## 1 1D porous tubular g-C<sub>3</sub>N<sub>4</sub> capture black phosphorus quantum dots

2 as 1D/0D metal-free photocatalysts for oxytetracycline hydrochloride

## 3 degradation and hexavalent chromium reduction

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As an "up-and-coming" two-dimensional (2D) material, black phosphorus (BP) 19 has attracted much attention due to its abundant metal-free properties and broad 20 application prospects in photocatalysis. This study introduces a promising 21 22 sunlight-driven metal-free photocatalyst for oxytetracycline hydrochloride 23 degradation and hexavalent chromium reduction in water and wastewater. The roles of BP quantum dots (BPQDs) in the distribution of electrons and photocatalytic 24 performances were well identified by experimental and density 25 functional theory (DFT) calculations. As expected, the specially designed 26 structure shows 27 unusual photocatalytic efficiency toward the gradation of oxytetracycline hydrochloride  $(0.0276 \text{ min}^{-1})$  and reduction of valent chromium  $(0.0404 \text{ min}^{-1})$ . 28 f þ Reactive species, namely,  $\bullet O_2^-$  and  $h^+$ 29 comprised the primary photocatalytic ride degradation. This work highlights that mechanisms for oxytetracycline 30  $-C_3$  (TCN) with BPQDs facilitates the charge spatial 31 the combination of tubular tal 32 tic process, and provides alternative strategy for design separation in the hoto 33 of highly active and metal-free nanomaterials toward environmental remediation and 34 sustainable solar-to-chemical energy conversion.

35 Keywords

BPQDs; Tubular g-C<sub>3</sub>N<sub>4</sub>; Cr(VI) reduction; Oxytetracycline hydrochloride; Density
functional theory

38

39 1. Introduction

40 Today, the dramatic increase in global energy demand is still hugely dependent 41 on fossil fuel combustion, which has been producing tremendous anthropogenic greenhouse gases [1-4]. Reducing greenhouse gases emissions and coping with 42 43 related global warming is one of the major challenges facing humanity in the 21st 44 century [5-8]. Moreover, various antibiotic contamination and heavy metal pollutants 45 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 46 ful to develop environmentally sustainable energy technologies to so 47 energy crisis and 48 environmental problems [12-14]. Fortunately, solar vergy photocatalytic technology grabs extreme attention due to its highly sustainable 49 nontoxic nature and low cost [15, 16]. In view of maximizing the use of solar energy, it is significant important to select 50 past decades, amounts of semiconductor the suitable photocatalysts [17 51 photocatalysts (TiO<sub>2</sub>, Bi Cl, 2nO and AgI, etc.) have been employed for 52 on) and energy conversion [18-20]. However, most of the 53 environmental rediż photocataysts are metal containing semiconductors which have 54 reported 55 environmentally harmful effects and limited quantity [21]. Hence, it is necessary for 56 investigators to construct a metal-free photocatalyst with amounts of earth elements (C, N and P, etc.) and high efficiency [22]. 57

To address above tasks, the nonmetallic conjugated semiconductor  $g-C_3N_4$  has been widely used in photocatalysis field because of its outstanding chemical and thermal stability, unique band gap structure, environmentally friendly nature and 61 visible light response [22]. Nevertheless, the photocatalytic property of pristine g-C<sub>3</sub>N<sub>4</sub> is not satisfactory due to the sluggish exciton dissociation, small surface area 62 63 and insufficient light absorption [23]. So far, many strategies (element doping, heterojunction, and morphological engineering, etc.) have been explored to overcome 64 the drawbacks of pure g-C3N4. To date, one-dimensional (1D) nanomaterials with 65 66 open channel have received much attention owing to their decreased mass transfer resistance, reduced diffusion distance, enhanced photogenerated carriers separation, 67 and increased light absorption [24, 25]. For example, Guo et al. 68 a hydrothermal method to obtain P-doped hexagonal tubular g-C<sub>3</sub>N<sub>4</sub> via 69 is of melamines in phosphorous acid [26]. As a result, a convenient, effective, and simple method for 70 synthesizing the highly efficient tubular g-CN photocatalyst is still a challenging 71 72 and predictable task.

hosphorus (BP) has received numerous Metal-free semiconductor 73 scientific interests on acc unt of excellent electrical and optical properties, high 74  $200 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ), as well as outstanding solar light absorption 75 charge mobility out capacity since the first preparation of atom-thick layer BP in 2014 [27, 28]. Notably, 76 77 BP has been used as a cocatalyst to promote the separation of photocavitation-electron 78 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 H<sub>2</sub> 79 production, and the amount of H<sub>2</sub> can reached approximately 0.64  $\mu$ mol h<sup>-1</sup> [28]. 80 Recently, 0D BPQDs have been widely used in photocatalytic area when the lateral 81 82 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-C<sub>3</sub>N<sub>4</sub> nanosheets through sonication approach and high-vacuum stirring
method, respectively [30, 31].

88 Bearing these in mind, for the first time, we employed a facile ice-assisted 89 ultrasonic method to obtain a metal-free BPQDs loaded TCN (BPTCN) nanohybrid with 1D tubular structure. In this system, BPQDs with an avera 90 size of 3.32 nm were dispersed onto the tubular g-C<sub>3</sub>N<sub>4</sub>. Various 91 pollutant systems (oxytetracycline hydrochloride (OTC-HCl), tetracycline (TC), and rhodamine B 92 93 (RhB)) and heavy metal Cr(VI) ions in wastewater were effectively mv removed and reduced by such well-confined BPTCN heterostructure. In addition, the 94 ut BPTCN were investigated, and the roles underlying photocatalytic mecha 95 C<sub>3</sub>N<sub>4</sub> in photocatalytic process were also highlighted. of BPQDs and tubular g 96 hd structure and strong electronic interaction of obtained 97 Meanwhile, the troi materials were calculated by density functional theory (DFT) calculation. This work 98 99 indicates a new paradigm for constructing metal-free photocatalyst with unique 100 tubular structure for effective photocatalytic organic pollutants degradation and green energy conversion. 101

102

103 2. Experimental Section

104 **2.1.** Catalysts synthesis

105	The reagents used in this work and the synthesized steps of tubular $g-C_3N_4$ (TCN
106	and bulk g-C <sub>3</sub> N <sub>4</sub> (CN) were depicted in the Supporting information. De-ionized water
107	(18.25 M $\Omega$ .cm) from Millipore system was applied in the whole experiment. The
108	BPQDs were obtained from Nanjing XFNANO, Inc. (XF208, Size, 1-10 nm;
109	Concentration, 0.1 mg/mL; Ratio of monolayer > 80%). As for preparing
110	BPQDs/TCN hybrids (denoted as BPTCN), 0.1 g of TCN was dispersed in 10 mL of
111	DI water. Then, 10 mL commercial BPQDs dispersion was mixed with the above
112	suspension. This mixture was stirred for 4 h and subsequently sonicated in an ice bath
113	for 4 h. The obtained suspension was centrifuged at 6750 h to 50 360 s to collect the
114	residual particles. The final precipitate was dried in exacuum oven at 40 $^{\circ}$ C for 12 h.
115	All chemicals were analytical grade and were used without additional purification in
116	this work.

## 117 **2.2 Characterization**

The transmission electron microscope (TEM), high-resolution TEM (Tecnai G2 118 Necron microscopy (SEM Hitachi S4800) tests were used to F20, FEI) and sch 119 ung determine the morphology structure of samples. The Fourier transform infrared 120 spectrum (FTIR) analysis was conducted by Bruker Vertex 70 instrument with KBr 121 122 pellet method. The X-ray diffraction (XRD) measurement was obtained by a Bruker 123 D8 Advance diffractometer. The X-ray photoelectron spectroscopy (XPS) results were 124 recorded on Escalab 250Xi instrument with an Al Ka X-ray source. The total organic carbon (TOC) data was collected on a Shimadzu TOC-LCPH analyzer. The electron 125 126 spin response (ESR) signal was detected on JEOL JES-FA200 spectrometer. The 127 three-dimensional excitation-emission matrix fluorescence spectra (3D EEMs) and

- 128 photoluminescence (PL) were carried out on LS-55 fluorescence spectrophotometer.
- 129 The detailed electrochemical measurement experiments were presented in Supporting
- 130 information.

## 131 **2.3 Photocatalytic Activity**

### 132 **2.3.1** Photodegradation of oxytetracycline hydrochloride

To investigate the photocatalytic activity of the samples, the degradation of 133 OTC-HCl (10 mg/L pH=7) was performed under visible liph 134 irradiation. The chemical structure and physicochemical properties of OT 135 32] were presented in Table S1. And the light source was from a 300 We enon lamp (PLS-SXE300, light 136 ther ( $\lambda > 420$  nm). The emission intensity was ~  $300 \text{ mW/cm}^2$ ) with the UV c 137 lto\* spectrum of the visible light and the corresponding photocatalytic reaction system 138 Briefly, 30 mg of sample was dispersed in were described in our previous 139 50 mL of pollutant aqueous solution. Before illumination, the suspension was churned 140 obtain the adsorption desorption equilibrium. The reaction 141 in the dark for OTC-HCl suspension (2 mL) was taken out at intervals of 15 min and filtered through 142 143 a 0.22 µm membrane filter. The concentrations of OTC-HCl suspension were analyzed by a Shimadzu UV-vis spectrophotometer (UV-2700) with absorbance at its 144 characteristic absorption peaks of 353 nm. The photo-degradation intermediate 145 products of OTC-HCl were determined by a LC-MS/MS instrument, and the specific 146 147 method was shown in supporting information. In addition, Escherichia coli bacteria were used to assess the potential risk of intermediates and detailed procedures wereprovided in the Supporting information.

150 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<sub>t</sub>/C<sub>0</sub>) = -K<sub>app</sub>t. Among 151 them, k<sub>app</sub> is the apparent rate constant; C<sub>t</sub> and C<sub>0</sub> are t-time and initial concentrations 152 153 of OTC-HCl, respectively. In this work, the quenchers were EDTA-2Na, TEMPOL and tertiary butanol (TBA), which could assimilate reactive species of h<sup>+</sup>, •O<sub>2</sub><sup>-</sup>, and 154 •OH, respectively. The contributions of each reactive species to the verall OTC-HCl 155 photodegradation kinetics were calculated using following 156  $R_{\bullet OH} = \ \frac{K_{\bullet OH}}{K_{app}} \approx \ \frac{(K_{app} - K_{TBA})}{K_{app}}$ 157 (1)
$$\begin{split} R_{\bullet O2^{-}} &= \ \frac{K_{\bullet O2^{-}}}{K_{app}} \approx \ \frac{(K_{app} - K_{TEMPOL})}{K_{app}} \\ R_{h+} &= \ \frac{K_{h+}}{K_{app}} \approx \ \frac{(K_{app} - K_{EDTA-2Na})}{K_{app}} \end{split}$$
158 (2)159 (3)

# 163 **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.

## 170 **2.3.3 Photoreduction of Cr(VI)**

The photocatalytic Cr(VI) reduction experiment was chosen to further evaluate 171 the photocatalytic reducing activity of BPTCN. Then, the reaction solution pH value 172 was adjusted by H<sub>2</sub>SO<sub>4</sub> (0.1 M) and NaOH (0.1 M) solutions. Before irradiation, 50 173 174 mg of the resultant sample was added into 50 mL of Cr(VI) solution (based on Cr in a 175 K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution, 10 mg/L), followed by stirring for 60 min to attain an 176 adsorption-desorption equilibrium in the absence of light. Approximately 2 mL of the reaction suspension was withdraw at given time intervas 177 min) and its concentration was determined by a UV-vis spectrophotom () nm) according to 178 the 1,5-diphenylcarbazide method [35, 36]. 179

## 180 **2.4 DFT calculations**

The DFT based simulations were conducted by using the Cambridge Serial Total 181 in the Materials Studio (MS) program. The Energy Package (CASTEP) imp 182 Perdew-Burke-Ernzerhof (IBE) generalized gradient approximation (GGA) was used 183 functions. for Considering that PBE functional 184 exchange-c will elañ underestimate the bind gap of semiconductors, Heyd-Scuseria-Ernzerhof (HSE06) 185 hybrid functional was used in electronic calculations. The cut-off energy for plane 186 wave basis was set to 340 eV, using the energy tolerance and force convergence 187 criteria per atom of 1  $\times$  10<sup>-5</sup> eV and 0.02/0.05 eV Å<sup>-1</sup> for the electronic structure 188 calculations. A Monkhorst-Pack grid of  $3 \times 3 \times 1$  for K-points was sampled in the first 189 Brillouin zone to do self-consistent calculations. The rectangle lattice constants of the 190 samples were shown in Table S2. The outer valence electron arrangement of each 191

192	element was 2 s <sup>2</sup> 2p <sup>2</sup> for C, 2 s <sup>2</sup> 2p <sup>3</sup> for N, $3s^2 3p^3$ for P. The density of states (DOS)
193	were calculated by using the tetrahedron method (Blöchl corrections).

194

## 195 3. Results and discussion

**3.1 Morphology structure** 

197 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. 198 Obviously, TCN and BPTCN reveal a tubular structure with a c 199 neter of 6-8 µm (Fig. 1b and Fig. 1c). From Fig. 1e, the TEM analysis furth 200 fied that the perfect 201 nanotube was successfully prepared. In contrast e CN possess stacked sheets structure with some pores (Fig. 1d). Furtherp the spherical morphology of 202 BPODs was revealed in Fig. 1f, the color of the as-prepared BPQDs suspension was 203 distribution size of the pure BPQDs was brown (inset of Fig. 1f) and the 204 determined by counting me hod (Fig. S1). According to Fig. S1, the average diameter 205 ould be measured to be 3.32 nm. From Fig. 1g, a certain le ø 206 size of the BPOI part amount of BPQDs can be detected from the edge of the sample of BPTCN. The TEM 207 208 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 209 information about the two parts of TCN and BPQDs. From the magnified image of 210 Fig. 1g (Fig. 1i), the obvious lattice fringe (0.22 nm) could be measured in the side of 211 BPQDs, which was in good agreement with the (002) facet of BPQDs (JCPDS 212 87-1526) [31, 37]. In addition, the intensity profiles along the red arrows in Fig. 1i 213

- 214 were shown in Fig. 1j. Such intimate interfacial interactions between 1D TCN and
- 215 BPQDs may cause an improved photocatalytic activity for BPTCN.



TCN, and (c) BPTCN, espectively. TEM images of (d) CN, (e) TCN, (f) pure BPQDs
solution and (g) RPTCN, respectively. (h) TEM EDS spectrum and (i) HRTEM
images of BPTCN. (j) Intensity profiles along the red arrows in (i).

221 **3.2** Crystal and chemical structure

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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  $g-C_3N_4$  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 227 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 228 229 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 BPQDs. As shown in 230 231 Fig. 2b, the XRD pattern of multiple recycled BPTCN was similar to the XRD pattern 232 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 233 FTIR spectra of the samples of CN, TCN, and BPTCN. The string **EXIR** signals of all 234 samples between 1000 cm<sup>-1</sup> and 1750 cm<sup>-1</sup> were related to 235 pical aromatic CN heterocycles, while the peaks in the range of  $3000 \times 500$  cm<sup>-1</sup> and the peak at about 236 809 cm<sup>-1</sup> were respectively attributed to the stretching mode of the bridged or terminal 237 amino group and the characteristic triazine wcles [29, 39, 40]. Furthermore, a new 238 assigned to the P-C stretching mode [31], peak located at ~ 560 cm<sup>-1</sup> (F 239 which indicates the presence of basic CN frameworks and BPQDs in the BPTCN 240 composites. The termation of the P–C bond may be related to the inherent protruding 241 edge (coordinativel) unsaturated atoms) of BPQDs, which contributes to the 242 hybridization between tubular g-C<sub>3</sub>N<sub>4</sub> and BPQDs [31]. 243

244 XPS analysis was performed to study the chemical states and the surface 245 chemical composition of TCN and BPTCN. The high-resolution XPS analysis of P 2p, 246 N 1s and C 1s were implemented. The peak of O element at 532.4 eV (Fig. 2d) was 247 assigned to the chemisorbed oxygen [41]. The C 1s XPS of TCN was depicted in Fig. 248 2e, in which the fitted peaks located at 284.8 eV and 288.1eV were assigned to the

249	graphitic carbon (C-C) and sp <sup>2</sup> -bonded carbon (N-C=N) [28]. Interestingly, for
250	BPTCN, a small negative shift (0.1 eV) was detected relative to that of all C-related
251	peaks for TCN. It could be explained that a strong interaction between TCN and
252	BPQDs (electron transfer from the binary hybrids) [28, 29]. The N 1s spectra of TCN
253	in Fig. 2f were decomposed into four peaks at 404.5, 400.5, 399.2, and 398.5 eV,
254	which were ascribed to charging effects of $\pi$ -excitations, the surface uncondensed
255	amino groups (C–NH <sub>x</sub> ), the tertiary nitrogen groups (N–(C) <sub>3</sub> ), and the sp <sup>2</sup> -hybridized
256	nitrogen of the triazine rings (C=N-C), respectively [42, 43]. Similarly, the binding
257	energies of N 1s in BPTCN shift to higher binding energies by around 0.2 eV,
258	indicating that the weakened electron screening erect due to the decrease of the
259	electron density [28, 44, 45]. Three distinct parks at about 128.4, 131.1, and 133.4 eV
260	could be observed in the high XPS resolution of P 2p spectra for BPTCN (Fig. 2g).
261	The first two peaks at 128.4 eV and 24.1eV were ascribed to P $2p_{3/2}$ and P $2p_{1/2}$ ,
262	respectively [46]. And the greatest peak at 133.4 eV was resulted from oxidized
263	phosphorus (P <sub>x</sub> O <sub>2</sub> , binding energies, P-OH or P-H <sub>2</sub> O bond, indicating that the interior
264	surface of BPQDs was slightly oxidized or the reaction of $P_xO_y$ and BPQDs in water
265	[29, 43, 47].



Fig. 2. (a) XRD patterns and (c) FTIR spectrum of CN TCN, and BPTCN,
respectively. Inset of (a) was (b) XRD patterns f 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.

# 271 **3.3** Theoretical calculation of exctranic structure

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272 To further analysi ronic band structure and strong electronic interaction the e an DFT calculations were carried out [48]. From Fig. 3a-c, the 273 of the obtained ma 274 optimized geometric structures of CN, BPQDs, and BPTCN composite were observed, 275 and the rectangle lattice constants of those samples were shown in Table S2. 276 Moreover, the density of states (DOS) (including the total DOS (TDOS) and the 277 projected DOS (PDOS)) and the band structures of the samples were depicted in Fig. 3d-f and Fig. 4. From the calculation results, the  $E_g$  of CN, BPQDs, and BPTCN were 278 2.70, 0.93, and 0.063 eV, respectively. It can be accepted that  $E_g$  and energy levels 279 play an important role in determining the photocatalytic properties of photocatalysts, 280

281	and the narrowed $E_g$ may result in stronger light absorption region, faster electron
282	migration, and better photocatalytic performance [49, 50]. However, the calculated $E_g$
283	of BPTCN (only 0.063 eV) can hardly be obtained by this method, which could be
284	conducive to the inherent defect of DFT methods [50, 51]. As described in Fig. 3d-f,
285	band structure diagram curve of BPTCN was denser than that of other materials,
286	which means that there are more electrons and thus generate more photogenerated
287	carriers in the photocatalysis process. Furthermore, as shown in Fig. 3d, the valence
288	band top (VBT) and conduction band bottom (CBB) of CN was located at G point and
289	H point, respectively. The VBT and CBB of BPQDs were both located at G point (Fig.
290	3e). These results indicated that the CN was an indicate band gap semiconductor, and
291	the BPQDs was direct band gap semicondul tor The TDOS and PDOS elucidated
292	orbital states of electrons in the samples, as lepicted in Fig. 4 [52]. From Fig. 4a, the
293	VBT of CN were occupied by 623 21 and N 2s, 2p orbitals, whereas the CBB was
294	mainly composed of C 2r and N 2p orbitals, which was different from those of
295	BPQDs (VBT and CBL Pos, 2p) (Fig. 4b) and BPTCN (VBT: C 2s, 2p, N 2s, 2p,
296	and P 2s, 2p; CBB: (2p, N 2p and P 2p) (Fig. 4c). It could be found that the VBT of
297	the BPTCN has been upshifted, which could be attributed to the hybridization of C 2p,
298	N 2p and P 2p leading towards the narrow band gap [37, 53]. Hence, the redistributed
299	electrons are beneficial to the efficient charge separation and avoid the recombination
300	of lightgenerated carriers, thus enhancing the photocatalytic performance of the
301	highly-uniform BPTCN hybrid.



Fig. 4. TDOS and PDOS of CN (a), BPQDs (b) and BPTCN (c). 308

#### **3.4 Photocatalytic activities** 309

### 3.4.1 Photocatalytic degradation of oxytetracycline hydrochloride 310

The photocatalytic activity of the synthesized BPTCN was concerned with its 311

ability to degrade antibiotics under visible light irradiation ( $\lambda > 420$  nm). As a stable 312

313 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 314 before irradiation (Fig. S2). As depicted in Fig. 5, the photolysis curve of OTC-HCl 315 shows the negligible self-degradation of OTC-HCl without photocatalyst. Only 32.37% 316 of OTC-HCl in solution can be photodegraded within 60 min by CN, but TCN 317 318 exhibits better degradation efficiency (48.59%) for OTC-HCl under the same 319 conditions, manifesting that CN's photocatalytic activity has been enhanced by unique morphology and structure of TCN. Impressively, BPQDs a 320 N indicates the good photocatalytic degradation (18.91% and 81.05%) 321 -HCl in imitated wastewater. As describe in Fig. 5b, the apparent c constant ( $K_{app}$ ) of OTC-HCl 322 degradation over BPTCN was 0.0276 min<sup>-1</sup> was 4.78 times than that of CN 323 wb.  $(0.00577 \text{ min}^{-1})$  and 2.36 times than that of TCN (0.0117 min^{-1}). This could be 324 the surface of tubular g-C<sub>3</sub>N<sub>4</sub> can result in explained that the loading of B 325 decreasing recombination of the pace charge carriers and more carriers could be used 326 here ore, the intimate interfacial interactions between 1D 327 to attack OTC-I tubular g-C<sub>3</sub>N<sub>4</sub> and BPODs were beneficial for improved OTC-HCl degradation. 328 BPTCN hybrid obtains the TOC removal efficiency of 58.62% after 120 min, 329 indicating that the BPTCN hybrid shows outstanding mineralization ability in the 330 photocatalytic reaction (Fig. 5c). Moreover, the apparent quantum efficiency (AQE) 331 of BPTCN was measured according to Zhou's studies [54]. Fig. S4 exhibits the initial 332 rate of OTC-HCl was measured to be 0.43  $\mu$ mol L<sup>-1</sup> min<sup>-1</sup>, and the AQE ( $\lambda$  = 420 nm) 333 was equal to 0.15%. 334

335	To prove the reusability and universality of the resultant samples, the multiple
336	cycle experiments of OTC-HCl and photodegradation of TC and RhB were further
337	evaluated. From Fig. 5d, BPTCN hybrid maintained its photocatalytic efficiency
338	except for a 2.16% decrease after six successive cycles, which may be caused by the
339	loss of materials during the recycling process. Furthermore, the recycled BPTCN kept
340	its intrinsically crystal structure from the results of the XRD characterizations of the
341	used and fresh BPTCN (Fig. 2b). Moreover, the results of organic element analysis
342	further proved the stability of BPTCN (Table S3). The universality of BPTCN was
343	evaluated by RhB and TC degradation under visible-light invitation. In Fig. S5, no
344	matter which pollutant (RhB or TC) was degraded the photocatalytic efficiency was
345	in order of BPTCN (99.43% or 77.11%) > T(N,97.94% or 62.44%) > CN (31.86%
346	or 33.09%). Obviously, the better catalytic performance was obtained when the
347	BPQDs and the tubular g-C <sub>3</sub> N <sub>4</sub> introate interacted, indicating that the heterostructures
348	in BPTCN were essential or facilitating the photocatalytic degradation efficiency.
349	The analysis mentioned above indicate that BPTCN is a recoverable and effective
350	catalyst which is suitable for various organic pollutant systems. Furthermore, a
351	comparison of degradation of organic pollutants by various photocatalysts were listed
352	in Table S4.



CN, TCN, and BPTCN; (b) Fig. 5. (a) Photocatalytic degradation of OTC 354 Pseudo first-order kinetic fitting curves a sponding apparent rate constants 355 the 356  $(K_{app})$ ; (c) The photocatalytic degra and TOC removal curves of OTC-HCl on atio BPTCN sample; (d) The c nt for the degradation of OTC-HCl by the 357 358 fresh and used BPTC

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359 3D EEMs is envitive and fast method for the analysis of dissolved organic material, which can distinguish between transformations and changes of dissolved 360 organic material [55]. As can be seen from Fig. S6a, the fluorescent characteristics 361 362 detected in the original OTC-HCl aqueous solution were negligible, probably due to the presence of a carbonyl group that reduced the fluorescent signal [56]. With the 363 augmentation of reaction time (15-45 min, Fig. S6b-d), an obvious fluorescence peak 364 was observed and significantly enhanced in the region with the wavelength at  $\lambda_{Ex}/\lambda_{Em}$ 365 = (320-390 nm)/(430-500 nm) (humic acid intermediates peaks) [57]. However, 366

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, H<sub>2</sub>O and CO<sub>2</sub> [58, 59].

371 To further verify the afore-mentioned results, it was necessary to explore the 372 possible intermediates and analysis the reasonable photodegradation pathway of OTC-HCl. The MS spectra, molecular weights, molecular structural formulas and 373 possible degradation path information of the formed intermed 374 ere depicted in Fig. S7, Table S5 and Fig. 6, respectively. The product 375 m/z = 461.1 was identified as the original OTC-HCl molecule As an electrophilic radical, 376 hydroxyl radicals react with organic compounds my through the reaction of OH 377 addition to double bond, H-abstraction, and lectron transfer. Hydroxyl radicals were 378 dominating active species dur atalytic process. OTC-HCl 1 stems from 379 OH is an aromatic ring and •OH further react with tertiary 380 OTC-HCl by the attack of • on density augment of N in NH<sub>2</sub> group, thus formed 381 amine on account OTC-HCl 2 [61]. CTC-HCl 4 is originated from OTC 2 degradation through the 382 383 dehydroxylation and deamidation reaction. OTC-HCl can also loss an N-methyl to produce OTC-HCl 3 [40]. Intermediate OTC-HCl 3 has two possible degradation 384 pathways. One is to further loss hydroxyl, N-methyl and amide to produce OTC-HCl 385 4. Further degradation of OTC-HCl 4 leads the generation of OTC-HCl 5 via the 386 demethylation reaction, deamination reaction, and addition reaction of the benzene 387 ring. OTC-HCl 5 transform to OTC-HCl 6 through the loss of hydroxyl group. 388

Another is to remove N(CH<sub>3</sub>)H, amide group, hydroxyl group, due and get the intermediate OTC-HCl 7. Since the N(CH<sub>3</sub>)H, hydroxyl group and amide group are easily oxidized, these functional groups can be detached to form OTC-HCl 7. OTC-HCl 7 lost a hydroxyl group and then undergoes ring-opening of benzene ring, formed intermediate OTC-HCl 8. The degradation of OTC-HCl 8 then leads to the generation of OTC-HCl 9 via deacetylation reaction, loss of methyl group and being oxidized [58].



396

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

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 401 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. 402 403 coli. In the photocatalytic process, the inhibition rate of the reaction solution increases 404 during the first 30 min, and then greatly decreases when the irradiation duration 405 exceeds 30 min. Similar results have been reported previously [62-64], and the 406 increase in toxicity might be caused by the generation of additional toxic 407 intermediates of OTC-HCl in the photocatalytic process. However, the toxicity of the reaction solution was drastically eliminated due to min rali 408 tion by further irradiation. Therefore, it was confirmed that the toxicity of 409 action solution could be reduced throughout the degradation process. In addition, the chemical oxygen 410 demand (COD) value of the initial solution me intermediate solution were 411 analyzed according to Wen's research [6. The COD of the original OTC-HCl 412 solution and the reaction solut irradiation) were 46.04 and 18.92 mg/L, 413 respectively. The change in COD value indicates that the photodegradation solution 414 innecuously. Taken together, the above analysis suggests that 415 was easier to be ated BPTCN composite hows good biodegradability and exhibits desirable property in 416 417 toxicity reduction, thereby leading to a great potential for wastewater treatment.

## 418 **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 423 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) 424 aqueous solution does not spontaneously undergo photolysis [66]. The BPTCN 425 exhibits the best photoreduction capacity of Cr(VI) removal (94.71%), while 17.61%, 426 22.49% and 81.59% of Cr(VI) photoreduction was achieved over BPQDs, CN and 427 428 TCN, respectively. The hugely promoted photoreduction ability of BPTCN might be 429 ascribed to the rapid separation and transfer of space carriers caused by the loading of BPQDs on the surface of tubular  $g-C_3N_4$  [67]. From Fig. 430 intensity of the absorption peak of Cr(VI) at 540 nm gradually decreased 431 e irradiation time increases. The inset in Fig. 7b shows that the or of Cr(VI) aqueous solution 432 changed from red to colourless, implying that the oncentration of Cr(VI) has been 433 434 lessened. The experimental data were whed in depth by a pseudo first-order res kinetic model, where  $E_a$  is ln ( appt (Fig. 7c). The apparent Cr(VI) removal 435 rate constants for CN, TCN and IPTCN were 0.00369 min<sup>-1</sup>, 0.0262 min<sup>-1</sup> and 0.0404 436 jourly, the highest  $K_{app}$  for BPTCN was ~10.95 times than min<sup>-1</sup>, respective 437 Ob that of CN. In addition, a comparison of Cr(VI) reductions over various photocatalysts 438 were listed in Table S6. 439

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





Fig. 7. (a) Photocatalytic activities of the obtained for the reduction of Cr(VI) ımp 461 in aqueous solution; (b) Temporal absorp of Cr(VI) with BPTCN catalysts 462 n sp under visible light irradiation; The n (b) is the digital photographs of Cr(VI) 463 nse aqueous solution after react o first-order kinetic fitting curves and the 464 corresponding Kapp va ct of different pH values on Cr(VI) reduction. 465 466 3.5 Degradation r nanism analysis

## 467 **3.5.1 Optical and electrochemical analysis**

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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) 474 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 475 476 and BPQDs [33]. Band gaps  $(E_g)$  of the resultant samples were typically calculated by 477 Tauc method (inset of Fig. 8a) [40]. The sample of TCN had a narrower band gap 478 (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 479 480 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 CLUs ions of CN and 481 TCN were -0.71 and -0.84 eV, respectively. And the energy 482 and structure of TCN was exhibited in Fig. 10. It can be seen from Fig. S1 and Table S7 that the SBET value 483 (15.505 m<sup>2</sup>/g), and the obvious of TCN (28.574  $m^2/g$ ) was 1.84 times that f 484 increase in specific surface area may be due to the unique 1D porous tubular structure. 485 The larger S<sub>BET</sub>, pore size an olume of TCN could provide numerous 486 site, facilitating the charge carrier transfer during the 487 boundaries and more activ However, the  $N_2$  adsorption-desorption isotherms and pore photocatalytic pi 488 size distribution curve of TCN and BPTCN were similar, because loading BPQDs on 489 490 TCN did not change the specific surface area of BPTCN [29]. Relative to TCN, it 491 could be acknowledged that the specific surface area was not the key factor to change the photocatalytic performance of BPTCN. 492

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

496 be caused by the bigger S<sub>BET</sub> [33]. BPTCN displayed a shorten PL lifetime compared to TCN, indicating a nonradiative pathway from the charge transfer across the 497 498 interface (P-C bonds) between TCN and BPQDs [31]. Furthermore, the behavior of 499 photoinduced electron-hole pairs separation and migration were further analyzed by 500 photoluminescence emission spectroscopy. Under the light irradiation of 340 nm 501 wavelength, the sample of CN showed a strong intrinsic luminescence emission peak 502 located at about 470 nm, indicating the high recombination of electron-hole pairs (Fig. 8d). The PL peak decreases dramatically for TCN and BPT N hich manifested 503 lower recombination rate of photogenerated electron-hole 504 1, 72]. The reason for the above results was that the 1D porous tubula structure reduces the diffusion 505 distance of the carriers to the surface, hence effect very separating the efficiency of 506 electron-hole pairs, which was in accordance with TRPL spectroscopy. 507 chemical (PEC) properties of BPTCN, the To verify the enhanced ph 508 transient photocurrent responses for three light on-off cycles were carried out under 509 T31 The saturated photocurrent density of BPTCN (about 510 visible light (Fi 0.225  $\mu$ A cm<sup>-2</sup>) and TCN (about 0.205  $\mu$ A cm<sup>-2</sup>) was bigger than that of CN (about 511 0.15  $\mu$ A cm<sup>-2</sup>), manifesting that the porous tubular structure and introduction of 512 513 BPQDs could facilitate photoinduced charge carriers separation/transport [24, 74]. Furthermore, the resultant catalysts showed reproducible and prompt photocurrent 514 responses upon exposure to simulated solar illumination, which supported that all 515 samples possess outstanding PEC stability. Electrochemical impedance spectra (EIS) 516

517 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 Nyquist 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 performed that the BPTCN possessed excellent PEC properties.



524 Fig. 8. (a) UV-vis diffuse reflectance spectra of samples and (inset graph) band gap
525 of CN and TCN; (b) VB-XPS spectra of CN and TCN; (c, d) Time-resolved PL

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spectra and PL spectra of samples; (e) Photocurrent responses under visible lightirradiation and (f) EIS Nyquist plots for CN, TCN and BPTCN.

## 528 **3.5.2** Radical trapping experiment and ESR test

529 Active species capture experiments and ESR spectroscopy were conducted to 530 identify key reactive species to better understand the photocatalytic mechanism [76]. 531 In this work, the quenchers were EDTA-2Na, TEMPOL and tertiary butanol (TBA), which could assimilate reactive species of  $h^+$ ,  $\bullet O_2^-$ , and  $\bullet OH$ , respectively [77]. From 532 the results of Fig. 9a and Fig. 9b, the main reactive sp cie involved in the 533 photodegradation reaction for BPTCN were  $\bullet O_2^-$  and  $h^+$ . 534 er, the role of •OH cannot be covered either. Moreover, the  $K_{app}$  for OTAHCl degradation were 0.00568, 535 TA-2Na, TEMPOL, and TBA, 0.00266, and 0.0181 min<sup>-1</sup> in the presence of 3 536 respectively. According to formulas 1-3, the relative contributions of  $h^+$ ,  $\bullet O_2^-$ , and 537 •OH to the OTC-HCl removal alated to be 79.42%, 90.36%, and 34.64%, 538 respectively (Fig. 9c). Due to the influence of the convoluted radical chemistry, the 539 total contribution to the photocatalytic system exceeds 100% [34, 78]. Hence, the  $\cdot O_2^-$ 540 and  $h^+$  comprised the primary catalytic mechanisms for OTC-HCl degradation. 541 Noticeably, the ESR spectra was performed to further proved that  $\bullet O_2^-$  and  $\bullet OH$  could 542 be produced during the BPTCN system. As described in Fig. 9d, the four main peaks 543 (1: 1: 1: 1) of  $\bullet O_2^-$  were observed in the obtained samples under the condition of light, 544 whereas no ESR peaks for all samples could be detected in the dark. As expected, the 545 main peaks of the BPTCN were obviously higher than those of CN and TCN. Similar 546 phenomenon was detected in Fig. 9e, strongest ESR spectra with relative intensities of 547

548 1:2:2:1 corresponding to the DMPO-•OH adduct were apparently observed in the
549 case of the BPTCN. This indicates that BPTCN can produce more reactive groups,
550 and the better photocatalytic activity could be attributed to the unique tubular
551 structure and the introduction of BPQDs.



Fig. 9. (a, b) Photocatalytic act e BPTCN for the degradation of OTC-HCl 553 feren 554 under the condition of di quenchers; (c) rate constants for photocatalytic degradation of O 555 he presence of various reactive species scavengers and percent contribution incurred from the corresponding reactive species; ESR spectra 556 of radical adducts tapped by DMPO spin-trapping in BPTCN dispersion in the dark 557 and under visible light irradiation (d) in methanol dispersion for DMPO $-\bullet O_2^-$  and (e) 558 559 in aqueous dispersion for DMPO-•OH.

552

560 Given the aforementioned analysis, a plausible photocatalytic mechanism for 561 OTC-HCl degradation and Cr(VI) reduction over BPTCN can be observed in Fig. 10. 562 The CB and VB potentials of TCN were located at -0.84 eV and +1.67 eV,



- (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
- 587 cycle photostability and electrons transfer.



Fig. 10. Possible photocatavtic mechanism scheme of the carriers separation process
on the interface of RPT/N under visible light irradiation.

591 **4.** Conclusion

588

In conclusion, 0D/1D mixed-dimensional BPTCN nanohybrids was successfully prepared by loading BPQDs of  $\sim 3.32$  nm in size onto the TCN of  $\sim 6-8$  µm 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 598 wastewater could reach 81.05% under visible light irradiation, and its AQE ( $\lambda = 420$ nm) was equal to 0.15%. In this system, the loading of BPQDs on the surface of 599 600 tubular g-C<sub>3</sub>N<sub>4</sub> could result in decreasing recombination of the space charge carriers and more carriers could be used to attack OTC-HCl. Furthermore, DFT calculation 601 602 was applied to deeper study the electronic band structure and strong electronic 603 interaction of obtained materials. This research exposes a promising prospect for the 604 design and synthesis of a variety of metal-free nanomaterials functional in solar-to-chemical energy conversion and environmental remed 605

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