1	Tube wall delamination engineering induces photogenerated carrier separation
2	to achieve photocatalytic performance improvement of tubular $g-C_3N_4$
3	Ting Wu ^{a, 1} , Qingyun He ^{a,1} , Zhifeng Liu ^{a,*} , Binbin Shao ^a , Qinghua Liang ^a , Yuan Pan
4	^a , Jing Huang ^a , Zan Peng ^a , Yang Liu ^a , Chenhui Zhao ^a , Xingzhong Yuan ^a , Lin Tang ^a ,
5	Shanxi Gong ^b .
6	^a College of Environmental Science and Engineering, Hunan University and Key
7	Laboratory of Environmental Biology and Pollution Control (Hunan University),
8	Ministry of Education, Ministry of Education, Changsha 410082, P.R. China
9	^b School of Chemistry and Chemical Engineering, Guangxi University, Nanning
10	530004, PR China
11	
12	* Corresponding authors at:
13	^a College of Environmental Science and Engineering, Hunan University and Key
14	Laboratory of Environmental Biology and Pollution Control (Hunan University),
15	Ministry of Education, Changsha 410082, P.R. China
16	E-mail: zhifengliu@hnu.edu.cn (Z. Liu)

 1 The authors contribute equally to this paper.

18	Abstract: Morphology adjustment is a feasible method to change the
19	physicochemical properties of photocatalysts. The issue that excessively thick tube wall
20	of tubular g-C ₃ N ₄ is not conducive to the electron migration from inside to the surface
21	thus inhibiting the separation of photogenerated carriers has always been ignored.
22	Potassium ions were used to regulate the structure of the tubular supramolecular
23	precursor by breaking hydrogen bonds, thereby promoting the synthesis of delaminated
24	laminar tubular g-C ₃ N ₄ (K-CN), which not only shortened the transfer distance of
25	photogenerated electrons but also provided abundant reaction active sites. Experiments
26	and DFT calculations were combined to reveal the details of the physicochemical
27	properties of K-CN. The photocatalytic capacity of K-CN for tetracycline
28	hydrochloride (TCH) degradation and $\rm H_2O_2$ generation were 83% and 133 $\mu M,$
29	respectively. This work not only synthesized a novel delaminated tubular g-C ₃ N ₄ but
30	also provided a strategy and inspiration for structure and performance optimization for
31	tubular g-C ₃ N ₄ .

Key words: Supramolecular self-assembly, Photocatalysis, delamination, tubular
 g-C₃N₄, DFT calculation

34 **1. Introduction**

The environment and energy are closely related to human life [1, 2]. Protecting the 35 36 ecological environment and promoting new energy production are the permanent goals of human development [3-5]. As one of the most used broad-spectrum antibiotics, 37 tetracycline (TC) has been widely used in the medical industry and animal husbandry 38 [6]. Worryingly, residual antibiotics are discharged into water in large quantities, which 39 may pose a risk of environmental biological distortion [7-9]. Therefore, antibiotic 40 pollution control and remediation should be taken seriously. In addition, the depletion 41 42 of natural resources has become a major threat to human development. As a new liquid solar fuel and a disinfectant, hydrogen peroxide (H₂O₂) has attracted more and more 43 attention [10]. In the recent several years, photocatalysis has been proved as a 44 45 sustainable approach to environmental remediation and energy production due to its use of solar energy [11, 12]. Importantly, developing photocatalysts with stable and high 46 catalytic performance is the key to promoting the application of this technology in 47 48 practice application. Graphitic carbon nitride (g-C₃N₄) due to its ideal band-gap structure, simple synthesis and cheap raw materials has been widely used in 49 photocatalysis field [13-15]. Additionally, unlike the metal-containing semiconductor 50 photocatalysts (e.g., metal sulfides, metal oxides), the non-metallic g-C₃N₄ is prepared 51 52 by calcining at high temperature and composed of strong C-N conjugate bonds, so it is difficult for photogenerated electrons and holes to reduce or oxidize g-C₃N₄ to damage 53 its structure and properties, which lead to a high photocatalytic capacity and 54 photostability of g-C₃N₄ [16-18]. The triazine rings or heptazine rings are connected by 55

56	amino groups to form the g-C ₃ N ₄ plane and the weak van der Waals force traction
57	between the interlayers makes the g-C ₃ N ₄ appear a layered crystal structure, which
58	promotes g-C ₃ N ₄ possess the potential to expose abundant active sites to contact with
59	the target molecules [19, 20]. Nevertheless, due to the rapid photo-generated charges
60	recombination, low specific surface area and low visible light responsiveness, the
61	photocatalytic ability of the initial g-C ₃ N ₄ is so limited [21]. In order to further promote
62	the photocatalytic performance of g-C ₃ N ₄ , many methods have been explored, such as
63	building defects [22], element doping [23-25], heterojunction construction [15, 26-29],
64	etc. In addition, the crystallinity, morphology and size also affect the physical and
65	chemical properties of the materials [18, 30, 31]. Therefore, constructing g-C ₃ N ₄ with
66	different morphologies is another effective method to promote its physicochemical
67	properties. To date, the zero-dimensional quantum dots [32], one-dimensional
68	nanofibers and nanotubes[33], two-dimensional nanosheets [34], three-dimensional
69	nanospheres and nanoflower [35] have been reported. However, on account of the easy
70	agglomeration of quantum dots, solid structure of nanofibers and nanowires, as well as
71	easy overlap of nanosheets, tubular structure is considered to be the ideal morphology
72	of g-C ₃ N ₄ due to its large exposure surface area and abundant active sites, which is
73	beneficial to improve photocatalytic efficiency [36]. Although a large number of reports
74	on the synthesis of tubular g-C ₃ N ₄ have been published, such as template method [37],
75	thermal polymerization [36, 38], and self-assembly [39] etc. However, due to the harsh
76	synthesis conditions, tedious steps and difficult operation, the development of these
77	method was slow [40, 41]. For example, Ge et al. assisted melamine polymerization

with HNO₃ and HIO₃ to form g-C₃N₄ tube, in which the mixed acid were required to 78 affect the hydrolysis and self-assembly process of melamine to achieve morphological 79 80 adjustment [42]. And Cao et al. used H₂SO₄ to induce melamine to produce a melaminecyanourate supramolecule that self-assembled to form a tubular g-C₃N₄ precursor. 81 Besides, combining some other materials such cyanic acid, phosphoric acid, boric acid 82 and urea etc. with melamine to achieve the formation of tubular morphology were also 83 reported [33, 39, 43, 44]. Nevertheless, a multi-component system often increases the 84 complexity of the operation. Although numerous studies on tubular g-C₃N₄ have been 85 86 reported, the shortcoming that the highly stacking of polymeric layers in tube wall inhibiting the separation of photogenerated electrons has always been neglected for a 87 long time. Despite 2D thin g-C₃N₄ nanosheets have been prepared by chemical or 88 89 physical exfoliation of bulk g-C₃N₄ [45, 46], the harsh reaction conditions and low yield limit the widespread use of these methods. Then due to the difficulty of maintaining the 90 tubular structure under the highly destructive chemical and physical mechanical action, 91 92 there are few reports on the exfoliation of tubular g-C₃N₄.

Apparently, it is necessary to find a safe and simple method to overcome the above drawbacks with the purpose to reduce the degree of polymeric layers stacking while ensuring the integrity of the tubular structure, so as to improve the separation efficiency of photogenerated carriers of tubular g-C₃N₄. Hydrothermal treatment of solely melamine would partially hydrolysis to yield melamine and cyanuric acid, which would self-assemble though highly saturated and directional hydrogen bonding to obtain tubular supramolecular precursors [47-49]. The relatively weak hydrogen bond

structure in the supramolecular precursors provides the possibility for the structural 100 adjustment of tubular g-C₃N₄ tube wall. In recently, the introduction of potassium ions 101 with large atomic radius would change the interlayer spacing of g-C₃N₄ have been 102 reported. For example, Song et al. introduced K ions into the heptazine ring space to 103 hinder the accumulation of heptazine rings, thus to obtain g-C₃N₄ nanosheets with 104 increased interlayer spacing [50]. Xiong et al. also proved that with the assistance of 105 potassium ions, the spacing of the prepared g-C₃N₄ layers increased due to the lattice 106 expansion [51, 52]. However, in the direct thermal polymerization, the prepared $g-C_3N_4$ 107 108 still presented a highly stacked block structure.

Herein, inspired by the characteristics mentioned above, a method to synthesize 109 delaminated tubular g-C₃N₄ by potassium ions regulated supramolecular precursors 110 111 firstly and followed thermal polymerization was designed. In order to simulate the effect of the introduced potassium atoms on K-CN, the density functional theory (DFT) 112 calculation and a series of experiments were carried out to deeply reveal the reasons for 113 114 the improvement of photocatalytic performance. This work explored a mild method for synthesizing a novel delaminated tubular g-C₃N₄ through potassium ions regulated 115 supramolecular self-assembly and thermal polymerization. And the influence of 116 potassium ions on the growth process and structure of K-CN was discussed. Then the 117 application of the prepared K-CN in environmental remediation and energy production 118 was studied. This study provided a reference for the development of thin-walled tubular 119 120 g-C₃N₄ with high photocatalytic performance.

121

122 **2.** Experimental section

123 2.1. Catalyst preparation

All the chemicals used in this work were purchased from Sinopharm Chemical 124 Reagent Co., Ltd. (PR China). The reagent purity was AR grade and used without 125 further purification. In a typical process, the K-CN was synthesized firstly though a 126 hydrothermal treatment that 10 mmol melamine was added to 80 mL distilled water and 127 heated at 80 °C for 30 min to obtain a clear solution, and then a certain amount of 128 potassium bromide (KBr, 1 mmol, 3 mmol, 5 mmol, 10 mmol) was added to the above 129 130 solution and continued to heat for another 30 min. Then the mixed solution was transferred to a 100 mL autoclave and hydrothermally heated at 180 °C for 10 h. 131 Collecting the recrystallized solids by filtering and dried at 60 °C for 12 h. The soft and 132 133 white crystal was put into a crucible and calcined at 550 °C under the protection of nitrogen for 2 h at a heating rate of 5 °C min⁻¹ in a tube furnace. The as-prepared 134 samples were named as K-CN-1, K-CN-2, K-CN-3 and K-CN-4, respectively. The 135 synthesis process of KOCN (tubular g-C3N4 regulated by KHCO₃) and BCN (tubular 136 g-C₃N₄ regulated by NH₄Br) was the same as that of K-CN but with different structural 137 regulators. KOCN and BCN used 3 mmol KHCO3 and 3 mmol NH4Br as the regulator, 138 respectively. The TCN was synthesized consistent with K-CN but without introducing 139 KBr. As for CN, 5 g melamine was directly calcined in the same conditions as K-CN. 140 The formation mechanisms of TCN and K-CN were illustrated as Scheme 1. 141 142

143 2.2. Characterization

144	The powder X-ray diffraction (XRD) was tested by a Bruker D8 advanced X-ray
145	diffractometer with Cu-K α radiation (λ =0.15406 nm). The Fourier Transform Infrared
146	(FTIR) spectra was obtained by an IRAffinity-1 spectrometer (Shimadzu, Japan) with
147	KBr pellet method. The UV-vis diffuse reflectance spectrum (DRS) was measured by
148	UV-vis spectrophotometer (Lambda 750, Perkin-Elmer). The morphology was
149	observed by scanning electron microscope (SEM, Zeiss HD) and transmission electron
150	microscope (TEM, Titan G260-300). Photoluminescence (PL) spectra was recorded by
151	a fluorescence spectrometer (Hitachi F-7000, Japan) with the excitation wavelength at
152	300nm. The X-ray photoelectron spectroscopy (XPS) was performed by a spectrometer
153	(Thermo Scientific K-Alpha). The Brunauer-Emmett-Teller (BET) specific surface
154	areas and pore-size distribution were collected by an automated gas sorption instrument
155	(Micrometrics ASAP 2420, USA). The photocurrent and electrochemical impedance
156	spectroscopy (EIS) were recorded by electrochemical analyzer (CHI 660C, China) with
157	a three electrodes system. The electron spin resonance (ESR) single was detected by a
158	X-band Elexsys system spectrometer (Bruker, Germany) with 5, 5-dimethyl-1-
159	pyrroline N-oxide (DMPO) as a trapping agent. The total organic carbon (TOC) was
160	determined by a Total Organic Carbon Analyzer (TOC-L shimazu, Japan) to analyze
161	the mineralization rate of pollutants.

162

163 2.3. DFT Calculations

The DFT calculations were performed on the Material Studio 8.0 software (MS).Firstly, the molecular model was optimized by Perdew-Burke-Ernzerhof (PBE) in

166 generalized gradient approximation (GGA). In order to ensure the accuracy of 167 electronic properties, the density of state (DOS), and the electron localization function 168 (ELF) were calculated by HSE06 hybrid functional. The energy cut-off was set to 435.4 169 eV and 340 eV in geometry optimization and electronic calculation process, 170 respectively. The convergence criteria for the residual force was set to $2.0 \times e^{-6}$ eV atom⁻¹ 171 ¹ in the structure relaxation process. The Brillouin zone was sampled by a $3 \times 2 \times 1$ K-172 point grid. The

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174 2.4. Photocatalytic performance evaluation

The photocatalytic performance was evaluated by degradation of TCH and 175 production of H₂O₂. The photocatalysis experiment was conducted under a 300 W 176 177 xenon lamp, through a 420 nm cut-off filter to intercept visible light. Typically, as for TCH degradation, in a quartz glass reactor, 20 mg photocatalyst was added to 50 mL 178 TCH solution with a concentration of 10 mg L⁻¹, pH=4.86. Firstly, a dark treatment was 179 180 performed for 30 min before the light radiation to reach the adsorption-desorption equilibrium. Then, the photocatalytic reaction was carried out for 1.5 h under the visible 181 light irradiation (λ >420 nm), the suspension was taken out in a 10 min interval and pass 182 through a 0.45 µm membrane filter to obtain clear solution. The concentration of TCH 183 solution was determined by a UV-vis spectrophotometer at the absorption wavelength 184 of 357 nm. 185

Photocatalytic production of H₂O₂ was carried out by adding 20 mg photocatalyst
into 40 mL distilled water, and 10 mL isopropyl alcohol was used as sacrificial agent

8

of holes. The pH of the reactor suspension was 6. Before photocatalytic reaction, the 188 suspension was stirred in the dark for 30 min with bubbling O₂ simultaneously to reach 189 the equilibrium of O₂ adsorption-desorption. Then the production of H₂O₂ was also 190 performed under a 300W xenon lamp for 1 h. The photocatalytic capacity of H₂O₂ 191 production was assessed by measuring the production of H₂O₂ at 10 mins intervals. The 192 concentration of H₂O₂ was measured by iodimetry, reported as [53], that was, 3 mL 193 reaction solution was taken and filtered through 0.45 µm membrane, then 1 mL 194 potassium hydrogen phthalate (C8H5KO4) solution at a concentration of 0.1 mol L⁻¹ and 195 1 mL potassium iodide (KI) solution at a concentration of 0.4 mol L⁻¹ were added into 196 the solution and left standing for 30 min for color development $(H_2O_2+3I^++2H^+\rightarrow$ 197 I_3^+ 2H₂O). The concentration of I_3^- was detected by a UV-vis spectrophotometer at the 198 199 wavelength of 350 nm. The whole experiment was carried out at a settled temperature of 25±3 °C to prevent the produced H₂O₂ from decomposition. The decomposition 200 behavior of H₂O₂ was studied by decomposing H₂O₂ with an initial concentration of 201 202 0.5 mM.

203

204 **3. Results and discussions**

205 3.1. Morphology characteristic

The morphology of the synthesized photocatalysts were characterized by SEM and TEM. As shown in Fig. 1a, the SEM images of as-prepared CN by calcination of melamine showed a typically thick block morphology and the TCN displayed a regular tubular structure (Fig.1b). Besides, the diameter and length of TCN and K-CN-2 were

210	about $2\sim3$ µm and $15\sim30$ µm, respectively. Distinctively, shown as Fig.1c and Fig.
211	S1a, K-CN-2 had an exfoliated and delaminated tube wall with thickness of 15nm,
212	which might result in K-CN-2 exposed bigger surface area than that of CN and TCN.
213	And the delaminated and thin tube wall shortened the transfer distance of
214	photogenerated electrons, which suppressed the recombination of photo-generated
215	carriers, thus lead to the promotion of photocatalytic properties. Correspondingly,
216	shown as Fig.1e and Fig.1f, TEM images further demonstrated that TCN and K-CN-2
217	had hollow tubular structures, and K-CN-2 possessed thinner tube walls than TCN,
218	which was inferred from the more transparent TEM images of K-CN-2 than TCN (Fig.
219	S1b). The elemental mapping showed that K-CN-2 contained only a very small amount
220	of potassium element, from which it could be inferred that potassium ions mainly
221	played a role in structural adjustment rather than doping in the prepared K-CN (Fig.1g).
222	In order to more clearly understand the regulation mechanism of potassium ions
223	on the structure of K-CN, tubular precursors treated with different concentrations of
224	potassium ions were investigated. In the absence of KBr, the end of the tubular
225	precursors presented a smooth and neat cross-section (Fig. S2a). After the introduction
226	of KBr, as the concentration of KBr increased, the ends of the tubular precursor were
227	gradually cut into strips (Fig. S2b-d), which might be due to the destruction of the
228	hydrogen bond between the melamine and cyanuric acid in the tubular precursor. In
229	order to explore the reasons for the destruction of hydrogen bonds, KHCO3 and NH4Br
230	were also used to adjust the growth process of the tubular precursors, respectively. The
231	result showed that the cross section of the tubular precursor treated by 3 mmol KHCO ₃

also showed strip-like cracks, which was the same as that treated with 3 mmol KBr (Fig. 232 S2e), while the cross section of the tubular precursor treated by 3 mmol NH₄Br was 233 234 relatively flat (Fig. S2f), indicating that the hydrogen bond was destructed by potassium ions. In addition, SEM (Fig. S2a'-d') also showed that with the increase of potassium 235 ions concentration, the degree of wall delamination was increased. The reason might 236 attribute to that, the high concentration of potassium ions would promote the destruction 237 of hydrogen bonds between melamine and cyanic acid molecules and lead to changes 238 in the supramolecular structure. Ascribing to structural destruction of the 239 240 supramolecular precursor, the highly ordered polycondensation of the tubular precursor was inhibited during the thermal polymerization process. At the same time, the adjacent 241 interleaved supramolecular layers polymerize with each other. Thus, a large degree of 242 243 delamination of the tube wall was occurred. The SEM of KOCN (Fig. S2e') showed that KOCN possessed a similar degree of delamination as K-CN-2 due to the same 244 content of potassium ion content was used for structure adjustment. The Fig. S2f 245 246 showed that the prepared BCN possessed a tubular structure with porous surface but no delamination, which further proved that the delamination of tubular g-C₃N₄ wall was 247 caused by potassium ions. 248

Accordingly, it could be speculated that the hydrothermal treatment process induced the formation of tubular structure. And the introducing of potassium ion induced the exfoliation and delamination of tube wall in K-CN-2, resulting in a thinwalled multilayer tubular structure, which was beneficial to increase the specific surface area of the prepared photocatalyst. The nitrogen adsorption–desorption

isotherms was used to provide a favorable evidence for this phenomenon. Shown as Fig. 254 2a, compared with CN, the specific surface area of TCN and K-CN-2 were greatly 255 256 increased. And attributing to the delamination tube wall, K-CN-2 possessed the largest porosity and specific surface area that of 0.27 cm³g⁻¹ and 37.59 m²g⁻¹, respectively, 257 higher than TCN and nearly three times that of CN. The type IV isothermal desorption 258 curve and the H3 type hysteresis ring indicated that K-CN-2 was mainly a mesoporous 259 structure, which originated from the slit holes formed by the stacking of g-C₃N₄ layers 260 in the tube walls. The BJH pore size distribution curve inset in Fig. 2b also showed 261 262 strong peaks at 22-29 nm, further indicating that the prepared samples mainly contained mesoporous structure, which was benefited to expose more active sites and improve 263 photocatalytic performance. 264

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266 3.2. Crystal structure

Firstly, in order to understand the growth process of the tubular supramolecular 267 precursor, the tubular precursors were preliminarily explored by XRD. Shown as Fig. 268 S3, with the increase of hydrothermal treatment time, the XRD diffraction peak 269 intensity of the precursors were gradually decreased, and some new diffraction peaks 270 were appeared at low diffraction angles ($2\theta \approx 10^{\circ}$ -11°), indicating that melamine was 271 partially hydrolyzed in the hydrothermal process. The new peaks came from the 272 intermediate formed by melamine and its hydrolyzed product. After the potassium ions 273 introducing, the peaks at $2\theta \approx 13^{\circ}$ and 17.6° completely disappeared, which proved that 274 potassium ions affected the growth process and regulated the crystal structure of the 275

tubular g-C₃N₄ precursor. Then, the crystal structure of the prepared CN, TCN and K-276 CN were also analyzed by XRD. The changes of the crystal structure before and after 277 278 the introduction of potassium ions and the influence of potassium ions content on the crystal structure were analyzed. In the Fig. 2c, all the prepared samples possessed the 279 typical (100) and (002) lattice plane, corresponding to 20 located at 12.95° and 27.53°, 280 which corresponded to the in-plane continuous extension of tri-s-triazine units and 281 stacking of π -conjugated graphitic monolayers, respectively [37]. Interestingly, 282 compared with the initial CN, the diffraction peak of the (100) crystal plane of TCN 283 284 and K-CN slightly shifted to the left. But there was no obvious further shift after potassium ions introducing. On the contrary, the (002) crystal plane diffraction peak of 285 TCN has no obvious shift while K-CN gradually shift to right with the increase of 286 287 potassium ion dosage. According to the Bragg formula, $2d\sin\theta = n\lambda$ (d is lattice spacing, θ is diffraction angle, n is diffraction order, generally 1, λ is incident wavelength), the 288 spacing distance between (100) lattice plane calculated as $d_{CN} = 0.68$ nm, $d_{TCN} = d_{K-CN-1}$ 289 290 $_2 \approx 0.69$ nm. It could be inferred that hydrothermal process lead to a wider spacing of the in-plane heptazine ring unites, which caused by the irregular alignment of heptazine 291 rings due to hydrogen bond breakage [54, 55]. Besides, the stack spacing of the K-CN 292 monolayer in (002) lattice plane was calculated as $d_{CN} = d_{TCN} \approx 0.324$ nm, $d_{K-CN-2} =$ 293 0.322 nm, proving that potassium ions adjustment decreased the stack spacing of the 294 K-CN monolayer, which ascribed to that potassium ions could promote the 295 polymerization of supramolecular precursors and facilitate lattice remodeling [56]. 296 Under the conditions that potassium ions promoted thermal polymerization and 297

hydrogen bond destruction, thermal polymerization of supramolecular precursor not
only occurred in a single supramolecular layer, but also happened between adjacent and
intersecting supramolecular layers. This would lead to part of the g-C₃N₄ nanosheets to
deviate from its original position, thereby realizing the delamination of the tube wall. A
concise schematic diagram on potassium ion regulated the structure of tubular g-C₃N₄
was displayed as Scheme S1.

The results of FTIR also proved that the hydrothermal treatment and potassium 304 regulation affected the structure of g-C₃N₄. As shown in Fig. 2d, the absorption bands 305 at 806 cm⁻¹ representing the breathing model of tri-s-triazine unit [57]. And the several 306 absorption peaks around 1080-1680 cm⁻¹ were the characteristic absorption bands of 307 the stretching vibration of N-C=N heterocycle [58]. The signal at 1239 cm⁻¹, 1319 cm⁻¹ 308 ¹ and 1408 cm⁻¹ corresponded to the stretching vibration of C-NH-C and the absorption 309 band at 1640 cm⁻¹, 1574 cm⁻¹ represented the C=N stretching vibration [59-61]. 310 Compared with CN, the absorption bands of the tri-s-triazine ring and N-C=N 311 heterocycle in TCN were enhanced. This was corresponding to the XRD results that 312 hydrothermal treatment led to the increase of lattice spacing of (100) plane, that the 313 greater the lattice spacing, the larger the stretching vibration of N-C=N. The further 314 increased absorption band of N-C=N in K-CN might be ascribed to the attractive 315 interaction between the residual potassium ions located in the g-C₃N₄ pore cage and N 316 atom in N-C=N heterocycle [56]. The intense band at 3150-3180 cm⁻¹ associated with 317 the stretches of the N-H from unpolymerized amino groups and O-H bond from 318 adsorbed H₂O molecules [62]. The enhanced absorption peak of TCN was caused by 319

the destruction of the periodic arrangement of the heptazine rings, exposing more terminal amino groups. And the high absorption intensity in K-CN might come from the delamination of the tube wall, which provided a larger specific surface area and facilitated the H₂O adsorption. Analogously, the new signal peak in TCN and K-CN at 2372 cm⁻¹ was derived from the adsorbed CO₂ molecules in the tubular porous structure [63].

The XPS was performed to understand the surface chemical state of the prepared 326 samples. The binding energy was corrected by the standard C peak that was 284.8 eV. 327 328 Fig. 3a showed the survey spectra contained only C, N and O elements, without K element, which might be due to the low content of potassium. The O 1s might come 329 from the absorbed H₂O and CO₂ molecules [60, 64]. The high-resolution XPS spectra 330 331 of N 1s was shown as Fig. 3b. Three main peaks at 398.6 eV, 400 eV, 401.2 eV represented sp² hybridized nitrogen in C-N=C, bridged nitrogen in N-(C)3 and C-NH_x 332 functional groups, respectively. The peak at 404.4 eV assigned to π -excitation [64]. It 333 was worth noting that the XPS results represent the information at the thickness of 3-5 334 nm on the surface of the material. Compared with CN, the N 1s peaks of TCN and K-335 CN-2 were greatly improved due to the larger exposed surface area in tubular structure 336 [64]. However, the decreased peak intensity of K-CN-2 relative to TCN was attributed 337 to the better crystallinity of the K-CN-2 and the reduced surface exposed atoms, which 338 was consistent with the results of XRD. Same as N 1s, the intensity of the C 1s peaks 339 changed in the same way. Shown as Fig. 3c, the band energy at 284.8 eV was the 340 standard carbon peak that was sp² hybridized C-C bonds. The peaks at 288.2 eV and 341

286.2 eV corresponded to (N)2-C=N in C-N heterocycle and edge C atom in the C-NH₂
groups, respectively. The peaks at 288.6 eV and 293.8 eV assigned to C-O bond of
absorbed CO₂ molecules and π-excitation.

Compared to CN and TCN, the N 1s binding energy at 398.5 eV and C 1s binding 345 energy at 288.0 eV of K-CN-2 shifted to a lower position, which due to the electron 346 cloud of residual potassium atoms covered on the surface of surrounding N and C atoms, 347 enhancing the shielding effect, so as to result in a decrease of binding energy [65]. To 348 further clarify the role of potassium atoms in K-CN, the high-resolution XPS spectra of 349 350 K 2p was conducted to investigate the chemical state of potassium. Shown as Fig. 3d, two detected peaks at 293.9 eV and 292.9 eV corresponded to the energy loss of C 1s 351 and electron orbits of K 2p_{3/2}, indicated the formation of the K-N bond [63]. Therefore, 352 353 it could be seen that another reason for the decrease in the binding energy of N 1s was that the electrons of potassium atom transferred to nitrogen atoms. However, the peak 354 of Br 3d was almost undetectable due to the low content (Fig. 3f). Combining XRD 355 analysis and XPS results, it could be inferred that the residual potassium atoms tended 356 to embed in the nitrogen pot of g-C₃N₄ though K-N bonds. This was profited from that 357 the lone pairs electrons of nitrogen atoms in the nitrogen pot were conducive to the 358 bonding of K-N [66]. In addition, the large spacing of (100) crystal plane (~0.69 nm), 359 was large enough to accommodate potassium atoms with a size of 0.275 nm. 360

The DFT calculation was also used to predict the effect of K and Br on the electronic structure of $g-C_3N_4$, and the three-dimensional models of DFT calculation were shown as Fig. S4. The electron localization function (ELF) can be used to describe the

364	delocalization and immobilization of electrons, which is an effective theoretical tool for
365	analyzing the types of chemical bonds. The value of ELF is defined between 0-1, where
366	ELF = 0 represents vacuum or a region between two atomic orbitals, usually
367	corresponding to ionic bonds. $ELF = 0.5$ represents the homogeneous electron gas of
368	the metal, corresponding to the metal bond. $ELF = 1$ represents a high degree of
369	electronic localization, corresponding to a covalent bond [67]. Shown as Fig. 4a, the
370	high degree of electron localization in the nitrogen pot was derived from the lone pair
371	electrons of N atom. In g-C ₃ N ₄ , the valence electrons mainly exist on N atoms, and the
372	higher electrophilic of N atoms than C atoms made N atom show anion properties [51].
373	After the introduction of K atoms, they were embedded in the nitrogen pot by
374	electrostatic coulomb action, thus the lone pair electrons arrangement of N was changed,
375	as shown in Fig. 4b. And there was an ELF minimum region between K and adjacent
376	N atoms, where the charge density was almost 0, indicating the existence of ionic
377	interaction between K-N [51]. In addition, because the atomic radius of Br was almost
378	twice that of N and C, it was difficult to replace the N and C atoms in g-C ₃ N ₄ . Therefore,
379	Br atoms embedded in nitrogen pot was simulated and the structure was optimized. The
380	result showed that the presence of Br lead to the deformation of the nitrogen pot, which
381	was caused by the repulsion between the N atoms in nitrogen pot and Br atoms (Fig.
382	4c). Besides, due to the change of the g-C ₃ N ₄ structure, the local electron configuration
383	was changed (Fig. 4c). Then the work function proved that the presence of K and Br
384	atoms would reduce the energy required for electrons to escape from the material bulk
385	to the surface. Displayed as Fig. 4d-f, the work function (WF) of CN, K-CN and BCN

was 4.86, 3.06 and 4.03 eV, respectively. The smaller the work function of the material, 386 the weaker the binding force for electrons to escape from the potential well to the 387 surface, making it easier for the electrons to separation and migrate to photocatalyst 388 surface. The partial density of states (PDOS) showed that the valence band (VB) of CN 389 was mainly consisted of N 2p orbital, and the conduction band (CB) was consisted by 390 C 2p and N 2p orbital (Fig. 4g). Slightly different, in addition to C 2p, N 2p likewise 391 contributed to the CB of K-CN. Besides, the K 2p also played a very important role on 392 the CB structure due to the exist of K-N bond and electron transfer from K to N atoms, 393 394 which leaded to the fermi level of K-CN moved to the lower energy (Fig. 4h). And the CB of K-CN was staggered with the fermi energy level, indicating that K-CN had a 395 metallic band structure, which favored the separation of photogenerated charges [59]. 396 397 In addition, Br 2p contributed to both CB and VB of g-C₃N₄, and mainly acted on VB (Fig. 4i). According to the calculation results of DFT, it was shown that the presence of 398 K and Br would change the electronic structure of g-C₃N₄. 399

400

401 3.3. Optical characteristics

The photocatalytic performance of the photocatalyst is affected by many factors in the same time. Light absorption capacity is a prerequisite for photocatalysis. The light absorption capacity of the prepared materials was tested by UV-vis DRS. Presented as Fig. 5a, the absorption edges of TCN and K-CN (~ 475 nm) were slightly red-shifted compared to CN (~ 462 nm), indicating that the light response ranges of TCN and K-CN were further extended to the visible light region, allowing a wider range of visible

light can be utilized, which was advantageous to the enhancement of photocatalytic 408 performance. In addition, due to the existence of abundant mesoporous structures in 409 410 tubular samples, the incident light was diffusely reflected multiple times, increasing light absorption capacity [68]. The light absorption capacity of the K-CN samples were 411 slightly weaker than that of the TCN, which might be caused by the narrowed layer 412 spacing of K-CN and the orderly arrangement of the heptazine rings, resulting in the 413 weakening of internal diffuse reflection. The band gap of prepared samples was 414 calculated by transformed Kubelka-Munk function (Eq. (1)) [69]: 415

416
$$\alpha hv = A(hv - E_g)^{n/2}$$
 (1)

a, h, v and A represent absorption coefficient, Planck constant, frequency of incident 417 light and a constant, respectively. E_{g} is the band gap energy of the prepared samples 418 419 and n depends on the type of semiconductor, that direct bandgap semiconductor, n = 4, indirect bandgap semiconductor, n=1. Due to g-C₃N₄ is indirect bandgap semiconductor, 420 n=1 is carried out to calculate the band gap [70]. The calculation result showed that the 421 band gap of CN and TCN were 2.60 eV and 2.43 eV, respectively. And the band gap of 422 K-CN-2 was between CN and TCN, that around 2.51 eV (inset in Fig. 5a). The potential 423 of CB and VB is the main factor to determine the redox ability of photocatalyst. 424 According to the XPS-VB spectra (Fig. 5b) and the Eq. (2) [53]: 425

426
$$E_{\rm NHE}/{\rm V}=\varphi+E_{\rm VB-XPS}-4.44$$
 (2)

That 4.44 and φ (4.2 eV) correspond to the vacuum level and electron work function of the XPS analyzer, respectively; *E*_{NHE}: normal hydrogen electrode potential. The top of VB potential (*E*_{VB}) of CN, TCN and K-CN-2 were calculated to 1.53, 1.39 and 1.44 eV 430 (vs NHE), respectively. Combined with the E_g , the bottom of CB potential (E_{CB}) could 431 be speculated as -1.07, -1.04 and -1.07 eV (vs NHE), respectively. Besides, VB-XPS 432 spectra of the prepared samples also represented the potential difference between E_{VB} 433 and Fermi level (E_F) [71]. Then the E_F value could be obtained according to the Eq. (3):

$$E_{\rm F} = E_{\rm VB} - E_{\rm VB-XPS} \qquad (3)$$

Therefore, the E_F of CN, TCN and K-CN-2 matched to -0.15, -0.24, and -0.33 eV, 435 respectively. Fig. 5c displayed the detail energy band potential distribution, that there 436 was only a slight change in the value of E_{VB} , while the E_{CB} of TCN showed an obvious 437 438 upward shift compared to CN, indicating that the change from the block to the tube mainly affected the valence band potential. The E_{CB} of K-CN-2 was located between 439 CN and TCN proving that potassium atoms has influence on the electronic structure of 440 441 g-C₃N₄, which might result from the change of electron distribution on the C-N heterocyclic ring [55]. In addition, the E_F level of TCN was higher than that of CN and 442 continued to increase after potassium regulation, further indicating that both the 443 444 morphological structure change and potassium regulation could lead to the change of electronic structure. 445

PL spectrum was used to evaluate the recombination efficiency of photogenerated electrons (e^{-}) and holes (h^{+}) at excitation wavelength of 320 nm (Fig. 5d). CN exhibited the strongest emission peak at 463 nm wavelength, while the emission intensity of TCN and K-CN-2 was significantly decreased, which due to the tubular structure could lead to the electron directional transfer and thus reduce the electron-hole pairs recombination [72]. Furthermore, since the tube wall of K-CN was exfoliated and delaminated to form a multilayer and thin tube wall, the distance of photogenerated carriers transferred from
the interior to the surface was shortened. Therefore, the recombination of
photogenerated electron-hole pairs was inhibited effectively and led to the lowest PL
emission peak of K-CN-2 [44]. In addition, a small amount of K ions embedded in the
K-CN plane played an important role of electron channels [52], which further inhibited
the recombination of photo-generated charges.

The electrochemical performance is another major factor affecting the 458 photocatalytic capacity, which reveals the efficiency of photogenerated carrier 459 excitation and transmission. According to the Nyquist plots of electrochemical 460 impedance Spectra (EIS) (Fig. 6a), CN had a minimum semicircle radius, while the arc 461 radius of tubular samples significantly increased. Indicating that tubular structure had 462 463 a larger impedance than the bulk CN. Frustratingly, the increase of impedance would inhibit the interfacial electron transport, which was not conducive to the improvement 464 of photocatalytic efficiency. Transient photocurrent response spectra (TPR) of the 465 samples were also tested at a 20 s on/off cycle to investigate the excitation 466 characteristics of photogenerated electrons (Fig. 6b). Due to the influence of material 467 impedance, the photocurrent showed a corresponding phenomenon, that was, CN 468 presented higher photocurrent intensity than TCN and K-CN-2. The results of EIS and 469 TPR were inconsistent with the theoretical simulation. The possible reason was that in 470 DFT calculation, the calculation models of CN and K-CN were both based on single-471 layer g-C₃N₄, while in the actual synthesized materials, the bulk CN and tubular K-CN 472 showed differences in their morphology and crystallinity, resulting in deviation between 473

the results of calculation and experimental. In addition, the electrochemical 474 characteristics were related to the thickness of the electrode. The greater the thickness, 475 476 the smaller the charge-transfer resistance, corresponding to a low EIS intensity [73, 74]. During the preparation of electrode materials, the bulk CN had the largest particle 477 thickness, which made CN had the smallest charge-transfer resistance. Similarly, the 478 tube wall structure of TCN was thicker than K-CN, and thus exhibited a smaller charge-479 transfer resistance than K-CN. Therefore, K-CN exhibited the largest charge-transfer 480 resistance and showed the largest EIS intensity. Correspondingly, K-CN showed the 481 482 smallest TPR intensity. This indicated that the morphology had an important effect on the electrochemical performance of the material. Although the photochemical property 483 test revealed that TCN and K-CN-2 had low photogenerated electron-hole pairs 484 485 separation and transfer ability, the photocatalytic performance of TCN and K-CN-2 cannot be evaluated due to their photocatalytic performance were determined by 486 multiple factors. 487

488

489 3.4 Photocatalysis experiment

The photoelectrochemical performance test results revealed the complexity of the factors that affect the photocatalyst performance. In order to understand the actual photocatalytic capability of the as-prepared samples, a series of photocatalytic capability tests was conducted, including the degradation of organic pollutants TCH and production of emerging green energy H₂O₂.

The photocatalytic degradation efficiency of the prepared samples was shown in

22

Fig. 7a. The degradation ability was ordered as K-CN-2 > K-CN-1 > K-CN-3 > TCN > 496 CN. Concretely, TCH was degraded 51% by using bulk CN after 1.5 h of visible light 497 498 irradiation, and the degradation efficiency was significantly improved by using TCN and K-CN. The K-CN-2 showed the optimum degradation capacity, up to 83%, which 499 was 32% and 10% higher than CN and TCN, respectively. The outstanding degradation 500 rate was resulting from the strong visible light absorption capacity, large specific 501 surface area and low electron-hole recombination efficiency. Then the total organic 502 carbon (TOC) test was used to reveal the organic molecule mineralization ability of CN, 503 504 TCN and K-CN-2 (Fig.7b). The result also demonstrated that K-CN-2 possessed the maximum TCH mineralization efficiency (80.6%), while CN and TCN showed 505 relatively low mineralization efficiency that of 44.4% and 67.8%, respectively, which 506 507 further confirmed a strong photocatalytic property of K-CN-2.

In addition, the environmental adaptability and reusability of photocatalysts are an 508 important index to evaluate the properties of photocatalysts. In the actual water 509 environment, the concentration of pollutants is usually variable. Therefore, the 510 photocatalytic efficiency was explored under different concentration gradients (5, 10, 511 20, 30 mg/L). The result showed that, the degradation efficiency was decreased with 512 the increasing of TCH concentrations (Fig. 7c). The possible reason can be attributed 513 to the limited catalytic active sites and high concentration of pollutant molecules 514 hindering the light absorption of the photocatalyst. Besides, in the natural water 515 environment, a variety of anionic electrolytes are commonly found, which may have 516 impacts on the performance of the photocatalyst. Several representative anions 517

including HCO3⁻, SO4²⁻, NO3⁻ and Cl⁻ were selected to investigate the effect on 518 degradation of TCH. The 5 mM NaHCO₃, Na₂SO₄, NaNO₃ and NaCl were used as 519 sources to provide related anions. Shown as Fig. 7d, SO₄²⁻, NO₃⁻ and Cl⁻ has little effect 520 on the degradation of TCH. Differently, in the system containing HCO₃, the reaction 521 rate increased significantly during the first 15 minutes, and the reaction rate remained 522 almost stagnant during the subsequent degradation process. The possible reason for the 523 increased degradation rate was that HCO3⁻ can react with ·OH to produce ·CO3⁻ radical 524 (Eq. (4)), which played an important role in the degradation of TCH [75]. 525 526 Although CO_3^- has a much lower oxidizing capacity than OH, but it has a longer lifetime. However, due to the low oxidation potential of $\cdot CO_3^-$, TCH could not be 527 mineralized and a large number of intermediate products were attached to the 528 529 photocatalyst, resulting in a stagnant state of the later reaction.

530 $HCO_3^- + \cdot OH \rightarrow \cdot CO_3^- + H_2O$

PH is an important factor affecting the performance of photocatalyst, therefore, 531 532 the degradation experiments under different pH conditions (3, 5, 7, 9, 11) were carried out. The results showed that the prepared samples maintained good photocatalytic 533 performance under a wide pH range (Fig.7e). At the same time, the reusing experiment 534 showed only 7% reducing of photocatalytic degradation ability after four times reusing 535 (Fig. 7f). The SEM of K-CN-2 after four cycles TCH degradation showed no obvious 536 structural damage (Fig. S5a) and the XRD also showed a slight decrease in crystallinity 537 (Fig. S5c), which indicated that the prepared K-CN has excellent photo-stability. 538

(4)

In order to prove the universal applicability of the synthesized samples in the field

of photocatalysis, we tried to use the prepared photocatalyst for H₂O₂ production under oxygen saturation condition with isopropanol as sacrificial agent. As shown in Fig. 8a, K-CN-2 showed the strongest H₂O₂ evolution capacity, up to 133 μ M, which was beyond 2 and 1.5 times that of CN and TCN. H₂O₂ can be partially decomposed by reacting with electrons and holes followed the pathway of Eq.s (5)-(8), therefore the generation and decomposition of H₂O₂ was a dynamic equilibrium process [10].

- 546 $H_2O_2 + H^+ + e^- \rightarrow H_2O + \cdot OH$ (5)
- 547 $H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$ (6)
- 548 $H_2O_2+h^+ \rightarrow H^++\cdot HO_2$ (7)
- 549 $H_2O_2+2h^+ \rightarrow 2H^++O_2$ (8)

The formation rate constant (K_f) and decomposition rate (K_d) constant of H₂O₂ were simulated by zero-order and first-order dynamics to understand the formation and decomposition characteristics of H₂O₂. The K_f and K_d were obtained by fitting the data of H₂O₂ production in Fig. 8a with Eq. (9) [53]:

554 $H_2O_2 = \frac{K_f}{K_d} \times \{1 - \exp(-K_d \times t) \quad (9)$

Shown as Fig. 8b, K-CN-2 had the highest value of K_f (2.34 µM min⁻¹) and lowest value of K_d (0.002 min⁻¹), which determined the significant increased H₂O₂ production capacity of K-CN-2 than CN and TCN. In addition, the practical decomposition characteristics of H₂O₂ test was also conducted by decomposing the H₂O₂ aqueous solution with initial concentration at 0.5 mM. Shown as Fig. 8c, after one hour of visible light irradiation, CN, TCN and K-CN-2 did not show significant H₂O₂ decomposition, which was about 1%. Relatively, K-CN-2 possessed the minimum decomposition efficiency, less than 1%. The high generation efficiency and low decomposition
efficiency demonstrated the feasibility of K-CN-2 in the field of photocatalytic H₂O₂
production. In order to evaluate the conversion efficiency of solar energy into chemical
energy, the solar energy conversion (SCC) efficiency was calculated according to Eq.s
(10)-(12) [76]:

567
$$H_2O+\frac{1}{2}O_2 \to H_2O_2 \ (\Delta G=117 \text{ kJ mol}^{-1})$$
 (10)

568
$$E_{\text{light}}(W) = irradiance (W m^{-2}) \times irradiated area (m^2)$$
 (11)

569 SCC efficiency (%)=
$$\frac{\left[\bigtriangleup G^{\theta} \left(\operatorname{J} \operatorname{mol}^{-1} \right) \right] \times [vield of H_2 O_2 (\operatorname{mol})]}{E_{\operatorname{light}}(W) \times T(s)}$$
(12)

 ΔG^0 is the free energy of H₂O₂ formation (117 kJ mol⁻¹); E_{light} is the total input solar 570 energy; T is the reaction time for H₂O₂ production (3600 s); irradiance is 0.076 W \cdot cm⁻ 571 ²; irradiated area is 38.4 cm². Accordingly, the conversion efficiency of K-CN to 572 573 produce H₂O₂ was calculated to be about 0.01%. Generally, strong oxidation may lead to the destruction of the catalyst and affect its performance. But the reusing experiment 574 of H₂O₂ production showed that the photocatalytic performance did not decrease 575 significantly after four times reusing (Fig.8d). Besides, the SEM and XRD of recycled 576 K-CN after H₂O₂ production showed no obvious structural damage (Fig. S5b-c), 577 indicating the high stability of the K-CN in oxidizing environment. 578

In general, the obtained tubular K-CN equipped with a stable tubular structure and delaminated tube wall, which can shorten the electron transport distance and facilitate the electron transfer from the inner surface to the outer surface. Subsequently, the recombination rate of electron-hole pairs was suppressed. In addition, the large specific surface area of K-CN exposed abundant active sites. Furthermore, the potassium atoms embedded in the C-N heterocyclic ring may play a role as electron channels, which
further effectively inhibited the recombination of the photo-generated charges in K-CN.
And the wider visible light response range of K-CN than CN improved visible light
utilization. Therefore, the K-CN displayed a better TCH degradation capacity and
higher H₂O₂ production capacity than the conventional CN and unmediated TCN.

589

590 4. Photocatalytic mechanism

In order to reveal the mechanism of TCH photodegradation and H₂O₂ production 591 592 in detail, a series of free radical capture experiments were carried out to determine the main active species in the photocatalytic process. And the ESR spectra was also 593 conducted to prove the presence of free radicals. As for TCH degradation, 1 mmol 594 595 ethylenediamine tetraacetic acid disodium (EDTA-2Na), 4-hydroxy-2,2,6,6tetramethylpiperidine-N-oxyl (TEMPOL) and isopropyl alcohol (IPA) were used as 596 scavenger of h^+ , $\cdot O_2^-$ and $\cdot OH$, respectively. Slightly different, 1 mmol AgNO₃ and 597 598 TEMPOL were used to quench e^- and $\cdot O_2^-$ respectively in H₂O₂ production experiment to investigate the path of H₂O₂ production. 599

600

601 4.1. TCH degradation

It could be seen from Fig. 9a that after presenting EDTA-2Na and TEMPOL, the degradation efficiency of TCH was greatly reduced, only 24.4% and 26.1% TCH was degraded, while the IPA slightly affected the degradation efficiency of TCH, indicating that h^+ and $\cdot O_2^-$ were the main active species for TCH degradation. In addition, the data of the active radical scavenging experiment for TCH degradation in Fig. 9a were deeply
analyzed through the quasi-first-order kinetic model to explore the contribution strength
of each active species in the TCH degradation system. According to the Eq.s (13)-(14)
[77]:

610
$$\ln\left(\frac{C_{t}}{C_{0}}\right) = -K_{app}t \qquad (13)$$

611
$$R_{\rm I} = \frac{K_{\rm I}}{K_{\rm app}} \approx \frac{K_{\rm app} - K_{\rm i}}{K_{\rm app}}$$
(14)

 K_{app} is the apparent rate constant of TCH degradation. K_{I} (I = O_{2}^{-} , OH^{-} , h⁺) is the rate 612 constant for TCH degradation in the presence of $\cdot O_2^-$, $\cdot OH$ and h⁺ respectively. K_i (i = 613 TEMPOL, IPA, EDTA-2Na) represents the rate constants of TCH degradation in the 614 presence of the corresponding quenchers. $R_{\rm I}$ is the fraction contribution of the 615 corresponding radical. The scavenger I (TEMPOL, IPA, EDTA-2Na) is corresponding 616 617 to the i radical ($\cdot O_2^-$, $\cdot OH$, h⁺). The result described as Fig. 9b showed the rate constant for TCH degradation were 0.001, 0.003 and 0.008 min⁻¹ in the presence of EDTA-2Na, 618 TEMPOL and IPA, respectively. According to the Eq. (14), the contribution of h^+ , $\cdot O_2^-$ 619 and \cdot OH were 90.3%, 64.6% and 10.7%, respectively. These results proved that h^+ 620 and $\cdot O_2^-$ played important roles in TCH degradation. Noting that, due to the complex 621 free radical chemistry involved in photocatalytic system, the total contribution over 100% 622 [77]. Furthermore, the ESR spectra of $\cdot O_2^-$ and $\cdot OH$ were investigated by DMPO spin-623 trapping under visible light and dark to further prove the formation of active free 624 radicals. Shown as Fig. 9c, four main DMPO- \cdot O₂ signal peaks with an intensity ratio 625 of 1:1:1:1 appeared under visible light irradiation and the intensity was increased with 626 the extension of radiation time, indicating that K-CN-2 produced $\cdot O_2^-$ under visible 627

628

629

light. Besides, the signal peaks with an intensity ratio of 1:2:2:1 in Fig. 9d corresponded to DMPO- \cdot OH, confirming the formation of \cdot OH, albeit only in small quantities.

According to the results of radical trapping and ESR spectra, combing with the 630 structure and physicochemical properties of K-CN, the photocatalytic degradation 631 mechanism of TCH was speculated as Fig. 10(a-b). Firstly, the large specific surface 632 area and porosity of K-CN facilitated the full contact of TCH molecules with active 633 sites. Subsequently, under the irradiation of direct incident light and diffuse reflection 634 light (Fig. 10a), the VB of K-CN were excited to generate photogenerated electron-hole 635 636 pairs both on the surface layer and inner delaminated layer simultaneously. Profiting from the delaminated and thin tube wall of K-CN and the shortened the transfer distance, 637 the photo-generated electrons could migrate to the surface of the inner delaminated 638 639 layer and the outer surface layer rapidly. So that the recombination of photo-generated electron-hole pairs was suppressed, and the photocatalytic performance was promoted. 640 Besides, a small number of K-N bridge electron channels in K-CN accelerated the 641 horizontal transfer of electrons in the tube wall, which further reduced the 642 recombination of photogenerated carriers. Subsequently, the photogenerated electrons 643 on the CB reacted with the O_2 molecules on the photocatalyst surface to generate O_2^- , 644 which had strong oxidability to oxidize TCH to CO₂ and H₂O. Secondly, the holes 645 remained on the VB was another major oxidizing pathway for TCH degradation (Fig. 646 10b). The whole TCH degradation process followed Eqs. (15)-(17): 647

- $O_2 + e^- \rightarrow \cdot O_2^- \tag{15}$
- $O_2^-+TCH \rightarrow CO_2^-+H_2O \qquad (16)$

$$h^{+}+TCH \rightarrow CO_{2}+H_{2}O \qquad (17)$$

651

$4.2. H_2O_2$ production

In the capture experiment of producing H₂O₂ (Fig. 9e), after presenting AgNO₃ and TEMPOL, the yields of H₂O₂ were reduced by 79.6% and 63.7% respectively. And the contribution rate of free radicals to H₂O₂ production was also calculated by the Eqs. (S1)-(S2) in supplementary information. Displayed as Fig. 9f, the result showed that the contribution of e^- and $\cdot O_2^-$ for H₂O₂ production were 79.3% and 64%, respectively, which proved that both two-step single-electron (Eqs. (18)-(21)) and one-step doubleelectron (Eq. (22)) existed simultaneously in the H₂O₂ generation [78].

$$O_2 + e^- \rightarrow O_2^-$$
(18)

$$661 \qquad \qquad \cdot O_2^- + H^+ \to HO_2^{-} \qquad (19)$$

$$HO_2^- + e^- \rightarrow HO_2^-$$
(20)

$$HO_2^- + H^+ \rightarrow H_2O_2$$
(21)

$$O_2 + 2e^- + 2H^+ \rightarrow H_2O_2 \qquad (22)$$

Synoptically, the H₂O₂ generation mechanism can be summarized as follows: firstly, the large porosity of K-CN enabled it to fully absorb O₂ molecules and provided sufficient substrates for H₂O₂ production. After the K-CN was excited to generate electron-hole pairs under visible light, photogenerated electrons were transferred to the CB of K-CN and reacted with O₂ molecules to produce H₂O₂ by the two-step singleelectron and one-step two-electron processes simultaneously (Fig. 10b (left)). Detailly, in the single-electron process, a photogenerated electron in the CB reacted with a O₂

molecule to generated $\cdot O_2^-$, which was immediately reacted with a proton to produce 672 HO_2^{-1} . Then another one electron reacted with HO_2^{-1} to generate HO_2^{-1} , which was finally 673 combined to a proton to produce H₂O₂. In the two-electron processes, O₂ molecules 674 were directly accepted two electrons and reacted with two protons to produce H₂O₂. In 675 order to visualize the H₂O₂ production process accompanied by the slightly H₂O₂ 676 decomposition, the decomposition process of H₂O₂ was also shown in Fig. 10c (left), 677 similar to the H₂O₂ production process, both the single-hole (Eq. (23)) and double-hole 678 (Eq. (24)) decomposition paths also existed. And the holes also played an important 679 role in H₂O₂ decomposition (Eq.s (25)-(26)). The process of H₂O₂ decomposition 680 followed Eq.s (23)-(26) [79]. 681

$$H_2O_2 + H^+ + e^- \rightarrow H_2O + \cdot OH \qquad (23)$$

683
$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$$
 (24)

$$H_2O_2 + h^+ \rightarrow OH^+ + OH_2$$
(25)

685 $H_2O_2 + 2h^+ \rightarrow O_2 + 2H^+$ (26)

686

687 **5.** Conclusion

In summary, we demonstrated that the exfoliated and delaminated tubular g-C₃N₄ could be synthesized by potassium ions adjustment. Firstly, K ions destroyed the hydrogen bonds of the supramolecular precursors to form an irregular supramolecular layer, and then during the thermal polymerization process, the irregular adjacent supramolecular layers undergone interleaved thermal polymerization reactions. Under the promotion of potassium ions, the degree of polymerization was enhanced, causing

part of the synthesized g-C₃N₄ layer to deviate from the original position, thereby 694 achieving the delamination of the tube wall. The delaminated and thin multilayer tube 695 wall with large specific surface area not only increased reactive sites, but also inhibited 696 the recombination of photogenerated carriers due to the shorted transportation distance. 697 Due to the strong visible light harvesting ability, low photogenerated carrier 698 recombination rate and a large number of reactive sites, K-CN exhibited significant 699 photocatalytic degradation ability of TCH (83 %) and outstanding photocatalytic H₂O₂ 700 production capacity (133 μ M) under visible light ($\lambda \ge 420$ nm). The solar-chemical 701 702 conversion efficiency of H₂O₂ production was about 0.01%. Besides, the prepared K-CN maintained excellent photocatalytic stability in a wide pH range and oxidizing 703 environment. The hole and electron played an important role in TCH degradation and 704 705 H₂O₂ production, respectively, and their contribution rates were 90.3% and 79.3%, severally. Furthermore, K-CN showed good degradation ability for TCH pollutants with 706 a concentration of 5 to 30 mg/L, and the photocatalytic activity of K-CN remained 707 stable even in the presence of common anions. This work provided a new inspiration 708 and reference for optimizing the photochemical properties of photocatalysts by 709 structural adjustment. 710

711

712 **Conflicts of interest**

There are no conflicts of interest to declare.

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32

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725 **References**

- 726 [1] T. Wu, X. Liu, Y. Liu, M. Cheng, Z. Liu, G. Zeng, B. Shao, Q. Liang, W. Zhang, Q. He, W. Zhang, Application
- of QD-MOF composites for photocatalysis: Energy production and environmental remediation, Coord.
 Chem. Rev., 403 (2020) 213097.
- 729 [2] S. Iqbal, Z. Pan, K. Zhou, Enhanced photocatalytic hydrogen evolution from in situ formation of few-
- 730 layered MoS2/CdS nanosheet-based van der Waals heterostructures, Nanoscale, 9 (2017) 6638-6642.
- 731 [3] Y. Pan, X. Liu, W. Zhang, Z. Liu, G. Zeng, B. Shao, Q. Liang, Q. He, X. Yuan, D. Huang, M. Chen, Advances
- in photocatalysis based on fullerene C60 and its derivatives: Properties, mechanism, synthesis, and
 applications, Appl. Catal. B-Environ., 265 (2020) 118579.
- [4] W. Zhang, Z. Zeng, Z. Liu, J. Huang, R. Xiao, B. Shao, Y. Liu, Y. Liu, W. Tang, G. Zeng, J. Gong, Q. He,
 Effects of carbon nanotubes on biodegradation of pollutants: Positive or negative?, Ecotoxicol. Environ.
 Saf., 189 (2020) 109914.
- 737 [5] Q. He, P. Xu, C. Zhang, G. Zeng, Z. Liu, D. Wang, W. Tang, H. Dong, X. Tan, A. Duan, Influence of
 738 surfactants on anaerobic digestion of waste activated sludge: acid and methane production and
 739 pollution removal, Crit. Rev. Biotechnol., 39 (2019) 746-757.
- [6] H. Li, S. Sun, H. Ji, W. Liu, Z. Shen, Enhanced activation of molecular oxygen and degradation of
 tetracycline over Cu-S4 atomic clusters, Appl. Catal. B-Environ., 272 (2020) 118966.
- 742 [7] B. Shao, Z. Liu, G. Zeng, Y. Liu, Q. Liang, Q. He, T. Wu, Y. Pan, J. Huang, Z. Peng, S. Luo, C. Liang, X. Liu,
- 743 S. Tong, J. Liang, Synthesis of 2D/2D CoAl-LDHs/Ti3C2Tx Schottky-junction with enhanced interfacial
- 744 charge transfer and visible-light photocatalytic performance, Appl. Catal. B-Environ., 286 (2021) 119867.
- [8] Z. Peng, X. Liu, W. Zhang, Z. Zeng, Z. Liu, C. Zhang, Y. Liu, B. Shao, Q. Liang, W. Tang, X. Yuan, Advances
 in the application, toxicity and degradation of carbon nanomaterials in environment: A review, Environ
 Int, 134 (2020) 105298.
- 748 [9] S. Xiao, M. Cheng, H. Zhong, Z. Liu, Y. Liu, X. Yang, Q. Liang, Iron-mediated activation of persulfate
 749 and peroxymonosulfate in both homogeneous and heterogeneous ways: A review, Chem. Eng. J., 384
 750 (2020) 123265.
- [10] X. Zhao, Y. You, S. Huang, Y. Wu, Y. Ma, G. Zhang, Z. Zhang, Z scheme photocatalytic production of
 hydrogen peroxide over Bi4O5Br2/g-C3N4 heterostructure under visible light, Appl. Catal. B-Environ.,
 278 (2020) 119251.
- [11] J. Huang, X. Liu, W. Zhang, Z. Liu, H. Zhong, B. Shao, Q. Liang, Y. Liu, W. Zhang, Q. He,
 Functionalization of covalent organic frameworks by metal modification: Construction, properties and
 applications, Chem. Eng. J., 404 (2021) 127136.
- [12] Q. Liang, B. Shao, S. Tong, Z. Liu, L. Tang, Y. Liu, M. Cheng, Q. He, T. Wu, Y. Pan, J. Huang, Z. Peng,
 Recent advances of melamine self-assembled graphitic carbon nitride-based materials: Design,
 synthesis and application in energy and environment, Chem. Eng. J., 405 (2021) 126951.
- 760 [13] D. Zhao, C.L. Dong, B. Wang, C. Chen, Y.C. Huang, Z. Diao, S. Li, L. Guo, S. Shen, Synergy of Dopants
 761 and Defects in Graphitic Carbon Nitride with Exceptionally Modulated Band Structures for Efficient
 762 Photocatalytic Oxygen Evolution, Adv. Mater., 31 (2019) e1903545.
- 763 [14] X. Wang, K. Maeda, A. Thomas, K. Takanabe, G. Xin, J.M. Carlsson, K. Domen, M. Antonietti, A metal764 free polymeric photocatalyst for hydrogen production from water under visible light, Nat Mater, 8 (2009)
 765 76-80.
- 766 [15] M.-Y. Ye, Z.-H. Zhao, Z.-F. Hu, L.-Q. Liu, H.-M. Ji, Z.-R. Shen, T.-Y. Ma, 0D/2D Heterojunctions of
 767 Vanadate QuantumDots/Graphitic Carbon Nitride Nanosheets for Enhanced Visible-Light-Driven
 768 Photocatalysis, Angew. Chem.-Int. Edit., 56 (2017) 8527.

769 [16] B. Weng, M.-Y. Qi, C. Han, Z.-R. Tang, Y.-J. Xu, Photocorrosion Inhibition of Semiconductor-Based
770 Photocatalysts: Basic Principle, Current Development, and Future Perspective, ACS Catal., 9 (2019)
771 4642-4687.

- [17] S. Iqbal, A. Bahadur, S. Anwer, M. Shoaib, G. Liu, H. Li, M. Raheel, M. Javed, B. Khalid, Designing
 novel morphologies of l-cysteine surface capped 2D covellite (CuS) nanoplates to study the effect of CuS
- morphologies on dye degradation rate under visible light, CrystEngComm, 22 (2020) 4162-4173.
- 775 [18] W. Hussain, A. Badshah, R.A. Hussain, D. Imtiaz ud, M.A. Aleem, A. Bahadur, S. Iqbal, M.U. Farooq,
- H. Ali, Photocatalytic applications of Cr 2 S 3 synthesized from single and multi-source precursors, Mater.
 Chem. Phys., 194 (2017) 345-355.
- [19] L.L. YunZheng, Bo Wang, and Xinchen Wang, Graphitic Carbon Nitride Polymers toward Sustainable
 PhotoredoxCatalysis, Angew. Chem.-Int. Edit., 54 (2015) 12868-12884.
- [20] L. Lin, Z. Yu, X. Wang, Crystalline Carbon Nitride Semiconductors for Photocatalytic Water Splitting,
 Angew. Chem.-Int. Edit., 58 (2019) 6164-6175.
- [21] Q. Liang, X. Liu, J. Wang, Y. Liu, Z. Liu, L. Tang, B. Shao, W. Zhang, S. Gong, M. Cheng, Q. He, C. Feng,
 In-situ self-assembly construction of hollow tubular g-C3N4 isotype heterojunction for enhanced visible-
- 784 light photocatalysis: Experiments and theories, J. Hazard. Mater., 401 (2020) 123355.
- [22] J. Yuan, X. Liu, Y. Tang, Y. Zeng, L. Wang, S. Zhang, T. Cai, Y. Liu, S. Luo, Y. Pei, C. Liu, Positioning
 cyanamide defects in g-C3N4: Engineering energy levels and active sites for superior photocatalytic
 hydrogen evolution, Appl. Catal. B-Environ., 237 (2018) 24-31.
- [23] Z. Liu, Y. Jiang, X. Liu, G. Zeng, B. Shao, Y. Liu, Y. Liu, W. Zhang, W. Zhang, M. Yan, X. He, Silver
 chromate modified sulfur doped graphitic carbon nitride microrod composites with enhanced visiblelight photoactivity towards organic pollutants degradation, Compos. Pt. B-Eng., 173 (2019) 106918.
- 791 [24] S. Luo, Z. Zeng, G. Zeng, Z. Liu, R. Xiao, P. Xu, H. Wang, D. Huang, Y. Liu, B. Shao, Q. Liang, D. Wang,
- Q. He, L. Qin, Y. Fu, Recent advances in conjugated microporous polymers for photocatalysis: designs,
 applications, and prospects, J. Mater. Chem. A, 8 (2020) 6434-6470.
- [25] S. Iqbal, A. Bahadur, M. Javed, O. Hakami, R.M. Irfan, Z. Ahmad, A. AlObaid, M.M. Al-Anazy, H.B.
 Baghdadi, H.S.M. Abd-Rabboh, T.I. Al-Muhimeed, G. Liu, M. Nawaz, Design Ag-doped ZnO
 heterostructure photocatalyst with sulfurized graphitic C3N4 showing enhanced photocatalytic activity,
 Mater. Sci. Eng. B-Adv. Funct. Solid-State Mater., 272 (2021) 115320.
- [26] B. Shao, J. Wang, Z. Liu, G. Zeng, L. Tang, Q. Liang, Q. He, T. Wu, Y. Liu, X. Yuan, Ti3C2Tx MXene
 decorated black phosphorus nanosheets with improved visible-light photocatalytic activity:
 experimental and theoretical studies, J. Mater. Chem. A, 8 (2020) 5171-5185.
- [27] B. Shao, Z. Liu, G. Zeng, H. Wang, Q. Liang, Q. He, M. Cheng, C. Zhou, L. Jiang, B. Song, Twodimensional transition metal carbide and nitride (MXene) derived quantum dots (QDs): synthesis,
 properties, applications and prospects, J. Mater. Chem. A, 8 (2020) 7508-7535.
- [28] R.M. Irfan, M.H. Tahir, S.A. Khan, M.A. Shaheen, G. Ahmed, S. Iqbal, Enhanced photocatalytic H2
 production under visible light on composite photocatalyst (CdS/NiSe nanorods) synthesized in aqueous
 solution, J. Colloid Interface Sci., 557 (2019) 1-9.
- 807 [29] S. Iqbal, Spatial Charge Separation and Transfer in L-Cysteine Capped NiCoP/CdS Nano808 Heterojunction Activated with Intimate Covalent Bonding for High-Quantum-Yield Photocatalytic
 809 Hydrogen Evolution, Appl. Catal. B-Environ., 274 (2020) 119097.
- 810 [30] Y.S. Jun, J. Park, S.U. Lee, A. Thomas, W.H. Hong, G.D. Stucky, Three-dimensional macroscopic
- assemblies of low-dimensional carbon nitrides for enhanced hydrogen evolution, Angew. Chem.-Int.
- 812 Edit., 52 (2013) 11083-11087.

- [31] A. Bahadur, W. Hussain, S. Iqbal, F. Ullah, M. Shoaib, G. Liu, K. Feng, A morphology controlled surface
- sulfurized CoMn2O4 microspike electrocatalyst for water splitting with excellent OER rate for binder free electrocatalytic oxygen evolution, J. Mater. Chem. A, 9 (2021) 12255-12264.
- [32] G. Li, Z. Lian, W. Wang, D. Zhang, H. Li, Nanotube-confinement induced size-controllable g-C3N4
 quantum dots modified single-crystalline TiO2 nanotube arrays for stable synergetic
 photoelectrocatalysis, Nano Energy, 19 (2016) 446-454.
- [33] B. Li, Q. Fang, Y. Si, T. Huang, W.-Q. Huang, W. Hu, A. Pan, X. Fan, G.-F. Huang, Ultra-thin tubular
 graphitic carbon Nitride-Carbon Dot lateral heterostructures: One-Step synthesis and highly efficient
- 821 catalytic hydrogen generation, Chem. Eng. J., 397 (2020) 125470.
- [34] Y. Wang, L. Li, Y. Wei, J. Xue, H. Chen, L. Ding, J. Caro, H. Wang, Water Transport with Ultralow
 Friction through Partially Exfoliated g-C3 N4 Nanosheet Membranes with Self-Supporting Spacers,
 Angew. Chem.-Int. Edit., 56 (2017) 8974-8980.
- [35] E. Mari, P.-C. Tsai, M. Eswaran, V.K. Ponnusamy, Efficient electro-catalytic oxidation of ethylene
 glycol using flower-like graphitic carbon nitride/iron oxide/palladium nanocomposite for fuel cell
 application, Fuel, 280 (2020) 118646.
- 828 [36] X. Zhao, Y. Zhang, X. Zhao, X. Wang, Y. Zhao, H. Tan, H. Zhu, W. Ho, H. Sun, Y. Li, Urea and Melamine
- Formaldehyde Resin-Derived Tubular g-C3N4 with Highly Efficient Photocatalytic Performance, ACS Appl.
 Mater. Interfaces, 11 (2019) 27934-27943.
- [37] Y. Guo, Q. Liu, Z. Li, Z. Zhang, X. Fang, Enhanced photocatalytic hydrogen evolution performance of
 mesoporous graphitic carbon nitride co-doped with potassium and iodine, Appl. Catal. B-Environ., 221
 (2018) 362-370.
- [38] Z. Jiang, X. Zhang, H.S. Chen, X. Hu, P. Yang, Formation of g C3N4 Nanotubes towards Superior
 Photocatalysis Performance, ChemCatChem, 11 (2019) 4558-4567.
- [39] S. Guo, Z. Deng, M. Li, B. Jiang, C. Tian, Q. Pan, H. Fu, Phosphorus-Doped Carbon Nitride Tubes with
- a Layered Micro-nanostructure for Enhanced Visible-Light Photocatalytic Hydrogen Evolution, Angew.
 Chem.-Int. Edit., 55 (2016) 1830-1834.
- [40] X.H. Dai, ZW; Waterhouse, GIN ; Fan, H ; Ai, SY, Ordered graphitic carbon nitride tubular bundles
 with efficient electron-hole separation and enhanced photocatalytic performance for hydrogen
 generation Appl. Catal. A-Gen., 566 (2018) 200-206.
- [41] M. Cao, J. Zuo, Y. Huang, Z. Liu, Synthesis of tubular g-C3N4 via a H2SO4-assisted precursor selfassembly strategy for enhanced photocatalytic degradation of organic pollutant, J. Mater. Sci.-Mater.
 Electron., 31 (2019) 2022-2029.
- [42] G. Ge, Z. Zhao, Combining iodic acid and nitric acid to fabricate carbon nitride tubes for enhanced
 hydrogen evolution under visible light, Catal. Sci. Technol., 9 (2019) 266-270.
- [43] F. Hou, Y. Li, Y. Gao, S. Hu, B. Wu, H. Bao, H. Wang, B. Jiang, Non-metal boron modified carbon
 nitride tube with enhanced visible light-driven photocatalytic performance, Mater. Res. Bull., 110 (2019)
 18-23.
- 850 [44] W. Wang, Q. Niu, G. Zeng, C. Zhang, D. Huang, B. Shao, C. Zhou, Y. Yang, Y. Liu, H. Guo, W. Xiong, L.
- 851 Lei, S. Liu, H. Yi, S. Chen, X. Tang, 1D porous tubular g-C3N4 capture black phosphorus quantum dots as
- 1D/0D metal-free photocatalysts for oxytetracycline hydrochloride degradation and hexavalent
 chromium reduction, Appl. Catal. B-Environ., 273 (2020) 119051.
- [45] J. Xu, L. Zhang, R. Shi, Y. Zhu, Chemical exfoliation of graphitic carbon nitride for efficient
 heterogeneous photocatalysis, J. Mater. Chem. A, 1 (2013) 14766.
- 856 [46] Y.-J. Yuan, Z. Shen, S. Wu, Y. Su, L. Pei, Z. Ji, M. Ding, W. Bai, Y. Chen, Z.-T. Yu, Z. Zou, Liquid exfoliation

- of g-C3N4 nanosheets to construct 2D-2D MoS2/g-C3N4 photocatalyst for enhanced photocatalytic H2
- 858 production activity, Appl. Catal. B-Environ., 246 (2019) 120-128.
- [47] N.A. Wasio, R.C. Quardokus, R.P. Forrest, C.S. Lent, S.A. Corcelli, J.A. Christie, K.W. Henderson, S.A.
- 860 Kandel, Self-assembly of hydrogen-bonded two-dimensional quasicrystals, Nature, 507 (2014) 86-89.
- 861 [48] V.R.P. Anupama Ranganathan, and C. N. R. Rao, Hydrothermal Synthesis of Organic Channel
- Structures: 1:1 Hydrogen-Bonded Adducts of Melamine with Cyanuric and Trithiocyanuric Acids, J. Am.
 Chem. Soc, 121 (1999) 1752-1753.
- [49] C. Zhou, R. Shi, L. Shang, L.-Z. Wu, C.-H. Tung, T. Zhang, Template-free large-scale synthesis of gC3N4 microtubes for enhanced visible light-driven photocatalytic H2 production, Nano Research, 11
 (2018) 3462-3468.
- [50] S. Song, C. Lu, X. Wu, S. Jiang, C. Sun, Z. Le, Strong base g-C 3 N 4 with perfect structure for
 photocatalytically eliminating formaldehyde under visible-light irradiation, Appl. Catal. B-Environ., 227
 (2018) 145-152.
- 870 [51] T. Xiong, W. Cen, Y. Zhang, F. Dong, Bridging the g-C3N4 Interlayers for Enhanced Photocatalysis,
 871 ACS Catal., 6 (2016) 2462-2472.
- [52] T. Xiong, H. Wang, Y. Zhou, Y. Sun, W. Cen, H. Huang, Y. Zhang, F. Dong, KCl-mediated dual electronic
 channels in layered g-C3N4 for enhanced visible light photocatalytic NO removal, Nanoscale, 10 (2018)
- 874 8066-8074.
- [53] C. Feng, L. Tang, Y. Deng, J. Wang, J. Luo, Y. Liu, X. Ouyang, H. Yang, J. Yu, J. Wang, Synthesis of LeafVein-Like g-C3N4 with Tunable Band Structures and Charge Transfer Properties for Selective
 Photocatalytic H2O2 Evolution, Adv. Funct. Mater., 30 (2020) 2001922.
- [54] Y. Kang, Y. Yang, L.C. Yin, X. Kang, L. Wang, G. Liu, H.M. Cheng, Selective Breaking of Hydrogen Bonds
 of Layered Carbon Nitride for Visible Light Photocatalysis, Adv. Mater., 28 (2016) 6471-6477.
- [55] Y. Xu, C. Qiu, X. Fan, Y. Xiao, G. Zhang, K. Yu, H. Ju, X. Ling, Y. Zhu, C. Su, K+-induced crystallization of
 polymeric carbon nitride to boost its photocatalytic activity for H2 evolution and hydrogenation of
 alkenes, Appl. Catal. B-Environ., 268 (2020) 118457.
- [56] Y. Li, S. Ouyang, H. Xu, X. Wang, Y. Bi, Y. Zhang, J. Ye, Constructing Solid-Gas-Interfacial Fenton
 Reaction over Alkalinized-C3N4 Photocatalyst To Achieve Apparent Quantum Yield of 49% at 420 nm, J.
- Am. Chem. Soc., 138 (2016) 13289-13297.
- [57] J. Fu, B. Zhu, C. Jiang, B. Cheng, W. You, J. Yu, Hierarchical Porous O-Doped g-C3 N4 with Enhanced
 Photocatalytic CO2 Reduction Activity, Small, 13 (2017).
- [58] Y. Gao, Y. Zhu, L. Lyu, Q. Zeng, X. Xing, C. Hu, Electronic Structure Modulation of Graphitic Carbon
 Nitride by Oxygen Doping for Enhanced Catalytic Degradation of Organic Pollutants through
 Peroxymonosulfate Activation, Environ. Sci. Technol., 52 (2018) 14371-14380.
- [59] J. Bi, L. Zhu, J. Wu, Y. Xu, Z. Wang, X. Zhang, Y. Han, Optimizing electronic structure and charge
 transport of sulfur/potassium co doped graphitic carbon nitride with efficient photocatalytic
 hydrogen evolution performance, Appl. Organomet. Chem., 33 (2019).
- [60] X. Yang, F. Qian, G. Zou, M. Li, J. Lu, Y. Li, M. Bao, Facile fabrication of acidified g-C3N4/g-C3N4
 hybrids with enhanced photocatalysis performance under visible light irradiation, Appl. Catal. B-Environ.,
 193 (2016) 22-35.
- [61] Y. Zeng, C. Liu, L. Wang, S. Zhang, Y. Ding, Y. Xu, Y. Liu, S. Luo, A three-dimensional graphitic carbon
- 898 nitride belt network for enhanced visible light photocatalytic hydrogen evolution, J. Mater. Chem. A, 4
 899 (2016) 19003-19010.
- 900 [62] N. Tian, K. Xiao, Y. Zhang, X. Lu, L. Ye, P. Gao, T. Ma, H. Huang, Reactive sites rich porous tubular

- 901 yolk-shell g-C3N4 via precursor recrystallization mediated microstructure engineering for
 902 photoreduction, Appl. Catal. B-Environ., 253 (2019) 196-205.
- 903 [63] H. Shen, M. Li, W. Guo, G. Li, C. Xu, P, K co-doped porous g-C3N4 with enhanced photocatalytic
 904 activity synthesized in vapor and self-producing NH3 atmosphere, Appl. Surf. Sci., 507 (2020) 145086.
- 905 [64] J. Yang, Y. Liang, K. Li, G. Yang, K. Wang, R. Xu, X. Xie, One-step synthesis of novel K+ and cyano

groups decorated triazine-/heptazine-based g-C3N4 tubular homojunctions for boosting photocatalytic
H2 evolution, Appl. Catal. B-Environ., 262 (2020) 118252.

- 908 [65] Y. Liu, J. Tian, Q. Wang, L. Wei, C. Wang, C. Yang, Enhanced visible light photocatalytic activity of g-
- C3N4 via the synergistic effect of K atom bridging doping and nanosheets formed by thermal exfoliation,
 Opt. Mater., 99 (2020) 109594.
- 911 [66] S. Hu, F. Li, Z. Fan, F. Wang, Y. Zhao, Z. Lv, Band gap-tunable potassium doped graphitic carbon
 912 nitride with enhanced mineralization ability, Dalton Trans., 44 (2015) 1084-1092.
- 913 [67] V. Maurya, K.B. Joshi, Electron Localization Function and Compton Profiles of Cu2O, J. Phys. Chem.
 914 A, 123 (2019) 1999-2007.
- 915 [68] J. Ran, T.Y. Ma, G. Gao, X.-W. Du, S.Z. Qiao, Porous P-doped graphitic carbon nitride nanosheets for
- synergistically enhanced visible-light photocatalytic H2 production, Energy Environ. Sci., 8 (2015) 37083717.
- [69] H. Bang Truong, B. The Huy, S. Kumar Ray, Y.-I. Lee, J. Cho, J. Hur, H2O2-assisted photocatalysis for
 removal of natural organic matter using nanosheet C3N4-WO3 composite under visible light and the
 hybrid system with ultrafiltration, Chem. Eng. J., 399 (2020) 125733.
- [70] L. Chen, D. Zhu, J. Li, X. Wang, J. Zhu, P.S. Francis, Y. Zheng, Sulfur and potassium co-doped graphitic
 carbon nitride for highly enhanced photocatalytic hydrogen evolution, Appl. Catal. B-Environ., 273 (2020)
 119050.
- [71] G. Ba, Z. Liang, H. Li, N. Du, J. Liu, W. Hou, Simultaneous formation of mesopores and homojunctions
 in graphite carbon nitride with enhanced optical absorption, charge separation and photocatalytic
- 926 hydrogen evolution, Appl. Catal. B-Environ., 253 (2019) 359-368.
- 927 [72] Z. Tong, D. Yang, Y. Sun, Y. Nan, Z. Jiang, Tubular g-C3 N4 Isotype Heterojunction: Enhanced Visible-
- Light Photocatalytic Activity through Cooperative Manipulation of Oriented Electron and Hole Transfer,
 Small, 12 (2016) 4093-4101.
- [73] J. Choi, F.S. Kim, Photoanode Thickness Optimization and Impedance Spectroscopic Analysis of DyeSensitized Solar Cells based on a Carbazole-Containing Ruthenium Dye, J. Korean Phys. Soc., 72 (2018)
 639-644.
- [74] S. Wang, J. Li, R. Zhang, L. Li, Charge transfer resistance of copper and nickel thin film electrodes in
 nano dimensions, Mater. Lett., 198 (2017) 61-64.
- [75] X. Wang, J. Jia, Y. Wang, Combination of photocatalysis with hydrodynamic cavitation for
 degradation of tetracycline, Chem. Eng. J., 315 (2017) 274-282.
- 937 [76] Y. Shiraishi, T. Takii, T. Hagi, S. Mori, Y. Kofuji, Y. Kitagawa, S. Tanaka, S. Ichikawa, T. Hirai, Resorcinol-
- formaldehyde resins as metal-free semiconductor photocatalysts for solar-to-hydrogen peroxide energy
 conversion, Nat Mater, 18 (2019) 985-993.
- [77] P. Chen, L. Blaney, G. Cagnetta, J. Huang, B. Wang, Y. Wang, S. Deng, G. Yu, Degradation of Ofloxacin
 by Perylene Diimide Supramolecular Nanofiber Sunlight-Driven Photocatalysis, Environ. Sci. Technol., 53

942 (2019) 1564-1575.

- 943 [78] F. Xu, Z. Mo, J. Yan, J. Fu, Y. Song, W. El-Alami, X. Wu, H. Li, H. Xu, Nitrogen-rich graphitic carbon
- 944 nitride nanotubes for photocatalytic hydrogen evolution with simultaneous contaminant degradation,

- 945 J. Colloid Interface Sci., 560 (2020) 555-564.
- 946 [79] H.-i. Kim, O.S. Kwon, S. Kim, W. Choi, J.-H. Kim, Harnessing low energy photons (635 nm) for the
- 947 production of H2O2 using upconversion nanohybrid photocatalysts, Energy Environ. Sci., 9 (2016) 1063-
- 948 1073.
- 949