- Highly porous carbon nitride by supramolecular preassembly of monomers for 1
  - photocatalytic removal of sulfamethazine under visible light driven
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Abstract: 12

Many organic and inorganic compounds have been developed as visible light driven 13 14 photocatalysts for environment and energy application. In this work, a metal-free carbon doping-carbon nitride (BCM-C<sub>3</sub>N<sub>4</sub>) nanocomposite was synthesized by 15 introducing barbituric acid and cyanuric acid during the polymerization of melamine. 16 The BCM-C<sub>3</sub>N<sub>4</sub> was characterized by structure, porosity, optical performance, and 17 photoelectrochemical properties. Results demonstrated that BCM-C<sub>3</sub>N<sub>4</sub> sample 18 19 exhibited higher surface area, lower fluorescence intensity, better photocurrent signals and more efficient charge transfer in comparison to pure C<sub>3</sub>N<sub>4</sub>. The BCM-C<sub>3</sub>N<sub>4</sub> 20 exhibits excellent photocatalytic degradation ability of sulfamethazine (SMZ) under 21 visible light irradiation. Much superior photocatalytic activity and high pollutant 22 mineralization rate was achieved by BCM-C<sub>3</sub>N<sub>4</sub>, where it was 5 times than that of 23 pristine C<sub>3</sub>N<sub>4</sub>. The effect of initial SMZ concentrations on photocatalyst was also 24 investigated. Additionally, the trapping experiments and electron spin resonance tests 25 demonstrated that the main active species, such as  $\cdot O_2^-$  and  $h^+$ , could be produced 26 under light irradiation. This work might provide an effective approach to the design of 27 low-cost and highly efficient photocatalysis degradation systems for water treatment. 28 Key words: Carbon doping  $\mathbf{x} - \mathbf{C}_{3}\mathbf{N}_{4}$ , Photocatalysis, Charge transfer, Sulfamethazine, 29

Accel Water treatment 30

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#### 32 1. Introduction

Water contaminated by antibiotics is becoming a worldwide environmental issue 33 [1-6]. Potentially negative concerns of these antibiotics active compounds contain 34 abnormal physiological processes, reproductive damage, increased cancer incidences, 35 and enhanced toxicity of chemical mixtures [7, 8]. The contaminants are in low 36 concentration at present, but tend to be accumulated in long periods of time. 37 Sulfonamide antibiotics have been detected at concentrations up to 900 mg  $\rm kg^{-1}$  in 38 manure, which can be transported to surface water, groundwater and soils. 39 Sulfamethazine (SMZ 4-amino-N-[4,6-dimethyl-2-pyrimidinyl] benzenesulfonamide), 40 which belongs to the sulfonamide group of antibiotics, is commonly used in 41 veterinary industry [9]. Traditional methods, including physical adsorption [10-14], 42 chemical reactions [15, 16], and biological degradation [17-20], may be effective for 43 remediation. However, pollutants just transfer from water phase to another phase with 44 these methods, and may cause the secondary pollution if there is no suitable further 45 treatment [21-23]. 46

Semiconductor photocatalysis technique has aroused widespread concern and has 47 been successfully employed to solve the environmental problems [24-28]. Also, it is 48 an economic and environmental technology [29]. The solar photocatalysis process 49 including three steps: (i) light harvest, (ii) photocarrier separation or transport, and (iii) 50 surface reaction [30]. Unfortunately, photocarriers are easy to recombine via the 51 long-distance transportation. To solve the problem and enhance the solar conversion 52 efficiency, the photocarrier transfer kinetics should be accelerated to reach fast 53 separation of the photoexcited electron-hole pairs with novel material or new 54 55 structural design. Among the numerous photocatalysts, graphic carbon nitride  $(g-C_3N_4)$ has gained much interest as an innovative material with desirable visible-light 56 response and medium band gap of 2.7eV [31, 32]. As an earth-abundant, low-cost, 57 biocompatible, and chemically stable photocatalyst, g-C<sub>3</sub>N<sub>4</sub> can easily be fabricated 58 59 from melamine, urea, etc. [33]. It has been developed as a metal-free visible-light sensitive photocatalyst in 2009 and applied in all kinds of photocatalytic branches, 60 such as H<sub>2</sub>/O<sub>2</sub> evolution from water splitting [34, 35], contaminant degradation [36], 61

62 CO<sub>2</sub> reduction [37], and so on. However,  $g-C_3N_4$  has a low efficiency under visible 63 light due to the high recombination of photo-generated electron ( $e^-$ )-hole ( $h^+$ ) pairs. 64 Thus, different techniques have been employed to improve the efficiency of  $g-C_3N_4$ . 65 One strategy for improving the charge carrier separation and photocatalytic efficiency 66 is to dope carbon nitride with heteroatoms [38] or heterojunction [39-41] or metal 67 nanoparticles [42-44].

To date, researchers have reported that nonmetal element doping  $g-C_3N_4$ 68 enhanced visible-light photocatalytic activity, such as doping with P, B, C, Cl, and S 69 [45-48]. For example, Deng et al. prepared P-doped g-C<sub>3</sub>N<sub>4</sub> and presented improved 70 photocatalytic activity for the simultaneous removal of Cr(VI) and 2,4-DCP under 71 visible light irradiation [49]. Recently, triazine derivatives doped with melamine 72 through hydrogen bonding led to carbon nitride structures attracted widespread 73 attention owing to its outstanding catalytic and photocatalytic activity. g-C<sub>3</sub>N<sub>4</sub> can be 74 easily modified by standard organic protocols such as barbituric acid, which was 75 proposed by Wang et al. [50]. Thomas et al using dimethyl sulfoxide as a solvent to 76 synthesize C<sub>3</sub>N<sub>4</sub> based on the cyanuric acid-melamine (CM) complex, which can 77 exhibited superior photocatalytic activity when compared with the bulk material [51]. 78 Shalom et al. presented hollow carbon nitride structures for degradation of rhodamine 79 B dye, using a CM complex in different solvents as a starting product [52]. Also, 80 Zheng et al. prepared optimized carbon-doped g-C<sub>3</sub>N<sub>4</sub> and enhanced the reaction rate 81 for the degradation of phenol and persistent organic pollutants when compared with 82 conventional g-C<sub>3</sub>N<sub>4</sub>[53]. Mesoporous carbon nitride was synthesized using different 83 nonionic surfactants by Peer et al [54]. These results indicated that carbon doped 84 85 g-C<sub>3</sub>N<sub>4</sub> could act as a good catalyst for environment management. However, the weak efficiency of carbon doped g-C\_3N\_4 may due to the limited surface area (40-60  $m^2\,g^{\text{-1}})$ 86 [55, 56]. Furthermore, a few studies are concerning the degradation system of the 87 typical organic micropollutants in water such as SMZ via carbon doped g-C<sub>3</sub>N<sub>4</sub>. 88

In this work, we report a high-surface area, high-porosity carbon nitrides by a facile one-step approach. This technique using the ethanol as the solvent, taking advantage of both melamine-cyanuric acid and the barbituric acid as monomers to

form supramolecular carbon nitride (BCM- $C_3N_4$ ) via electrostatic interactions or 92 hydrogen bond. The BET surface area of BCM- $C_3N_4$  was up to 179 m<sup>2</sup> g<sup>-1</sup>. With the 93 high surface area and porosity, the synthesized carbon nitrides presented desirable 94 optical properties, and their wide band gap improved visible light absorption, which 95 made them more suitable for photocatalytic applications. The photocatalytic activity 96 was tested by measuring the degradation of SMZ under visible light illumination with 97 the presence of photocatalyst. The chemical structure, morphology, and optical 98 99 properties of the resulting carbon nitrides were characterized. The performance including degradation efficiency and photocatalytic stability of the photocatalyst 100 under visible light was observed. The effects of initial concentration and the removal 101 rate of total organic carbon were also discussed. The predominant radicals in the 102 photodegradation system were discussed by radicals trapping experiment and electron 103 spin-resonance spectroscopy (ESR) analysis. Meanwhile, a possible degradation 104 pathway of SMZ was proposed. It is anticipated that this metal-free photocatalyst can 105 be a promising candidate for other degradation systems. 106

# 107 **2. Experimental**

108 2.1 Materials

109 Melamine (>99%), cyanuric acid (>98%), barbituric acid (>99%), and 110 Sulfamethazine (>99%) were purchased from Sinopharm Chemical Reagent Co., Ltd 111 (Shanghai, China). All the reagents and materials were of analytical grade and used as 112 received without additional purification or treatment. De-ionized water (18.25 M $\Omega$ .cm) 113 was used in the whole experiment.

114 2.2 Characterization

The specific surface area, pore volume and pore size of  $g-C_3N_4$ , BCM- $C_3N_4$  were measured by the Brunauer-Emmett-Teller (BET) adsorption method (Micromeritics Instrument Corporation, TRI-STAR3020, USA). The photoluminescence (PL) spectra were recorded with Hitachi F-7000 fluorescence spectrophotometer at an excitation

wavelength of 365 nm. The UV-Vis diffuse reflectance spectra (DRS) were 119 performed on a UV-Vis spectrophotometer (Cary 300, USA) with an integrating 120 sphere. The crystal phase of the samples was determined by a D/max-2500 X-ray 121 diffractometer (XRD; Rigaku, Japan) using Cu Ka radiation ( $\lambda = 0.15406$  nm) in the 122 region of  $2\theta$  from 10° to 80°. X-ray photoelectron spectrum (XPS) of the samples was 123 obtained by using an ESCALAB 250Xi spectrometer (Thermo Fisher, USA) with Al 124  $K\alpha$  radiation (hv = 1486.6 eV). Their morphology was examined by transmission 125 electron microscope (TEM, JEOL JEM-2100F). The light irradiation source was a 300 126 W Xe arc lamp (CEL-HXF300, Beijing). The visible light used in this study was 127 obtained by cutting UV light ( $\lambda$ <420 nm) with a filter (Beijing China Education 128 Au-light Co., Ltd). The total organic carbon (TOC) was applied to analyze the 129 mineralization degree of organic contaminants on Analytik Jena AG (Multi N/C 130 Manus 2100). 131

2.3 Preparation of samples 132

#### 2.3.1 Synthesis of $g-C_3N_4$ 133

In a typical synthesis process, 10 g of melamine was placed into a ceramic 134 crucible with a cover and then loaded into the central region of a muffle furnace. The 135 crucible was firstly heated to 550 °C with a heating rate of 2.3 °C min<sup>-1</sup> and 136 maintained at 550 °C for 4h, and then cooled down naturally. After cooling to ambient 137 temperature, the obtained yellow agglomerate (g-C<sub>3</sub>N<sub>4</sub>) was ground into powder. 138

2.3.2 Synthesis of BCM- $C_3N_4$ 139

The BCM-C<sub>3</sub>N<sub>4</sub> was prepared from melamine, cyanuric acid, and barbituric acid by 140 modified method [57, 58]. 5.0 g of melamine, 5.0 g of cyanuric acid, and 0.5 g of 141 barbituric acid were first dispersed in 100 mL of ethanol to form suspension. The 142 suspension was next stirred at ambient temperature for 2 h, followed by sonication at 143 room temperature for an additional 1 h. The suspension was then dried on a hot plate 144 at 90 °C until no obvious liquid found. The calcination procedure was exhibited in the 145

part of 2.3.1. For comparison,  $CM-C_3N_4$  sample was obtained without barbituric acid.

### 147 2.4 Photodegradation evaluation

The photodegradation activities of obtained samples were investigated via the 148 degradation of SMZ in aqueous solution under a 300W Xe lamp in an aqueous 149 solution under visible light (> 420 nm). In photocatalytic degradation experiment, 50 150 mg of powder photocatalyst was dispersed into 50 mL of SMZ ( $10 \text{ mg L}^{-1}$ ) solution. 151 Before illumination, the suspensions were stirred in dark for 1 h to reach the 152 adsorption-desorption equilibrium. After that, the mixture solutions were illuminated 153 under visible light. At a given time interval of irradiation, aliquots were separated 154 from the suspension. The SMZ concentration was determined using an HPLC Series 155 1100 (Agilent, Waldbronn, Germany) equipped with a UV-vis detector. The Column 156 was C-18 column (4.6  $\times$  250 mm) at the temperature of 30 °C. The mobile phase was 157 water-acetonitrile (80:20, v/v) with 0.1% acetic acid at the flow rate of 1 mL min<sup>-1</sup>. 158 The sample volumes for injection were all 20 uL and the wavelength of detector was 159 270 nm. 160

# 161 2.5 Photoelectrochemical measurement

Photoelectrochemcial tests were carried out on a CHI 660D workstation in a 162 three-electrode model, utilizing a Pt electrode (40×0.55 mm, 99%) as the counter 163 electrode and an Ag/AgCl electrode as the reference electrode. A 300 W Xe lamp was 164 used as a light source. Typically, the working electrodes were prepared as follows: 10 165 mg of the photocatalyst was suspended in 1 mL of 0.5% nation solution to make 166 slurry. Then, 100  $\mu$ L of the slurry dropped onto a 1 cm  $\times$  2 cm FTO slice with an 167 effective working area of  $1 \text{ cm}^2$ . The electrochemical impedance spectroscopy (EIS) 168 was performed in 100 mL of 0.2 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution with the above 169 three-electrode system. 170

171 *2.6 Active species trapping experiment* 

The active species trapping were ethylenediaminetetraacetic acid disodium salt (EDTA-2Na), benzoquinone (BQ), and isopropanol (IPA), which were introduced as the scavengers to detect holes ( $h^+$ ), superoxide radicals ( $\bullet O_2^-$ ) and hydroxyl radicals ( $\bullet OH$ ), respectively. The experiment was analyzed by 1 mM scavengers to degrade SMZ in an aqueous solution under visible light (> 420 nm).

### 177 **3. Results and discussion**

# 178 *3.1 Crystal structure and morphology*

Direct evidence for the g-C<sub>3</sub>N<sub>4</sub> formation was obtained by FT-IR spectroscopy, XRD, and XPS. The FT-IR spectra of g-C<sub>3</sub>N<sub>4</sub>, CM-C<sub>3</sub>N<sub>4</sub>, and BCM-C<sub>3</sub>N<sub>4</sub> were shown in Fig. 1. According to the FT-IR spectrum of g-C<sub>3</sub>N<sub>4</sub>, several bands in the 1200-1700 cm<sup>-1</sup> region are attributed to the typical stretching vibrations of C-N heterocycles. The peak at 805 cm<sup>-1</sup> belongs to the triazine. These results are highly consistent with the previous reports [59].

The XRD patterns of g-C<sub>3</sub>N<sub>4</sub>, CM-C<sub>3</sub>N<sub>4</sub>, and BCM-C<sub>3</sub>N<sub>4</sub> were also investigated, 185 and the results were depicted in Fig. 2. All samples had a similar XRD pattern which 186 could be ascribed to a typical graphite-like structure. The peak of g-C<sub>3</sub>N<sub>4</sub> at 13.1° is 187 ascribed to the (100) inplanar ordering of tri-s-triazine units. The strong interplanar 188 stacking peak at 27.2° corresponding to the (002) interlayer stacking. Compared to the 189 g-C<sub>3</sub>N<sub>4</sub>, the (100) peak of BCM-C<sub>3</sub>N<sub>4</sub> is significantly weakened, which is a feature of 190 BCM- $C_3N_4$  with mesoporous structure. Also, the (002) peak of BCM- $C_3N_4$  obviously 191 became weaker and broader, which was ascribed to the addition of cyanuric acid 192 and/or barbituric acid [60]. 193

194 XPS test results of C, N, and O for  $g-C_3N_4$  and BCM- $C_3N_4$  were presented in Fig. 195 3. The survey of BCM- $C_3N_4$  displayed that the elements of the samples were C, N, 196 and O. The C1s binding energy region (284.9 eV) was ascribed to alkyl carbon 197 (C=C-C or C-H), most likely either adventitious carbon adsorbed on the surface or 198 any sp<sup>3</sup> graphitic carbon formed during pyrolysis. The peak at 288.4 eV was attributed 199 to the signals of sp<sup>2</sup> carbon (N-C=N) presented in the backbone of  $g-C_3N_4$ . These

signals are usually observed in the XPS spectrum of carbon nitrides. The N 1s peak at 200  $398.8 \pm 0.2$ eV and  $404.1 \pm 0.2$ eV correspond to sp<sup>2</sup> hybridized aromatic N in tri-ring 201 (C-N=C) and positively charged localization, respectively. The peak with a high 202 binding energy at 399.7  $\pm$  0.1 eV is assigned to nitrogen (N-(C)<sub>3</sub>) at the structural 203 edges of g-C<sub>3</sub>N<sub>4</sub>. The peak located at  $400.9\pm$  0.1 indicated the presence of amino 204 functions (C-N-H), originating from the terminal amino groups on the surface [61]. As 205 for O 1s spectrum, it exhibited the predominant characteristic peak at 529.9 eV. As 206 shown in Table. S1, the surface atomic ratio from XPS revealed that the C/N molar 207 ratio of the BCM-C<sub>3</sub>N<sub>4</sub> nanosheet (0.67) was much smaller than that of the  $g-C_3N_4$ 208 (0.94), indicating the presence of surface carbon vacancies in the BCM-C<sub>3</sub>N<sub>4</sub> 209 nanosheet. The above results were consistent with the previous reports, confirming 210 the successful of preparation of  $g-C_3N_4$  [62]. 211

The morphological of g-C<sub>3</sub>N<sub>4</sub> and BCM-C<sub>3</sub>N<sub>4</sub> have been characterized by the 212 TEM images. As shown in Fig. 4a and Fig. 4b the pristine g-C<sub>3</sub>N<sub>4</sub> presented stacked 213 sheets structure and smooth surface. After addition of the barbituric acid and cyanuric 214 acid, the BCM-C<sub>3</sub>N<sub>4</sub> obviously displayed thin nanosheet structures and randomly 215 distributed mesopores, which significantly differed from the mainly dense and stacked 216 sheets of the pristine  $g_{-C_3N_4}$  (Fig. 4c). As shown in Fig. 4d, many pores, 217 approximately 5-10 nm, were embedded in a porous BCM-C<sub>3</sub>N<sub>4</sub>. These surface pores 218 existed on BCM- $C_3N_4$  can provide a lot of active sites and improve mass 219 transportation, which can be further utilized for photocatalytic degradation. 220

To further study the surface morphology and pore volume in the as-prepared samples, the nitrogen adsorption-desorption isotherms experiments have been performed in Fig. S1 and Table 2. The BET surface area and pore volume of BCM-C<sub>3</sub>N<sub>4</sub> were calculated to be 179.03 m<sup>2</sup> g<sup>-1</sup> and 0.56 cm<sup>3</sup> g<sup>-1</sup>, respectively. Photodegradation is a surface reaction. The increase surface area and pore volume may offer more active sites for the pollutants, enhancing its photocatalytic efficiency. The results mentioned above as supported by the TEM and further demonstrate the successful preparation of BCM- $C_3N_4$  which possesses nanosheet structure with pores on the surface [63, 64].

# 230 *3.2 Optical property, photoluminescence, and photo electrochemical properties*

DRS were used to study the optical absorption properties of the  $g-C_3N_4$ , CM-C<sub>3</sub>N<sub>4</sub>, 231 and BCM-C<sub>3</sub>N<sub>4</sub> samples. As shown in Fig. 5a, g-C<sub>3</sub>N<sub>4</sub> has an adsorption at 453 nm 232 which fitted with the previous report [65]. After doping the barbituric acid and 233 cyanuric acid with melamine, the absorption edge gradually moved to longer edge, 234 which can significantly enhance the visible light absorption. The energy band gap of 235 semiconductors can be determined from the intercept of the tangents to the plots of 236  $(\alpha hv)^2$  versus hv [66]. As presented in Fig. 5b, we can obtain that the band gap of 237 CM-C<sub>3</sub>N<sub>4</sub> and BCM-C<sub>3</sub>N<sub>4</sub> are 2.32 eV and 2.02 eV, respectively, which are narrower 238 than the g-C<sub>3</sub>N<sub>4</sub> (2.68 eV). The carbon doping of BCM- $C_3N_4$  could change its band 239 gap obviously. Furthermore, the conduction band and valence band of the samples 240 could be calculated by the equation as following [67]: 241

242 
$$E_{CB}=X-E_C-1/2E_g$$
  
243  $E_{VB}=E_{CB}+E_g$ 

Where *X* is the electronegativity of the semiconductor, and the value for  $g-C_3N_4$  is 4.72 eV,  $E_C$  is the energy of free electrons on the hydrogen scale (about 4.5 eV vs NHE). According the data above, the  $E_{CB}$  and  $E_{VB}$  of BCM-C<sub>3</sub>N<sub>4</sub> are calculated to be -0.79 eV and +1.23 eV, respectively. The  $E_{CB}$  and  $E_{VB}$  of  $g-C_3N_4$  are calculated to be -1.12 eV and +1.56 eV, respectively.

(1)

(2)

To confirm the photo-response ability and photogenerated charges recombination efficiency in the photocatalyst, the transient photocurrent measurement was introduced. As shown in Fig. 5c, it can be seen that all the electrodes exhibited rapid and stable photocurrent response under light illumination. The transient photocurrent of BCM-C<sub>3</sub>N<sub>4</sub> increased by 2.5 times compared to pristine  $g-C_3N_4$ . Large

enhancement of transient photocurrent in the BCM-C<sub>3</sub>N<sub>4</sub> sample was indeed observed, 254 indicating that the better separation of photogenerated charges carriers and more 255 efficient electron transportation at the interfaces. EIS is another method to explain the 256 electron-transfer efficiency at the electrodes. Fig. 5d presented an overview of the 257 semicircular Nyquist plots for the samples, and g-C<sub>3</sub>N<sub>4</sub> showed the bigger diameter, 258 which implied that the poor electrical conductivity may inhibit the electron transfer. 259 The BCM-C<sub>3</sub>N<sub>4</sub> shows smaller arc radius than g-C<sub>3</sub>N<sub>4</sub>, which could be attributed to 260 the doping of barbituric acid. 261

PL was measured to study the separation efficiency of photogenerated charge carriers of as-fabricated semiconductor photocatalyst. The samples were excited by the wavelength of 360 nm, because the light in this wavelength could initiate both the bandgap transition of photocatalyst. The PL intensities of BCM-C<sub>3</sub>N<sub>4</sub> are found to be greatly lowered in comparison with that of  $g-C_3N_4$  in Fig. 6a, which reflect the charge carrier may be suppressed by doping cyanuric acid and barbituric acid.

For better understanding the process of charge separation and transfer in the 268 samples, fluorescence decay time was provided. As shown in Fig. 6b, the change in 269 the tendency of decay time can be determined. It could be clearly seen that, when 270 cyanuric acid and barbituric acid were integrated with the pristine g-C<sub>3</sub>N<sub>4</sub>, the 271 emission lifetime of BCM-C<sub>3</sub>N<sub>4</sub> was decreased from 7.45 ns to 5.12 ns (shown in 272 Table 2). The reduced decay lifetime and quenched PL suggest more effective 273 charge-carrier formation and faster interfacial charge transfer occurring in the doping 274 photocatalyst due to the emergence of non-radiative quenching pathways. 275

276 *3.3 Photocatalytic activity and photocatalyst stablity* 

The photocatalytic activities of as-prepared  $g-C_3N_4$ , CM-C<sub>3</sub>N<sub>4</sub>, and BCM-C<sub>3</sub>N<sub>4</sub> samples composites were evaluated by the decomposition of the micropollutant SMZ under visible light irradiation. Before irradiation, the dark adsorption test was carried out. The adsorption efficiency of samples was added in Table S1. There was no obvious increase of adsorption for all the samples after 60 min dark reaction. As revealed in Fig. 7a, when all the samples were exposed to visible light, the BCM-C<sub>3</sub>N<sub>4</sub> showed a photocatalytic degradation rate over 90% for SMZ. However, the degradation rate of pristine g-C<sub>3</sub>N<sub>4</sub> was 20%, which was the lowest removal efficiency among those there photocatalysts. It suggested that BCM-C<sub>3</sub>N<sub>4</sub> showed excellent photocatalytic performance, which may due to the high efficient of photoinduced electron-hole pairs separation.

Different initial concentrations of SMZ (5-100 mg  $L^{-1}$ ) were also applied to test the activities of the photocatalysts (Fig. 7b). With the increasing concentration, the removal efficiency was decreased from 98% (5 mg  $L^{-1}$ ) to 22% (100 mg  $L^{-1}$ ) in 1 h. This negative effect explained that a higher concentration of SMZ would decrease the photon adsorption on catalyst. The results indicated that lower SMZ concentration was more beneficial to gain higher removal efficiency. Also, in the practical wastewater treatment, dilution was essential in the process of pretreatment.

The ability to deep mineralize organic pollutants is crucial for environmental governance. In this work, the mineralization for SMZ could be measured by TOC analysis. As shown in Fig. 7c, the removal efficiency of TOC in SMZ aqueous solution was slower than that of SMZ decomposition, about 60% of TOC could be removed for 2 h visible light irradiation. The result demonstrated that BCM- $C_3N_4$ exhibited superior photocatalytic activity in the SMZ degradation with a favorable mineralization ability.

To discuss the stability of BCM- $C_3N_4$ , the sample had been performed four reaction runs under the same conditions. For each cycle, the catalyst was collected after the centrifugation, washing, and drying for the next test. Compare fresh BCM- $C_3N_4$  with aged BCM- $C_3N_4$ , little inhibition was observed in SMZ degradation. As presented in Fig. 7d, photodegradation efficiencies of SMZ solution exhibited no obvious reduction, even after four circles. To further demonstrate the stability of the 308 BCM- $C_3N_4$ , the FT-IR and XRD of the fresh and used samples have been provided for 309 comparison in the Fig. S2 and Fig. S3.

310 3.4 Degradation mechanism of  $BCM-C_3N_4$ 

To identify main reactive species involved in photocatalytic degradation process, 311 conducted. ethylenediamintetraacetic scavenger tests were acid disodium 312 (EDTA-2Na), 1,4-Benzoquinone (BQ), and isopropanol (IPA), were adopted as the 313 scavengers of hole ( $h^+$ ), super oxide radical( $\bullet O_2^-$ ), and hydroxyl radical ( $\bullet OH$ ), 314 respectively [68, 69]. As depicted in Fig.8a and 8b, it is obvious that the 315 photocatalytic performance decrease after adding the EDTA-2Na or BQ. The activity 316 was inhibited by 1mM EDTA-2Na and the degradation rate of SMZ decreased from 317 98.09% to 25.93%. This result suggested that EDTA-2Na acts as h scavenger, which 318 will consume the reactive species and further reduce the activity of BCM-C<sub>3</sub>N<sub>4</sub>. With 319 the addition of BQ, the photocatalytic activity of BCM- $C_3N_4$  decreased from 98.09% 320 to 35.85%, which implies the  $\cdot O_2$  was also the major species in the degradation of 321 SMZ. However, in the presence of IPA, the photodegradation rate of SMZ exhibited 322 no obvious decrease, revealing that •OH active species were the minor factor in the 323 photocatalytic reaction. Based on the above results, it could be deduced that the  $h^+$ , 324  $\cdot O_2^{-}$ , and  $\cdot OH$  played an important role in the photodegradation of BCM- $C_3N_4$ . 325

To further confirm the reactive oxygen species evolved in the photocatalysis over 326 BCM-C<sub>3</sub>N<sub>4</sub> nanocomposite, the ESR with 5,5-dimethyl-1-pyrroline N-oxide (DMPO) 327 in aqueous solution was performed.[39] As shown in Fig. 8c, four obvious signals 328 with BCM-C<sub>3</sub>N<sub>4</sub> in methanol were produced, which could be assigned to DMPO- $\cdot$ O<sub>2</sub><sup>-</sup> 329 under light illumination. There is no  $\cdot O_2^-$  signal in the dark, but an increasing signal 330 of DMPO- $\cdot$ O<sub>2</sub><sup>--</sup> could be observed with visible light irradiation. Moreover, the signal 331 of •OH was also detected in DMPO system when exposed to light in Fig. 8d. The 332 scavenger test and ESR result confirmed that  $\cdot O_2$  and  $\cdot OH$  exist in the BCM- $C_3N_4$ 333 system under visible light irradiation. 334

335 On the basis of the above results, a possible mechanism is proposed to explain the high photocatalytic activity of the as-prepared BCM-C<sub>3</sub>N<sub>4</sub> in Fig. 9. BCM-C<sub>3</sub>N<sub>4</sub> has 336 higher specific surface area and numerous active sites for the reaction process. Under 337 visible light irradiation, the BCM-C3N4 could generate electrons and holes. The 338 electrons on the CB of BCM-C<sub>3</sub>N<sub>4</sub> (-0.79 eV), which are more negative than E 339  $(O_2/O_2)$  (-0.33 eV), are a good reductant that could efficiently reduce oxygen 340 molecules adsorbed on the surface of the photoanode to •O2-. Moreover, super-oxide 341 radicals  $\cdot O_2^-$  are the most important oxidizing species and then induces the SMZ 342 degradation. The standard redox potential of •OH/OH is +2.38 eV, which is more 343 positive than the VB position of BCM-C<sub>3</sub>N<sub>4</sub> (+1.23 eV). Thus, the photogenerated 344 hole ( $h^+$ ) cannot react with H<sub>2</sub>O to produce •OH over BCM-C<sub>3</sub>N<sub>4</sub> nanosheet. The 345 generated •OH may attributed to the conversion of the  $Q_2$ . In conclusion, the 346 predominant active species ( $\bullet O_2^-$  and  $h^+$ ) as well as the converted products ( $\bullet OH$ ) 347 could effectively degrade SMZ into CO<sub>2</sub> and H<sub>2</sub>O, etc. According to the above 348 analysis, the reaction process can be list as following equations: 349

350 BCM-C<sub>3</sub>N<sub>4</sub>+ 
$$hv \rightarrow$$
 BCM-C<sub>3</sub>N<sub>4</sub> (h<sup>+</sup>+e<sup>-</sup>) (3)  
351 O<sub>2</sub> + e<sup>-</sup>  $\rightarrow$  O<sub>2</sub><sup>-</sup> (4)  
352  $\cdot$  O<sub>2</sub><sup>-</sup> + e<sup>-</sup> + 2H<sup>+</sup>  $\rightarrow$  H<sub>2</sub>O<sub>2</sub> (5)

353 
$$H_2O_2 + e^- \rightarrow OH^+ OH$$
 (6)

354 (•O<sub>2</sub>,  $h^+$  and •OH)+SMZ  $\rightarrow$  degradation products (CO<sub>2</sub>+H<sub>2</sub>O) (7)

#### 355 **4. Conclusion**

In conclusion, a visible light driven mesoporous catalyst has been successfully prepared via carbon doping and thermal process. We have shown that the optical and electronic properties of carbon nitride polymer can be easily modified by nonmetal doping. Under visible light irradiation, the BCM- $C_3N_4$  composite could remove 98% of SMZ in 1 h, which was more efficient than that of pristine  $C_3N_4$  (removed 20% of

SMZ in 1 h). The PL, transient photocurrent, and fluorescence decay time studies 361 revealed that effective electron-hole separation in the excited state made it an 362 effective photocatalyst. The active species  $\bullet O_2^-$ ,  $h^+$  and  $\bullet OH$  were produced and were 363 deduced by scavenger tests and ESR in the catalyst system. Furthermore, the visible 364 light photoactivity of the as-prepared photocatalyst under different pollutant 365 concentration was also investigated. The study may provide new insight into the 366 strategies for the design and utilization of highly efficient and stable non-metal 367 photocatalyst for visible light driven degradation of pollutants. 368

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# 377 **References**

- 378 [1] G. Zeng, M. Chen, Z. Zeng, Nature 499 (2013) 154.
- 379 [2] G. Zeng, M. Chen, Z. Zeng, Science 340 (2013) 1403.
- 380 [3] Y. Feng, J.-L. Gong, G.-M. Zeng, Q.-Y. Niu, H.-Y. Zhang, C.-G. Niu, J.-H. Deng,
- 381 M. Yan, Chem. Eng. J. (2010) 487-494.
- [4] T. Fan, Y. Liu, B. Feng, G. Zeng, C. Yang, M. Zhou, H. Zhou, Z. Tan, X. Wang, J.
  Hazard. Mater. 160 (2008) 655-661.
- 384 [5] D. Huang, W. Xue, G. Zeng, J. Wan, G. Chen, C. Huang, C. Zhang, M. Cheng, P.
- 385 Xu, Water Res. 106 (2016) 15-25.
- 386 [6] L. Qin, G. Zeng, C. Lai, D. Huang, C. Zhang, P. Xu, T. Hu, X. Liu, M. Cheng, Y.
- 387 Liu, Sens. Actuators B: Chem. 243 (2017) 946-954.
- [7] S. Zhong, C. Zhou, X. Zhang, H. Zhou, H. Li, X. Zhu, Y., J. Hazard. Mater. 276
  (2014) 58-65.
- 390 [8] C. Zhou, H. Li, H. Zhou, H. Wang, P. Yang, S. Zhong, J. Sep. Sci. 38 (2015)
- 391 1365-1371.

- 392 [9] C. Zhang, C. Lai, G. Zeng, D. Huang, C. Yang, Y. Wang, Y. Zhou, M. Cheng,
- 393 Water Res. 95 (2016) 103-112.
- 394 [10] P. Xu, G.M. Zeng, D.L. Huang, C.L. Feng, S. Hu, M.H. Zhao, C. Lai, Z. Wei, C.
- 395 Huang, G.X. Xie, Z.F. Liu, Sci. Total Environ.424 (2012) 1-10.
- 396 [11] J.-L. Gong, B. Wang, G.-M. Zeng, C.-P. Yang, C.-G. Niu, Q.-Y. Niu, W.-J. Zhou,
- 397 Y. Liang, J. Hazard. Mater. 164 (2009) 1517-1522.
- 398 [12] Y. Zhang, G.-M. Zeng, L. Tang, D.-L. Huang, X.-Y. Jiang, Y.-N. Chen, Biosens.
- Bioelectron. 22 (2007) 2121-2126.
- 400 [13] Y. Cheng, H. He, C. Yang, G. Zeng, X. Li, H. Chen, G. Yu, Biotechnol. Adv. 34
  401 (2016) 1091-1102.
- 402 [14] X.-j. Hu, J.-s. Wang, Y.-g. Liu, X. Li, G.-m. Zeng, Z.-l. Bao, X.-x. Zeng, A.-w.
- 403 Chen, F. Long, J. Hazard. Mater. 185 (2011) 306-314.
- 404 [15] M. Cheng, G. Zeng, D. Huang, C. Lai, P. Xu, C. Zhang, Y. Liu, J. Wan, X. Gong,
- 405 Y. Zhu, J. Hazard. Mater. 312 (2016) 184-191.
- 406 [16] D.-L. Huang, R.-Z. Wang, Y.-G. Liu, G. M. Zeng, C. Lai, P. Xu, B.-A. Lu, J.-J.
- 407 Xu, C. Wang, C. Huang, Environ. Sci. Pollut. Res.22 (2015) 963-977.
- 408 [17] L. Tang, G.-M. Zeng, G.-L. Shen, Y.-P. Li, Y. Zhang, D.-L. Huang, Environ Sci.
  409 Technol. 42 (2008) 1207-1212.
- 410 [18] D.-L. Huang, G.-M. Zeng, C.-L. Feng, S. Hu, X.-Y. Jiang, L. Tang, F.-F. Su, Y.
- 411 Zhang, W. Zeng, H,-L. Kia, Environ Sci. Technol. 42 (2008) 4946-4951.
- 412 [19] C. Yang, H. Chen, G. Zeng, G. Yu, S. Luo, Biotechnol. Adv. 28 (2010) 531-540.
- 413 [20] D. Huang, L. Liu, G. Zeng, P. Xu, C. Huang, L. Deng, R. Wang, J. Wan,
- 414 Chemosphere 174 (2017) 545-553.
- 415 [21] M. Cheng, G. Zeng, D. Huang, C. Lai, P. Xu, C. Zhang, Y. Liu, Chem. Eng. J.
- 416 284 (2016) 582-598.
- 417 [22] D. Huang, C. Hu, G. Zeng, M. Cheng, P. Xu, X. Gong, R. Wang, W. Xue, Sci.
- 418 Total Environ. 574 (2017) 1599-1610.
- 419 [23] C. Zhang, G. Zeng, D. Huang, C. Lai, C. Huang, N. Li, P. Xu, M. Cheng, Y. Zhou,
- 420 W. Tang, Rsc Adv. 4 (2014) 55511-55518.
- 421 [24] Y. Song, J. Tian, S. Gao, P. Shao, J. Qi, F. Cui, Appl. Catal. B: Environ. 210

- 422 (2017) 88-96.
- [25] Y.-q. Gao, N.-y. Gao, Y. Deng, Y.-q. Yang, Y. Ma, Chem. Eng. J. 195-196 (2012)
  248-253.
- [26] C. Guo, J. Xu, S. Wang, Y. Zhang, Y. He, X. Li, Catal. Sci. Technol. 3 (2013)
  1603.
- 427 [27] C. Lai, M.-M. Wang, G.-M. Zeng, Y.-G. Liu, D.-L. Huang, C. Zhang, R.-Z. Wang,
- 428 P. Xu, M. Cheng, C. Huang, Appl. Surf. Sci. 390 (2016) 368-376.
- [28] M. Cheng, G. Zeng, D. Huang, C. Lai, C. Zhang, Y. Liu, Chem. Eng. J. 384 (2017)
  98-113.
- 431 [29] X. Liu, N. Chen, Y. Li, D. Deng, X. Xing, Y. Wang, Sci. Rep. 6 (2016) 39531.
- 432 [30] W. Che, W. Cheng, T. Yao, F. Tang, W. Liu, H. Su, Y. Huang, Q. Liu, J. Liu, F. Hu,
- 433 Z. Pan, Z. Sun, S. Wei, J. Am. Chem. Soc. 139 (2017) 3021-3026.
- 434 [31] D. Tang, G. Zhang, Appl. Surf. Sci. 391 (2017) 415-422.
- 435 [32] D. Lu, G. Zhang, Z. Wan, Appl. Surf. Sci. 358 (2015) 223-230.
- 436 [33] D. Masih, Y. Ma, S. Rohani, Appl. Catal. B: Environ. 206 (2017) 556-588.
- 437 [34] D. Zheng, X.-N. Cao, X. Wang, Angew, Chem. Int. Edit. 55 (2016) 11512-11516.
- 438 [35] Y. Zheng, L.H. Lin, B. Wang, X.C. Wang, Angew. Chem. Int. Edit. 54 (2015)
  439 12868-12884.
- [36] W. Chen, Y.-X. Hua, Y. Wang, T. Huang, T.-Y. Liu, X.-H. Liu, J. Catal. 349 (2017)
  8-18.
- 442 [37] S.W. Cao, J.X. Low, J.G. Yu, M. Jaroniec, Adv. Mater. 27 (2015) 2150-2176.
- 443 [38] J. Wen, X Xie, X. Chen, X. Li, Appl. Surf. Sci. 391 (2017) 72-123.
- 444 [39] F. Chen, Q. Yang, Y. Wang, J. Zhao, D. Wang, X. Li, Z. Guo, H. Wang, Y. Deng,
- 445 C. Niu, G. Zeng, Appl. Catal. B: Environ. 205 (2017) 133-147.
- 446 [40] J. Wang, L. Tang, G. Zeng, Y. Deng, Y. Liu, L. Wang, Y. Zhou, Z. Guo, J. Wang,
- 447 C. Zhang, Appl. Catal. B: Environ. 209 (2017) 285-294.
- 448 [41] J. Xia, M. Ji, J. Di, B. Wang, S. Yin, Q. Zhang, M. He, H. Li, Appl. Catal. B:
- 449 Environ. 191 (2016) 235-245.
- 450 [42] J. Wang, L. Tang, G. Zeng, Y. Liu, Y. Zhou, Y. Deng, J. Wang, B. Peng, ACS
- 451 Sustainable Chem. Eng. 5 (2017) 1062-1072.

- 452 [43] F. Chen, Q. Yang, J. Sun, F. Yao, S. Wang, Y. Wang, X. Wang, X. Li, C. Niu, D.
- 453 Wang, G. Zeng, ACS Appl. Mater. Interfaces 8 (2016) 32887-32900.
- [44] C. Zhang, C. Lai, G. Zeng, D. Huang, L. Tang, C. Yang, Y. Zhou, L. Qin, M.Cheng, Biosens. Bioelectron. 81 (2016) 61-67.
- [45] W. Iqbal, C. Dong, M. Xing, X. Tan, J. Zhang, Catal. Sci. Technol. 7 (2017)
  1726-1734.
- 458 [46] C. Liu, Y. Zhang, F. Dong, A.H. Reshak, L. Ye, N. Pinna, C. Zeng, T. Zhang, H.
- 459 Huang, Appl. Catal. B: Environ. 203 (2017) 465-474.
- [47] S. Guo, Z. Deng, M. Li, B. Jiang, C. Tian, Q. Pan, H. Fu, Angew. Chem. Int. Ed.
  55 (2016) 1830-1834.
- [48] Y. Yao, H. Chen, J. Qin, G. Wu, C. Lian, J. Zhang, S. Wang, Water Res.101 (2016)
  281-291.
- 464 [49] Y. Deng, L. Tang, G. Zeng, Z. Zhu, M. Yan, Y. Zhou, J. Wang, Y. Liu, J. Wang,
- 465 Appl. Catal. B: Environ. 203 (2017) 343-354.
- 466 [50] J. Zhang, X. Chen, K. Takanabe, K. Maeda, K. Domen, J.D. Epping, X. Fu, M.
- 467 Antonietti, X. Wang, Angew. Chem. Int. Ed. 49 (2010) 441-444.
- 468 [51] Y.-S. Jun, E.Z. Lee, X. Wang, W.H. Hong, G.D. Stucky, A. Thomas, Adv. Funct.
  469 Mater. 23 (2013) 3661-3667.
- 470 [52] M. Shalom, S. Inal, C. Fettkenhauer, D. Neher, M. J. Am. Chem. Soc. 135 (2013)
  471 7118-7121.
- 472 [53] Q. Zheng, D.P. Durkin, J.E. Elenewski, Y. Sun, N.A. Banek, L. Hua, H. Chen,
- 473 M.J. Wagner, W. Zhang, D. Shuai, Environ. Sci. Technol. 50 (2016) 12938-12948.
- 474 [54] M. Peer, M. Lusardi, K.F. Jensen, Chem. Mater. 29 (2017) 1496-1506.
- 475 [55] X. Wang, K. Maeda, A. Thomas, K. Takanabe, G. Xin, J.M. Carlsson, K. Domen,
- 476 M. Antonietti, Nature Mater. 8 (2009) 76-80.
- 477 [56] P. Yang, H. Ou, Y. Fang, X. Wang, Angew. Chem. Int. Ed. 56 (2017) 3992-3996.
- 478 [57] S. Guo, Z. Deng, M. Li, B. Jiang, C. Tian, Q. Pan, H. Fu, Angew. Chem. Int. Ed.
- 479 55 (2016) 1830-1834.
- 480 [58] M. Shalom, M. Guttentag, C. Fettkenhauer, S. Inal, D. Neher, A. Llobet, M.
- 481 Antonietti, Chem. Mater. 26 (2014) 5812-5818.

- [59] S. Yan, Z. Li, Z. Zou, Langmuir 25 (2009) 10397-10401. 482
- [60] L. Lin, H. Ou, Y. Zhang, X. Wang, ACS Catal. 6 (2016) 3921-3931. 483
- [61] K. Schwinghammer, M.B. Mesch, V. Duppel, C. Ziegler, J.r. Senker, B.V. Lotsch, 484
- J. Am. Chem. Soc. 136 (2014) 1730-1733. 485
- [62] S. Yan, Z. Li, Z. Zou, Langmuir, 26 (2010) 3894-3901. 486
- [63] J. Zhang, F. Huang, Appl. Surf. Sci. 358 (2015) 287-295. 487
- [64] S. Panneri, P. Ganguly, M. Mohan, B.N. Nair, A.A.P. Mohamed, K.G. Warrier, 488
- 489 U.S. Hareesh, ACS Sustainable Chem. Eng. 5 (2017) 1610-1618.
- [65] C. Feng, Z. Wang, Y. Ma, Y. Zhang, L. Wang, Y. Bi, Appl. Catal. B: Environ. 205 490
- (2017) 19-23. 491
- [66] Z. Wan, G. Zhang, X. Wu, S. Yin, Appl. Catal. B: Environ. 207 (2017) 17-26. 492
- [67] F. Chen, Q. Yang, S. Wang, F. Yao, J. Sun, Y. Wang, C. Zhang, X. Li, C. Niu, D. 493
- Wang, G. Zeng, Appl. Catal. B: Environ. 209 (2017) 493-505. 494
- [68] Y. Shang, X. Chen, W. Liu, P. Tan, H. Chen, L. Wu, C. Ma, X. Xiong, J. Pan, 495
- Appl. Catal. B: Environ. 204 (2017) 78-88 496
- [69] F. Chen, Q. Yang, Y. Zhong, H. An, J. Zhao, T. Xie, Q. Xu, X. Li, D. Wang, G. 497
- SS-56 Zeng, Water Res. 101 (2016) 555-563. 498
- 499

- 500 Figure captions:
- Fig. 1 The FT-IR analysis of  $g-C_3N_4$ , CM-C<sub>3</sub>N<sub>4</sub>, and BCM-C<sub>3</sub>N<sub>4</sub>
- Fig. 2 The XRD pattern of  $g-C_3N_4$ , CM-C<sub>3</sub>N<sub>4</sub>, and BCM-C<sub>3</sub>N<sub>4</sub>
- 503 Fig. 3 The XPS spectra of g-C<sub>3</sub>N<sub>4</sub> and BCM-C<sub>3</sub>N<sub>4</sub>: (a) survey spectra, (b) high
- resolution C 1s, and (c) high resolution N 1s
- 505 Fig. 4 TEM images of as-prepared photocatalysts: (a) low and (b) high resolution of
- $g-C_3N_4$ , (c) low and (d) high resolution of BCM- $C_3N_4$
- 507 Fig. 5 (a) UV-vis adsorption spectra and digital photograph of the as-prepared samples,
- (b) the plots of  $(ahv)^{1/2}$  vs photon energy (hv), (c) transient photocurrent response for
- 509 the samples, and (d) the EIS for the samples
- Fig. 6 (a) photoluminescence (PL) spectra and (b) the fitting curves of fluorescence
  decay of samples
- Fig. 7 (a) Photodegradation rate of SMZ on different photocatalyst samples, (b) effect
- of initial concentration of SMZ on BCM- $C_3N_4$ , (c) The photodegradation and TOC removal curves of SMZ on BCM- $C_3N_4$ , (and (d) The cycling runs in the
- photodegradation of SMZ over BCM- $C_3N_4$  under visible light irradiation (> 420 nm).
- Fig. 8 The photocatalytic degradation plots of SMZ over BCM- $C_3N_4$  (a, b) with the
- addition of hole,  $\bullet O_2^-$  and  $\bullet OH$  radical scavenger under visible light irradiation and ESR spectra of radical adducts trapped by DMPO in the BCM- $C_3N_4$  dispersion under both the dark and visible light irradiation (> 420 nm) condition: (c) in methanol dispersion for DMPO- $\bullet O_2^-$ ; (d) in aqueous dispersion for DMPO- $\bullet OH$
- 521 Fig. 9 A schematic illustration of degradation of SMZ on BCM-C<sub>3</sub>N<sub>4</sub> under visible
- 522 light irradiation
- 523