- Ternary Z-scheme heterojunction of Bi₂WO₆ with reduced 1 graphene oxide (rGO) and meso-tetra (4-carboxyphenyl) 2 porphyrin (TCPP) for enhanced visible-light photocatalysis 3 4 Kai Hu,^{a,1} Changya Chen,^{a,1} Yuan Zhu,^{a,1} Guangming Zeng,^{*,a} Binbin Huang,^{*,a} Wenqian Chen,^b 5 Shaoheng Liu,^c Chao Lei,^d Bisheng Li,^a Yang Yang^a 6 7 ^aCollege of Environmental Science and Engineering, Hunan University and Key Laboratory of Environmental Biology and Pollution Control (Hunan University), Ministry of Education, Changsha 8 9 410082, P.R. China. ^bDepartment of Chemical Engineering and Technology, Imperial C 10 Exhibition Road, 11 London SW7 2AZ, UK. 12 ^cCollege of Chemistry and Material Engineering, Hunan L rsity of Arts and Science, Changde 415000, Hunan, P.R. China. 13 ^dSchool of Hydraulic Engineering, Changsha of Science & Technology, Changsha 14 15 410114, China. 16 17 * Corresponding author at: Coll ge of Environmental Science and Engineering, Hunan University, China Tel.: +86–731–88822754; fax: +86–731–88823701. E-mail 18 Changsha, Hunan 410082,
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ABSTRACT: A highly efficient and new ternary TCPP/rGO/Bi₂WO₆ Z-scheme 22 heterojunction was designed and fabricated via a facile hydrothermal approach and a 23 24 liquid ultrasonic route in sequence. The crystal structures, morphologies, microstructures, chemical compositions, elemental states, optical and photo-25 26 electrochemical properties of the heterojunction were characterized. This Z-scheme TCPP/rGO/Bi₂WO₆ photocatalyst has significantly enhanced photocatalytic activity for 27 the tetracycline (TC) degradation under the irradiation of visible light ($\lambda > 420$ nm) 28 within 60 min, as compared to pure Bi₂WO₆, rGO/Bi₂W TCPP/Bi₂WO₆ 29 composites. The effects of the photocatalyst dosages, 30 utant concentrations. coexisting ions and illumination conditions on the physical degradation were investigated. 31 According to the trapping experiments and electron spin resonance analyses, the hole 32 (h⁺) and superoxide radical ($\cdot O_2^-$) mainly contribute to the TC decomposition in the 33 m. The photodegradation process in the TCPP/rGO/Bi₂WO₆ photocatal 34 TCPP/rGO/Bi₂WO₆ ternary composites can be well described by the proposed Z-35 results indicate that more efficient charge separation, better 36 scheme mechani light absorption, and larger surface area from the developed photocatalyst collectively 37 contribute to the excellent photocatalytic performances. Besides, the photocatalyst has 38 great stability and recyclability with a removal efficiency of 79.27% even after five 39 40 times of repeated treatment. This work reports a new strategy for the preparation of Zscheme heterojunction photocatalyst with high photocatalytic activity and provides an 41 42 alternative for the effective removal of antibiotic wastewater through photocatalysis. **Keywords:** heterojunction; TCPP/rGO/Bi₂WO₆; photocatalysis; mechanism; 43

44 tetracycline degradation

45 **1. Introduction**

46 Due to large scale industrialization and urbanization, environmental issues have become a very severe problem that threatens the safety of human life and hinders the 47 sustainable development of society [1-5]. Photocatalytic oxidation is a new technology 48 49 that uses photocatalysts to convert light energy into chemical energy, which subsequently lead to the generation of the hole (h⁺), hydroxyl radical (•OH) and 50 superoxide radical $(\bullet O_2^{-})$ for the degradation of pollutants [6]. It has attracted increasing 51 interest, since it, is recognized as one of the most effective apprentice and the second seco 52 The due to its superior properties of sustainable energy source, avoidance econdary pollution, 53 economical cost, and easy operation [7,8]. Since T_{2} was discovered as the earliest 54 bot catalysis because of its strong 55 photocatalyst, it has been widely used in the field oxidizing ability, non-toxicity, low cost and you photochemical stability [9,10]. 56 However, TiO₂ can only absorb the travolet light from approximate 4% of the solar 57 spectral range, which results in the inefficient utilization of solar energy and greatly 58 ormunce and further application [11,12]. Therefore, it is 59 limits the photocatalytic net ble-respond photocatalysts. 60 necessary to explore nei

Bismuth tungston oxide (Bi₂WO₆) (BWO) is a typical Aurivillius oxide with 61 perovskite layered structure constructed from alternating $(Bi_2O_2)^{2+}$ and WO_4^{2-} layers, 62 63 which has been extensively investigated as effective photocatalysts over the years [13-15]. Firstly, the narrow energy gap of BWO (2.80 eV) means it has strong visible-light 64 harvesting ability, which greatly improves the utilization efficiency of light energy as 65 compared to TiO₂ [16, 17]. In addition, BWO possesses a large surface area, and the 66 interlayer space of the sandwich structure can provide sufficient active sites for 67 photocatalytic reaction. The stable physicochemical properties of BWO also give it the 68

69 ability to resist the photo-corrosion and to be recycled for many times. Although BWO exhibits excellent photocatalytic performances toward organic pollutant degradation, 70 its photocatalytic activity is still limited by some factors. The maximum light absorption 71 72 wavelength of BWO is only at around 460 nm, which means it still cannot fully utilize 73 the solar energy [18]. Besides, most $e^{-}h^{+}$ pairs recombine immediately after the photoexcitation, resulting in relatively low separation efficiency [19]. Among many 74 75 proposed approaches, constructing heterojunction structure has been regarded as an effective approach and widely used to overcome the drawbacks of BWO in order to 76 77 achieve better photocatalytic performance [20-24]. Therefore, coosing an appropriate material that matches well with BWO has become a ke 78 igning a highly efficient heterojunction photocatalyst. 79

Porphyrin is the main component of chlorophil, wich plays a central role in the 80 photosynthesis of green plants. Inspired b ature, porphyrin has been widely used 81 the as both appealing photosensitizers an ffective electron donors in the photocatalytic 82 egradation processes [25-28]. Among the 83 hydrogen generation and contrart and various porphyrin molecules, moso-tetra (4-carboxyphenyl) porphyrin (TCPP) was 84 chosen to couple with BWO to construct heterojunction photocatalyst in this work, 85 mainly due to the following reasons: (1) benefiting from its conjugated macrocyclic π -86 87 electrons structure, TCPP possesses a narrow band gap and a wide photoabsorption 88 range in visible-light spectral; (2) the lowest unoccupied molecular orbital (LUMO, 89 -0.60 eV) and the highest occupied molecular orbital (HOMO, +1.10 eV) of TCPP is 90 well-matched with the CB (+0.46 eV) and VB (+3.26 eV) of BWO to design a Z-91 scheme heterostructure, which will dramatically contribute to the separation of photoinduced e⁻-h⁺ pairs [29]; (3) TCPP has a high chemical stability and the carboxylic 92 93 groups in TCPP make it combines with the BWO tightly [26]. However, no relevant 94 information have been reported before.

Graphene is a two-dimensional material consisting of sp2-hybridized single-layer 95 carbon atoms with excellent electrical conductivity, mechanical properties and large 96 97 specific surface area [30-32]. To further enhance the photocatalytic activity of Zscheme TCPP-BWO heterojunction, reduced graphene oxide (rGO) was incorporated 98 into the system to produce ternary composites as excellent photocatalyst. The 99 100 introduction of rGO not only enables the photocatalyst to better adsorb organic 101 contaminants due to its π - π structure, but can also expand the visible-light response range by its great photo-response property [33]. Moreover, the high electron mobility 102 of rGO can effectively restrain the e⁻-h⁺ recombination and 103 heir separation, 104 thereby improving the photocatalytic performance of photocatalyst.

As a typical antibiotic, tetracycline (TC) has been videly used to treat diseases of 105 can be absorbed by the organism, the human and many animals. Since only 30 106 ΤC remaining part enters the environmer a unite and feces and extensively distributed 107 other hand, the residues of TC result in the 108 in all kinds of water bodies [34 1. **D**n generation of antibiotic-registar pathogens and cause the transfer of antibiotic 109 resistance genes, which pose serious threats to the human health and ecological safety 110 [35]. Removing TO from the environment has become an urgent issue to be solved. 111 112 Moreover, photocatalytic degradation of organic dye rhodamine B (RhB) has been 113 extensively studied by a series of photocatalysts based on graphene/Bi₂WO₆ system (Table S1) [36-44], but few studies have been reported by using this system for the 114 photocatalytic degradation of TC. Therefore, in this work, TC was selected as the 115 116 targeted contaminant to evaluate the photocatalytic activity of the prepared catalyst under the illumination of visible light (>420 nm). 117

118 To the best of our knowledge, it was the first time to combine BWO, TCPP and

rGO together to construct a Z-scheme TCPP/rGO/BWO heterojunction photocatalyst. 119 In this work, the superior photocatalytic performance of TCPP/rGO/BWO was studied, 120 and the effects of the photocatalyst dosages, pollutant concentrations, coexisting ions 121 122 and illumination conditions on the photodegradation were carefully investigated. Moreover, the mechanism of the enhanced visible-light photocatalytic activity acquired 123 by TCPP/rGO/BWO was explored in depth. We hope this work may provide a novel 124 125 and efficient Z-scheme heterojunction photocatalyst for effective removal of antibiotic wastewater. 126

127 **2. Materials and methods**

128 2.1 Materials



Bismuth nitrate (Bi(NO₃)₃ 5H₂O), sodium tuns tate (Na₂WO₄ 2H₂O), acetic acid 129 (CH₃COOH), absolute ethanol (C_2H_6O) and tetracycline (TC) were purchased from 130 why hen year that the second s Sinopharm (Shanghai, China). Meso-tethe(4-8 131 obtained from Macklin (Shanghai, Cuna) Graphene oxide dispersion (GO, 2mg/mL) 132 was acquired from Hengqiu (Suchea, a). All chemical reagents were used without 133 further purification. Mili-Q wate was used throughout the study with a resistivity of 134 135 18 M Ω at room to per

136 **2.2 Fabrication of photocatalysts**

137 2.2.1 Fabrication of rGO/BWO

In a typical procedure, $Bi(NO_3)_3$ 5H₂O (0.97 g) was dissolved in acetic acid (10

139 mL), followed by adding ultrapure water (30 mL) and graphene oxide dispersion (10

140 mL). The mixture was magnetic stirred for 30 min to prepare solution A. Meanwhile,

- 141 Na₂WO₄ 2H₂O (0.33 g) was added to ultrapure water (20 mL) to obtain solution B.
- 142 Then, A was added into B dropwise before magnetic stirring for 1 h. The mixed solution
- 143 was sealed in a 100 mL Teflon-lined stainless-steel autoclave and kept at 180 $\,^{\circ}$ C for 12

h, followed by cooling to room temperature naturally. Finally, the resultant solids were washed by absolute ethanol and ultrapure water for three times each, and then dried at 60 \degree for 4 h in a vacuum oven and named as rGO/BWO (1.72 wt%). The pure BWO was also synthesized by hydrothermal method under the same conditions except the absence of GO.

149 2.2.2 Fabrication of TCPP/rGO/BWO

150 The TCPP/rGO/BWO composites were fabricated via a liquid ultrasonic route. Firstly, rGO/BWO (0.5 g) was added to absolute ethanol (40 mL) and ultrasonicated 151 152 for 30 min to make it evenly dispersed. Next, a given amount of TCPP was added to this suspension and the mixture was ultrasonicated for 153 The. xture was then 154 continuously stirred at room temperature until the solvent was completely volatilized. Finally, the solids were dried at 60 $^{\circ}$ C for 4 h in a varuum oven. The as-prepared 155 TCPP/rGO/BWO composites with 0.0 025, 0.50 and 0.75 wt% TCPP 156 TCPP_{0.05}/rGO/BWO, concentrations TCPP_{0.10}/rGO/BWO, 157 were recorded and TCPP_{0.75}/rGO/BWO, respectively. 158 TCPP_{0.25}/rGO/BWO, TCPP_{0.50}/r (Qù

159 **2.3 Characterization**

The crystalline properties of the fabricated powders were measured by X-ray 160 diffraction (XRD, D Advance, Bruker, Germany). The morphology and structure were 161 observed by scanning electron microscopy (SEM, Supra55, Zeiss, Germany) and 162 163 transmission electron microscopy (TEM, JEM-2100, JEOL, Japan), and the element constitution was detected by energy-disperse X-ray spectroscopy (EDS). The functional 164 group of the samples was characterized by Fourier transform infrared spectroscopy (FT-165 166 IR, Nicolet 6700, Thermo Fisher, America). The surface chemical compositions and elemental states were analyzed by X-ray photoelectron spectroscopy (XPS, Escalab 167 250Xi, Thermo Fisher, America). The Brunauer–Emmett–Teller (BET) surface areas of 168

169 as-prepared materials were measured using a surface area and porosity analyzer 170 (Quadrasorb EVO, Quantachrome, America) by nitrogen adsorption–desorption. The 171 optical properties of various photocatalysts were examined by UV–Vis diffuse 172 reflectance spectra (UV-Vis DRS, UH4150, Hitachi, Japan). The existence of free 173 radical during the photocatalytic reaction was confirmed by electron spin response 174 (ESR, JES-FA200, JEOL, Japan) using 5,5-dimethyl-1-pyrroline N-oxide (DMPO) as 175 spin-trapped reagent.

176 **2.4 Photocatalytic experiments**

177 The photocatalytic performance of the as-prepared cataly is was investigated by the photodegradation of TC by using a 300 W Xe lamp equ cutoff filter ($\lambda >$ 178 179 420 nm) as the light source. Typically, a photocatalyst (30 mg) was dispersed into a TC aqueous solution (15 mg/L, 100 mL) and constantly magnetic stirred for 30 min in the 180 dark conditions to get the adsorption-desorption equilibrium and subsequently exposed 181 the Mution (3 mL) was withdrawn from the to the illumination of visible light. T 182 centrifuged to remove the catalyst particles. 183 system at predetermined interval tipe and the TC concentrations were measured by detecting the maximum absorbance at 357 184 vis pect ophotometer (UV-2700, Shimadzu). 185 nm through an U

186 The photodegr dation efficiency of TC was assessed by the following formula:

187
$$\eta = \frac{c_0 - c_t}{c_0} \times 100\%$$
 (1)

where C_0 represents the initial TC concentration and C_t represents the TC concentration at time t, respectively.

190 **2.5 Photo-electrochemical measurements**

191 The photo-electrochemical measurements were conducted on electrochemical 192 workstation through a standard three-electrode model with saturated calomel electrode 193 as reference electrode, platinum filament as counter electrode and conductive glass coated with photocatalyst as working electrode, respectively. The three-electrode system was performed in 0.2 M Na₂SO₄ electrolyte solution and exposed to the illumination of visible light (>420 nm) provided by a 300 W Xe lamp. The detailed fabrication steps of the working electrode were as follows: 0.5% Nafion solution (1 mL) was prepared firstly and the material (10 mg) was dispersed into the liquid by half an hour of ultrasonication. Then 1 cm² area of 1.0 cm ×2.0 cm conductive glass was coated by the slurry and dried in an oven at 110 \mathbb{C} for 1 h.

201 **3. Results and discussions**

202 **3.1 Characterization**

203 **3.1.1 XRD**



The crystal structure of the as-synthesized BWO, rGO/BWO, TCPP/BWO and 204 TCPP/rGO/BWO composites was characterized by (Fig. S1). All the samples XR 205 32.80°, 47.19°, 55.83°, 58.61°, show eight diffraction peaks situated at 206 68.82°, 76.08° and 78.50°, corresponding to the (113), (200), (220), (313), (226), (400), 207 (333) and (240) crystal planes d ombic phase Bi₂WO₆ (JCPDS card, No. 73-208 troduction of rGO and TCPP do not change the crystalline 1126), which indicates the i 209 210 structure of BWC [45]. dition, diffraction peaks belonging to GO are not found in the rGO/BWO and CPP/rGO/BWO composites, probably due to the low amount and 211 the reduction of GO, while similar observation was also found in the previous study 212 213 [46]. Likewise, the XRD patterns of TCPP/BWO and TCPP/rGO/BWO composites do not show any characteristic diffraction peak of TCPP, which is attributed to the trace 214 loading of TCCP on the supports. However, the intensity of diffraction peaks decreases 215 216 slightly with the increasing TCPP content in the TCPP/rGO/BWO composites, indicating that the TCPP may have an adverse effect on the crystallinity of BWO crystal 217 218 to some extent.

219 **3.1.2 SEM, EDS and TEM**

SEM, EDS and TEM were applied to investigate the morphologies, elementary 220 221 compositions and microstructures of the as-prepared rGO/BWO and 222 TCPP_{0.25}/rGO/BWO composites. It is observed that the rGO/BWO has a spherical 223 morphology and a flower-like nanostructure with particle diameter of approximately 5.0 µm, which is composed of numerous crisscross nanoplates of BWO (Fig. 1a). The 224 rough exterior texture of the BWO nanoplates is associated with the coverage of the 225 stratiform rGO nanosheets. In addition, the numerous interstice and holes existing 226 227 among the nanoplates are in favor of the penetration and absorption of light and the transport of reactive substrates [47]. After introducing TCRP, TSP0.25/rGO/BWO 228 229 remains the flower-like microsphere as well, whereas the BWO nanoplate substrates is partly coated with the smaller TCPP nanosheets (Fig. 1 230 And some microspheres of rGO/BWO and TCPP_{0.25}/rGO/BWO composites were clearly observed in the low-231 The EDS mapping analyses (Fig. 1c-f) magnification SEM images (Fig. 232 demonstrate the co-existence an up for ny distribution of Bi, W, C and N elements in 233 TCPP_{0.25}/rGO/BWO composites, which is highly consistent with the following XPS 234 results (see below). Authomore, the TEM image (Fig. 2a) clearly shows that 235 TCPP_{0.25}/rGO/BWC is an individual microsphere, which agrees well with above SEM 236 result. In the HRTEM image of TCPP_{0.25}/rGO/BWO (Fig. 2b), highly transparent 237 238 graphene nanosheets can be observed at the edge of composite, indicating the successfully deposition of rGO onto the BWO nanoplates in the microsphere. The 239 crystal lattice of BWO nanoplates with interplanar distances of 0.315 nm is assigned to 240 241 the (113) lattice planes of BWO in TCPP_{0.25}/rGO/BWO [48]. The diffraction ring in the selective area electron diffraction (SAED) pattern of TCPP_{0.25}/rGO/BWO (inset of Fig. 242 243 2a) corresponds to the (113), (220), and (313) crystal planes of orthorhombic phase

244 Bi₂WO₆, which is consistent with the XRD and HRTEM results. Therefore, the SEM,

EDS and TEM characterization results confirm the successful preparation of the Z-

scheme TCPP/rGO/BWO heterojunction photocatalyst.

247 **3.1.3 FT-IR**

FT-IR tests were performed to analyze the functional groups of samples and to 248 confirm the presence of rGO and TCPP in the TCPP_{0.25}/rGO/BWO composites. Shown 249 in Fig. S3 is the FT-IR spectra of pure TCPP, BWO, as well as rGO/BWO, TCPP/BWO 250 and TCPP_{0.25}/rGO/BWO composites. In the spectrum of BWO, the typical peaks at 251 568.2 cm⁻¹, 727.9 cm⁻¹ and 1386.8 cm⁻¹ are ascribed to the 61–0, W–O stretching 252 vibration modes and W–O–W bridging stretching modes, respectively. These peaks are 253 still present in the rGO/BWO, TCPP/BWO and TCPP_{0.25}/GO/BWO composites, 254 indicating that no structural change of BWO occurred. The characteristic peaks at 255 1627.1 cm⁻¹ and 1558.9 cm⁻¹ appeared in the rCG/BVO composites are assigned to the 256 the C=O and C=C stretching mode of The successful incorporation 257 between BWO and rGO. The entry ce beaks at 727.9 cm^{-1} and 1386.8 cm^{-1} in the 258 rGO/BWO composites are attributed to the interface interaction between BWO and 259 rGO [49]. In the exectrum of the TCPP, the typical absorption bands in $600-1500 \text{ cm}^{-1}$ 260 are originated from the symmetrical and asymmetric stretching vibration of the pyrrole 261 ring (i.e. v (N–N), v (C–N), v (C=C) and v (C=N)) [50]. Besides, the characteristic 262 peaks at 1682.8 cm⁻¹, 1417.8 cm⁻¹ and 1275.9 cm⁻¹ are ascribed to the C=O, COO⁻ and 263 -OH stretching vibrations, respectively, which indicate the existence of carboxyl group 264 in the TCPP [51]. In the spectrum of TCPP/BWO composites, the new appeared peaks 265 compared to the BWO at 1627.1 cm⁻¹, 1226.4 cm⁻¹ and the enhanced peak at 1386.8 266 cm⁻¹ are attributed to the red-shift of C=O, -OH and COO⁻ stretching vibrations, 267 respectively, indicating that the BWO and TCPP have combined with each other 268

successfully. In addition, the broad band at 3430.2 cm⁻¹ appeared in all samples is related to the stretching vibrations of -OH. Furthermore, the FT-IR spectrum of TCPP_{0.25}/rGO/BWO composite inherit the features of both rGO/BWO and TCPP/BWO binary complexes, implying that the BWO, rGO and TCPP are coupled together perfectly to form the TCPP_{0.25}/rGO/BWO ternary composites. These results confirm the successful construction of the different rGO/BWO, TCPP/BWO and TCPP_{0.25}/rGO/BWO composites.

276 **3.1.4 XPS**

XPS analyses were carried out to reveal the chemical compositions and elemental 277 states on the surface of pure BWO and TCPP_{0.25}/rGO/BWG . The full survey 278 spectra (0–1100 eV) of both samples are shown in Fig. S4a, and Bi, W, O, C and N are 279 indeed found in the TCPP_{0.25}/rGO/BWO composites. The high-resolution XPS spectra 280 0.2 rGO/BWO, as well as C 1s and N of Bi 4f, W 4f and O 1s for both BWO and TC 281 1s for only TCPP_{0.25}/rGO/BWO are er eved. From the high-resolution Bi 4f spectrum 282 158.7 eV and 164.0 eV are attributed to the in Fig. S4b, the binging energy 283 ittly .e Bi $4f_{7/2}$ and Bi $4f_{5/2}$, suggesing that the bismuth species exist as Bi³⁺ oxidation state in 284 the BWO. Two peaks of W 4 located at 35.0 eV and 37.0 eV are corresponding to the 285 W $4f_{7/2}$ and W $4f_{5/2}$, which are the characteristics of W⁶⁺ oxidation state in BWO phase 286 (Fig. S4c). In the high-resolution O 1s spectrum, three individual peaks situated at 529.7, 287 288 531.8 and 533.2 eV belong to the lattice oxygen (Bi-O-W), the external hydroxyl groups (O–H), and the adsorbed oxygen species at the surface of BWO respectively 289 (Fig. S4d) [52,53]. Compared to the pristine BWO, the peaks of Bi 4f, W 4f and O 1s 290 over the TCPP_{0.25}/rGO/BWO composite all display an evident shift toward a high 291 binding energy, suggesting the formation of strong chemical interactions among the 292 BWO, rGO and TCPP. In the high-resolution C 1s spectrum, three fitting peaks situated 293

at 284.6, 286.4 and 288.7 eV are attributed to the C–C, C–O and O–C=O bonds respectively (Fig. S4e) [46,54]. The weak peaks of C–O and C=O indicate that GO was well reduced to rGO after combining with BWO [55]. In addition, one main peak situated at 399.7 eV in the N 1s spectrum over the TCPP_{0.25}/rGO/BWO is assigned to the N element in the TCPP (Fig. S4f). The XPS result is in good accord with the FT-IR result, which further verifies that the TCPP_{0.25}/rGO/BWO composite has been successfully prepared.

301 **3.1.5 BET**

The nitrogen sorption isotherms of BWO, rGO/BWO and TCPP_{0.25}/rGO/BWO 302 were carried out by BET analysis (Fig. S5a). According to the ation of IUPAC 303 organization, all the isotherms can be categorized as type IV why a H₃ hysteresis loop, 304 305 implying the presence of mesopores [56]. The corresponding Barrett–Joyner–Halenda (BJH) analyses (Fig. S5b) illustrate that most of he ores in the BWO, rGO/BWO and 306 xe range of 2–20 nm (especially at 4 nm). As TCPP_{0.25}/rGO/BWO are mainly in the 307 shown in Table S2, the BET sp cite ace area is calculated to be 9.24, 13.08 and 308 16.15 m²/g for BWO, rGC/BWO and TCPP_{0.25}/rGO/BWO respectively, while their 309 corresponding perce volumes are measured to be 0.027, 0.033, and 0.043 cm^3/g . The 310 results indicate that the introduction of rGO and TCPP can significantly enhance the 311 surface area and pore volume of BWO. The large surface area and good porous structure 312 313 of TCPP_{0.25}/rGO/BWO can provide more surface active sites and improve the transportation of the contaminant molecules and active radicals, which may result in 314 the enhanced photodegradation ability of the TCPP_{0.25}/rGO/BWO composite [57]. 315

316 **3.1.6 Optical property**

317 Optical properties of the pristine BWO, rGO/BWO, TCPP/BWO and 318 TCPP/rGO/BWO composites with different contents of TCPP were measured by UV- 319 Vis DRS (Fig. S6). The absorption edge of pristine BWO is approximately at 460 nm, while the incorporation of rGO successfully extends the light absorption to the visible 320 321 light region. In addition, the traditional peaks of S-band at 420 nm and the four Q-bands 322 at around 520, 560, 595 and 650 nm of TCPP are observed in all the TCPP modified composites, which confirms the successful introduction of TCPP again. Importantly, 323 the TCPP/rGO/BWO composites show an even larger range of light absorption to the 324 325 entire visible spectrum compared with the rGO/BWO, and the visible light absorption intensity of TCPP/rGO/BWO enhances with the increasing of TCPP. This result reveals 326 that the construction of Z-scheme TCPP/rGO/BWO heterojunction can greatly improve 327 the optical absorption, which provide a possibility to promite ration of photo-328 induced electron-hole pairs and give rise to an enhanced photocatalytic activity. 329 Moreover, the band gap energy (E_g) of the pure BVO can be acquired from UV-330 vis DRS results according to the following 331 $\alpha h v = A (h v - E_a)^{n/2}$ 332 (2)333 where α represents the absorptio ent, *h* is Planck constant, *v* stands for the light frequency, hv represents th energy of the incident photon, A is the proportionality 334 constant, E_g represents lergy gap. Additionally, n is equal to 1 and 4 for a direct 335 and indirect optical transition type of semiconductors, respectively. The n value of 336 BWO is 1 [59,60], and the E_g of BWO is estimated to be 2.80 eV. Furthermore, the VB 337 338 and CB of BWO can be determined by the following formula [61]:

339
$$E_{CB} = X - E^e - \frac{1}{2}E_g \tag{3}$$

$$E_{VB} = E_g + E_{CB} \tag{4}$$

where *X* represents the electronegativity of the semiconductor, which is calculated from the geometric average value of the electronegativity of constituent atoms in the semiconductor (6.36 eV for BWO) [62]. E^e stands for the energy of free electrons on the hydrogen scale (4.50 eV). E_g is the energy gap. Herein, applying the relevant data to the eqs. (3) and (4), the CB and VB of BWO is calculated to be +0.46 eV and +3.26 eV.

347 **3.2 Photocatalytic performance**

348 **3.2.1 Photocatalytic behavior of different materials**

As depicted in Fig. 3a, the photocatalytic activities of different materials 349 350 developed in this study were investigated by the photodegradation of TC. The TC was hardly removed in the blank test without the addition of photocatalyst and hence the 351 effect of TC photolysis on the photocatalytic degradation reaction can be neglected. As 352 shown in Fig. S7, the adsorption capacity of TC VC GO/BWO and 353 TCPP_{0.25}/rGO/BWO was enhanced in turn because of the increased surface area and 354 355 pore volume, and the adsorption equilibrium was achieved within 30 min in the darkness. After the start of illumination, the To concentration in all the photocatalysis 356 experiments gradually decreased In particular, the photocatalytic 357 tin.e. d TCPP/BWO (70.53%) binary composites 358 performances of rGO/BWO (66 93 were significantly higher than BWO counterpart (48.61%) within 1 h of visible-light 359 irradiation. More importantly, all the TCPP/rGO/BWO ternary composites with 360 different TCPP coments had an even better photocatalytic efficiency under the same 361 362 conditions. The catalytic performance was enhanced when the TCPP content was 363 increased from 0.05% to 0.25% and the TCPP_{0.25}/rGO/BWO had the highest photodegradation efficiency of 83.60%. Furthermore, the variation of absorbance curve 364 during the photodegradation of TC over TCPP_{0.25}/rGO/BWO composite was also 365 recorded. As shown in Fig. 3b, the absorbance of TC significantly decreased with the 366 increased illumination time. This can be attributed to the enhanced adsorption capacity 367 for TC and the better utilization of light energy, as well as the higher separation 368

369 efficiency of the photoexcited charge carriers. However, the photocatalytic performance started to decrease with the further increasing of TCPP content. It can be due to the 370 covering of active sites on the surface of BWO by the redundant TCPP, resulting in the 371 372 decrease of the photocatalytic activity of TCPP/rGO/BWO composites. The complete decomposition of TC was investigated by TCPP_{0.25}/rGO/BWO under visible-light 373 illumination. As shown in Fig. S8, the degradation rate of TC gradually decreased with 374 375 the prolongation of time and the complete removal of TC was ultimately achieved in 360 min, which is mainly due to the competition effect between the accumulated 376 377 intermediates and TC molecules during the photocatalysis process. In addition, another typical antibiotic ciprofloxacin (CIP) was chosen to further test alytic activity of 378 BWO, rGO/BWO and TCPP_{0.25}/rGO/BWO, and the vesult suggests that 379 380 TCPP_{0.25}/rGO/BWO also had an excellent photocallytic performance for CIP degradation compared to the BWO and r O. Fig. S9). 381

382 3.2.2 Effect of photocatalyst dosage

The amount of photocataly type 383 an application is an important factor related to both the photocatalytic performance and the economic cost. As shown in Fig. 4a, a 384 series of photocatelyst losages (from 0.10 g/L to 1.00 g/L) were chosen to investigate 385 their influence on the photocatalytic performance. The photodegradation efficiency of 386 TC rapidly increased from 61.89% to 83.60% when the dosages of TCPP_{0.25}/rGO/BWO 387 388 increases from 0.10 g/L to 0.30 g/L. When the catalyst dosage continued to increase to 0.50 g/L, the degradation efficiency was only slightly increased to 85.36%. 389 Nevertheless, the photocatalytic degradation efficiency decreases when the catalyst 390 391 dosage went beyond 1.00 g/L, which can be due to the higher turbidity and the resultant worse transmissivity of the TC solution [63]. Therefore, a modest catalyst dosage is 392 393 essential to achieve the maximum TC degradation efficiency, and here the photocatalyst dosage located at 0.30 g/L was chosen as the optimal dosage for the following
investigations.

396 **3.2.3 Effect of initial TC concentrations**

397 The effect of initial TC concentrations (ranging from 20 to 100 mg/L) on the photodegradation of TC by TCPP_{0.25}/rGO/BWO composite is depicted in Fig. 4b. The 398 results clearly show that the higher initial TC concentration leads to a lower TC removal 399 efficiency, where 83.60%, 73.55%, 64.79%, 51.89% and 44.88% of TC were removed 400 at the initial TC concentration of 15, 25, 35, 45 and 55 mg/L, respectively. This 401 phenomenon is mainly attributed to two reasons: (1) the increase of TC concentration 402 reduces the light penetration and prevents the photons from 403 the surface of 404 contaminant molecules [64]; (2) more intermediates are generated and accumulated in 405 the higher TC concentration, which compete with TC molecules for the reactive egridation of TC [65]. Therefore, the oxidizing species in the system and inhibit the 406 sary or the photodegradation of TC solution appropriate initial concentration is ne 407 g/L of TC was chosen as the optimal initial in the practical applications. Hereir 408 concentration throughout the following investigations. 409

410 3.2.4 Effect of imprganic amons

It is well-known that various anions exist in wastewater and may affect the 411 photodegradation performance of catalyst [66,67]. Therefore, the effect of inorganic 412 413 anions on the TC decomposition over TCPP_{0.25}/rGO/BWO photocatalyst was investigated by the addition of three model sodium salts (NaNO₃, NaCl and Na₂CO₃) 414 with a concentration of 0.05 M into the TC solution, mainly due to the fact that the 415 416 photocatalytic degradation process is slightly influenced by the presence of Na⁺ [68]. As shown in Fig. 4c, NO₃⁻ and Cl⁻ had minor effects on the photodegradation of TC, 417 418 which is probably due to the competition between the anions and the TC molecule for the active sites of TCPP_{0.25}/rGO/BWO during the photocatalytic process [69]. In addition, NO₃⁻ exhibited a weaker suppression effect than Cl⁻ because the photolysis of NO₃⁻ can generate a small quantity of •OH, which to some extent can facilitate the decomposition of TC [70]. However, the addition of CO_3^{2-} can significantly decrease the photodegradation efficiency of TC compared to those of NO₃⁻ and Cl⁻ as CO_3^{2-} can act as an effective scavenger of h⁺, leading to the reduction of photocatalytic performance towards TC degradation [71].

426 **3.2.5 Effect of light irradiation conditions**

The energy of photocatalytic reaction comes from the conversion of light energy, 427 so the light irradiation conditions have a significant infigure on *photocatalytic* 428 429 performance [72]. Fig. 4d shows the decomposition efficiency of TC over TCPP_{0.25}/rGO/BWO photocatalyst within different irradiation conditions by using a 430 300 W xenon lamp equipped with or without the optical filter. In the dark condition, no 431 was observed after the system reached the obvious decrease of TC concentrati 432 adsorption equilibrium within 3 m . re efficient photodegradation reaction of TC 433 (88.97%) was achieved in full spectrum light irradiation without the filter ($\lambda > 350$ nm) 434 as opposed to the degralation process (83.60%) with the filter ($\lambda > 420$ nm). Enhanced 435 TC degradation resulted from the full spectrum light irradiation was also observed 436 without the catalyst. This phenomenon can be attributed to the greater photon energy 437 438 provided by the light of shorter wavelength. Thus, the experimental data show that TCPP_{0.25}/rGO/BWO with excellent absorbency in the entire visible-spectrum exhibits 439 440 a promising application potential in the disposal of actual water bodies.

441 **3.2.6 The stability of catalyst**

442 Another major concern of the photocatalytic system is the stability and 443 recyclability of the catalyst [73-75]. To investigate the reusability of the 444 TCPP_{0.25}/rGO/BWO photocatalyst, recycling experiments were conducted by the photodegradation of TC. As displayed in Fig. 5a, the TC removal efficiency of 445 TCPP_{0.25}/rGO/BWO remained 79.27% with only 4.33% decrease after five times of 446 447 repeated treatment. Moreover, the XRD patterns (Fig. 5b) of TCPP_{0.25}/rGO/BWO photocatalyst before and after five cycles of TC photodegradation were characterized, 448 and no obvious changes of the diffraction peaks could be observed, indicating the steady 449 crystal structure. As shown in the SEM image of the post-test sample (Fig. S10), 450 TCPP_{0.25}/rGO/BWO still maintained a spherical morphology and a flower-like 451 nanostructure and essentially no obvious changes were of served. In this case, 452 TCPP_{0.25}/rGO/BWO exhibits a strong stability in the phot cess and shows 453 454 a great potential in the real wastewater application.

455 **3.3 Photo-electrochemical properties**

Devising photocatalysts with higher se ration efficiency of photogenerated 456 portant direction in the field of photocatalysis charge carriers has always been an i 457 research, because the charge ser are on fficiency plays a key role in determining the 458 photocatalytic property of the catalyst. The photocurrent response is often used to 459 evaluate the photocatal st's capability of generating and separating the photoinduced 460 charge carriers. He ein, the photocurrent responses of pristine BWO, rGO/BWO, 461 TCPP/BWO and TCPP_{0.25}/rGO/BWO composites are displayed in Fig. S11a. All the 462 463 BWO composites exhibited higher photocurrent intensity compared with the pristine BWO. Specifically, the TCPP_{0.25}/rGO/BWO composites possessed the highest 464 photocurrent density (0.65 μ A/cm²), which is 3.6 times higher than that of pure BWO 465 (0.18 µA/cm²), 1.9 times of rGO/BWO (0.35 µA/cm²) and 1.5 times of TCPP/BWO 466 $(0.43 \,\mu\text{A/cm}^2)$. The result indicates that the incorporation of BWO with rGO and TCPP 467 greatly suppress the recombination of photo-excited charges and highly promote their 468

separation, and the TCPP_{0.25}/rGO/BWO heterostructure is successfully constructed by the internal interactions rather than the simple physical mixture of the components.

Electrochemical impedance spectra (EIS) was also carried out to investigate the 471 472 photo-electrochemical properties of the as-prepared catalysts. Generally, a smaller arc radius represents a higher charge migration and separation rate of sample. As shown in 473 Fig. S11b, the arc radius is in the order of BWO > rGO/BWO > TCPP/BWO > 474 TCPP_{0.25}/rGO/BWO, which indicates that the TCPP_{0.25}/rGO/BWO has the highest 475 migration and separation efficiency of photoinduced charges. In addition, the EIS result 476 477 of various photocatalysts has a great consistency with the above photocurrent test and their photocatalytic activity. Therefore, the superior photoelectool nical properties 478 479 of TCPP_{0.25}/rGO/BWO ternary composite compared to pristine BWO and its binary 480 composites can be categorically proved.

481 **3.4 Mechanisms of enhanced photocatalytic ativ**

OH and $\cdot O_2^-$ radical species are the primary 482 Previous studies show that the osition of organic pollutants and play a key contributors to the photocatalytic decor 483 role in the process [76,77]. To reveal the photodegradation mechanisms and the 484 predominant radical species in TCPP_{0.25}/rGO/BWO system, the trapping experiments 485 were conducted by using 1.0 mmol of ethylenediaminetetraacetic acid disodium 486 (EDTA-2Na), benzoquinone (BQ) and isopropanol (IPA) as the scavengers of h^+ , $\bullet O_2^-$ 487 488 and •OH, respectively. As illustrated in Fig. 6, the photocatalytic degradation efficiency of TC did not significantly decrease (from 83.60% to 69.69%) after the addition of IPA, 489 which implies that •OH is involved but does not play a dominant role in the 490 491 photodegradation process. However, the presence of EDTA-2Na and BQ greatly suppressed the TC decomposition (from 83.60% to 33.08% and 45.40% for EDTA-2Na 492 and BQ, respectively), suggesting that h^+ and $\bullet O_2^-$ mainly contributed to the TC 493

494 photodegradation in the TCPP $_{0.25}$ /rGO/BWO system.

ESR analysis was carried out to directly prove the generation of $\cdot O_2^-$ and $\cdot OH$ in 495 the photocatalytic reaction. As displayed in Fig. S12a, four typical signals of 496 497 $DMPO-O_2^-$ for $TCPP_{0.25}/rGO/BWO$ are observed when expose to the illumination of visible light, and the signals intensity increases with the prolong of time, while no 498 signals are found in the darkness. Besides, the similar phenomenon is also observed in 499 Fig. S12b, which represents the ESR signals of DMPO-•OH. These results demonstrate 500 the presence of $\bullet O_2^-$ and $\bullet OH$ in the TCPP_{0.25}/rGO/BWO system [12,78,79], which are 501 consistent with the trapping experiments. 502 The enhanced photocatalytic activity over TCPP₀ 503 composites is closely related to the interfacial charge transfer between BWO and TCPP. Based on the 504 energy band structures of BWO and TCPP, there are wo possible mechanisms to 505 elucidate the charge transfer and TC degradation plocess in the TCPP_{0.25}/rGO/BWO 506 light, both BWO and TCPP can be excited by composites. Upon exposing to the visi 507 the incident photon owing to their nat w band gaps and the electrons on the VB 508 (HOMO) simultaneously jump into the CB (LUMO) and leave the same number of 509 holes in the VB (HONO), bading to the generation of photoinduced e^--h^+ pairs. In 510 accordance with the common double-transfer mechanism, the photogenerated electrons 511 on the LUMO of TCPP will transfer to the CB of BWO and the resultant photoinduced 512 513 holes on the VB of BWO will migrate to the HOMO of TCPP. Nevertheless, the CB level of BWO (+0.46 eV) is below the energy level of the O_2/O_2^- redox couple (-0.33) 514 eV), which is thermodynamically unable to reduce O_2 to produce O_2^- [80]. Similarly, 515 516 •OH can't be produced either in the photocatalytic process because the HOMO level of TCPP (+1.10 eV) is beyond the energy level of the OH^{-}/OH redox couple (+2.29 eV) 517 518 [81]. However, this assumption contradicts with the above-mentioned conclusion that

519 $\bullet O_2^-$ and $\bullet OH$ do exist in the TCPP_{0.25}/rGO/BWO system, which has been proved by the trapping experiments and ESR analyses. So the common double-transfer 520 mechanism cannot explain the reaction process in the TCPP_{0.25}/rGO/BWO system. 521 522 Herein, we propose another more reasonable Z-scheme mechanism to elucidate the photocatalytic degradation process, and the schematic description is given in Scheme 523 1. The electrons on the CB of BWO can spontaneously transfer to the HOMO of TCPP 524 525 because of the formed electric field between them, making BWO and TCPP served as hole-rich and electron-rich reservoir, respectively. For instance, in the previously 526 reported material Bi₂Fe₄O₉/Bi₂WO₆, electrons in the CB of Bi₂/O₆ transfer to the VB 527 of Bi₂Fe₄O₉, which has been elucidated by the Z-scheme mechanism that work [24]. 528 Similar example is also found in Z-scheme BiOI/Ag@AgI heterojunction 529 photocatalysts [82]. In such a way, the photoexc ted $-h^+$ pairs can be efficiently 530 separated by the interfacial transfer process between the two components in the Z-531 scheme TCPP_{0.25}/rGO/BWO heterojy tion. Desides, the presence of rGO in this Z-532 separation of charges and suppress their scheme system can further promote 533 recombination by collecting and shuttling electrons through its unique π - π structure 534 [83]. Thus, the superior photo-electrochemical properties over TCPP_{0.25}/rGO/BWO, 535 which has been confirmed by the photocurrent and EIS results, can be rationally 536 537 explained by the above discussion. The holes accumulated in the VB of BWO then can 538 immediately decompose the TC molecules or oxidize H₂O to produce •OH for TC degradation subsequently because the VB level of BWO (+3.26 eV) is below the 539 energy level of the OH^{-/}•OH redox couple (+2.29 eV). At the same time, the electrons 540 541 accumulated in the LUMO of TCPP can reduce O_2 to generate O_2^- to degrade TC because the LUMO level of TCPP (-0.60 eV) is higher than the energy level of the 542 O_2/O_2 redox couple (-0.33 eV). In summary, this photoexcited charge transfer 543

process perfectly match the result of photocurrent, EIS, ESR and trapping experiments, which confirms the successful construction of Z-scheme TCPP_{0.25}/rGO/BWO heterojunction.

547 In addition to the highly efficient charge separation, the considerable improvement of photocatalytic activity over the TCPP_{0.25}/rGO/BWO is also the result of the higher 548 photoenergy utilization efficiency and larger surface area. According to the above DRS 549 550 results, the introduction of rGO and TCPP to BWO greatly broadens the range of light absorption to the entire visible spectrum and increases the absorption intensity, which 551 can further generate more photoinduced e^- -h⁺ pairs and consequently more free radicals, 552 resulting in the enhanced photocatalytic activity. Moreover nce of rGO and the pr 553 554 TCPP in the TCPP_{0.25}/rGO/BWO can highly increase the surface area and pore volume 555 for holding more contaminants and creating bigger feaction interspace, which has been the more efficient charge separation, the confirmed by the results of BET. Overall 556 arfact area all in together contribute to the better light absorption, and the larg 557 ctivity of Z-scheme TCPP_{0.25}/rGO/BWO 558 remarkably enhanced photoca alvi heterojunction towards the egratiation of TC. 559

560 **4. Conclusion**

In conclusion, TCPP/rGO/BWO was designed and successfully fabricated as a 561 novel Z-scheme heterojunction photocatalyst for TC removal. The resulting 562 TCPP_{0.25}/rGO/BWO photocatalyst has the best photocatalytic performance (removal of 563 83.60% TC) compared with BWO, rGO/BWO, TCPP/BWO and other 564 TCPP/rGO/BWO composites with different TCPP contents. The hole (h⁺) and 565 superoxide radical $(\bullet O_2^{-})$ are the major contributors for the TC decomposition in the 566 TCPP_{0.25}/rGO/BWO system according to the results of trapping experiments and ESR 567 568 analysis. Additionally, the TCPP_{0.25}/rGO/BWO photocatalyst has a great recyclability 569 and stability, as it still had high removal efficiency for TC (79.27%) even after being used for five times. A Z-scheme mechanism is proposed to elucidate the charge transfer 570 process in the TCPP_{0.25}/rGO/BWO ternary composite, in which BWO and TCPP serve 571 as the hole-rich and electron-rich reservoir respectively and hence the photoexcited e⁻-572 h^+ pairs can be efficiently separated. The key improvements of this work are: (1) a facile 573 method combining hydrothermal approach with liquid ultrasonic route was developed 574 575 to synthesize ternary TCPP/rGO/BWO composites; (2) compared to the widely studied graphene/BWO composites, the ternary Z-scheme TCPP/rGO/BWO composites with 576 577 low TCPP content can significantly enhance the photocatalytic activity of the material (from 66.93% to 83.60% for TC removal efficiency); (\$ previous works 578 mainly focused on the investigation of photocatalytic degradation of organic dyes (e.g., 579 580 RhB) by using graphene/BWO-based composites, a more recalcitrant antibiotic (e.g., TC) was degraded by a novel TCPP/ $\sqrt{0}$ material; and (4) the enhanced 581 GOGWO is systematically elaborated from photocatalytic performance of TCPP 582 eparation, better light absorption, and larger 583 three aspects (i.e. more efficient char surface area), which are confirmed by characterizations such as photocurrent, EIS, DRS 584 and BET. This work provid s a new insight for novel photocatalysts preparation by 585 combining porphyric and semiconductor that have matching energy band structure and 586 promote their application in antibiotic wastewater treatment. 587

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