spectrometer. In Fig. 10a, the signal of $\bullet O_2^-$ was increased with the increase of

visible light irradiation time, while no signal of $\cdot O_2^-$ was found in dark condition. As shown in Fig. 10b, it can be observed that the weak signal of $\cdot OH$ was also found in DMPO system when exposed with light. The ESR results were in good agreement with the previous trapping experiment.

On the basis of all the results and discussions, a deep understanding on the excellent photocatalytic activity of CN-SA was obtained. Under visible light, the electrons of CN-SA samples are excited from the valence band (VB) to conduction band (CB) and left holes in the VB. Electrons on the CB could capture the oxygen molecules to form •O 2⁻ reacted with H⁺ and generated H₂O₂, which was further excited by electrons and ch •OH. Holes (h⁺) on the CB also can directly reaction with pollutants. As a re reactive radicals like $\bullet O_2^-$, h⁺, and •OH could synergistically oxidize TC and SMZ u ple-light irradiation. The enhanced nde photocatalytic activity could be due to several facurs: better light absorption induces to produce more charge carriers and efficient ation. Therefore, the CN-SA sample showed the better photocatalytic activity fo contaminant removal.

4. Conclusions

In summary, we developed a facile method to design a distorted carbon nitride by simply copolymerizing urea and salicylic acid. It was demonstrated in experimental results that the salicylic acid doping in PCN framework significantly improved the light harvesting and band structure of PCN. The photoelectrochemical results indicated that the photogenerated charge carriers of CN-SA samples were more efficiently separated and transferred than that of PCN. Based on above, the CN-SA exhibited the improved activities for the degradation of aquatic organic pollutants. The optimized CN-SA-0.05 displays a reaction rate of 0.0327 min⁻¹ for TC

removal, which was 2 times larger than that of PCN. Also, the photocatalytic activity of CN-SA was evaluated by degradation of SMZ in aqueous. The SMZ photocatalytic degradation rate constant of CN-SA-0.05 was 0.0823 min⁻¹, which was about 3 folds that of PCN (0.0293 min⁻¹). In addition, the activity of modified CN-SA remains stable after four successive cycles. According to the radical species trapping experiments and electron spin resonance analyses, $\cdot O_2^-$ and h⁺ were the main active species involved in the degradation of organic pollutants. We expect the synthesis method of the organic acid modified carbon nitride would inspire the design of other organic

photocatalysts.

Acknowledgements



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Figure captions:

Fig. 1 (a) Powder XRD patterns, (b-d) FT-IR spectra of CN and CN-SA -x samples

Fig. 2 High-resolution XPS spectra of (a) survey, (b) C 1s, (c) N 1s and (d) O 1s for CN-SA-0.05.

Fig. 3 SEM images of (a) CN and (b) CN-SA-0.05 samples. TEM images of (c) CN and (d) CN-SA-0.05 samples.

Fig. 4 (a) UV-visible light absorption spectra, (b) band gap of PCN and CN-SA samples. (c) Mott-Schottky plots and (d) VB-XPS of PCN and CN-SA-0.05.

Fig. 5 (a) Photocatalytic degradation of TC over PCN and CN-SA samples. (b) degradation rate of TC on PCN and CN-SA samples (c) effect of initial concentration of TC on CN-SA-0.05, (d) effect of catalyst dosage of TC on CN-SA-0.05

Fig. 6 (a) Recycling of the CN-SA-0.05 toward ne regradation of SMZ under visible light irradiation over four cycles, (b) FT-IR spectra and (c-d) SEM images of fresh and used CN-SA-0.05 before and after reactions.

Fig. 7(a) Photocatalytic degradation of SMZ over PCN and CN-SA samples under visible light irradiation, (b) Kindra fit of the egradation of SMZ on PCN and CN-SA samples

Fig. 8 (a) Room temperature steady state photoluminescence (PL) emission spectra (b) time-resolved fluorescence decay spectra of PCN and CN-SA sample with an excitation wavelength of 365 nm, (c) Transient photocurrent, (d) electrochemical impedance spectroscopy (EIS) Nyquist plots of PCN and CN-SA samples.

Fig. 9 Reactive species trapping experiments of CN-SA-0.05 under visible light irradiation.

Fig. 10 ESR spectra of CN-SA-0.05 dispersion under both the dark and visible light irradiation (>

420 nm) condition: (a) in methanol dispersion for DMPO-•O2-, (b) in aqueous dispersion for

DMPO-•OH.

