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## ARTICLE

# Synthesis and characterization of BiPO<sub>4</sub>/g-C<sub>3</sub>N<sub>4</sub> nanocomposites with significantly enhanced visible-light photocatalytic activity for Benzene degradation

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In order to enhance the photocatalytic activity of g-C<sub>3</sub>N<sub>4</sub> under visible light region, the BiPO<sub>4</sub>/g-C<sub>3</sub>N<sub>4</sub> nanocomposites photocatalysts with different BiPO<sub>4</sub> contents were prepared through hydrothermal with calcination method. Through N<sub>2</sub> adsorption-desorption measurement, the BiPO<sub>4</sub>/g-C<sub>3</sub>N<sub>4</sub> showed large surface area (234.8 m<sup>2</sup> g<sup>-1</sup>) and small pore diameter and the incorporation of BiPO<sub>4</sub> caused a red-shift of g-C<sub>3</sub>N<sub>4</sub> in visible light region by UV-vis diffuse reflection spectroscopy. The photocatalytic degradation of benzene over BiPO<sub>4</sub>/g-C<sub>3</sub>N<sub>4</sub> was investigated. The degradation of benzene could get 73% in 2 wt% BiPO<sub>4</sub>/g-C<sub>3</sub>N<sub>4</sub> photocatalysts under optimum reaction conditions, which was 6 times compared with pure g-C<sub>3</sub>N<sub>4</sub> at the same conditions. The improved photoactivity of BiPO<sub>4</sub>/g-C<sub>3</sub>N<sub>4</sub> could be ascribed to its effective separation of photogenerated hole-electron pairs between BiPO<sub>4</sub> and g-C<sub>3</sub>N<sub>4</sub>. Furthermore, the BiPO<sub>4</sub>/g-C<sub>3</sub>N<sub>4</sub> photocatalysts showed excellent stability. By using the *in situ* FTIR technique, ethyl acetate, carboxylic acid and aldehyde could be regarded as the intermediate products, and CO<sub>2</sub> and H<sub>2</sub>O were produced as the final products. Through Electron spin resonance (ESR), OH· and O<sub>2</sub>·<sup>-</sup> were examined in the photocatalytic degradation of benzene.

## 1 Introduction

The effective applications on solar energy conversion and environmental pollutions removal by semiconductor photocatalysts have attracted considerable attention in modern society<sup>1-4</sup>. In the past decade, traditional photocatalyst TiO<sub>2</sub> has still been extensively investigated owing to its merits, such as the nontoxicity, low cost and excellent stability against photocorrosion<sup>5-8</sup>. However, it can only be activated by the ultraviolet light ( $\lambda < 400$  nm), which only constitutes about 4% of the solar spectrum, due to its wide bandgap (anatase 3.4 eV) and have low separation efficiency of electron-hole pairs formed in photocatalytic processes<sup>7</sup>. Therefore, it is necessary to fabricate efficient new types of photocatalysts responded to visible light in order to improve the utilization of solar energy<sup>9-11</sup>.

Recently, graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>), which is as organic semiconductor materials, are increasing interest due to the constructed plastic optoelectronic systems and the chemical structure of organic semiconductor materials

since Wang et al. reported that g-C<sub>3</sub>N<sub>4</sub> showed a good photocatalytic performance for hydrogen or oxygen product by water splitting under visible light irradiation<sup>12</sup>. For g-C<sub>3</sub>N<sub>4</sub>, the catalysts possess high stability respect to thermal and chemical attacks due to its tri-s-triazine ring structure and high condensation. Meanwhile, it features a semiconductor band gap of 2.7 eV corresponding to an optical wavelength of 460 nm, which belongs to visible light region<sup>13</sup>. With an attractive electronic structure, g-C<sub>3</sub>N<sub>4</sub> is an ideal semiconductor and is valuable for photocatalysis driven applications. According to the literatures<sup>14-17</sup>, the conduction band (CB) of g-C<sub>3</sub>N<sub>4</sub> is located at about -1.3 V vs. NHE (pH = 7). Whereas its valence band (VB) top locates at about 1.4 V, resulting in a small thermodynamic driving force for organic pollutants oxidation. Furthermore, the photocatalytic efficiency of bulk g-C<sub>3</sub>N<sub>4</sub> is limited due to fast recombination of electron-hole pairs formed in photocatalytic process. In order to resolve this problem, several routes have been used including non-metal doping (boron<sup>18</sup>, fluorine<sup>19</sup> and sulfur<sup>20</sup>), optimizing porous structure<sup>17</sup>, and coupling g-

42  $C_3N_4$  with semiconductor<sup>21, 22</sup>. In these methods, there is a  
43 great interest in heterostructure of semiconductor catalytic  
44 performance. Through the coupling, synergistic effect may  
45 be achieved. High utilization efficiency of solar light can  
46 be achieved by the narrow band gap semiconductor<sup>15, 23</sup>.  
47 Simultaneously, high separation rate of photoinduced  
48 electrons-hole pairs can be realized due to the interaction  
49 of the two semiconductors. Bismuth salt photocatalysts  
50 (such as  $Bi_2WO_6$ <sup>24</sup>), which reported by other groups,  
51 exhibited superior photocatalytic activity for the pollutions  
52 degradation.  $BiPO_4$ , as one of them, finds applications in  
53 catalysis and can be used for separating radioactive  
54 elements<sup>25, 26</sup>.  $PO_4^{3-}$ , which possesses a large negative  
55 charge, is postulated to help the electron-hole pairs  
56 separation, which plays an important role in its excellent  
57 photocatalytic activity.

58 Benzene is regarded as the priority hazardous substance  
59 due to its high toxicity, confirmed carcinogenicity, and  
60 environmental persistence because it is widely used as a  
61 solvent in industrial processes<sup>27-30</sup>. Therefore, how to  
62 effectively remove benzene from the ambient environment  
63 is necessary by mild technology.

64 Herein, we synthesized a new inorganic-organic  
65  $BiPO_4/g-C_3N_4$  nanocomposites photocatalysts by  
66 hydrothermal with simple calcination method. It was  
67 found the photodegradation activity of  $BiPO_4/g-C_3N_4$  for  
68 benzene was greatly enhanced under visible light  
69 irradiation comparing with the pure  $g-C_3N_4$ . And the  
70  $BiPO_4/g-C_3N_4$  nanocomposites photocatalyst show  
71 excellent stability during the photochemical reactions. The  
72 mechanism for this enhanced photocatalytic benzene  
73 degradation can be ascribed to the large surface area,  
74 strong absorption in visible light and excellent charge  
75 transfer between  $BiPO_4$  and  $g-C_3N_4$  based on the  
76 photoluminescence results.

## 77 Experimental section

78 All chemicals were used as received without any further  
79 modification.  $Bi(NO_3)_3 \cdot 5H_2O$ ,  $NaH_2PO_4 \cdot 2H_2O$ , Melamine  
80 and anhydrous ethanol were purchased from Tianjin  
81 Kermel Chemical Reagents Development Centre. The  
82 distilled water was used in experimental process.

## 84 Photocatalysts preparation

86  $BiPO_4$  was synthesized by hydrothermal process.  
87 Typically, 8 mmol of  $Bi(NO_3)_3 \cdot 5H_2O$  was soluted into  
88 160 mL distilled water under magnetic stirring. Then 28.8  
89 mmol  $NaH_2PO_4 \cdot 2H_2O$  was added into the mixture and  
90 stirred for 1 h. The resulting suspension was transferred  
91 into a Teflon-lined stainless steel autoclave and maintained  
92 at 160 °C for 24 h. The products were washed three times  
93 with distilled water and anhydrous ethanol respectively  
94 before it dried at 120 °C for 8 h.

95  $BiPO_4/g-C_3N_4$  with different amount of  $BiPO_4$  was  
96 synthesized by calcination method. In a typical procedure,  
97  $BiPO_4$  (0.016, 0.036, 0.048 and 0.065 for sample 1 wt%  
98 Bi-CN, 2 wt% Bi-CN, 3 wt% Bi-CN and 4 wt% Bi-CN,  
99 respectively) was dissolved in 2 mL of anhydrous ethanol,  
100 and then 15.8 mmol melamine was added and dispersed by  
101 ultrasonic for 5 min. The mixtures were dried at 85 °C  
102 overnight to remove ethanol. Subsequently, the as  
103 prepared mixtures were put into a crucible with cover and  
104 heated to 500 °C for 2 h with a heating rate of 20 °C min<sup>-1</sup>  
105 and 520 °C for another 2 h in a muffle furnace. The pure  
106  $g-C_3N_4$  was also prepared for comparison purpose.

## 108 Characterization

110 The crystal structure of the samples was investigated by  
111 X-ray diffraction (XRD) using a powder X-ray  
112 diffractometer (LabX-6000, Shimadzu, Japan,  $\lambda = 1.5406$   
113 Å) with a scan rate of 0.02° s<sup>-1</sup> over a 2 $\theta$  range from 20 to  
114 70°. The morphology of the samples was detected by using  
115 transmission electron microscopy (TEM; JEOL JEM-2100;  
116 accelerating voltage, 200 kV). UV-vis diffuse reflection  
117 spectra were recorded on a Shimadzu UV-500  
118 spectrophotometer, using  $BaSO_4$  as reference. The pore  
119 structure of the obtained sample was characterized by  $N_2$   
120 adsorption using an adsorption apparatus (Quantachrome  
121 NOVA Instruments V 2.2 gas sorption analyzer). Specific  
122 surface area of the samples was determined from the  
123 Brunauer-Emmett-Teller (BET) equation, and pore volume  
124 was determined from the total amount adsorbed at relative  
125 pressures near unity. The photoluminescence (PL) spectra  
126 were surveyed by an Edinburgh FL/FS900  
127 spectrophotometer. The electron spin resonance (ESR)  
128 signals of the radicals trapped by 5, 5-dimethyl-1-pyrroline  
129 N-oxide (DMPO) were detected at ambient temperature  
130 with a Bruker (E500) spectrometer. The irradiation source  
131 was a Quanta-Ray Nd: YAG pulsed laser system ( $\lambda = 532$   
132 nm, 10 Hz). The settings for the ESR spectrometer were as  
133 follows: center field = 3510 G; sweep width = 200 G;  
134 microwave frequency = 9.85 GHz; modulation frequency  
135 = 100 kHz and power = 20 mW. To minimize  
136 measurement errors, the same quartz capillary tube was  
137 used throughout the ESR measurements.

## 139 Photocatalytic activity test

141 The photocatalytic degradation of gaseous benzene was  
142 carried out under visible light, using a 500W Xe lamp  
143 (Shanghai Seagull Colored Optical Glass Co., Ltd.) with a  
144 UV-cutoff filter ( $\lambda > 400$  nm). Photocatalytic degradation  
145 of benzene was conducted in a Pyrex glass cylindrical  
146 reactor with the volume of 120 mL. 0.1 g of the catalysts  
147 was put at the bottom of the reactor. Then, benzene vapor  
148 was mixed with the air (78% nitrogen, 21% oxygen as  
149 reaction gas) and introduced into the reactor at room  
150 temperature. Once the concentration of the reactants had

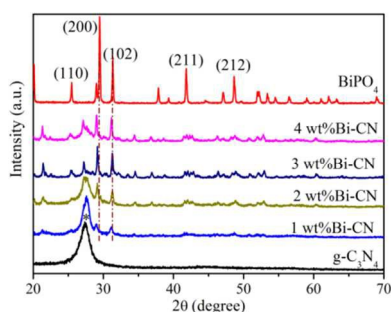
151 been stabilized, the inlet and outlet ports were shut off.  
 152 After adsorption equilibration in the dark for 1 h, the lamp  
 153 was turned on to allow the photoreaction to proceed. The  
 154 concentration of benzene was analyzed by gas  
 155 chromatogram (Agilent7890A) with HP-5 capillary  
 156 column (30 m×320 μm×0.25 μm).

157 The *in situ* FTIR measurement was carried out in a  
 158 home-built IR cell (about 120 mL), equipped with two  
 159 NaCl windows and a sample holder for the catalyst wafer  
 160 to analyze the degradation mechanism of benzene.  
 161 Benzene vapor mixture with the dry air, which pretreated  
 162 through a drying column packed with desiccant and  
 163 molecular sieves, was introduced to the IR cell at room  
 164 temperature. When the sample was saturated with reaction  
 165 gas, the inlet and outlet ports were shut off. After  
 166 adsorption equilibration in the dark for 1 h, the 500 W Xe  
 167 lamp (Shanghai Seagull Colored Optical Glass Co.) with a  
 168 UV-cutoff filter ( $\lambda > 400$  nm) were used as visible light. A  
 169 Bruker VERTEX 70 FT-IR equipped with a DTGS  
 170 detector was employed for recording of the FTIR spectra.

## 171 Results and discussion

### 172 Characterization of the BiPO<sub>4</sub>/g-C<sub>3</sub>N<sub>4</sub> nanocomposites

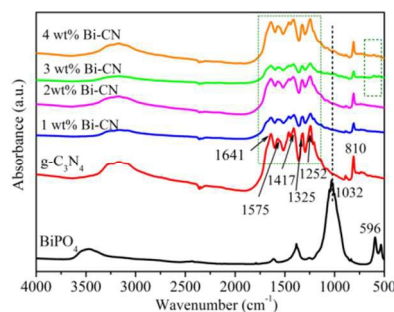
173 XRD pattern is used to investigate the phase structures  
 174 of the samples, and the typical diffraction patterns are  
 175 shown in Fig. 1. The peak at 27.4° in the XRD patterns of  
 176 the samples is due to the stacking of the conjugated  
 177 aromatic system, which is indexed for graphitic materials  
 178 as the (002) peak of the g-C<sub>3</sub>N<sub>4</sub><sup>13</sup>. For BiPO<sub>4</sub>, Evidently,  
 179 the same diffraction peaks of BiPO<sub>4</sub> (JCPDS 15-0766)  
 180 have been detected, in which the peaks at 25.5°, 29.5°,  
 181 31.3°, 41.9° and 48.7° are corresponding to the diffraction  
 182 peaks of (110), (200), (102), (211) and (212) crystal planes  
 183 of BiPO<sub>4</sub><sup>31</sup>. For BiPO<sub>4</sub>/g-C<sub>3</sub>N<sub>4</sub> samples, these peaks are  
 184 intensified with the increasing amount of BiPO<sub>4</sub>, while the  
 185 ones belonging to C<sub>3</sub>N<sub>4</sub> gradually decreased. The intensity  
 186 of the peak is decreased which indicated that BiPO<sub>4</sub>  
 187 nanoparticles may be wrapped in the interlayer of g-C<sub>3</sub>N<sub>4</sub>  
 188 and weaken the force of interlayer stacking, accordingly.  
 189 In addition, no impurity peaks were observed.



201 **Fig 1.** XRD patterns of the BiPO<sub>4</sub>, pure g-C<sub>3</sub>N<sub>4</sub> and Bi-  
 202 CN.

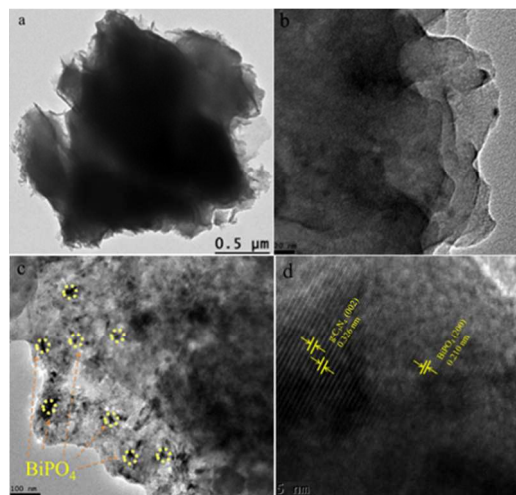
203 Fig. 2 shows a comparison of the FTIR spectra of BiPO<sub>4</sub>, 1  
 204

205 032 cm<sup>-1</sup> and 596 cm<sup>-1</sup> could be attributed to δ(PO<sub>4</sub>) and  
 206 ν(PO<sub>4</sub>), respectively<sup>32</sup>. For the g-C<sub>3</sub>N<sub>4</sub>, the broad band at 3  
 207 155 cm<sup>-1</sup> is attributed to stretching modes of NH and  
 208 NH<sub>2</sub>. The band at 1 325 cm<sup>-1</sup> corresponds to C(sp<sup>2</sup>)-N  
 209 stretching, and the band at 1 641 cm<sup>-1</sup> assigns to C(sp<sup>2</sup>)=N  
 210 stretching modes. The 807 cm<sup>-1</sup> band is attributed to s-  
 211 triazine ring vibration modes. The C-NH-C unit is found  
 212 in melem (1 252 and 1 325 cm<sup>-1</sup>)<sup>33</sup>. It can be clearly seen  
 213 that the main characteristic peaks of g-C<sub>3</sub>N<sub>4</sub> and BiPO<sub>4</sub> all  
 214 appeared in the Bi-CN photocatalysts.



226 **Fig 2.** FTIR spectra of the BiPO<sub>4</sub>, pure g-C<sub>3</sub>N<sub>4</sub> and Bi-  
 227 CN.

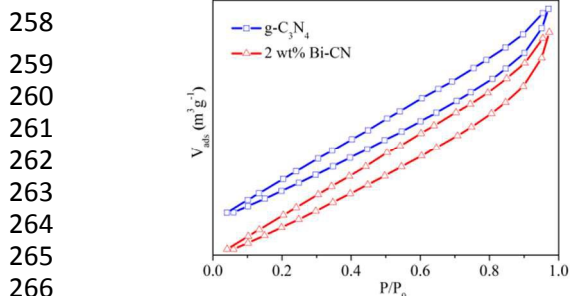
228 The existence of BiPO<sub>4</sub> in the g-C<sub>3</sub>N<sub>4</sub> was visualized by  
 229 the TEM observations, as shown in Fig. 3. The g-C<sub>3</sub>N<sub>4</sub>  
 230 shows layer structure (Fig. 3a and b), which is consistent  
 231 with results reported previously. BiPO<sub>4</sub> nanoparticles with  
 232 average size of about 20 nm were well dispersed in the g-  
 233 C<sub>3</sub>N<sub>4</sub> phase (Fig. 3c). The HRTEM reveals that the fringe  
 234 spacing of 0.326 nm can be indexed to the (002) crystal  
 235 planes of g-C<sub>3</sub>N<sub>4</sub> (Fig. 3d), while the lattice spacing of  
 236 0.210 nm can be assigned to the (200) facets of BiPO<sub>4</sub>.



237 **Fig 3.** TEM images of pure g-C<sub>3</sub>N<sub>4</sub> (a and b) and 2 wt%  
 238 Bi-CN (c) and HRTEM image (d) of 2 wt% Bi-CN.

240 Fig. 4 shows N<sub>2</sub> adsorption-desorption isotherms of the  
 241 2 wt% Bi-CN and pure g-C<sub>3</sub>N<sub>4</sub>. The 2 wt% Bi-CN and  
 242 pure g-C<sub>3</sub>N<sub>4</sub> were found to be of IV-type isotherms  
 243 according to the BDDT classification. The hysteresis loops  
 244 for the 2 wt% Bi-CN and g-C<sub>3</sub>N<sub>4</sub> were similar, which

245 shown the incorporation of BiPO<sub>4</sub> didn't affect the specific  
 246 surface area of g-C<sub>3</sub>N<sub>4</sub>. The BET surface areas of the 2 wt%  
 247 Bi-CN and g-C<sub>3</sub>N<sub>4</sub> were 234.8 and 232.6 m<sup>2</sup> g<sup>-1</sup>,  
 248 respectively (see Table 1). The large surface area can  
 249 provide more photocatalytic active sites and will be  
 250 beneficial for the photocatalytic application. Meanwhile,  
 251 the pore size of 2 wt% Bi-CN was calculated as 2.432 nm  
 252 based on the N<sub>2</sub> adsorption-desorption isotherms,  
 253 exhibiting a character of mesoporous materials. It has been  
 254 reported that large pore volume might be beneficial for the  
 255 catalytic activity, while a small average pore diameter  
 256 might also be one of the reasons for the increasing  
 257 catalytic activity<sup>34, 35</sup>.

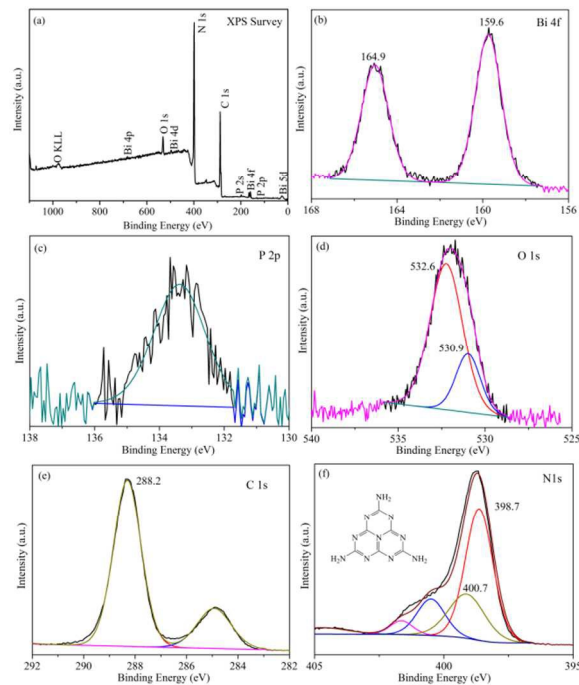


267 **Fig 4.** N<sub>2</sub> adsorption-desorption isotherms of 2 wt% Bi-CN  
 268 and pure g-C<sub>3</sub>N<sub>4</sub>.

269 **Table 1** Physical properties of 2 wt% Bi-CN and g-C<sub>3</sub>N<sub>4</sub>.

Catalyst	Surface Area (m <sup>2</sup> /g)	Pore Volume (m <sup>3</sup> /g)	Average Pore Diameter (nm)
2 wt% Bi-CN	234.8	0.301	2.432
g-C <sub>3</sub> N <sub>4</sub>	232.6	0.286	2.441

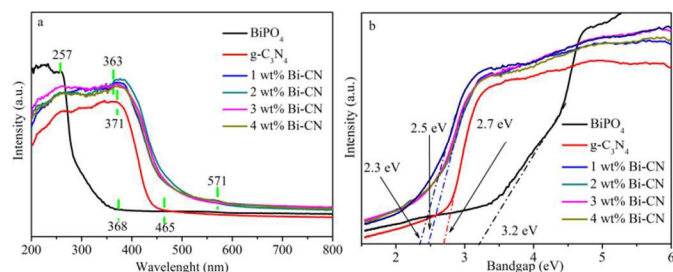
270 Fig. 5a-5f shows the XPS spectra of 2 wt% Bi-CN. Fig.  
 271 5a is the XPS survey spectrum of the sample which  
 272 contains the peaks of Bi 4p, Bi 4d, Bi 4f, Bi 5d, O KLL, O  
 273 1s, P 2s, P 2p, N 1s, and C 1s. The peaks at 164.9 eV and  
 274 159.6 eV can be assigned to the binding energies of Bi 4f  
 275 5/2 and Bi 4f 7/2 (Fig. 5b), which indicates the existence  
 276 of a trivalent oxidation state for Bi<sup>3+</sup>. A broad signal peak  
 277 at about 132.7 eV suggests that the P in the sample exist in  
 278 the oxidation state of P<sup>5+</sup> (Fig. 5c)<sup>33</sup>. For the O 1s, the peak  
 279 at 530.9 eV is attributed to the crystal lattice oxygen, while  
 280 the peak at 532.6 eV is related to adsorbed oxygen (Fig.  
 281 5d). The binding energy of 288.2 eV can be corresponded  
 282 to the C-N-C coordination in the C 1s (Fig. 5e). In the N 1s  
 283 spectrum several binding energies can be separated (Fig.  
 284 5f). The main signal shows occurrence of C-N-C groups  
 285 (398.7 eV) and tertiary nitrogen N-(C)<sub>3</sub> groups (400.7  
 286 eV)<sup>37</sup>.



287

288 **Fig 5.** XPS survey spectrum of 2 wt% Bi-CN (a) and its high-  
 289 resolution XPS spectra: (b) Bi 4f, (c) P 2p, (d) O 1s  
 290 and (f) N 1s.

291 The absorption range of light plays an important role in  
 292 the photocatalysis, especially for the visible light  
 293 photodegradation of contaminants. Fig 6a shows the UV-  
 294 vis DRS of the as-synthesized samples. As it can be  
 295 observed, BiPO<sub>4</sub> only can absorb UV light, which  
 296 absorbance region is from 257 to 368 nm. However, for  
 297 pure g-C<sub>3</sub>N<sub>4</sub> and Bi-CN samples, strong absorption in the  
 298 visible region can be appeared, which absorbance region is  
 299 from 371 to 465 nm and Bi-CN samples exhibit absorption  
 300 edge of 571 nm together with an increased light absorption,  
 301 which has a significant redshift (ca. 106 nm) compared  
 302 with g-C<sub>3</sub>N<sub>4</sub>. The results indicated that loading of BiPO<sub>4</sub>  
 303 improved the light absorption ability. There are two major  
 304 reasons to explain the resultd. Firstly, the interaction of  
 305 heterojunction between BiPO<sub>4</sub> and g-C<sub>3</sub>N<sub>4</sub> effectively  
 306 enhances the separation of electron-hole pairs account for  
 307 the band gap transition of photo-generated electrons and  
 308 then enhanced the absorption in the visible light region<sup>31</sup>.  
 309 Secondly, as a colour change of the composites samples,  
 310 which become darker, that is, from pale yellow to grey,  
 311 along with a increasing amount of BiPO<sub>4</sub> was introduced  
 312 into the g-C<sub>3</sub>N<sub>4</sub> would also cause the absorbance  
 313 enhanced<sup>38</sup>. The band gap of the pure g-C<sub>3</sub>N<sub>4</sub> is estimated  
 314 to be about 2.7 eV (Fig 6b). It is noteworthy that the band  
 315 gap of Bi-CN samples, which is from 2.3 to 2.5 eV due to  
 316 incorporation different amount of BiPO<sub>4</sub>, tends to be  
 317 smaller than that of pure g-C<sub>3</sub>N<sub>4</sub>, indicating that the  
 318 absorption of the Bi-CN samples is shifted to the lower  
 319 energy region.



320  
321 **Fig 6.** UV-visible DRS spectra (a) and curves of  $(\alpha h\nu)^{1/2}$   
322 vs. photon energy (b) of the  $\text{BiPO}_4$ , pure  $\text{g-C}_3\text{N}_4$  and Bi-  
323 CN with different amount of  $\text{BiPO}_4$ .

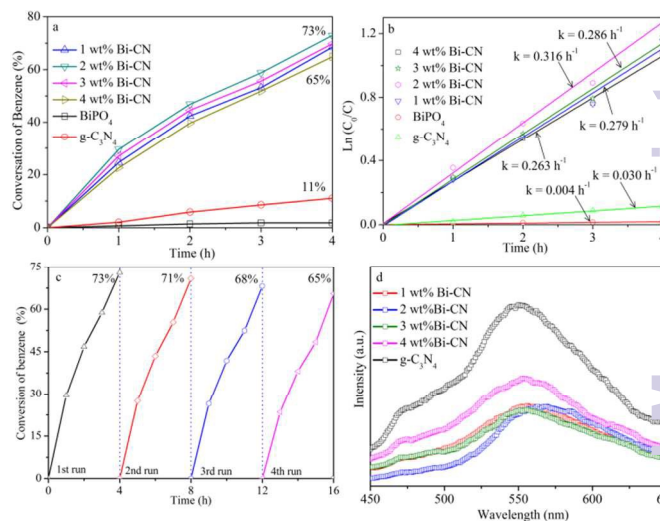
324  
325 **Photocatalytic degradation performance of the**  
326  **$\text{BiPO}_4/\text{g-C}_3\text{N}_4$  photocatalysts**

327  
328 The photocatalytic degradation of gaseous benzene over  
329 the  $\text{BiPO}_4/\text{g-C}_3\text{N}_4$  photocatalysts was illustrated in Fig. 7a.  
330 As shown in Fig. 7a, the photocatalytic activities of  $\text{BiPO}_4$   
331 and  $\text{g-C}_3\text{N}_4$  were very low under visible light. The  
332 conversion of benzene was only 2% and 11%, respectively.  
333 In contrast, Bi-CN samples presented much higher photo  
334 degradation activity for benzene under the same conditions.  
335 Especially, the conversion of benzene over 2 wt% Bi-CN  
336 achieved 73% after 4 h under visible light irradiation. The  
337 Bi-CN exhibit a higher photocatalytic activity for the  
338 decomposition of gaseous benzene compared to pure  $\text{g-C}_3\text{N}_4$   
339 under visible light irradiation, which is due to its  
340 strong absorption in visible-light region (from 571 to 363  
341 nm) and excellent charge separation characteristics.  
342 However, the removal of benzene decreased with  
343 increasing amount of  $\text{BiPO}_4$ , which might result from the  
344 additional recombination of photo induced electron-hole  
345 pairs in the excess amount of  $\text{BiPO}_4$  particles and  
346 decreasing the diffraction intensity assigned to  $\text{g-C}_3\text{N}_4$   
347 because the crystal had important role in photocatalytic  
348 oxidation process<sup>39, 40</sup>.

349 The photocatalytic reaction followed a pseudo-first-  
350 order reaction, and the rate constant of benzene  
351 decomposition over 2 wt% Bi-CN, which was estimated to  
352 be about  $0.316 \text{ h}^{-1}$ , was faster than the other samples (Fig.  
353 7b). Furthermore, the photochemical stability of 2 wt% Bi-  
354 CN was tested. As shown in Fig. 7c, the benzene  
355 degradation efficiency declines only about 8% after four  
356 consecutive runs. Therefore, the as-synthesized  $\text{BiPO}_4/\text{g-}$   
357  $\text{C}_3\text{N}_4$  photocatalyst exhibits excellent stability in the  
358 visible light photochemical degradation reactions.

359 The PL spectroscopy is usually utilized to investigate  
360 the separation of the photogenerated electron-hole pairs  
361 during photocatalytic process<sup>41, 42</sup>. Fig. 7d shows the PL  
362 spectra of  $\text{g-C}_3\text{N}_4$  and Bi-CN. The PL spectrum of  $\text{g-C}_3\text{N}_4$   
363 shows a strong emission, which indicates the electrons and  
364 holes recombine rapidly. By contrast, for Bi-CN  
365 photocatalysts, there was weak PL peak observed,

366 indicating that the photogenerated electron-hole pairs  
367 recombination was very slow. It is concluded that the  
368 heterojunction of  $\text{BiPO}_4$  and  $\text{g-C}_3\text{N}_4$  may act as an active  
369 center for decreasing the recombination of photoinduced  
370 electron-hole pairs. On the other hand, according to the  
371 result of the  $\text{N}_2$  adsorption-desorption, Bi-CN showed  
372 large specific surface area, which means that its surface  
373 can provide more photocatalytic active sites.

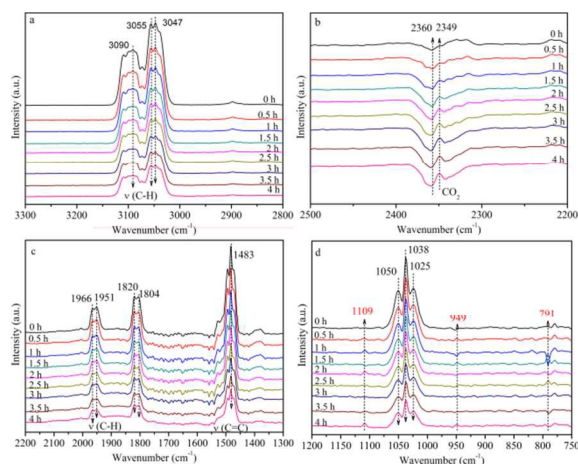


375 **Fig. 7.** (a) Photocatalytic degradation of benzene using  
376 the as-prepared the  $\text{BiPO}_4$ , pure  $\text{g-C}_3\text{N}_4$  and Bi-CN  
377 photocatalysts 1-5 ( $[\text{benzene}]_0 = 115 \text{ ppm}$ ,  $[\text{catalysts}]_0 =$   
378  $100 \text{ mg}$ ,  $I_0 = 200 \text{ mW cm}^{-2}$ ). (b) The variation of  $\ln(C/C_0)$   
379 of benzene by different processing routes. (c) Cyclic  
380 photodegradation of benzene over 2 wt% Bi-CN under  
381 visible light irradiation. (d) PL spectra of  $\text{g-C}_3\text{N}_4$  and Bi-  
382 CN.

383  
384 **In situ FTIR study of photodegradation mechanism of**  
385 **benzene**

386  
387 Real-time monitoring of transient events occurring on  
388 the catalyst during the reaction and the surface adsorbed  
389 species, which were detected by *in situ* FTIR, will give an  
390 important insight into the reaction mechanisms. In this  
391 work, a set of IR transmittance spectra are obtained during  
392 the photocatalytic oxidation of benzene over 2 wt% Bi-CN  
393 (Fig. 8). Prior to light irradiation ( $t=0$ ), when benzene  
394 reached adsorption equilibrium on the surface of the 2 wt%  
395 Bi-CN, strong peaks due to gas-phase benzene appeared at  
396  $3090$ ,  $3055$  and  $3047 \text{ cm}^{-1}$ , which are assigned to the C-  
397 H stretching mode of benzene, respectively<sup>43</sup> (Fig. 8a).  
398 The band of  $1483 \text{ cm}^{-1}$  is associated with C=C stretching.  
399 The vibrational bands at  $1804$ ,  $1820$ ,  $1951$ , and  $1966$   
400  $\text{cm}^{-1}$  are assigned to C-H out-of-plane bending mode<sup>44</sup> (Fig.  
401 8c). The bands at  $1050$ ,  $1038$  and  $1025 \text{ cm}^{-1}$  could be  
402 ascribed to C-H in-plane deformation vibrations<sup>43</sup> (Fig. 8d).  
403 After reaction, the intensity of bands at  $3090$ ,  $3055$  and  
404  $3047 \text{ cm}^{-1}$  decreased significantly with increasing reaction

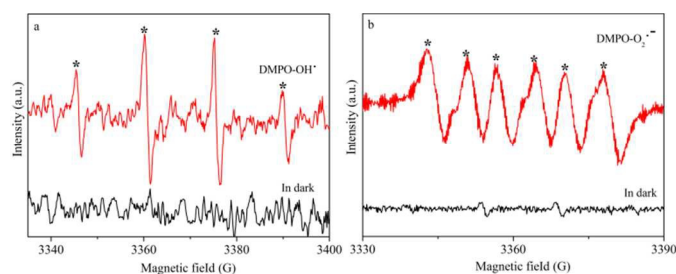
405 time. After 4 h, most of benzene was decomposed.  
 406 Meanwhile, the bands at 2 360 and 2 342  $\text{cm}^{-1}$  (Fig. 8b)  
 407 corresponding to  $\text{CO}_2$  increased as the reaction proceeded,  
 408 and some new surface species, which appeared at 1 109,  
 409 949 and 791  $\text{cm}^{-1}$ , were evidenced by the FTIR spectra in  
 410 Fig. 8d. Among them, bands at 1 109  $\text{cm}^{-1}$  is assigned to  
 411 the C-O-C stretching vibration which existed in ester<sup>45</sup>.  
 412 The 949  $\text{cm}^{-1}$  band is assigned to O-H out-of-plane  
 413 deformation vibration of carboxylic acid, and 791  $\text{cm}^{-1}$  is  
 414 assigned to C-H deformation vibration of aldehyde<sup>46</sup>. On  
 415 the basis of the previous reports and the results,  
 416 ethylacetate, carboxylic acid and aldehyde are the  
 417 intermediate products during the photocatalytic  
 418 degradation of benzene,  $\text{CO}_2$  and  $\text{H}_2\text{O}$  are produced as the  
 419 final product.



420 **Fig. 8.** (a-d) Infrared spectra recorded as a function of  
 421 irradiation time following the photooxidation of toluene  
 422 over 2 wt% Bi-CN photocatalyst.

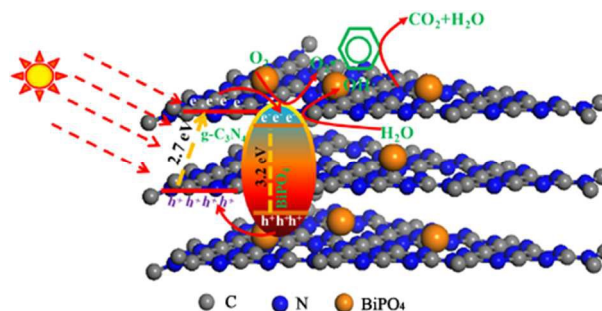
423 In order to detect the reactive species evolved during the  
 424 photocatalytic reaction process, such as hydroxyl radical  
 425 and superoxide radical species, the electron spin resonance  
 426 (ESR) technique was usually used<sup>47</sup>. As shown in Fig. 9a,  
 427 four characteristic peaks of  $\text{DMPO-OH}\cdot$  with intensity  
 428 1:2:2:1 can be observed with visible light irradiated  
 429 aqueous dispersions of 2 wt% Bi-CN. Similarly, the  
 430 stronger six characteristic peaks of the  $\text{DMPO-O}_2^{\cdot-}$   
 431 adducts are also observed with visible light irradiated  
 432 methanol dispersions of 2 wt% Bi-CN in Fig 9b. ESR  
 433 results indicate that the generation of  $\text{OH}\cdot$  radical and  $\text{O}_2^{\cdot-}$   
 434 radical species is crucial during the reaction and it is  
 435 confirmed that both  $\text{OH}\cdot$  and  $\text{O}_2^{\cdot-}$  radicals are produced on  
 436 the surface of 2 wt% Bi-CN and  $\text{OH}\cdot$  radicals with strong  
 437 oxidation capability act as the predominant species.

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446 **Fig. 9.** ESR spectra of radical adducts trapped by DMPO  
 447 in 2 wt% Bi-CN dispersions after 60 s visible-light  
 448 irradiation ( $\lambda > 400 \text{ nm}$ ): (a)  $\text{DMPO-OH}\cdot$  formed in  
 449 irradiated aqueous dispersions; (b)  $\text{DMPO-O}_2^{\cdot-}$  formed in  
 450 irradiated methanol dispersions.

451 Based on the above results, the photocatalytic  
 452 mechanism may be proposed in Scheme 1. Under visible  
 453 light irradiation, electrons ( $e^-$ ) are excited from the VB of  
 454  $\text{g-C}_3\text{N}_4$  and created holes ( $h^+$ ) in the VB. Normally, these  
 455 charge carriers quickly recombine and only a fraction of  
 456 electrons could participate in the photocatalytic reaction.  
 457 However, when  $\text{g-C}_3\text{N}_4$  is connected with  $\text{BiPO}_4$  to form  
 458 composites, these photoinduced electrons on the CB of  $\text{g-}$   
 459  $\text{C}_3\text{N}_4$  tend to transfer to  $\text{BiPO}_4$  particles due to their  
 460 excellent electronic conductivity, improving to hole-  
 461 electron separation. The transferred electrons will  
 462 accumulate on the  $\text{BiPO}_4$  nanoparticles and presumably as  
 463 interface bound exciton pairs to capture the adsorbed  $\text{O}_2$   
 464 and  $\text{H}_2\text{O}$  on  $\text{g-C}_3\text{N}_4$  surface to form  $\text{OH}\cdot$  and  $\text{O}_2^{\cdot-}$ , and  
 465 then participate in photocatalytic oxidation reaction.  
 466 Meanwhile, on the VB of  $\text{g-C}_3\text{N}_4$ , the high separation  
 467 efficiency of photogenerated electron-hole pairs is result  
 468 in the increase of the number of holes, which could  
 469 directly enhance the moderate performance of  
 470 mineralization ability.



471 **Scheme. 1.** Schematic diagram showing the possible  
 472 mechanism for the photocatalytic degradation of benzene  
 473 over the  $\text{BiPO}_4/\text{g-C}_3\text{N}_4$ .

## 475 Conclusions

476 In summary, we have successfully synthesized  $\text{BiPO}_4/\text{g-}$   
 477  $\text{C}_3\text{N}_4$  by hydrothermal with calcination method for  
 478 efficient photocatalytic degradation of gaseous benzene  
 479 under visible light irradiation. The photocatalytic activities  
 480 of  $\text{BiPO}_4/\text{g-C}_3\text{N}_4$  on benzene degradation under visible  
 481 light irradiation increase to about 6.0 times as high as

482 those of pure g-C<sub>3</sub>N<sub>4</sub>. The significant enhancement on  
483 photocatalytic performance was ascribed to strong  
484 absorption in visible light and rapid photogenerated  
485 electron transfer rate and charge separation efficiency in  
486 BiPO<sub>4</sub>/g-C<sub>3</sub>N<sub>4</sub>. Through *in situ* FTIR technique, phenol,  
487 carboxylic acid and aldehyde could be regarded as the  
488 intermediate products, and CO<sub>2</sub> and H<sub>2</sub>O are determined as  
489 the final product during the reaction process. Through ESR,  
490 OH· and O<sub>2</sub><sup>-</sup> are examined in the photocatalytic  
491 degradation of benzene. Such BiPO<sub>4</sub>/g-C<sub>3</sub>N<sub>4</sub>  
492 nanocomposites with high photocatalytic performances  
493 may provide an alternative of traditional catalysts to  
494 address energy conversion, green chemistry, and  
495 environmental issues.

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## 525 References

526  
527 1. C. T. Dinh, H. Yen, F. Kleitz and T. O. Do, *Angew Chem Int Ed*  
528 *Engl*, 2014, 53, 6618-6623.  
529 2. G. Manna, R. Bose and N. Pradhan, *Angew Chem Int Ed Engl*, 2014,  
530 53, 6743-6746.  
531 3. J. Tian, Z. Zhao, A. Kumar, R. I. Boughton and H. Liu, *Chem Soc*  
532 *Rev*, 2014, 43, 6920-6937.  
533 4. X. Wang, G. Sun, P. Routh, D. H. Kim, W. Huang and P. Chen,  
534 *Chem Soc Rev*, 2014, 43, 7067-7098.  
535 5. H.-E. Kim, J. Lee, H. Lee and C. Lee, *Applied Catalysis B:*  
536 *Environmental*, 2012, 125, 331-349.  
537 6. M. Pelaez, N. T. Nolan, S. C. Pillai, M. K. Seery, P. Falaras, A. G.  
538 Kontos, P. S. M. Dunlop, J. W. J. Hamilton, J. A. Byrne, K. O'Shea,  
539 M. H. Entezari and D. D. Dionysiou, *Applied Catalysis B:*  
540 *Environmental*, 2012, 125, 331-349.  
541 7. R. Asahi, T. Morikawa, H. Irie and T. Ohwaki, *Chem Rev*, 2014,  
542 114, 9824-9852.  
543 8. K. Lee, A. Mazare and P. Schmuki, *Chem Rev*, 2014, 114, 9385-  
544 9454.

545 9. J. L. Wang, C. Wang and W. Lin, *ACS Catalysis*, 2012, 2, 2630-  
546 2640.  
547 10. M. L. Marin, L. Santos-Juanes, A. Arques, A. M. Amat and M. A.  
548 Miranda, *Chem Rev*, 2012, 112, 1710-1750.  
549 11. D. Chen, H. Zhang, Y. Liu and J. Li, *Energy & Environmental*  
550 *Science*, 2013, 6, 1362-1387.  
551 12. X. Wang, K. Maeda, A. Thomas, K. Takanabe, G. Xin, J. M.  
552 Carlsson, K. Domen and M. Antonietti, *Nat Mater*, 2009, 8, 76-80.  
553 13. X. Bai, L. Wang, Y. Wang, W. Yao and Y. Zhu, *Applied Catalysis*  
554 *B: Environmental*, 2014, 152-153, 262-270.  
555 14. Z. a. Huang, Q. Sun, K. Lv, Z. Zhang, M. Li and B. Li, *Applied*  
556 *Catalysis B: Environmental*, 2015, 164, 420-427.  
557 15. M. J. Muñoz-Batista, M. Fernández-García and A. Kubacka,  
558 *Applied Catalysis B: Environmental*, 2015, 164, 261-270.  
559 16. L. Ge, C. C. Han, X. L. Xiao and L. L. Guo, *Applied Catalysis B:*  
560 *Environmental*, 2013, 142, 414-422.  
561 17. S. Cao and J. Yu, *The Journal of Physical Chemistry Letters*, 2014,  
562 5, 2101-2107.  
563 18. S. C. Yan, Z. S. Li and Z. G. Zou, *Langmuir*, 2010, 26, 3894-3901.  
564 19. Y. Wang, Y. Di, M. Antonietti, H. Li, X. Chen and X. Wang,  
565 *Chemistry of Materials*, 2010, 22, 5119-5121.  
566 20. G. Liu, P. Niu, C. H. Sun, S. C. Smith, Z. G. Chen, G. Q. (Max) Lu,  
567 and H. M. Cheng, *J. Am. Chem. Soc.* 2010, 132, 11642-11648.  
568 21. J. Chen, S. Shen, P. Guo, M. Wang, P. Wu, X. Wang and L. Guo,  
569 *Applied Catalysis B: Environmental*, 2014, 152-153, 335-341.  
570 22. Y. He, J. Cai, L. Zhang, X. Wang, H. Lin, B. Teng, L. Zhao, W.  
571 Weng, H. Wan and M. Fan, *Industrial & Engineering Chemistry*  
572 *Research*, 2014, 53, 5905-5915.  
573 23. S. Zhou, Y. Liu, J. M. Li, Y. Y. Wang, G. Y. Jiang, Z. Zhao, D. X.  
574 W, A. J. Duan, J. Liu and Y. C. Wei, *Applied Catalysis B:*  
575 *Environmental*, 2014, 158-159, 20-29.  
576 24. L. Ge, C. Han and J. Liu, *Applied Catalysis B: Environmental*,  
577 2011, 108-109, 100-107.  
578 25. G. Liu, S. Liu, Q. Lu, H. Sun and Z. Xiu, *Industrial & Engineering*  
579 *Chemistry Research*, 2014, 53, 13023-13029.  
580 26. Y. Liu, Y. Lv, Y. Zhu, D. Liu, R. Zong and Y. Zhu, *Applied*  
581 *Catalysis B: Environmental*, 2014, 147, 851-857.  
582 27. T. Marino, R. Molinari and H. Garcia, *Catalysis Today*, 2013, 206,  
583 40-45.  
584 28. H. Zhuang, Q. Gu, J. Long, H. Lin, H. Lin and X. Wang, *RSC*  
585 *Advances*, 2014, 4, 34315-34324.  
586 29. F. Villanueva, A. Notario, J. A. Adame, M. C. Millan, R. Mabilia  
587 and J. Albaladejo, *Environ Technol*, 2013, 34, 289-299.  
588 30. D. K. Ortega-Gonzalez, D. Zaragoza, J. Aguirre-Garrido, H.  
589 Ramirez-Saad, C. Hernandez-Rodriguez and J. Jan-Roblero, *Folia*  
590 *Microbiol (Praha)*, 2013, 56, 569-577.  
591 31. Z. Li, B. Li, S. Peng, D. Li, S. Yang and Y. Fang, *RSC Advances*,  
592 2014, 4, 35144-35188.  
593 32. B. Long, J. Huang and X. Wang, *Progress in Natural Science:*  
594 *Materials International*, 2012, 22, 644-653.  
595 33. Z. Li, S. Yang, J. Zhou, D. Li, X. Zhou, C. Ge and Y. Fang,  
596 *Chemical Engineering Journal*, 2014, 241, 344-351.  
597 34. C. Andriamiadamanana, C. Laberty-Robert, M. T. Sougrati, S.  
598 Casale, C. Davoisne, S. Patra and F. Sauvage, *Inorg Chem*, 2014,  
599 53, 10129-10139.  
600 35. M. Tahir, C. Cao, N. Mahmood, F. K. Butt, A. Mahmood, F. Idrees,  
601 S. Hussain, M. Tanveer, Z. Ali and I. Aslam, *ACS Appl Mater*  
602 *Interfaces*, 2014, 6, 1258-1265.  
603 36. W. C. Xu, G. Y. Zhou, J. Z. Fang, Z. Liu, Y. F. Chen and C. P.  
604 Cen, *Int. J. Photoenergy*, 2013, 234806  
605 37. S. Wang, D. Li, C. Sun, S. Yang, Y. Guan and H. He, *Applied*  
606 *Catalysis B: Environmental*, 2014, 144, 885-892.  
607 38. J. Yuan, Q. Gao, X. Li, Y. Liu, Y. Fang, S. Yang, F. Peng and X.  
608 Zhou, *RSC Adv.*, 2014, 4, 52332-52337.  
609 39. C. Xiong, X. Deng and J. Li, *Applied Catalysis B: Environmental*,  
610 2010, 94, 234-240.  
611 40. C.-Y. Yue, X.-W. Lei, R.-Q. Liu, H.-P. Zhang, X.-R. Zhai, W.-P.  
612 Li, M. Zhou, Z.-F. Zhao, Y.-X. Ma and Y.-D. Yang, *Crystal Growth*  
613 *& Design*, 2014, 14, 2411-2421.  
614 41. Y. Ren, Q. Zhao, X. Li, W. Xiong, M. Tade and L. Liu, *Journal of*  
615 *Nanoparticle Research*, 2014, 16, 2532.  
616 42. T. Simon, N. Bouchonville, M. J. Berr, A. Vaneski, A. Adrovic, D.  
617 Volbers, R. Wyrwich, M. Doblinger, A. S. Susha, A. L. Rogach, F.



- 618 Jackel, J. K. Stolarczyk and J. Feldmann, *Nat Mater*, 2014, 13,  
619 1013-1018.
- 620 43. S.V. Awate, R. K. Sahu, M. D. Kadgaonkar, R. Kumar and N. M.  
621 Gupta, *Catal. Today*, 2009, 141, 144-151.
- 622 44. W. C. Wu, L. F. Liao, C. F. Lien and J. L. Lin, *Phys. Chem. Chem.*  
623 *Phys.*, 2001, 3, 4456-4461.
- 624 45. H. P. Yang, R. Yan, H. P. Chen, D. H. Lee, D. T. Liang and C.G.  
625 Zheng, *Energy Fuels*, 2006, 20, 1321-1328.
- 626 46. N. Sivasankar and S. Vasudevan, *J. Phys. Chem. B* 2004, 108,  
627 11585-11590.
- 628 47. F. Dong, Z. Y. Wang, Y. H Li, W. K. Ho and S. C. Lee, *Environ.*  
629 *Sci. Technol.* 2014, 48, 10345-10353.