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1D porous tubular g-C₃N₄ capture black phosphorus quantum dots as 1D/0D metal-free photocatalysts for oxytetracycline hydrochloride degradation and hexavalent chromium reduction



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ABSTRACT

As an "up-and-coming" two-dimensional (2D) material, black phosphorus (BP) has attracted much attention due to its abundant metal-free properties and broad application prospects in photocatalysis. This study introduces a promising sunlight-driven metal-free photocatalyst for oxytetracycline hydrochloride degradation and hexavalent chromium reduction in water and wastewater. The roles of BP quantum dots (BPQDs) in the distribution of electrons and photocatalytic performances were well identified by experimental and density functional theory (DFT) calculations. As expected, the specially designed 0D/1D structure shows unusual photocatalytic efficiency toward the degradation of oxytetracycline hydrochloride (0.0276 min⁻¹) and reduction of hexavalent chromium $(0.0404 \text{ min}^{-1})$. Reactive species, namely, O_2^- and h^+ comprised the primary photocatalytic mechanisms for oxytetracycline hydrochloride degradation. This work highlights that the combination of tubular g-C₃N₄ (TCN) with BPQDs facilitates the charge spatial separation in the photocatalytic process, and provides alternative strategy for design of highly active and metal-free nanomaterials toward environmental remediation and sustainable solar-to-chemical energy conversion.

1. Introduction

Today, the dramatic increase in global energy demand is still hugely dependent on fossil fuel combustion, which has been producing tremendous anthropogenic greenhouse gases [1-4]. Reducing greenhouse gases emissions and coping with related global warming is one of the major challenges facing humanity in the 21 st century [5-8]. Moreover, various antibiotic contamination and heavy metal pollutants in water systems have a significant impact on human health due to their high toxicity and carcinogenic [9-11]. For this reason, it is fairly meaningful to develop environmentally sustainable energy technologies to solve the energy crisis and environmental problems [12–14]. Fortunately, solar energy photocatalytic technology grabs extreme attention due to its highly sustainable, nontoxic nature and low cost [15,16]. In view of maximizing the use of solar energy, it is significant important to select

the suitable photocatalysts [17]. Over the past decades, amounts of semiconductor photocatalysts (TiO2, BiOCl, ZnO and AgI, etc.) have been employed for environmental remediation and energy conversion [18-20]. However, most of the reported photocatalysts are metal containing semiconductors which have environmentally harmful effects and limited quantity [21]. Hence, it is necessary for investigators to construct a metal-free photocatalyst with amounts of earth elements (C, N and P, etc.) and high efficiency [22].

To address above tasks, the nonmetallic conjugated semiconductor g-C₃N₄ has been widely used in photocatalysis field because of its outstanding chemical and thermal stability, unique band gap structure, environmentally friendly nature and visible light response [22]. Nevertheless, the photocatalytic property of pristine g-C3N4 is not satisfactory due to the sluggish exciton dissociation, small surface area and insufficient light absorption [23]. So far, many strategies (element

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doping, heterojunction, and morphological engineering, etc.) have been explored to overcome the drawbacks of pure g-C3N4. To date, one-dimensional (1D) nanomaterials with open channel have received much attention owing to their decreased mass transfer resistance, reduced diffusion distance, enhanced photogenerated carriers separation, and increased light absorption [24,25]. For example, Guo et al. used a hydrothermal method to obtain P-doped hexagonal tubular g-C₃N₄ via hydrolysis of melamines in phosphorous acid [26]. As a result, a convenient, effective, and simple method for synthesizing the highly efficient tubular g-C₃N₄ photocatalyst is still a challenging and predictable task.

Metal-free semiconductor black phosphorus (BP) has received numerous scientific interests on account of excellent electrical and optical properties, high charge mobility (about $1000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), as well as outstanding solar light absorption capacity since the first preparation of atom-thick layer BP in 2014 [27,28]. Notably, BP has been used as a cocatalyst to promote the separation of photocavitation-electron pairs in the field of environmental treatment and photocatalytic water splitting [29]. For instance, Zhu et al. prepared a binary nanohybrid BP/CN for photocatalytic H₂ production, and the amount of H₂ can reached approximately $0.64 \,\mu mol \, h^{-1}$ [28]. Recently, 0D BPQDs have been widely used in photocatalytic area when the lateral size of BP is decreased to below 20 nm. Apart from the benefits of parental BP, BPQDs possess additional favorable characteristics like quantum confinement effects, prominent edge and high absorption co-efficient [29]. Very recently, Lei et al. and Kong et al. fabricated 0D/2D heterostructure combined ultrasmall BPQDs with ultrathin g-C₃N₄ nanosheets through sonication approach and high-vacuum stirring method, respectively [30,31].

Bearing these in mind, for the first time, we employed a facile iceassisted ultrasonic method to obtain a metal-free BPQDs loaded TCN (BPTCN) nanohybrid with 1D tubular structure. In this system, BPQDs with an average size of 3.32 nm were dispersed onto the tubular g-C₃N₄. Various organic pollutant systems (oxytetracycline hydrochloride (OTC-HCl), tetracycline (TC), and rhodamine B (RhB)) and heavy metal Cr(VI) ions in simulated wastewater were effectively removed and reduced by such well-confined BPTCN heterostructure. In addition, the underlying photocatalytic mechanisms about BPTCN were investigated, and the roles of BPQDs and tubular g-C₃N₄ in photocatalytic process were also highlighted. Meanwhile, the electronic band structure and strong electronic interaction of obtained materials were calculated by density functional theory (DFT) calculation. This work indicates a new paradigm for constructing metal-free photocatalyst with unique tubular structure for effective photocatalytic organic pollutants degradation and green energy conversion.

2. Experimental section

2.1. Catalysts synthesis

The reagents used in this work and the synthesized steps of tubular g- C_3N_4 (TCN) and bulk g- C_3N_4 (CN) were depicted in the Supporting information. De-ionized water (18.25 M Ω .cm) from Millipore system was applied in the whole experiment. The BPQDs were obtained from Nanjing XFNANO, Inc. (XF208, Size, 1–10 nm; Concentration, 0.1 mg/mL; Ratio of monolayer > 80%). As for preparing BPQDs/TCN hybrids (denoted as BPTCN), 0.1 g of TCN was dispersed in 10 mL of DI water. Then, 10 mL commercial BPQDs dispersion was mixed with the above suspension. This mixture was stirred for 4 h and subsequently sonicated in an ice bath for 4 h. The obtained suspension was centrifuged at 6750 rpm for 360 s to collect the residual particles. The final precipitate was dried in a vacuum oven at 40 °C for 12 h. All chemicals were analytical grade and were used without additional purification in this work.

2.2. Characterization

The transmission electron microscope (TEM), high-resolution TEM (Tecnai G2 F20, FEI) and scanning electron microscopy (SEM Hitachi S4800) tests were used to determine the morphology structure of samples. The Fourier transform infrared spectrum (FTIR) analysis was conducted by Bruker Vertex 70 instrument with KBr pellet method. The X-ray diffraction (XRD) measurement was obtained by a Bruker D8 Advance diffractometer. The X-ray photoelectron spectroscopy (XPS) results were recorded on Escalab 250Xi instrument with an Al K α X-ray source. The total organic carbon (TOC) data was collected on a Shimadzu TOC-LCPH analyzer. The electron spin response (ESR) signal was detected on JEOL JES-FA200 spectrometer. The three-dimensional excitation-emission matrix fluorescence spectra (3D EEMs) and photoluminescence (PL) were carried out on LS-55 fluorescence spectro-photometer. The detailed electrochemical measurement experiments were presented in Supporting information.

2.3. Photocatalytic activity

2.3.1. Photodegradation of oxytetracycline hydrochloride

To investigate the photocatalytic activity of the samples, the degradation of OTC-HCl (10 mg/L pH = 7) was performed under visible light irradiation. The chemical structure and physicochemical properties of OTC-HCl [32] were presented in Table S1. And the light source was from a 300 W xenon lamp (PLS-SXE300, light intensity was ~ 300 mW/cm^2) with the UV cutoff filter ($\lambda > 420 \text{ nm}$). The emission spectrum of the visible light and the corresponding photocatalytic reaction system were described in our previous work [33]. Briefly, 30 mg of sample was dispersed in 50 mL of pollutant aqueous solution. Before illumination, the suspension was churned in the dark for 2 h to obtain the adsorption desorption equilibrium. The reaction OTC-HCl suspension (2 mL) was taken out at intervals of 15 min and filtered through a 0.22 um membrane filter. The concentrations of OTC-HCl suspension were analyzed by a Shimadzu UV-vis spectrophotometer (UV-2700) with absorbance at its characteristic absorption peaks of 353 nm. The photo-degradation intermediate products of OTC-HCl were determined by a LC-MS/MS instrument, and the specific method was shown in Supporting information. In addition, Escherichia coli bacteria were used to assess the potential risk of intermediates and detailed procedures were provided in the Supporting information.

The experimental data (the degradation rates of OTC-HCl) were researched in depth by a pseudo first-order kinetic model, where E_q is ln (C_t/C_0) = $-K_{app}t$. Among them, k_{app} is the apparent rate constant; C_t and C_0 are t-time and initial concentrations of OTC-HCl, respectively. In this work, the quenchers were EDTA-2Na, TEMPOL and tertiary butanol (TBA), which could assimilate reactive species of h^+ , O_2^- , and OH, respectively. The contributions of each reactive species to the overall OTC-HCl photodegradation kinetics were calculated using following formulas [34]:

$$R \bullet OH = \frac{K \bullet_{OH}}{K_{app}} \approx \frac{(K_{app} - K_{TBA})}{K_{app}}$$
(1)

$$R \cdot O2 - = \frac{K_{\cdot O2-}}{K_{app}} \approx \frac{(K_{app} - K_{TEMPOL})}{K_{app}}$$
(2)

$$Rh+ = \frac{K_{h+}}{K_{app}} \approx \frac{(K_{app} - K_{EDTA-2Na})}{K_{app}}$$
(3)

R is the fractional contribution of a particular reactive species, and K_{TBA} , K_{TEMPOL} , and $K_{EDTA-2Na}$ is the apparent rate constant for OTC-HCl photodegradation in presence of the corresponding quenchers.

2.3.2. Reusability

To evaluate the reusability and stability of the samples, six successive cycles of experiments were performed for OTC-HCl degradation. Namely, the used sample after each cycle was collected through centrifugation and rinsed three times with ethanol and ultrapure water. Subsequently, the washed powder was dried for 8 h (60 °C) to conduct next photocatalytic cycle. Moreover, the XRD of the samples after six cycles was characterized and compared to that of the fresh samples.

2.3.3. Photoreduction of Cr(VI)

The photocatalytic Cr(VI) reduction experiment was chosen to further evaluate the photocatalytic reducing activity of BPTCN. Then, the reaction solution pH value was adjusted by H_2SO_4 (0.1 M) and NaOH (0.1 M) solutions. Before irradiation, 50 mg of the resultant sample was added into 50 mL of Cr(VI) solution (based on Cr in a K₂Cr₂O₇ solution, 10 mg/L), followed by stirring for 60 min to attain an adsorption-desorption equilibrium in the absence of light. Approximately 2 mL of the reaction suspension was withdraw at given time intervals (15 min) and its concentration was determined by a UV–vis spectrophotometer (540 nm) according to the 1,5-diphenylcarbazide method [35,36].

2.4. DFT calculations

The DFT based simulations were conducted by using the Cambridge Serial Total Energy Package (CASTEP) implemented in the Materials Studio (MS) program. The Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) was used for exchange-correlation functions. Considering that PBE functional will underestimate the band gap of semiconductors, Heyd-Scuseria-Ernzerhof (HSE06) hybrid functional was used in electronic calculations. The cut-off energy for plane wave basis was set to 340 eV, using the energy tolerance and force convergence criteria per atom of 1×10^{-5} eV and 0.02/0.05 eV Å⁻¹ for the electronic structure calculations. A Monkhorst-Pack grid of $3 \times 3 \times 1$ for K-points was sampled in the first Brillouin zone to do selfconsistent calculations. The rectangle lattice constants of the samples were shown in Table S2. The outer valence electron arrangement of each element was 2 s² 2p² for C, 2 s² 2p³ for N, 3s² 3p³ for P. The density of states (DOS) were calculated by using the tetrahedron method (Blöchl corrections).

3. Results and discussion

3.1. Morphology structure

The morphology and structure of the as-prepared samples were studied by SEM and TEM. As depicted in Fig. 1a, the CN has a smooth and lamellar-like morphology. Obviously, TCN and BPTCN reveal a tubular structure with a diameter of $6-8\,\mu m$ (Fig. 1b and c). From Fig. 1e, the TEM analysis further verified that the perfect nanotube was successfully prepared. In contrast, the CN possess stacked sheets structure with some pores (Fig. 1d). Furthermore, the spherical morphology of BPQDs was revealed in Fig. 1f, the color of the as-prepared BPQDs suspension was brown (inset of Fig. 1f) and the particle distribution size of the pure BPQDs was determined by counting method (Fig. S1). According to Fig. S1, the average diameter size of the BPQDs particle could be measured to be 3.32 nm. From Fig. 1g, a certain amount of BPQDs can be detected from the edge of the sample of BPTCN. The TEM EDS spectrum of BPTCN (Fig. 1h) also further demonstrated that the BPQDs were loaded on TCN. Moreover, high-resolution TEM (HRTEM) was given to obtain more information about the two parts of TCN and BPQDs. From the magnified image of Fig. 1g and i), the obvious lattice fringe (0.22 nm) could be measured in the side of BPQDs, which was in good agreement with the (002) facet of BPQDs (JCPDS 87-1526) [31,37]. In addition, the intensity profiles along the red arrows in Fig. 1i were shown in Fig. 1j. Such intimate interfacial interactions between 1D TCN and BPQDs may cause an improved photocatalytic activity for BPTCN.

3.2. Crystal and chemical structure

Fig. 2a presents the XRD patterns of CN, TCN, and BPTCN. As described in Fig. 2a, the XRD patterns of all obtained samples were very similar, indicating that the general structure of g-C₃N₄ remained well. The CN possesses two typical diffraction peaks at 27.3° ((002) plane) and 13.0° ((100) plane), which can be assigned to the interlayer stacking of graphite-like materials and the repeated tri-s-heterocycle packing, respectively (JCPDS 87-1526) [38]. Compared with CN, the peak centered at 27.3° becomes much broader and weaker, manifesting size-dependent properties of the 1D tubular structure [25]. In addition, no other peaks intensity was detected in the BPTCN due to the limited amount and the well dispersion of BPODs. As shown in Fig. 2b, the XRD pattern of multiple recycled BPTCN was similar to the XRD pattern of fresh BPTCN, which acknowledged that the recycled BPTCN kept the intrinsically crystal structure. As exhibited in Fig. 2c, there was no significant difference in the FTIR spectra of the samples of CN, TCN, and BPTCN. The strong FTIR signals of all samples between 1000 cm^{-1} and 1750 cm⁻¹ were related to the typical aromatic CN heterocycles, while the peaks in the range of $3000-3500 \text{ cm}^{-1}$ and the peak at about 809 cm⁻¹ were respectively attributed to the stretching mode of the bridged or terminal amino group and the characteristic triazine cycles [29,39,40]. Furthermore, a new peak located at $\sim 560 \text{ cm}^{-1}$ (Fig. S3) was assigned to the P-C stretching mode [31], which indicates the presence of basic CN frameworks and BPQDs in the BPTCN composites. The formation of the P-C bond may be related to the inherent protruding edge (coordinatively unsaturated atoms) of BPQDs, which contributes to the hybridization between tubular g-C₃N₄ and BPQDs [31].

XPS analysis was performed to study the chemical states and the surface chemical composition of TCN and BPTCN. The high-resolution XPS analysis of P 2p, N 1s and C 1s were implemented. The peak of O element at 532.4 eV (Fig. 2d) was assigned to the chemisorbed oxygen [41]. The C 1s XPS of TCN was depicted in Fig. 2e, in which the fitted peaks located at 284.8 eV and 288.1 eV were assigned to the graphitic carbon (C-C) and sp²-bonded carbon (N-C=N) [28]. Interestingly, for BPTCN, a small negative shift (0.1 eV) was detected relative to that of all C-related peaks for TCN. It could be explained that a strong interaction between TCN and BPQDs (electron transfer from the binary hybrids) [28,29]. The N 1s spectra of TCN in Fig. 2f were decomposed into four peaks at 404.5, 400.5, 399.2, and 398.5 eV, which were ascribed to charging effects of π -excitations, the surface uncondensed amino groups $(C-NH_x)$, the tertiary nitrogen groups $(N-(C)_3)$, and the sp²-hybridized nitrogen of the triazine rings (C=N-C), respectively [42,43]. Similarly, the binding energies of N 1s in BPTCN shift to higher binding energies by around 0.2 eV, indicating that the weakened electron screening effect due to the decrease of the electron density [28,44,45]. Three distinct peaks at about 128.4, 131.1, and 133.4 eV could be observed in the high XPS resolution of P 2p spectra for BPTCN (Fig. 2g). The first two peaks at 128.4 eV and 131.1 eV were ascribed to $P\ 2p_{3/2}$ and $P\ 2p_{1/2},$ respectively [46]. And the greatest peak at 133.4 eV was resulted from oxidized phosphorus (PxOy) binding energies, P-OH or P-H₂O bond, indicating that the interior surface of BPQDs was slightly oxidized or the reaction of P_xO_y and BPQDs in water [29,43,47].

3.3. Theoretical calculation of electronic structure

To further analysis the electronic band structure and strong electronic interaction of the obtained materials, DFT calculations were carried out [48]. From Fig. 3a–c, the optimized geometric structures of CN, BPQDs, and BPTCN composite were observed, and the rectangle lattice constants of those samples were shown in Table S2. Moreover, the density of states (DOS) (including the total DOS (TDOS) and the projected DOS (PDOS)) and the band structures of the samples were depicted in Figs. 3d–f and 4. From the calculation results, the E_g of CN,



Fig. 1. Microscopic characterization of obtained samples. SEM images of (a) CN, (b) TCN, and (c) BPTCN, respectively. TEM images of (d) CN, (e) TCN, (f) pure BPQDs solution and (g) BPTCN, respectively. (h) TEM EDS spectrum and (i) HRTEM images of BPTCN. (j) Intensity profiles along the red arrows in (i). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

BPQDs, and BPTCN were 2.70, 0.93, and 0.063 eV, respectively. It can be accepted that E_g and energy levels play an important role in determining the photocatalytic properties of photocatalysts, and the narrowed Eg may result in stronger light absorption region, faster electron migration, and better photocatalytic performance [49,50]. However, the calculated E_g of BPTCN (only 0.063 eV) can hardly be obtained by this method, which could be conducive to the inherent defect of DFT methods [50,51]. As described in Fig. 3d-f, band structure diagram curve of BPTCN was denser than that of other materials, which means that there are more electrons and thus generate more photogenerated carriers in the photocatalysis process. Furthermore, as shown in Fig. 3d, the valence band top (VBT) and conduction band bottom (CBB) of CN was located at G point and H point, respectively. The VBT and CBB of BPQDs were both located at G point (Fig. 3e). These results indicated that the CN was an indirect band gap semiconductor, and the BPQDs was direct band gap semiconductor. The TDOS and PDOS elucidated orbital states of electrons in the samples, as depicted in Fig. 4 [52]. From Fig. 4a, the VBT of CN were occupied by C 2 s, 2p and N 2 s, 2p orbitals, whereas the CBB was mainly composed of C 2p and N 2p orbitals, which was different from those of BPQDs (VBT and CBB: P 2 s, 2p) (Fig. 4b) and BPTCN (VBT: C 2 s, 2p, N 2 s, 2p, and P 2 s, 2p; CBB: C 2p, N 2p and P 2p) (Fig. 4c). It could be found that the VBT of the BPTCN has been upshifted, which could be attributed to the hybridization of C 2p, N 2p and P 2p leading towards the narrow band gap [37,53]. Hence, the redistributed electrons are beneficial to the efficient charge separation and avoid the recombination of lightgenerated carriers, thus enhancing the photocatalytic performance of the highly-uniform BPTCN hybrid.

3.4. Photocatalytic activities

3.4.1. Photocatalytic degradation of oxytetracycline hydrochloride

The photocatalytic activity of the synthesized BPTCN was concerned with its ability to degrade antibiotics under visible light irradiation $(\lambda > 420 \text{ nm})$. As a stable and refractory antibiotic, OTC-HCl was selected as the target pollutant in this work. 120 min dark reaction (stirring the samples and OTC-HCl solution) was carried out before irradiation (Fig. S2). As depicted in Fig. 5, the photolysis curve of OTC-HCl shows the negligible self-degradation of OTC-HCl without photocatalyst. Only 32.37% of OTC-HCl in solution can be photodegraded within 60 min by CN, but TCN exhibits better degradation efficiency (48.59 %) for OTC-HCl under the same conditions, manifesting that CN's photocatalytic activity has been enhanced by unique morphology and structure of TCN. Impressively, BPQDs and BPTCN indicates the good photocatalytic degradation (18.91 % and 81.05 %) of OTC-HCl in imitated wastewater. As describe in Fig. 5b, the apparent rate constant (K_{app}) of OTC-HCl degradation over BPTCN was 0.0276 min⁻¹, which was 4.78 times than that of CN $(0.00577 \text{ min}^{-1})$ and 2.36 times than that of TCN $(0.0117 \text{ min}^{-1})$. This could be explained that the loading of BPQDs on the surface of tubular g-C₃N₄ can result in decreasing recombination of the space charge carriers and more carriers could be used to attack OTC-HCl. Therefore, the intimate interfacial interactions



Fig. 2. (a) XRD patterns and (c) FTIR spectrum of CN, TCN, and BPTCN, respectively. Inset of (a) was (b) XRD patterns of the fresh and recycled BPTCN composite under study. High-resolution XPS spectra of (d) survey, (e) C 1s, (f) N 1s and (g) P 2p for TCN and BPTCN, respectively.

between 1D tubular g-C₃N₄ and BPQDs were beneficial for improved OTC-HCl degradation. BPTCN hybrid obtains the TOC removal efficiency of 58.62 % after 120 min, indicating that the BPTCN hybrid shows outstanding mineralization ability in the photocatalytic reaction (Fig. 5c). Moreover, the apparent quantum efficiency (AQE) of BPTCN

was measured according to Zhou's studies [54]. Fig. S4 exhibits the initial rate of OTC-HCl was measured to be $0.43 \,\mu$ mol L⁻¹ min⁻¹, and the AQE ($\lambda = 420 \text{ nm}$) was equal to 0.15 %.

To prove the reusability and universality of the resultant samples, the multiple cycle experiments of OTC-HCl and photodegradation of TC



Fig. 3. The crystal structure of CN (a), BPQDs (b) and BPTCN (c), blue, gray and pink spheres represent N, C and P atoms, respectively. And the calculated band structure, and the corresponding density of states for CN (d), BPQDs (e) and BPTCN (f), respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).



Fig. 4. TDOS and PDOS of CN (a), BPQDs (b) and BPTCN (c).

and RhB were further evaluated. From Fig. 5d, BPTCN hybrid maintained its photocatalytic efficiency except for a 2.16 % decrease after six successive cycles, which may be caused by the loss of materials during the recycling process. Furthermore, the recycled BPTCN kept its intrinsically crystal structure from the results of the XRD characterizations of the used and fresh BPTCN (Fig. 2b). Moreover, the results of organic element analysis further proved the stability of BPTCN (Table S3). The universality of the BPTCN was evaluated by RhB and TC degradation under visible-light irradiation. In Fig. S5, no matter which pollutant (RhB or TC) was degraded, the photocatalytic efficiency was in order of BPTCN (99.43 % or 77.11 %) > TCN (97.94 % or 62.44 %) > CN (31.86 % or 33.09 %). Obviously, the better catalytic performance was obtained when the BPQDs and the tubular $g-C_3N_4$ intimate interacted, indicating that the heterostructures in BPTCN were essential for facilitating the photocatalytic degradation efficiency. The analysis mentioned above indicate that BPTCN is a recoverable and effective catalyst which is suitable for various organic pollutant systems. Furthermore, a comparison of degradation of organic pollutants by various photocatalysts were listed in Table S4.

3D EEMs is a sensitive and fast method for the analysis of dissolved organic material, which can distinguish between transformations and changes of dissolved organic material [55]. As can be seen from Fig. S6a, the fluorescent characteristics detected in the original OTC-HCl aqueous solution were negligible, probably due to the presence of a



Fig. 5. (a) Photocatalytic degradation of OTC-HCl over CN, TCN, and BPTCN; (b) Pseudo first-order kinetic fitting curves and the corresponding apparent rate constants (K_{app}); (c) The photocatalytic degradation and TOC removal curves of OTC-HCl on BPTCN sample; (d) The cycling experiment for the degradation of OTC-HCl by the fresh and used BPTCN sample.



Fig. 6. Possible degradation pathways of OTC-HCl in BPTCN system.

carbonyl group that reduced the fluorescent signal [56]. With the augmentation of reaction time (15–45 min, Fig. S6b-d), an obvious fluorescence peak was observed and significantly enhanced in the region with the wavelength at $\lambda_{Ex}/\lambda_{Em} = (320–390 \text{ nm})/(430–500 \text{ nm})$ (humic acid intermediates peaks) [57]. However, when the irradiation time was gradually increased to 60 min or even 120 min, the intensity of the fluorescence peak was continuously weakened (Fig. S6e-f), which might be related to the photodegradation of the formed intermediates and the decomposition to smaller fragments, H₂O and CO₂ [58,59].

To further verify the afore-mentioned results, it was necessary to explore the possible intermediates and analysis the reasonable photodegradation pathway of OTC-HCl. The MS spectra, molecular weights, molecular structural formulas and possible degradation path information of the formed intermediates were depicted in Fig. S7, Table S5 and Fig. 6, respectively. The product iron at m/z = 461.1 was identified as the original OTC molecule [60]. As an electrophilic radical, hydroxyl radicals react with organic compounds mainly through the reaction of OH addition to double bond, H-abstraction, and electron transfer. Hydroxyl radicals were dominating active species during photocatalytic process. OTC 1 stems from OTC by the attack of 'OH in an aromatic ring and 'OH further react with tertiary amine on account of electron density augment of N in NH₂ group, thus formed OTC 2 [61]. OTC 4 is originated from OTC 2 degradation through the dehydroxylation and deamidation reaction. OTC can also loss an N-methyl to produce OTC 3 [40]. Intermediate OTC 3 has two possible degradation pathways. One is to further loss hydroxyl, N-methyl and amide to produce OTC 4. Further degradation of OTC 4 leads the generation of OTC 5 via the demethylation reaction, deamination reaction, and addition reaction of the benzene ring. OTC 5 transform to OTC 6 through the loss of hydroxyl group. Another is to remove N(CH₃)H, amide group, hydroxyl group, due and get the intermediate OTC 7. Since the N(CH₃)H, hydroxyl group and amide group are easily oxidized, these functional groups can be detached to form OTC 7. OTC 7 lost a hydroxyl group and then undergoes ring-opening of benzene ring, formed intermediate OTC 8. The degradation of OTC 8 then leads to the generation of OTC 9 via deacetylation reaction, loss of methyl group and being oxidized [58].

In order to investigate the potential risk of the reaction solution

(pure OTC-HCl and its products), the toxicity experiments were tested through the detection of the viable cell density of the Escherichia coli (E. coli) bacteria. Different inhibition of the blank control (3.64%) and initial OTC-HCl solution (52.35%) was observed from Fig. S8, indicating that the initial OTC-HCl solution had a significant adverse effect on E. coli. In the photocatalytic process, the inhibition rate of the reaction solution increases during the first 30 min, and then greatly decreases when the irradiation duration exceeds 30 min. Similar results have been reported previously [62-64], and the increase in toxicity might be caused by the generation of additional toxic intermediates of OTC-HCl in the photocatalytic process. However, the toxicity of the reaction solution was drastically eliminated due to mineralization by further irradiation. Therefore, it was confirmed that the toxicity of the reaction solution could be reduced throughout the degradation process. In addition, the chemical oxygen demand (COD) value of the initial solution and the intermediate solution were analyzed according to Wen's research [65]. The COD of the original OTC-HCl solution and the reaction solution (1 h irradiation) were 46.04 and 18.92 mg/L, respectively. The change in COD value indicates that the photodegradation solution was easier to be treated innocuously. Taken together, the above analysis suggests that BPTCN composite shows good biodegradability and exhibits desirable property in toxicity reduction, thereby leading to a great potential for wastewater treatment.

3.4.2. Photocatalytic reduction of hexavalent chromium

To better understand the catalytic capability of BPTCN, photoreduction of Cr(VI) in aqueous solution was also studied. In the absence of visible light (60 min), the suspensions were magnetically stirred to build the absorption-desorption equilibrium, and the adsorption values of Cr(VI) on the obtained nanomaterials were illustrated in Fig. S9. As shown in Fig. 7a, in the absence of photocatalyst, the concentration of Cr(VI) hardly changed throughout the process, which manifests that the Cr(VI) aqueous solution does not spontaneously undergo photolysis [66]. The BPTCN exhibits the best photoreduction capacity of Cr(VI) removal (94.71%), while 17.61%, 22.49% and 81.59% of Cr(VI) photoreduction was achieved over BPQDs, CN and TCN, respectively. The hugely promoted photoreduction ability of BPTCN might be ascribed to the rapid separation and transfer of space carriers caused by the loading of BPQDs on the surface of tubular g-C₃N₄ [67]. From Fig. 7b, the intensity of the absorption peak of Cr(VI) at 540 nm gradually decreases as the irradiation time increases. The inset in Fig. 7b shows that the color of Cr(VI) aqueous solution changed from red to colourless, implying that the concentration of Cr(VI) has been lessened. The experimental data were researched in depth by a pseudo first-order kinetic model, where E_q is ln (C_t/C₀) = $-K_{app}$ t (Fig. 7c). The apparent Cr(VI) removal rate constants for CN, TCN and BPTCN were 0.00369 min⁻¹, 0.0262 min⁻¹ and 0.0404 min⁻¹, respectively. Obviously, the highest K_{app} for BPTCN was ~10.95 times than that of CN. In addition, a comparison of Cr(VI) reductions over various photocatalysts were listed in Table S6.

During the photodegradation process, the rate of Cr(VI) reduction on the photocatalyst was immensely affected by the pH of the aqueous solution. And the photocatalytic reduction performance of BPTCN at various pH values was investigated, as shown in Fig. 7d. In this work, EDTA-2Na (10 mM) was selected to capture holes to achieve the remaining electrons to restore Cr(VI). The concentration of Cr(VI) remains unchanged within no light, indicating that both the visible light and the catalyst were indispensable elements in the reduction process. The photoreduction ratio increased clearly with the decrease of pH (91.25% 60 min, 94.71% 60 min, 83.01% 30 min, and 93.11% 30 min at pH 5.65, 4.65, 3.65, and 2.65, respectively). The above interesting phenomenon might be due to the following reasons [35,36,66,68]: (I) In the acidic condition, $Cr_2O_7^{2-}$ or $HCrO_4^{-}$ was the predominant Cr (VI) species, and the sufficient H⁺ could favors the conformation change from Cr(VI) to Cr(III) (described by Eq. (4)); and (II) at high pH, CrO₄²⁻ was the mainly specie, and the reaction process happens



Fig. 7. (a) Photocatalytic activities of the obtained samples for the reduction of Cr(VI) in aqueous solution; (b) Temporal absorption spectra of Cr(VI) with BPTCN catalysts under visible light irradiation; The inset in (b) is the digital photographs of Cr(VI) aqueous solution after reaction; (c) Pseudo first-order kinetic fitting curves and the corresponding K_{app} value; (d) Effect of different pH values on Cr(VI) reduction.

following Eq. (5). Furthermore, in the neutral or alkaline conditions, the $Cr(OH)_3$ precipitate was obtained and Cr(III) tends to cover the active sites of BPTCN, inhibiting its photocatalytic reduction performance [68]. Overall consideration, the catalysts were evaluated at pH = 4.65 in this study, and the BPTCN hybrids exhibit excellent photocatalytic reduction on Cr(VI).

 $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$ (4)

 $\text{CrO}_4^{2-} + 4\text{H}_2\text{O} + 3\text{e}^- \rightarrow \text{Cr(OH)}_3 + 5\text{OH}^-$ (5)

3.5. Degradation mechanism analysis

3.5.1. Optical and electrochemical analysis

To study the mechanism of improved photocatalytic performance of BPTCN heterojunctions, UV–vis DRS, BET, time-resolved fluorescence decay spectrum, PL spectra, transient photocurrent responses and EIS of the obtained samples were investigated. As depicted in Fig. 8a, the CN displayed the typical semiconductor absorption edge at ~ 470 nm, which accords with the existed studies [31,69]. Interestingly, TCN and BPTCN exhibited better absorption coefficient (480-520 nm) compared to CN, because the multiple reflections of incident light improved the ability of TCN and BPTCN to absorb visible light with its 1D porous tubular structure and BPQDs [33]. Band gaps (E_g) of the resultant samples were typically calculated by Tauc method (inset of Fig. 8a) [40]. The sample of TCN had a narrower band gap (2.51 eV) than CN (2.57 eV), resulting in more photogenerated carriers under visible light. From previous work [70], the VB potentials can be estimated from VB-

XPS spectrum (Fig. 8b), so the VB values of CN and TCN were calculated to be 1.86 and 1.67 eV, respectively. Combined with the value of E_{g} , the CB locations of CN and TCN were -0.71 and -0.84 eV, respectively. And the energy band structure of TCN was exhibited in Fig. 10. It can be seen from Fig. S10 and Table S7 that the SBET value of TCN (28.574 m^2/g) was 1.84 times that of CN (15.505 m^2/g), and the obvious increase in specific surface area may be due to the unique 1D porous tubular structure. The larger SBET, pore size and pore volume of TCN could provide numerous boundaries and more active sites, facilitating the charge carrier transfer during the photocatalytic process. However, the N₂ adsorption-desorption isotherms and pore size distribution curve of TCN and BPTCN were similar, because loading BPQDs on TCN did not change the specific surface area of BPTCN [29]. Relative to TCN, it could be acknowledged that the specific surface area was not the key factor to change the photocatalytic performance of BPTCN.

The dynamics of charge carriers were studied by time-resolved PL (TRPL) spectroscopy, as shown in Fig. 8c. The decay kinetics of TCN and BPTCN exhibits a longer average PL lifetime (6.60 and 6.58 ns) than that of CN (6.20 ns), which might be caused by the bigger S_{BET} [33]. BPTCN displayed a shorten PL lifetime compared to TCN, indicating a nonradiative pathway from the charge transfer across the interface (P–C bonds) between TCN and BPQDs [31]. Furthermore, the behavior of photoinduced electron–hole pairs separation and migration were further analyzed by photoluminescence emission spectroscopy. Under the light irradiation of 340 nm wavelength, the sample of CN showed a strong intrinsic luminescence emission peak located at about



Fig. 8. (a) UV-vis diffuse reflectance spectra of samples and (inset graph) band gap of CN and TCN; (b) VB-XPS spectra of CN and TCN; (c, d) Time-resolved PL spectra and PL spectra of samples; (e) Photocurrent responses under visible light irradiation and (f) EIS Nyquist plots for CN, TCN and BPTCN.

470 nm, indicating the high recombination of electron-hole pairs (Fig. 8d). The PL peak decreases dramatically for TCN and BPTCN, which manifested lower recombination rate of photogenerated electron-hole pairs [71,72]. The reason for the above results was that the 1D porous tubular structure reduces the diffusion distance of the carriers to the surface, hence effectively separating the efficiency of electron-hole pairs, which was in accordance with TRPL spectroscopy.

To verify the enhanced photoelectrochemical (PEC) properties of BPTCN, the transient photocurrent responses for three light on–off cycles were carried out under visible light (Fig. 8e) [73]. The saturated photocurrent density of BPTCN (about $0.225 \,\mu A \, cm^{-2}$) and TCN (about $0.205 \,\mu A \, cm^{-2}$) was bigger than that of CN (about $0.15 \,\mu A \, cm^{-2}$),

manifesting that the porous tubular structure and introduction of BPQDs could facilitate photoinduced charge carriers separation/transport [24,74]. Furthermore, the resultant catalysts showed reproducible and prompt photocurrent responses upon exposure to simulated solar illumination, which supported that all samples possess outstanding PEC stability. Electrochemical impedance spectra (EIS) was a useful technology to investigate the charge transfer dynamics in interfacial regions [16]. Generally, at the electrode surface, a smaller arc in the EIS Ny-quist plots suggest smaller charge-transfer resistance [75]. As depicted in Fig. 8f, the relative arc radii of three electrodes were in the order of CN > TCN > BPTCN, indicating the highest interfacial charge transfer rate in BPTCN. Overall, the above analysis and discussion



Fig. 9. (a, b) Photocatalytic activities of the BPTCN for the degradation of OTC-HCl under the condition of different quenchers; (c) rate constants for photocatalytic degradation of OTC-HCl in the presence of various reactive species scavengers and percent contributions incurred from the corresponding reactive species; ESR spectra of radical adducts tapped by DMPO spin-trapping in BPTCN dispersion in the dark and under visible light irradiation (d) in methanol dispersion for DMPO – O_2^- and (e) in aqueous dispersion for DMPO – OH.

performed that the BPTCN possessed excellent PEC properties.

3.5.2. Radical trapping experiment and ESR test

Active species capture experiments and ESR spectroscopy were conducted to identify key reactive species to better understand the photocatalytic mechanism [76]. In this work, the quenchers were EDTA-2Na, TEMPOL and tertiary butanol (TBA), which could assimilate reactive species of h⁺, O_2^- , and OH, respectively [77]. From the results of Fig. 9a and Fig. 9b, the main reactive species involved in the photodegradation reaction for BPTCN were O_2^- and h⁺. However, the role of OH cannot be covered either. Moreover, the K_{app} for OTC-HCl degradation were 0.00568, 0.00266, and 0.0181 min⁻¹ in the presence of EDTA-2Na, TEMPOL, and TBA, respectively. According to formulas 1–3, the relative contributions of h⁺, O_2^- , and OH to the OTC-HCl



Fig. 10. Possible photocatalytic mechanism scheme of the carriers separation process on the interface of BPTCN under visible light irradiation.

removal were calculated to be 79.42 %, 90.36 %, and 34.64 %, respectively (Fig. 9c). Due to the influence of the convoluted radical chemistry, the total contribution in the photocatalytic system exceeds 100 % [34,78]. Hence, the O_2^- and h^+ comprised the primary catalytic mechanisms for OTC-HCl degradation. Noticeably, the ESR spectra was performed to further proved that $^{\circ}O_2^{-}$ and $^{\circ}OH$ could be produced during the BPTCN system. As described in Fig. 9d, the four main peaks (1: 1: 1: 1) of O_2^- were observed in the obtained samples under the condition of light, whereas no ESR peaks for all samples could be detected in the dark. As expected, the main peaks of the BPTCN were obviously higher than those of CN and TCN. Similar phenomenon was detected in Fig. 9e, strongest ESR spectra with relative intensities of 1 : 2:2:1 corresponding to the DMPO-'OH adduct were apparently observed in the case of the BPTCN. This indicates that BPTCN can produce more reactive groups, and the better photocatalytic activity could be attributed to the unique tubular structure and the introduction of BPQDs.

Given the aforementioned analysis, a plausible photocatalytic mechanism for OTC-HCl degradation and Cr(VI) reduction over BPTCN can be observed in Fig. 10. The CB and VB potentials of TCN were located at -0.84 eV and +1.67 eV, respectively ($E_g = 2.51$ eV). Under visible light illumination, electrons (e⁻) in VB, primarily TCN, were excited to its CB, leaving positively charged holes (h⁺) in VB. As displayed in Fig. 10, Cr(VI) was reduced to Cr(III) by the lightgenerated e⁻ and 'O₂⁻ was yielded by capture of O₂. The TCN cannot oxidize H₂O or OH⁻ to 'OH, and the generated 'OH may root in the translation of the H₂O₂ (O₂⁻ can capture H⁺ to yield H₂O₂) [79]. As a result, the formed active species ('O₂⁻, 'OH, and h⁺) could effectively attack OTC-HCl. The reaction process can be described as following equations:

BPTCN + hv \rightarrow BPTCN (h ⁺	+ e ⁻)	(6)
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BPTCN
$$(e^-) \rightarrow BPQDs$$
 (e-) (7)

$$Cr^{6+} + BPQDs (e^{-}) \rightarrow Cr^{3+}$$
 (8)

$$O_2 + BPQDs (e^-) \rightarrow O_2^-$$
(9)

$$O_2^- + BPQDs (e^-) + 2H^+ \rightarrow H_2O_2$$
 (10)

$$H_2O_2 + BPQDs (e^-) \rightarrow OH + OH$$
(11)

$$h^+$$
, O_2^- and $OH + OTC-HCl \rightarrow$ degradation products (CO₂, H₂O etc.) (12)

The greater photocatalytic activity of BPTCN was clearly illustrated by the characterization analysis, and the detail reasons could be described as follows. On the one hand, 1D porous tubular structure reduces the diffusion distance of the carriers to the surface, therefore effectively separating the efficiency of electron–hole pairs. In addition, the photon absorption of BPTCN has been greatly improved due to the addition of BPQDs. On the other hand, BPQDs (acts as an electron mediator) were uniformly loaded on the surface of TCN to obtain a unique 0D/1D structure (interfacial P–C bonds), which retarded the recombination of carriers [80]. The P–C bonds build an intimate interaction between BPQDs with TCN, and thus facilitating cycle photostability and electrons transfer.

4. Conclusion

In conclusion, 0D/1D mixed-dimensional BPTCN nanohybrids was successfully prepared by loading BPQDs of ~ 3.32 nm in size onto the TCN of $\sim 6-8$ um in diameter by a facile ice-assisted ultrasonic method. The as-obtained BPTCN nanohybrids reveal better photocatalytic property for the removal of various organic pollutants (OTC-HCl, TC, and RhB) and reduction Cr(VI) than that of CN and TCN. Notably, the photocatalytic degradation of OTC-HCl by BPTCN in simulated wastewater could reach 81.05 % under visible light irradiation, and its AQE $(\lambda = 420 \text{ nm})$ was equal to 0.15 %. In this system, the loading of BPQDs on the surface of tubular g-C₃N₄ could result in decreasing recombination of the space charge carriers and more carriers could be used to attack OTC-HCl. Furthermore, DFT calculation was applied to deeper study the electronic band structure and strong electronic interaction of obtained materials. This research exposes a promising prospect for the design and synthesis of a variety of metal-free nanomaterials functional in solar-to-chemical energy conversion and environmental remediation.

CRediT authorship contribution statement

Wenjun Wang: Conceptualization, Methodology, Data curation, Writing - original draft. Qiuya Niu: Writing - review & editing. Guangming Zeng: Supervision, Project administration, Funding acquisition, Writing - review & editing. Chen Zhang: Supervision, Project administration, Funding acquisition. Danlian Huang: Resources, Supervision, Funding acquisition. Binbin Shao: Software. Chengyun Zhou: Validation, Data curation. Yang Yang: Validation, Data curation. Yuxin Liu: Data curation, Writing - review & editing. Hai Guo: Formal analysis. Weiping Xiong: Formal analysis. Lei Lei: Validation, Data curation. Shiyu Liu: Validation, Data curation. Huan Yi: Validation, Data curation. Sha Chen: Validation, Data curation. Xiang Tang: Validation, Data curation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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