Sulfur Doped Carbon Quantum Dots Loaded Hollow Tubular g-C₃N₄ as Novel Photocatalyst for Destruction of *Escherichia Coli* and Tetracycline Degradation under Visible Light

Wenjun Wang ^{a,1}, Zhuotong Zeng ^{b,1}, Guangming Zeng ^{a, *}, Chen Zhang ^{a, *}, Rong Xiao ^{b, *}, Chengyun Zhou ^a, Weiping Xiong ^a, Yang Yang ^a, Lei Lei ^a, Yang Liu ^a, Danlian Huang ^a, Min Cheng ^a, Yaya Yang ^a, Yukui Fu ^a, Hanzhuo Luo ^a, Yin Zhou ^a

a College of Environmental Science and Engineering, Hunan University and Key

Laboratory of Environmental Biology and Pollution Control (Uncan University), Minisy of Education, Changsha 410082, P.R. China;

b Department of Dermatology, Second Xiangya Hegital, Central South University, Changsha 410011, P R China.

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^{*} Corresponding authors at: College of Environmental Science and Engineering, Hunan University,

Changsha 410082, PR China.

E-mail addresses: zgming@hnu.edu.cn (G. Zeng), zhangchen@hnu.edu.cn (C. Zhang), xiaorong65@csu.edu.cn (R. Xiao).

¹These authors contribute equally to this article.

Abstract

Microbial contamination and antibiotic pollutions diffusely exist in wastewater system, and contaminated water poses a threat to public health. Therefore, there is a need to effectively remove biohazard and antibiotic contamination from wastewater systems. In this paper, sulfur doped carbon quantum dots (S-CQDs)/hollow tubular g-C₃N₄ photocatalyst (HTCN-C), prepared via ultrasonic assisted synthesis strategy, was regarded as an efficient catalyst for the degradation of antibiotic (tetracycline) and destruction of a typical Gram-negative bacterium (Escherichi *ali*) in imitated wastewater system. The unique structures of hollow tubu \overline{N}_4 and loading of modified carbon quantum dots enhanced electron ransfer and charge separation, leading to a significant improvement in photoc tab enficiency. Benefiting from these merits, the optimized catalysts (HTCN-C(2 exhibited superior performance with a e (TC) degradation and 99.99% destruction reaction rate of 0.0293 min⁻¹ for sible light irradiation. Moreover, the characterization of of Escherichia coli under ectra, photoluminescenc technique, transient photocurrent UV-Vis diffuse re tat responses and electrichemical impedance spectroscopy also verified the good optical and electrochemical properties of resultant samples. Our current work indicates that HTCN-C has great potential in degradation of antibiotic and destruction of bacterium for practical wastewater treatment.

Keywords

Hollow tubular g-C₃N₄; Bacterial destruction; Photocatalytic; modified CQDs

1. Introduction

The rapid development of economic has brought convenience to people in recent years, while it has also brought many serious environmental problems [1-5]. Due to the infectious waterborne diseases of biohazards and poor biodegradability of antibiotic, microbial contaminations and antibiotic pollutions were unwanted constituents in water system [6-10]. For example, *Escherichia coli*, as a pathogenic microorganism, can cause a variety of intestinal diseases. The existence of tetracycline (TC) can also lead to antibiotic resistance problem [11-13]. Therefore, finding an effe way to remove these contaminants in wastewater is of great importance [1 owever, there exist huge challenges and difficulties to effective elimination of these contaminants [17-19]. Conventional wastewater disinfection methods sur ultraviolet irradiation, microbial degradation, chlorination, and ozonation have been proposed and obtained good mited due to the high energy consumption, improvement, but their applicat noxious disinfection by-pro ucts enormous cost, and complex process [20-23].

Very recention semiconductor photocatalytic technique has attracted considerable attention in organic pollutants elimination, bacterial disinfection and energy generation for their non-byproducts, powerful photocatalytic ability, environment friendly and cost-effective advantages [24, 25]. Based on previous studies, it was vital to choose a "suitable" photocatalyst in the process of photocatalysis [26, 27]. The practical applications of traditional photocatalysts (ZnO, SnO₂, and TiO₂) were restricted by their low solar-energy utilization efficiency, wide band-gap, and high recombination rate of lightinduced e^{-}/h^{+} [28, 29]. Non-metal graphitic carbon nitride (g-C₃N₄), a fascinating organic semiconductor photocatalyst, has a great deal of advantages including reliable chemical inertness, appealing optical characteristics, excellent thermal stability, and proper band-gap, making it particularly suitable for applications in organic synthesis, bacterial disinfection, energy conversion and elimination of organic pollutants [30]. However, owing to the sluggish exciton dissociation, insufficient light absorption and low practical surface area, the photocatalytic activity of bulk g-C₃N₄ needs to be further enhanced [31]. Hence, different strategies such as morphological engineering, combination with conductive materials, element doping and co ructing vacancy defects have been proposed to address these intrinsic draw 32]. Photocatalytic processes generally occur on the surface of the phototalysts, so the modified g-C3N4 with nanostructures and unique morphology ex superior optical and chemical ate, various nanostructure morphologies properties than their bulk counterparts Ťo ires, particles, spheres, etc.) of $g-C_3N_4$ (ribbons, sheets, tubes, fiber photocatalysts have been su cessfully prepared. According to recent experimental and tim nsional (1D) g- C_3N_4 nanotubes have drawn tremendous theoretical studies one attention due to ther unique structure, which possess high surface photocatalytic efficiency, facilitated electron transfer rate and excellent optical properties [33-35]. The aforesaid g-C₃N₄ nanotubes can be synthesized by liquid-phase reactions, wet-chemical routes, and template-assisted processes [36]. However, these mentioned methods were not intrinsically controllable because of the condition of high pressure, various organic additives, and indelible template residues. Thus, a facile method to synthesis tubular g- C_3N_4 with large scale is highly desirable.

Carbon quantum dots (CQDs), as a carbon-based material, are particularly encouraging because of their robust chemical inertness, good biocompatibility, low toxicity and excellent optical properties. In the field of photocatalysis, CQD acts as a photosensitizer and an electron mediator to broaden photon absorption region and decrease photo-induced e⁻/h⁺ recombination [37]. Moreover, CQDs also exhibit upconversion properties. Several semiconductors photocatalysts such as Bi₂WO₆, TiO₂, g-C₃N₄, BiVO₄, and ZnO can be coupled with CQDs to enhance their photocatalytic efficiency, which were attributed to a longer visible light_also on region, more charge carriers, and higher electron-hole pair separation [3] ccording our group previous work, we reported a facile hydrothermal settegy for fabricating a novel 0D CQDs coupled 2D Bi₂WO₆ nanosheets composit anomaterials (denoted as CBW) [38]. The CBW heterostructures exhibited otter photocatalytic performance towards e orange than pure 2D Bi₂WO₆ under the degradation of bisphenol A and irradiation of visible and neur-infrared light. Based on density functional theory (DFT) e valence band-edge hybridization and complementary and experimenta SII conduction between sure 2D Bi₂WO₆ and CQDs could greatly enhance the electronhole pair separation of CBW composite nanomaterials. Hence, loading CQDs on a semiconductor photocatalyst was vital for improving its photocatalytic efficiency. Moreover, heteroatom S doping was introducted into carbonaceous material to enhance its electrical conductivity and optical properties, which accelerates the electron transport and produces good catalytic performance [39, 42, 43].

Motivated by the above considerations, we used a simple ultrasonic-assisted method for the fabrication of modified CQDs loaded hollow tubular g-C₃N₄ novel photocatalyst (HTCN-C). In the first place, hollow tubular g-C₃N₄ was prepared via a molecule self-assembly between melamine and cyanuric acid. Then, a facile ultrasonicassisted method was used to obtain HTCN-C (the detail procedures were proposed in Scheme 1 and supporting information). Notably, S-CQDs acted as a photosensitizer and an electron mediator to broaden photon absorption region and decrease photo-induced e^{-}/h^{+} recombination in this system. The unique structures of hollow bular g-C₃N₄ and loading of modified carbon quantum dots enhanced ele ansfer and charge separation, leading to a significant improvement for e photo-destruction of a typical Gram-negative bacterium (Escherichia col photo-degradation of TC in wastewater system. Our current study might bed light on fabricating of 0D/1D novel nanostructure for visible light utilization in g-C₃N₄-based photocatalyst with bacteria destruction and pol utant degradation.

2. Experimental Section

2.1. Reagents

Urea (CO(NH₂)₂), Melamine (C₃N₃(NH₂)₃), ethanol (E), tertiary butanol (TBA), 4-hydroxy-2,2,6,6-tetramethylpiperidinyloxy (TEMPOL), cyanuric acid, disodium ethylenediaminetetraacetate (EDTA-2Na), citric acid, acetone, Eosin Methylene Blue Agar, glutaraldehyde, l-cysteine and tetracycline (TC) were purchased from Sinopharm Corporation Ltd. (Shanghai, China). All materials or chemicals applied in this study were of analytical grade without additional purification.

2.2 Synthesis of the catalysts

The S-CQDs solution was obtained according to previous work with minor modifications [42]. To synthesize S-CQDs, 0.9607 g of citric acid (5 mmol) and 0.6058 g of 1-cysteine (5 mmol) was dissolved in 5 mL of distilled water, respectively. The above solution was mixed and stirred 30 min. Subsequently, the resulting suspension was transferred to a 50 mL Teflon-lined stainless autoclave and kept for 6 h at 200 $^{\circ}$ C. Next, the final product was subjected to dialysis for 12 h for vertices the purified S-CQDs solution. The diameter, the flattening width and the notenuar weight cut off of the dialysis bag were 22 mm, 34 mm and 3500 Da, respectively.

Pristine g-C₃N₄ were synthesized accordin our previous work [44]. The detailed procedures for preparing hollow tublar g-C₃N₄ were shown in the supporting information. As for preparing S low tubular g-C₃N₄ hybrids (HTCN-C), 0.2 g of hollow tubular g-C₃N₄ was scattered in 30 mL of distilled water. Subsequently, a 3 mL) of S-CQDs solution (0.1mg/mL) was injected into certain volume (and above suspension. The mixture was subsequently sonicated 1 h and stirred 1 h, and then vacuum dried at 85 °C for 20 h to remove the liquid. Moreover, the procedures of synthesized S-CQDs/hollow tubular g-C₃N₄ photocatalysts were proposed in Scheme 1. The final photocatalysts was marked as HTCN-C(x), where x represents the S-CQDs volume. In addition, a summary table reporting all prepared catalyst was displayed in Table S1 to make it easier to understand the preparation process.

2.3 Characterization

The X-ray diffraction (XRD) patterns of as-obtained samples were recorded on a D/max-2500 Advance X-ray diffractometer with Cu Ka radiation. The functional groups of resultant samples were detected by Fourier transform infrared (FT-IR, Bruker Vertex 70) spectrophotometer with KBr pellet method. The X-ray photoelectron spectroscopy (XPS) was acquired on Escalab 250Xi instrument with an Al Ka X-ray source. Transmission electron microscopy (TEM) and Scanning electron microscopy (SEM) images were used to determine the morphology and microstructure of the nanomaterials. The photoluminescence (PL) spectra and UV bsorption (DRS) spectra were detected on a Fluromax-4 spectrofluorome Cary 300 UV-vis spectrophotometer, respectively. The FLS980 flugcence spectrometer (excitation wavelength: 340 nm) was used to record time-uso ed transient PL decay spectra. Total organic carbon (TOC) was detected on a Shinadzu TOC-LCPH analyzer. ESR signals by a JEOL JES-FA200 spectrometer under of \bullet OH and \bullet O₂⁻ radicals were the irradiation of visible lig

2.4 Evaluation or photocatelytic properties

2.4.1 Photocatalytic degradation activity

Under visible light irradiation, the resultant samples were employed to degrade TC (20 mg/L) to study their photocatalytic activities. The visible light source was provided by a PLS-SXE 300 W Xenon lamp, and its light density parameter was 0.33 W/cm². Furthermore, the photocatalytic reaction system and the emission spectrum of the visible light was presented in Fig. S1. Typically, the catalyst dosage was 1 g/L. Before the photocatalytic procedure, the solid-liquid system was churned for 60 min in

the dark to achieve the adsorption-desorption equilibrium. The reaction TC suspension (2 mL) was taken out at a given interval time and filtered using a 0.45 µm membrane filter, and then analyzed by a Shimadzu UV-2700 spectrophotometer to record the concentration of TC (357 nm). The used photocatalyst was collected and rinsed several times with ultrapure water and ethanol to remove surface inclusions for next use, and five successive cycles of experiments were performed for TC degradation.

2.4.2 Photocatalytic disinfection capability

In addition, the bacterial disinfection activities of the result ocatalysts were estimated by using gram-negative strain Escherichia coli (a model bacterium. Before each experiment, all the glassware and F n Methylene Blue Agar were sterilized by an autoclave at 121 °C for 20 min. Indensity of the *E. coli* suspension ſh was ~ 3.0×10^9 colony forming units per milliliter (CFU/mL). Typically, 30 mg of HTCN-C was added into 49.5 m water with the condition of ultrasonication. insity was changed to 3.0×10^7 CFU/mL since 0.5 mL of Next, the final viable cell d dispersed in the above suspension. Similar to photobacterial stock s tioi degradation of TC, he suspension was also churned for 1h in the dark to reach the adsorption-desorption equilibrium. 100 µL of the aliquot samples were collected and diluted at given time intervals (10 min), and then spread on Eosin Methylene Blue Agar plate. All photocatalytic bacterial inactivation experiments were carried out triplicate, and the data shown were the average of these triplicates. Then, above plates were incubated at 37 °C for 20 h to measure the viable cell density. Besides, the control

experiments and blank reaction were carried out without photocatalysts and without light irradiation under the same condition, respectively.

2.5 Electrochemical measurements

CHI 660D electrochemical workstation was employed to record photocurrent density (PC), Mott-Schottky curve, and electrochemical impedance spectroscopy (EIS) of the resultant samples in a conventional three-electrode cell. The Ag/AgCl electrode and Pt electrode were served as reference electrode and counter electrode, respectively. And the prepared HTCN-C on 1cm×2 cm fluorine-doped tin oride (ETO) glass were regarded as the working electrodes. In this typical experimental light source was a 300 W Xeon lamp. And the electrolyte solution was 0.201 of Na₂SO₄ liquid. Under the condition of room temperature, all the electrochemical measurements were obtained without bias potential.

3. Results and discussion

3.1 Structural conractorizatio

The XRD patterns in Fig. 1a presented crystal phase structures of the samples of bulk g-C₃N₄, HTCN, and HTCN-C(x), x = 0.5, 1, 2 and 3. Consistent with the previous studies [45, 46], a stronger diffraction peak at ~ 27.4 ° and a weaker one at ~ 13.1 ° were found from XRD patterns of all the resultant samples, which were well indexed to g-C₃N₄ (JCPDS No. 87-1526). And the XRD pattern of pure S-CQDs was shown in Fig. S2. The peak at ~ 27.4 °(0 0 2 peak) was assigned to the stacking of conjugated aromatic system with an interlayer distance of 0.34 nm. However, the weaker one at ~ 13.1 °(1

0 0 peak) was assigned to in-plane structural packing motif of the tri-s-triazine units with a distance of 0.68 nm. There was no obvious difference with bulk g-C₃N₄, HTCN, and HTCN-C(x), manifesting that hollow tubular structure and the loading of S-CQDs did not affect the crystal structure of pure g-C₃N₄ in the preparation process. In addition, no additional peaks for S-CQDs were obtained might because of its poor crystallinity and limited amount in the composite [39, 47]. It was worth noticing that 27.4° diffraction peak slightly shifted with increasing of S-CQDs (Fig. S3). The reason for this phenomenon was that S-CQDs adjusted the distance of laver eflecting that S-CQDs was not limited to the shallow surface and the exit strong interfacial interaction between the S-CQDs and g-C₃N₄ [37 1. Furthermore, the loading of hollow tubular g-C₃N₄ by S-CODs was also by organic elemental analysis pr results (Table S2). Compared to the C/N molecratio (0.6517) of bulk g-C₃N₄, the higher C/N molar ratio (0.6959) of HT nd the content of sulfur element suggested the presence of S-CQDs

It was easy a find hat he samples of bulk g-C₃N₄, HTCN, and HTCN-C(x), x = 0.5, 1, 2 and 3 showed the similar framework in the typical FT-IR spectra (Fig. 1b). And FT-IR spectrum of pure S-CQDs was shown in Fig. S4. The typical characteristic peaks of g-C₃N₄ could be found in all photocatalysts, but the peaks of S-CQDs were scarcely obtained in resultant samples. This phenomenon suggested that the amount of S-CQDs was low and the loading of S-CQDs did not distinctly change the integral structure of pristine g-C₃N₄. As depicted in Fig. 1b, several major vibration bands at 3000 cm⁻¹ ~ 3500 cm⁻¹ might be attributed to the surface adsorbed hydroxyl species (C-OH) and free amino groups (N-H). Vibrations bands ranging from 1100 to 1700 cm^{-1} belongs to the distinctive stretch modes of C-N heterocycles and the band at about 808 cm^{-1} was consistent with the particular signal of triazine unit [47]. In addition, a slight peak at ~ 1135 cm^{-1} corresponded to C–S and C–O bonds, which could be regarded as the indirect evidence that S-CQDs/hollow tubular g-C₃N₄ hybrids were successfully synthesized (Fig. S5).

The morphology and microstructure of bulk g-C₃N₄, HTCN and HTCN-C(2) were checked by SEM, and the consistent results were showed in Fig. 2 depicted in Fig. 2a, bulk g-C₃N₄ prepared from direct calcination of melami nted an aggregated and chunky structure [33]. In contrast, the as-obtained HTCN and HTCN-C(2) mainly displayed a well-developed hollow tubular motohylo (Fig. 2b and Fig. 2c). The TEM measurement was introduced to further sturv the internal structure of bulk g-C₃N₄, HTCN and HTCN-C(2), and t were shown in Fig. 3. The bulk g-C₃N₄ revealed as numerous ultration mosheets with no pores (Fig. 3a). Fig. 3b and Fig. 3c she carbon nitride possessed hollow tubular structure with verified that the ıbehi abundant of pores, which was in consistent with the above SEM results. In addition, the N₂ adsorption-desorption isotherm experiments results were displayed in Fig. S6 and Table S3. The pore size, pore volume, and specific surface area of HTCN have been measured to be 23.057 nm, 0.204 cm³/g, and 32.982 m²/g, which were about 1.2-times, 2.8-times, and 2.6-times than that of pure $g-C_3N_4$ (18.548 nm, 0.061 cm³/g, and 10.625 m^2/g), respectively. In present study, the larger pore volume and enhanced specific surface area were caused by hollow porous tubular structure of HTCN, which could shorten the path of mass transfer and provide more reaction activity sites for improving the reaction probability and facilitating the photocatalytic performance of HTCN. According to Fig. 3d, a lot of S-CQDs were uniformly loaded on the surface of hollow tubular g-C₃N₄, and the lattice spacing of S-CQDs (0.21 nm) was determined by HRTEM. Fig. 3e and Fig. 3f reflected that the size of the pure S-CQDs was below 5 nm (average particle diameters were about 2 nm), the color of its solution was yellow, and its solution also showed homogeneous phase with no precipitations. What's more, the results of elemental mapping images (Fig. 3h-j) and the EDS (FTE) (Fig. 3g) were acknowledged that HTCN-C(2) contained S, N and C spects

X-ray photoelectron spectroscopy (XPS) surve spectrum results (Fig. 4a) also presented that the HTCN-C(2) were mainly r áde of oxygen, sulfur, nitrogen, and carbon. Among them, the peak of O element 532.4 eV (Fig. S7) was belonging to the chemisorbed oxygen [49, 50]. solution spectrum of C1s (Fig. 4b) showed eV and 288.1 eV. The former peak around 284.5 eV was two distinct peaks at 284.5 C. , and the latter peak presents the presence of C=O [51]. attributed to graph As revealed in Fig. 4. the N 1s peak was separated into four binding energy peaks at ~ 404.5 eV, 400.6 eV, 399.5 eV, and 398.8 eV, which could be assigned to the charging effects of π -excitations, pyrrolic type and pyridinic type N atoms (C-N=C, N-C₃, C-NH) [52]. In the analysis for S 2p (Fig. 4d), two significant peaks (165.1 eV and 163.8 eV) were observed. The lower peak (165.1 eV) was attributed to the C-S-C units, and the peak located at 163.8 eV was formed by replacing N atoms (C-S bonds) [53]. The analysis mentioned above performed that S-CQDs successfully decorated on the surface of HTCN with good dispersion.

3. 2 Optical and electrochemical properties

The optical and electrochemical properties of resultant samples were characterized and depicted in Fig. 5. From Fig. 5a and the inset image of Fig. 5a, the S-CQDs/hollow tubular g-C₃N₄ hybrid photocatalyst (HTCN-C) extended the optical absorption regions of bulk g-C₃N₄ (about 470 nm). HTCN-C and HTCN presented a red shift in the absorption region compared to bulk g-C₃N₄ due to the excellent light harvest ability of S-CQDs and the porous structure of HTCN (Porous structure d promote the multiple reflection of incident light) [54, 55]. Additionally, energy gap (Eg) of HTCN and HTCN-C(2) was calculated to be 2.53 eVd 2.47 eV via the Kubelk-Munk method (Fig. 5b). The HTCN-C(2) photocatal st a narrower bandgap than HTCN, leading to more lightgenerated electrons unter visible light irradiation. The value of 8 XPS spectra [46, 56]. As shown in Fig. 5c valence band (VB) could obtain and Fig. 5d, the VB potential of MTCN and HTCN-C(2) was estimated to be 1.62 eV Hence, the conduction band (CB) value of HTCN and HTCNand 1.53 eV, respectively vel C(2) was calculated to be -0.91 eV and -0.94 eV by the formula of $E_{CB} = E_{VB} - E_{g}$. Where E_{VB} , Eg and E_{CB} were VB potential, the band gap energy and CB potential, respectively. The detailed location of VB and CB band of HTCN-C(2) was illustrated in Scheme 2.

To better expound the mechanism of electron delivery, PL technique and the timeresolved fluorescence spectra were conducted. Typically, 5 mg of sample was scattered in 4 mL of distilled water, and the above solution was sonicated for 240 min to obtained the suspension. And the suspension exhibited maximal emission peak at about 465 nm with 340 nm excitation wavelength at room temperature measured by Fluromax-4 spectrofluorometer. From Fig. 5e, the sample of HTCN-C(2) exhibited the lowest PL intensity, indicating the excellent carriers separation, which was mainly caused by the hollow porous tubular structure of HTCN and the existence of S-CQDs [56, 57]. Furthermore, non-modified g-C₃N₄ exhibited the highest PL intensity in all prepared photocatalysts, demonstrating that the modified g-C₃N₄ could improve the photocatalytic activity by efficient reducing the recombination rate of carriers. Moreover, the time-resolved fluorescence decay spectrum sified above results and depicted in Fig. 5f. The fitting results were given Table S4. The average life-time $_{2}\tau_{2}^{2})/(A_{1}\tau_{1}+A_{2}\tau_{2})$. The $\tau_{average}$ $(\tau_{average})$ was calculated by the Eq of $\tau_{average} = (A_{average})$ of bulk g-C₃N₄, HTCN, and HTCN-C(2) were 6.16, 6.95 and 6.82 ns, respectively. and HTCN-C(2) were longer than bulk g-Consequently, the mean lifetime improved specific surface area. The values showed an C_3N_4 , which was due to the erated carriers over HTCN and HTCN-C(2) samples, and extended lifetimer hence promoting the process of interfacial charge migration [56]. Compared to HTCN, HTCN-C(2) displayed a shorten lifetime of electron/hole pairs, which could be ascribed to the presence of non-radiative quenching routes [58].

The transient photocurrent responses and electrochemical impedance spectroscopy were crucial factors to evaluated the separation and transfer efficiency of carriers. As displayed in Fig. 5g, HTCN exhibited a larger photocurrent intensity than bulk g-C₃N₄, and HTCN-C(2) showed the highest photocurrent signs indicating the best e⁻/h⁺ separation efficiency. It was easy to found that photocurrent intensity of HTCN-C(2) was approximately a 17.5- fold and 6.56- fold increase compared to bulk g-C₃N₄ and HTCN, respectively. Additionally, the transient photocurrent values of photocatalysts almost maintained repeatedly after several ON/OFF illumination cycles, indicating the good photoelectrochemical stability. The radius of arc was always connected with the charge transfer resistance at the electrode-electrolyte interface, and the EIS spectra of corresponding samples were shown in Fig. 5h. From Fig. 5h, the size of the arc radius order was HTCN-C(2) < HTCN < bulk g- $\sqrt{3}N$ and HTCN-C(2)presents a lowest charge transfer resistance and best interfa rge migration skill. These results were well fitted with PL and TRPL lysis, indicating hollow porous tubular structure of HTCN and loading of S ave synergistic effect to enhance the photocatalytic performance.

3.3 Photocatalytic activities and mochanisms

3.3.1 Photocatalytic degradation of TC

As a typical antibatic TC has been extensively applied in agriculture, animal husbandry and iatablogy. Previous researches illuminated that TC was a stable pharmaceutical and poorly metabolized in animals, and couldn't be degraded under light irradiation without photocatalysts [59, 60]. In this work, the photocatalytic properties of resultant composites were studied via the removal of TC in aqueous solution under visible light irradiation (Fig. 6a). Before visible light irradiation, the adsorption-desorption equilibrium was attained between TC and the samples under the condition of 1 h dark reaction [61]. As shown in Fig. S8, the adsorption efficiency of

TC for bulk g-C₃N₄, HTCN and HTCN-C(2) was only 2.98%, 3.88% and 5.37%, respectively. For Fig. 6a, different samples exhibited different photodegradation properties, which was in order of bulk $g-C_3N_4$ (30.16%) < HTCN (51.85%) < HTCN-C(0.5) (64.41%) < HTCN-C(1) (68.66%) < HTCN-C(3) (74.40%) < HTCN-C(2) (82.67%). Obviously, the removal capacity of HTCN-C photocatalysts were all better than bulk g-C₃N₄ and HTCN, indicating the presence of S-CQDs facilitated the photocatalytic degradation efficiency of HTCN. However, the photocatalytic activity of HTCN-C did not increase as the proportion of S-CQDs inc sed. It could be attributed to the fact that proper amount of S-CQDs could a electron mediator to accelerate separation of carriers, whereas excess ke S-CQDs would compete for photons with g-C₃N₄ and led to a lower reacti ites (inner filter effects) [62]. The re spe experimental results were deep studied via he pseudo-first-order kinetic model with an Eq of $\ln (C_t/C_0) = -K_{app}t$. kinetic curves (Fig. 6b) and apparent rate he HTCN-C(2) possessed the highest K_{app} (0.0293 min⁻¹), constant (inset in Fig. 6b), bigger than HTCN (0.0124 min⁻¹) and ~ 4.97-fold bigger than which was ~ 2.3 fold that of bulk $g-C_3N_4(0.0059 \text{ min}^{-1})$. Hence, the above-mentioned results were in line with the before properties characterization analysis, cofirming the sample of HTCN-C(2) has optimum photocatalytic activity.

In order to deeper evaluate the property of the photocatalyst of HTCN-C(2), total organic carbon (TOC) removal analysis and multiple cycles experimental were also investigated and the corresponding curves were described in Fig. 6c and Fig. 6d. From Fig. 6c, the mineralization efficiency of HTCN-C(2) could achieved 35.22% within 60

min visible light irradiation. Under the same reaction conditions, the used HTCN-C(2)was washed and collected for cycles experimental (Fig. 6d). After five repeated cycles, the photo-degradation efficiency of HTCN-C(2) showed negligible decrease (about 3.52% lost) and remained about 79.15% efficiency. The aforementioned results exhibited the sample of HTCN-C(2) has the ability to degrade TC into intermediate products or CO₂, and showed good chemical stability and reusability, which benefited the practical application. Furthermore, the recycled HTCN-C(2) was measured by XRD and FT-IR (Fig. 6e and Fig. 6f). It was acknowledged that the reled HTCN-C(2) kept its intrinsically crystal structure, exhibiting no appared ence between fresh and recycled HTCN-C(2). In addition, as illustrate in Table S2, the S/C ratio of recycled HTCN-C(2) was similar to that of fre h C(2). In a word, the sample of recyclible photocatalyst, which shows great HTCN-C(2) was an capable and application potential for practic blication.

3.3.2 Photocatalytic disinfection performance

E. coli inactivation was chosen for probing the disinfection ability of resultant samples, and corresponding results were depicted in Fig. 7. It could be observed that the influence of visible light on bacteria was insignificant, because the density of viable *E. coli* cells kept almost unchanged with light control and no photocatalysts. Furthermore, blank reaction (catalysts without light irradiation) was to prove that the material itself was also not toxic to bacteria under the condition of dark. But the amount of viable *E. coli* cells began to decrease after the addition of the samples in the visible light. From Fig. 7, only about 0.62-log and 2.36-log reduction of *E. coli* cells

by bulk g-C₃N₄ and HTCN were achieved under 40 min of visible light irradiation. In contrast, HTCN-C nanocomposites showed more excellent disinfection performance and about 4.21-log, 5.24-log, 6.88-log, and 5.63-log reduction of *E. coli* cells for HTCN-C(0.5), HTCN-C(1), HTCN-C(2), and HTCN-C(3), respectively. Apparently, HTCN-C(2) displays the highest inactivation efficiencies and meet the requirement of surface water treatment.

In the process of studying the mechanism of photocatalytic disinfection, bacterial regrowth experiment was an important index [63-66]. Hence nage of the cell he membrane and the morphological structure destructs of A ere investigated by SEM, and the corresponding preparation procedures r bacterial SEM study were put in the supporting information. Prior to photoca disinfection process, E. coli cells alv possessed a normal rod-like morphology as well as regular fuzzy elliptical outlines (Fig. 8a). In contrast, the typical rod e E. coli cell was destructed with holes and blogy after 30 min or 60 min visible light irradiation (Fig. showed an abnormal morph enon shown that the cell membrane was damaged during 8b and Fig. 8c). the inactivation process, which subsequently leads to severe leakage of intracellular components. The leakage of potassium ion (K⁺) could acted as an index to evaluate cell membrane permeability and evaluated membrane destruction, because K⁺ was virtually existing in bacteria. As shown in Fig. S9, there was little K⁺ leakage found in the light control, indicating a few cell death and structure destruction. However, quick leakage of K⁺ occurred in HTCN-C(2) photocatalytic disinfection system, suggesting that the cell was inactivated and the active species (h^+ , O_2^- and H_2O_2) were generated under the visible light irradiation [67-70].

3.3.3 Possible reaction mechanism

For better understanding the possible photocatalytic reaction mechanisms about antibiotic degradation and bacterial inactivation, the roles of major active substances were systemically researched. And the corresponding scavengers were TEMPOL, EDTA-2Na, and TBA, which could assimilate reactive species of $\cdot O_2^-$, h⁺, and $\cdot OH$, respectively [71]. From Fig. 9a, there was a significant photocatalytic activity deterioration with the addition of TEMPOL (5 mM) and EDTA mM), presenting the predominant roles of $\cdot O_2^-$ and h^+ in the photocatalytic r process. Moreover, slight inhibition (about 6.78% loss after 1 h) can be fund with the addition of TBA (5 mM), which indicated that ·OH also participates in degradation of TC. The relevant values of TC removal ratio with the presence of scavengers were shown in the inset of Fig. 9a. Hence, the main activ For HTCN-C(2) might be $\cdot O_2^-$ and h^+ . Some red in the process of bacterial inactivation with the exists similar results were discove). As described in Fig. 9b, $\cdot O_2^-$ and h⁺ still play an vital of various quenc role in controlling the process of inactivation, and OH acts as an assistant. Thus, $\cdot O2^{-1}$ and h⁺ affect the process of photocatalytic inactivation and the removal of TC, and the function of \cdot OH could not be ignored either. In order to further affirmed that \cdot O₂⁻ and •OH were yielded in the HTCN-C(2) photocatalytic system, and the ESR spin-trap measurement was conducted under visible light irradiation. From Fig. 9c and Fig. 9d, there was no signal peaks of DMPO- \cdot O²⁻ and DMPO- \cdot OH appeared in the darkness, while obvious intensity signals can be detected under visible light. Therefore, $\cdot O_2^-$, h^+ ,

and ·OH active species were generated and had synergistic effect during the photocatalytic process based on the ESR analysis and the trapping experiments.

Based on the aforementioned analyses and discussions, a deep mechanism for TC degradation and photocatalytic inactivation toward *Escherichia coli* over HTCN-C(2) composite under visible light irradiation was presented in Scheme 2. In this system, S-CQDs were acted as a photosensitizer and an electron mediator to broaden photon absorption region and decrease photo-induced e^{-}/h^{+} recombination. The electrons (e^{-}) of HTCN-C(2) composite were excited from VB to CB, and general holes (h^+) in the VB under visible light. The accumulated e⁻ can validly cap to obtain $\bullet O_2^-$, and $\cdot O_2^-$ could reacted with H⁺ to form H₂O₂. The obtained $\cdot OH$ of HTCN-C(2) may come of HTCN-C(2) also made from the conversion of the H_2O_2 . In addition contribution to reacting with TC and photo atalytic inactivation toward Escherichia O_2^- and •OH can participate in the process coli. In brief, reactive radicals s h and photo-degradation, which was consistent with ESR of photocatalytic inactivation periments. Hence, HTCN-C(2) displayed an excellent analysis and the app inactivation efficiency and superior photocatalytic degradation activity, which meet the requirement of surface water treatment.

4. conclusion

In summary, we have successfully fabricated modified CQDs loaded hollow tubular g-C₃N₄ novel photocatalyst (HTCN-C) via ultrasonic-assisted method. The hollow tubular g-C₃N₄ was prepared via a molecule self-assembly between melamine and cyanuric acid. Based on the characterization of morphologies and optical properties, the HTCN-C hybrid system was formed with modified CQDs loaded on the surface of hollow tubular g-C₃N₄. In this photocatalytic system, S-CQDs were acted as a photosensitizer and an electron mediator to broaden photon absorption region and decrease photo-induced carrier recombination. Compared to bulk g-C₃N₄, the optimal photocatalyst (HTCN-C(2)) displayed superior photocatalytic activity for TC degradation and photocatalytic inactivation toward Escherichia coli, with the 82.67% removal rate of tetracycline and the inactivation of 6.88 log₁₀ cm ¹ (about 99.99%) destruction rate) of bacterial cells under visible-light faction, respectively. Eventually, possible reaction mechanism for enhance g the photocatalytic activity of antibiotic degradation and bacterial inactivation aised. These results offered an Nu-based photocatalyst with advanced novel clue for the design of 0D/1D g-C nanostructure for practical waste

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Figure captions:

Scheme 1. Schematic illustration of the preparation for modified carbon quantum dots loaded hollow tubular carbon nitride (HTCN-C) samples.

Fig. 1. XRD patterns (a); FT-IR spectra (b) of samples of bulk $g-C_3N_4$, HTCN, and HTCN-C(x), x = 0.5, 1, 2 and 3.

Fig. 2. SEM images of samples of (a) bulk $g-C_3N_4$, (b) HTCN, and (c) HTCN-C(2), respectively.

Fig. 3. TEM images of (a) bulk g-C₃N₄, (b) HTCN, (c, d) HTCN-C(2) and (e) pure S-CQDs, respectively. The inset in (e) is the digital photographic of tune S-CQDs solution. (f) Corresponding size distribution graph of (e) pure SCQDs. The TEM EDS spectrum (g) and elemental mapping patterns (h, i, j) of (TCN-C(2).

Fig. 4. High-resolution XPS spectra of (a) servey, (b) C 1s, (c) N 1s and (d) S 2p for HTCN-C(2).

Fig. 5. (a) UV–vis diffuse reflectance spectra of samples and (b) band gap of HTCN and HTCN-C(2) XPS valuace band spectra of (c) HTCN and (d) HTCN-C(2), respectively. (e) PL spectra of samples and (f) Time-resolved PL spectra, (g) Photocurrent responses under visible light, (h) EIS Nyquist plots for bulk g-C₃N₄, HTCN and HTCN-C(2) samples.

Fig. 6. (a) Photocatalytic degradation of TC over as-obtained samples; (b) Pseudo firstorder kinetic fitting curves and the corresponding apparent rate constants (K_{app}); (c) The photocatalytic degradation and TOC removal curves of TC on HTCN-C(2) catalyst; (d) The cycling test for the degradation of TC by the fresh and used HTCN-C(2) catalyst; (e) XRD and (f) FT–IR survey for fresh and used HTCN-C(2) sample.

Fig. 7. Inactivation efficiencies of as-prepared samples toward *E. coli* $(3.0 \times 10^7 \text{ CFU/mL})$ under visible light irradiation.

Fig. 8. SEM images of *E. coli* treated by HTCN-C(2) hybrid photocatalysts under visible light irradiation at 0 min, 20 min, and 40 min.

Fig. 9. (a) Photocatalytic activities of the HTCN-C(2) sample for the degradation of TC under the condition of different quenchers; (b) Inactivation efficiency of the HTCN-C(2) sample toward *E. coli* under the condition of different underers; ESR spectra of radical adducts tapped by DMPO spin-trapping in ECN-C(2) dispersion in the dark and under visible light irradiation (c) in methanol dispersion for DMPO– \cdot O₂⁻ and (d) in aqueous dispersion for DMPO– \cdot OH Scheme 2. Possible photocatalytic methanism scheme of HTCN-C(2) composite for TC degradation and photocatalytic inactivation toward *Escherichia coli* under visible light irradiation.

37





Fig. 1. XRD patterns (a); FT-IR spectra (b) of samples of bulk g-C₃N₄, HTCN, and





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Fig. 8. SEM images of *E. coli* treated by HTCN-C(2) hybrid photocatalysts under

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Scheme 2. Possible photocatalytic mechanism scheme of HTUN-GC) composite for TC degradation and photocatalytic inactivation toward *Escienciality coli* under visible light irradiation.