

Differences of characteristics and performance with Bi3+ and Bi2O3 doping over TiO2 for photocatalytic oxidation under visible light

Article

Accepted Version

Huang, Q., Ye, J., Si, H., Yang, B., Tao, T., Zhao, Y., Chen, M. and Yang, H. ORCID: https://orcid.org/0000-0001-9940-8273 (2020) Differences of characteristics and performance with Bi3+ and Bi2O3 doping over TiO2 for photocatalytic oxidation under visible light. Catalysis Letters. pp. 1-13. ISSN 1011-372X doi: https://doi.org/10.1007/s10562-019-03017-w Available at https://centaur.reading.ac.uk/87158/

It is advisable to refer to the publisher's version if you intend to cite from the work. See <u>Guidance on citing</u>.

To link to this article DOI: http://dx.doi.org/10.1007/s10562-019-03017-w

Publisher: Springer

All outputs in CentAUR are protected by Intellectual Property Rights law, including copyright law. Copyright and IPR is retained by the creators or other copyright holders. Terms and conditions for use of this material are defined in the <u>End User Agreement</u>.



www.reading.ac.uk/centaur

CentAUR

Central Archive at the University of Reading

Reading's research outputs online

1	Differences of characteristics and performance with Bi ³⁺ and			
2	Bi₂O₃ doping over TiO₂ for photocatalytic oxidation under			
3	visible light			
4				
5	Qiong Huang ^{1, *} , Juan Ye ¹ , Han Si ¹ , Bo Yang ¹ , Tao Tao ¹ , Yunxia Zhao ¹ ,			
6	Mindong Chen ¹ and Hong Yang ^{1, 2, *}			
7				
8	¹ Jiangsu Collaborative Innovation Center of Atmospheric Environment and			
9	Equipment Technologies, Jiangsu Key Laboratory of Atmospheric Environmental			
10	Monitoring & Pollution Control, School of Environmental Science & Engineering,			
11	Nanjing University of Information Science & Technology, Nanjing 210044, China;			
12	² Department of Geography and Environmental Science, University of Reading,			
13	Whiteknights, Reading, RG6 6AB, UK			
14				
15	*Corresponding author 1: Dr. Qiong Huang			
16	School of Environmental Science and Engineering, Nanjing University of Information			
17	Science & Technology, Nanjing 210044, China			
18	Address: No. 219 Ningliu Road, Nanjing University of Information Science &			
19	Technology, School of Environmental Science and Engineering, 210044, Nanjing,			
20	China			
21	E-mail: hqhaixia@163.com (Q.H.)			
22	Tel: +86 25 58731090 Fax: +86 25 58731090			
23				
24	*Corresponding author 2: Dr. Hong Yang			
25	Department of Geography and Environmental Science, University of Reading,			
26	Whiteknights, Reading, RG6 6AB, UK			
27	E-mail: hongyanghy@gmail.com (H. Y.)			
28	Tel: +44 (0)1183787750			

Differences of characteristics and performance with Bi³⁺ and Bi₂O₃ doping over TiO₂ for photocatalytic oxidation under visible light

32

Abstracts: Bi-doped TiO₂ photocatalysts were synthesized by sol with a high-pressure 33 hydrothermal method and developed for the photocatalytic degradation of 34 35 formaldehyde under the visible light irradiation and ambient temperature. According to characterization, it could be found that some Bi-doped TiO₂ could be transformed into 36 the distinctive crystals phase of Bi₄Ti₃O₁₂, which was crucial for improving activity. 37 The excess Bi₂O₃ doping into TiO₂, such as Bi₂O₃-N/TiO₂ and Bi₂O₃-C/TiO₂, generated 38 a mixed oxides with Bi₂O₃ and Bi₄Ti₃O₁₂, was not beneficial to increase the activity of 39 HCHO oxidation, whereas Bi3+/TiO2 composed of TiO2 and Bi4Ti3O12 displayed a 40 higher activity with good stability. It was worth noteworthy that Bi³⁺/TiO₂ didn't show 41 the lowest binding energy. However, it exhibited a lower PL intensity, higher adsorption, 42 43 and activity due to the uniform particulates, high surface areas, and the strong interaction between TiO₂ and Bi₄Ti₃O₁₂, attributing to create superoxide radical anion 44 $(^{\circ}O_2^{-})$ and hydroxyl radical ($^{\circ}OH$). The present results of Bi³⁺/TiO₂ indicated that HCHO 45 could be effectively oxidized from 1.094 to 0.058 mg/m³ (94.7%) under visible light 46 irradiation within 36 h. The current research made effort to draw out the existing state 47 of Bi, which would be better, Bi^{3+} or Bi_2O_3 , doped in the TiO₂. 48

49 Keywords: TiO₂; Bi-doped; Photocatalytic oxidation; Formaldehyde; Visible light

- 50
- 51

52 1. Introduction

With the rapid development of economy and urbanization, decoration has turn into a 53 kind of popular lifestyle. A large number of new decorative materials and furniture have 54 been used in rooms, while they can release a variety of volatile organic compounds 55 (VOCs), such as formaldehyde [1,2], benzene [3,4], toluene [5,6] and so on [7]. Accordingly, 56 indoor air pollution has become an increasingly serious problem. As people spend more 57 time indoors than outdoors, people may suffer from a serious of greater impact on 58 human health, including nausea, dizzy, headache, leukemia, and even cancer^[8]. In 59 particular, formaldehyde (HCHO), one of the notorious carcinogenic and deformity-60 causing substances identified by the World Health Organization (WHO), has been 61 detected at elevated levels in various indoor environments ^[9]. Hence, seeking an 62 effective method to remove indoor HCHO has been an urgent task. To date, the main 63 strategies of eliminating HCHO include adsorption ^[10], photocatalysis ^[11, 12], low 64 temperature plasma^[13], and catalytic oxidation at ambient temperature^[14]. Considering 65 efficiency and practicality, photocatalytic oxidation using TiO₂ semiconductors is one 66 of advanced technologies and it is still receiving attentions from many researches ^[15, 16]. 67 Up to now, TiO₂ is still the most frequently used photocatalyst due to the high solar 68 sensitivity, chemical stability and low toxicity ^[17]. In addition, its high density of states 69 in bands enables the efficient photo to current conversion, and this makes TiO₂ more 70 active than other semiconductors, such as ZnO, SnO₂, ZrO₂, CdS and g-C₃N₄ ^[18]. 71 Therefore, TiO₂ has been widely applied in various photocatalytic fields, such as water 72 and gas stream treatment, and organic contaminant decomposition ^[19, 20]. However, 73 owing to its large band gap energy of 3.2 eV (λ <380nm), TiO₂ absorbs only ultraviolet 74 light rather than more visible light that including a large part of solar irradiation ^[21, 22]. 75 Furthermore, the overall quantum yield rate can be seriously impacted by the low 76 electron transfer rate and a high recombination rate of photo-induced electrons and 77 holes. In order to overcome those problems, lots of efforts have been made to adjust the 78 properties of TiO₂ with electronic, for example, the noble metal deposition ^[22], the other 79 semiconductor coupling ^[23], and metal cations or non-metal anions doping ^[24-27]. 80 Coupling of TiO₂ with Bi₂O₃^[28], as a promising semiconductor, has been found to be a 81

good strategy for elongating the light region to the visible and enhancing the 82 photocatalytic activity ^[29]. Bi₂O₃ is an excellent material for the photocatalytic 83 oxidation due to its narrow band gap of 2.8 eV and diversity in crystal structure with 84 doping of TiO₂. Some studies about the Bi₂O₃/TiO₂ composite or Bi-doped TiO₂ found 85 better performance of VOCs photocatalytic oxidation under the excitation of visible 86 light ^[30]. However, it is still unclear about the existence state of bismuth to improve the 87 oxidation activity over Bi-doped TiO₂, especially for Bi³⁺ or Bi₂O₃, which donate as 88 composite oxides (Bi_xTiO_y), or mixed oxides (Bi₂O₃-TiO₂), separately. Murcia-Lopez 89 et al. ^[31] synthesized a series of Bi³⁺-doped TiO₂ catalysts with 2wt% doping to evaluate 90 the photocatalytic oxidation of phenol under UV-vis illumination and they found that 91 the nominal content of Bi³⁺ in TiO₂ was the main reason for the increase in the 92 photocatalytic activity. Bentouami et al. ^[32] also found that the binding energy of Bi 93 detected by XPS wasn't the same as the one of Bi in Bi₂O₃, and the shift in binding 94 energies of XPS could be ascribed to some valence states higher than Bi³⁺. Bouattour 95 et al. ^[33] and Xu et al. ^[34] suggested that the doped Bi ions substitute some of the 96 97 titanium atoms in the form of compound oxidation, such as Ti-O-Bi, Sr_{1-x}Bi_xTi_{1-x}Fe_xO₃, and BiFeO₃, according to the results of XRD and XPS. Kang et al ^[35] found that Bi ions 98 inserted into TiO₂ could markedly improve CO₂ reduction to CH₄ due to the inhibited 99 recombination of photogenerated electron-hole. However, some scholars had a different 100 opinion that Bi₂O₃ rather than Bi³⁺ played an important role in the photocatalytic 101 oxidation over Bi-doped TiO₂. For instance, Li et al. ^[36] found that the flower-like 102 Bi₂O₃/TiO₂ with enrichment Bi₂O₃ quantum dots on the surface of photocatalyst 103 exhibited higher activity due to the strong interaction between Bi₂O₃ and TiO₂. Leung 104 ^[37] and Wang ^[38] et al. hold that heterojunction structures with mixed semiconductors, 105 such as TiO₂/ZnO/Bi₂O₃, 3D BiOCl_xBr_{1-x}/graphene oxide, could effectively improve 106 the separation efficiency of photogenerated electron/hole and increase the subsequent 107 photocatalytic activity. Meanwhile, some researcher suggested that bismuth might 108 coexist in the form of Bi³⁺ and Bi₂O₃ over Bi-doped TiO₂ photocatalysts. Li et al. ^[39] 109 reported an ordinary approach, doping Bi₂O₃ powder into TiO₂ sol, to synthesis Bi-110 doped TiO₂ photocatalyst. When the loading of Bi₂O₃ exceed 5mol%, Bi₂Ti₄O₁₁ phase 111

started to appear and showed a good crystallization. The calcination temperature had a 112 key effect on the chemical state of Bi, a direct effect on the photocatalytic activity. 113 Attributed to the synergetic effect of Bi_xTiO_y and TiO₂, the photocatalytic activity over 114 Bi-doped TiO₂ could be improved. Gao et al. ^[30] found that Bi₄Ti₃O₁₂ and Fe-doped 115 Bi₄Ti₃O₁₂ nanosheets, described with a formula of $(Bi_2O_2)^{2+}(Bi_2Ti_3O_{10})^{2-}$, which was 116 constructed with a TiO₆ octahedral and a $(Bi_2O_2)^{2+}$ monolayer, displayed a high 117 photocatalytic oxidation of bisphenol A and phenol, although not as good as Au-2%Fe/ 118 Bi₄Ti₃O₁₂ composite photocatalysts. According to the XPS analysis, XPS signals of 119 Bi₂O₃ powders could also be found. Prabhakaran et al. ^[40] reported that Bi-doped and Bi-120 N co-doped TiO₂ nanocomposites could exhibit preferable photocatalytic activities for 121 fabric dye under visible light illumination. However, the results of XRD were different 122 from the results of XPS. XRD spectra showed crystalline Bi₂O₃, while the positive shift 123 of XPS peaks corresponding to Bi4f_{7/2} and Bi4f_{5/2} might also be ascribed to Bi-O-Ti 124 bonds formation on the photocatalyst surface. 125

To summarize, it is still difficult to clarify the state of Bi, as composite oxides or mixed 126 127 oxides, for obtaining a high activity over Bi-doped TiO₂ photocatalysts. I t is still necessary to investigate the state of Bi in-depth and find the rules between bismuth and 128 TiO₂ in Bi-doped TiO₂ with composite oxides or mixed oxides. The most attractive 129 aspect of these photocatalysts is the synergistic combination of bismuth oxide and 130 titanium oxide, as doped Bi ions substitute titanium atoms in the form of compound 131 oxidation or doped Bi₂O₃ with TiO₂ in the form of heterojunction structure. Different 132 133 from previous studies that some simple approaches have been developed to synthesize Bi-doped TiO₂ photocatalysts with the formation of Bi_xTiO_y or Bi₂O₃-TiO₂, bismuth 134 135 and titanium oxide with composite oxides or mixed oxides were produced for photocatalytic oxidation of low concentration of HCHO under visible light irradiation 136 in this study. The possible mechanism of photocatalytic activities of BixTiOy and Bi2O3-137 TiO₂ was discussed. This research provides a better understanding of the different 138 composite oxides or mixed oxides in the process of photocatalytic oxidation of HCHO. 139

140 2. Materials and Methods

141 2.1. Syntheses of photocatalysts

All reagents, such as ethanol, glycerol and acetic acid, were analytical grade and were
used without further purification in the experiments. For comparison, three different
types of Bi-doped TiO₂ photocatalysts were prepared.

The first one was for Bi³⁺/TiO₂ as composite oxides. 14.3 mL tetrabutyl titanate was 145 added into 8.5 mL ethanol and 8.5 mL glycerol in a conical flask, denoted as solution 146 A with a constant magnetic stirring. 3.2 g bismuth nitrate (Bi(NO₃)₃·5H₂O) and 0.4 g 147 ammonium carbonate ((NH₄)₂CO₃) were dissolved into 8.5 mL ethanol, 8.5 mL 148 glycerol and 6.6 mL acetic acid, denoted as solution B with the magnetic mixture. Later, 149 the solution B dropped into solution A with constant agitation. The resulting solution 150 was stirred for 30 min and transfer into a stainless steel reactor for 2 days aging at 110 151 °C. Finally, the precipitate was centrifuged and scrubbed with using distilled water and 152 ethanol for three times, and then dried at 80 °C for 2.5 h and calcined at 450 °C for 8.5h 153 [41] 154

The second were for Bi₂O₃-C/TiO₂ and Bi₂O₃-N/TiO₂ as composite/mixed oxides. 3.2 155 g bismuth nitrate (Bi(NO₃)₃·5H₂O) was added into 100 mL distilled water with 156 157 magnetic stirred until complete dissolution. 30 mL of 4M NaOH aqueous solution was dropped until the pH at 12. With a continuous stirring for 12 h, the suspension was 158 centrifuged and washed with distilled water twice, and then dried at 60 °C and calcined 159 at 450 °C for 4h, denoted as Bi₂O₃-C powders, or not calcined at 450 °C for 4h, denoted 160 as Bi₂O₃-N powders, to obtain two different powders (Bi₂O₃-C and Bi₂O₃-N). After that, 161 another solution was prepared with the same way as Bi³⁺/TiO₂ without bismuth nitrate, 162 and then these Bi₂O₃-C or Bi₂O₃-N powders were added into the mixed solution 163 together under constant agitation. After that, the resulting solution was stirred for 30 164 165 min and transfer into a stainless steel reactor for 2 days aging at 110 °C. Finally, the precipitate was centrifuged and scrubbed with using distilled water and ethanol for three 166 times, and then dried at 80 °C for 2.5 h and calcined at 450 °C for 8.5h. These catalysts 167 were identified as Bi₂O₃-C/TiO₂ and Bi₂O₃-N/TiO₂. 168

169 The third one was for Bi_2O_3 -Ti O_2 as mixed oxides. Two types of powders, such as 170 Bi_2O_3 -N and Ti O_2 , were synthesized in the same way as above. And then, these two 171 kinds of Bi_2O_3 -N and Ti O_2 powders were mixed with mechanical blending, confirmed 172 as Bi₂O₃-TiO₂.

173 *2.2. Characterization*

The crystal structures of three different styles of photocatalysts were all detected by 174 using a D/max-RB X-ray diffractometer (XRD, D8 Advance, Bruker, Germany) 175 equipped with Cu K α radiation ($\lambda = 0.15406$ nm) in a 20 range of 10-80° and the 176 177 scanning speed was 4°/min. Raman spectra were measurement on Renishaw inVia Raman systems at ambient temperature and fitted with the 532 nm line of an Ar ion 178 laser as an excitation source. The microscopic morphological structure and particle size 179 of these prepared samples were observed by using a scanning electron microscope 180 (SEM, Hitachi S-4800, Hitachi, Japan) and a transmission electron microscope (TEM, 181 JEM-2100, JEOL, Japan). The Brunauer-Emmett-Teller (BET, ASAP-2020, 182 Micromeritics Instrument Corporation, USA) surface areas of the spent catalysts and 183 pre-treated were determined by using nitrogen adsorption at 77.3 K. The UV-vis spectra 184 (UV-vis, Lambda 950, Perkin-Elmer, USA) of samples were recorded with an 185 integrating sphere attachment. The scanning range was between 250 nm and 800 nm, 186 187 and BaSO₄ was used as a reference. The excited states of these catalysts composite were detected with photoluminescence (PL, MicOS, HORIBA Scientific, USA). In-situ 188 diffuse reflectance infrared transform spectrometry (DRIFTS, Nicolet 6700FTIR, 189 Thermo, USA) was carried out on a spectrometer fitted with a MCT detector and a high-190 temperature reaction chamber, which could supply all the necessary gas inlets or outlets 191 and allow for measuring and controlling the temperature. The spectra could be acquired 192 with an accumulation of 64 scans and a resolution of 4 cm⁻¹. IR spectra (Nicolet 410 193 FTIR, Thermo, USA) on KBr pellets of the samples were recorded on a spectrometer 194 at a resolution of 4 cm⁻¹. The concentration of the samples in KBr was maintained at 195 approximately 0.3%. The X-ray photoelectron spectroscopy (XPS, AXIS ULTRA DLD, 196 Shimadzu-Krotos, Japan) spectra were obtained by using an AlKa X-ray source (1486.6 197 eV) operated at 15 kV and 300 W with an ESCALAB250 Thermo VG to understand 198 the chemical binding energies of the Bi, Ti and O. Electron paramagnetic resonance 199 200 (EPR, JES-FA200, JEOL, Japan) spectra was collected from a spectrometer with employing an X-band microwave frequency (9.43GHz) and power (1.5mW) at room 201

202 temperature.

203 2.3. Activity evaluation of HCHO removal

The photocatalytic degradation of HCHO over Bi-doped TiO₂ catalysts was carried out 204 in a self-designed glass reactor (600×600×600 mm). 1mL HCHO (38wt%) was dropped 205 into a petri dish and removed into this glass reactor for five minutes. When the 206 concentration was $1.05 \pm 0.05 \text{ mg/m}^3$, the petri dish was moved out and another petri 207 dish with 0.4g photocatalyst powder was transferred into the glass reactor quickly. After 208 209 that, the glass reactor was immediately sealed by using a glass cover with vaseline. Through a small hole in the front of the glass reactor, the concentration of formaldehyde 210 was detected by using a formaldehyde meter (PPM-400st, PPM Technology, UK), 211 which designed to measure HCHO concentrations from 0 to 24.56 mg/m^3 in snatch 212 samples of air. A 36W energy-saving lamp (LED) providing the visible light was fixed 213 10cm above the catalyst. When the concentration became stable and the adsorption-214 desorption equilibrium remained, the energy-saving lamp was turned on and HCHO 215 concentration was measured using the PPM-400st meter for three times at every 12 h. 216 217 To investigate the photocatalytic activity of different catalysts, a set of gaseous experiments were carried out in the indoor environment. 218

219 **3. Results and discussion**

220 3.1 The activity of Bi-doped TiO₂ for HCHO oxidation

Fig. 1 shows the conversion of HCHO and stability under visible light irradiation over 221 different types of Bi-doped TiO₂ photocatalysts as a function of time. The conditions in 222 standard tests were composed of HCHO concentration $(1.05 \pm 0.05 \text{ mg/m}^3)$, reaction 223 temperature (20-30°C), LED type (36 W) and catalyst powder (0.40 g). In terms of the 224 blank and adsorption tests over TiO₂, Bi₂O₃ and Bi³⁺/TiO₂ catalysts under dark, the 225 concentration of HCHO decreased from 1.052 to 0.923 mg/m³ at 48h in the blank (Fig. 226 1 (A)), indicating that the glass reactor owned good airtightness without HCHO leakage. 227 Although the Bi^{3+}/TiO_2 photocatalysts exhibited better adsorption than TiO₂ and Bi₂O₃, 228 the adsorption amount of HCHO was still very low, even negligible. In terms of the 229 230 photocatalytic activity and stability over these Bi-doped TiO₂ catalysts, the photocatalytic activity and stability of Bi³⁺/TiO₂ were significantly higher than other 231

three kinds of Bi-doped TiO₂ catalysts due to the composition and structure (Fig. 1(B) 232 and (C)). The HCHO concentration decreased from 1.094 to 0.058 mg/m³ at 36h, even 233 below the limits value of standard (0.08 mg/m³). Moreover, the catalyst demonstrated 234 good stability with four consecutive tests. However, Bi₂O₃-N/TiO₂, Bi₂O₃-C/TiO₂, and 235 Bi₂O₃-TiO₂ catalysts showed the same activity for HCHO degradation and the 236 conversion was about 50% at 48h. Meanwhile, the stability of Bi₂O₃-N/TiO₂ was as bad 237 as its oxidation activity, without improving. Owing to the rapid recombination of 238 photogenerated electrons and holes, although Bi₂O₃ owned lower band gap energy (2.9 239 eV) than TiO₂ (3.2 eV), it exhibited the lowest activity for HCHO oxidation. 240









Fig. 1. Photocatalytic degradation of HCHO and stability over Bi-doped TiO₂ catalysts (A: blank
 and adsorption experiments under dark; B: photocatalytic oxidation of HCHO over Bi-doped TiO₂
 catalysts; C: stability experiments over Bi³⁺/TiO₂ and Bi₂O₃-N/TiO₂ with four times)

247 *3.2 XRD analysis*

Fig. 2 shows the XRD patterns of Bi-doped TiO₂ catalysts with different preparation methods calcinated at 450 °C for 8.5 h. For comparison, the XRD patterns of the asprepared pure Bi₂O₃ and TiO₂ were also provided. The XRD patterns of TiO₂ and Bi₂O₃ were corresponded to the anatase phase of TiO₂ (PDF # 21-1272) and the monoclinic phase of α -Bi₂O₃ (PDF # 41-1449), respectively. Both of them showed good crystal

structures with the sharp diffraction peaks accompanied by calcinating at 450 °C for 8.5 253 254 h and the crystal peaks were calculated by using the Scherrer equation attributed to (1 0 1) and (1 2 0) planes to be 11.9 nm and 84.3 nm. In terms of Bi-doped TiO₂ catalysts, 255 except for Bi₂O₃-TiO₂ mixed oxides, the XRD patterns of Bi³⁺/TiO₂ were assigned to 256 anatase TiO₂ and a new characteristic peak at 30.2° and 33.1° ascribed to the composite 257 oxide of Bi4Ti3O12 (PDF # 35-0795). Regarding Bi2O3-N/TiO2 and Bi2O3-C/TiO2 258 catalysts, the XRD patterns displayed almost the same diffraction peaks indexed to the 259 260 monoclinic phase of α -Bi₂O₃ and the composite oxide of Bi₄Ti₃O₁₂, implying that Bi₂O₃ with calcining or not had no effect on the crystal structure. This is due to that these two 261 kinds of Bi-doped TiO₂ catalysts composed of Bi₂O₃ and Bi₄Ti₃O₁₂ led to a lower 262 activity than Bi³⁺/TiO₂. In terms of Bi₂O₃-TiO₂ mixed oxide catalyst, the diffraction 263 peaks in the patterns were ascribed to the TiO₂ and α-Bi₂O₃, respectively. Therefore, 264 the above results indicated that the heterojunction structure with TiO₂ and Bi₄Ti₃O₁₂ 265 was the critical factor to obtain a high activity for HCHO oxidation, rather than the 266 incorporation of Bi₂O₃ and Bi₄Ti₃O₁₂, even with Bi₂O₃ and TiO₂. 267



268 269

Fig. 2. XRD patterns of TiO₂, Bi₂O₃, and Bi-doped TiO₂ catalysts

271



Samples	$S_{\rm BET}~({ m m^2/g})$	$V_{\rm p}~({\rm cm^{3}/g})$	d _p (nm)	
TiO ₂	59.53	0.11	5.76	
Bi ₂ O ₃	37.96	0.03	5.43	
Bi ³⁺ /TiO ₂	52.39	0.12	7.82	
Bi ₂ O ₃ -N/TiO ₂	27.3	0.07	6.73	
Bi ₂ O ₃ -C/TiO ₂	42.78	0.10	7.23	
Bi ₂ O ₃ -TiO ₂	50.51	0.11	6.67	

273 Table 1. Textural properties of TiO₂, Bi₂O₃, and Bi-doped TiO₂ catalysts



Fig. 3. Nitrogen adsorption-desorption isotherms and pore-size distribution curves of TiO₂, Bi₂O₃,
and Bi-doped TiO₂ catalysts

In general, the large surface areas of catalysts can provide more active sites to adsorbent 277 reactant molecules and then oxidize, which can effectively improve the activity of 278 279 HCHO oxidation. Fig. 3 shows N₂ adsorption-desorption isotherms and the appropriate pore size distribution curves of different types of Bi-doped TiO₂ catalysts. The 280 isotherms of TiO₂ displayed a type IV isotherm with a H2 hysteresis loops, which may 281 include typical "ink bottle" holes, tubular holes with uneven pore size distribution, or 282 283 densely packed spherical particle interstitial holes, etc. Bi-doped TiO₂ catalysts, except 284 for Bi³⁺/TiO₂, showed adsorption-desorption isotherms of type IV with an overlap of H2 and H3 hysteresis loops, resulting from bottle-ink and slit-like pores, signifying that 285 the pore sizes of these samples lied in the range of 2–50 nm. The result could also be 286

confirmed by the pore size distribution and the result of BET (Table 1) and SEM (Fig. 287 5), which demonstrated that the pore sizes of these samples were from 5 to 8 nm. 288 However, Bi³⁺/TiO₂ displayed two distinct hysteresis loops, implying that one of the 289 hysteresis loops was the channel in these particles and the other should be the 290 accumulation hole of the particles. The result implied that Bi³⁺/TiO₂ had larger channels, 291 which was also confirmed by the pore size distribution and the improved HCHO 292 adsorption. Bi³⁺/TiO₂ (S_{BET} =52.39 m²/g) exhibited the largest surface areas and pore 293 sizes among these different types of Bi-doped TiO₂ catalysts. In addition, the surface 294 areas of TiO₂ and Bi₂O₃ were calculated to be 59.53 m²/g and 37.96 m²/g, respectively. 295 Bi₂O₃ and Bi₂O₃-N/TiO₂ exhibited extremely low pore volume, which were aligned 296 with the adsorption-desorption isotherms, and these could significantly decrease the 297 adsorption of HCHO and be detrimental for the improvement of oxidation activity. 298 Therefore, the above results demonstrated that the specific surface areas maybe not the 299 most important factor for photocatalytic oxidation of HCHO, but it could display a 300 minor role in the activity enhancement. 301







Fig. 4. Raman spectra of Bi-doped TiO₂ catalysts



of anatase TiO_2 ^[39], indicating that the TiO_2 was one of the main phase structures in the 307 sample of Bi³⁺/TiO₂ and Bi₂O₃-TiO₂, which was consistent with the XRD results. While 308 for Bi₂O₃-N/TiO₂ and Bi₂O₃-C/TiO₂, it was difficult to detect the presence of anatase 309 TiO₂ by Raman spectra. More importantly, the Raman peak at 481 cm⁻¹ could be 310 assigned to the characteristic band of Bi₂O₃. Among these samples, the Bi₂O₃-C/TiO₂ 311 exhibited the strongest intensity due to Bi₂O₃ powder calcined at 450 °C for 4h. While 312 for Bi₂O₃-N/TiO₂, Bi₂O₃-C/TiO₂ and Bi³⁺/TiO₂, it was easy to find the presence of 313 Bi₄Ti₃O₁₂, not Bi₂O₃, by the XRD measurement, which was not corroborate well with 314 Raman spectra. That was because the composite oxides of Bi₄Ti₃O₁₂ contained the 315 characteristic band of Bi₂O₃. 316

317 *3.5 Morphology measurement*

The morphology structure of TiO₂, Bi₂O₃, and Bi-doped TiO₂ catalysts were 318 investigated by using SEM and TEM. TiO₂ showed an aggregated of lumpy particles 319 with a smooth surface, while Bi₂O₃ displayed some aggregated and smaller particles 320 with a rough surface attributed to nano-sized spherical Bi₂O₃ (Fig. 5(B)). Bi₂O₃-TiO₂ 321 322 (Fig. 5(C)) mixed oxides with TiO_2 and Bi_2O_3 exhibited the same image as the images of Fig. 5(A) and Fig. 5(B) without changing. Regarding Bi-doped TiO₂ catalysts (Fig. 323 5(D-F)), SEM image of Bi^{3+}/TiO_2 composites that were composed of mutually 324 aggregated spherical nanoparticles showed a uniform particulate state and it could 325 improve the adsorption of visible light and HCHO to increase the activity. While, 326 samples of Bi₂O₃-N/TiO₂ and Bi₂O₃-C/TiO₂ calcined at 450 °C for 8.5h displayed 327 irregular and smooth-surfaced lumps, indicated that there was a melting-328 recrystallization-remelting process for these composites. As can be seen in Fig. 5(G), 329 330 the observed lattice spacing of 0.234 nm was attributed to the (0 14 0) crystal planes of Bi₄Ti₃O₄, and lattice spacing of 0.243 nm and 0.166 nm (not shown) corresponded to 331 the (1 0 3) and (2 1 1) crystal planes of anatase TiO₂, respectively. However, the images 332 of Bi₂O₃-N/TiO₂ and Bi₂O₃-C/TiO₂ catalysts exhibited that these particles aggregated 333 together and produced a large number of lumps with a smooth surface due to roasted 334 Bi₂O₃ without doping into TiO₂. According to Fig. 5(H), the lattice spacing of 0.234 335 nm, 0.271 nm, 0.269 nm and 0.256 nm matched well with the (0 14 0) crystal planes of 336

- $Bi_4Ti_3O_4$ and the (-1 2 2), (2 2 0), and (-2 1 2) crystal planes of Bi_2O_3 (not shown). The
- above results were all in accordance with the XRD exhibited in Fig. 2.



340





 Bi^{3+}/TiO_2 , (E, H) Bi_2O_3 -N/TiO_2, and (F) Bi_2O_3 -C/TiO_2

345 3.6 Optical absorption properties

The corresponding UV-vis DRS and PL spectra of TiO₂, Bi₂O₃ and Bi-doped TiO₂ 346 catalysts are presented in Fig. 6. The absorption peak of pure TiO₂ at 380–780 nm could 347 be found as anatase TiO₂ and the band gap energy (E_g) was 3.1 eV, which displayed 348 349 visible light absorption and low E_g (3.2 eV) due to the incorporation of N or C with $(NH_4)_2CO_3$. The absorption intensities of Bi₂O₃ with the E_g of approximately 2.9 eV in 350 the visible region from 380 to 450 nm were markedly higher than those in other visible 351 regions. Bi₂O₃ displayed visible light absorption and low E_g , and it exhibited the worse 352 353 activity than other samples due to the rapid recombination of photogenerated e⁻ and h⁺. Therefore, Bi₂O₃ couldn't be used independently as an oxide catalyst for HCHO 354 oxidation and it needed to be combined with other semiconductors, such as TiO₂, to 355 form heterojunctions structure or others to improve the oxidation activity. In terms of 356 Bi-doped TiO₂ samples, Bi^{3+}/TiO_2 with the E_g of around 3.0 eV exhibited the highest 357 absorption at UV and visible regions, so it showed the highest activity for HCHO 358 degradation at ambient temperature. Bi2O3-N/TiO2 and Bi2O3-C/TiO2 displayed almost 359 the same visible light absorption and E_g (2.8 eV) owing to the rapid recombination of 360 photogenerated e⁻ and h⁺ with Bi₂O₃. Therefore, the samples of Bi₂O₃-N/TiO₂ and 361 Bi₂O₃-C/TiO₂ displayed poor activities for HCHO oxidation. The above results were all 362 consistent with the activity of Bi-doped TiO₂ for HCHO oxidation. 363

The PL spectra were designed to evaluate the excited state of photocatalysts and the 364 recombination rate of photoinduced e^{-} and h^{+} . In this study, the excitation wavelength 365 was 325 nm at room temperature and examined in the range of 350-900 nm with a 366 single scan mode. Fig. 6(C) shows the PL spectra of Bi₂O₃-N/TiO₂, Bi₂O₃-C/TiO₂, 367 Bi³⁺/TiO₂ and Bi₂O₃-TiO₂. Among these four samples, Bi₂O₃-C/TiO₂ exhibited the 368 highest PL intensity, indicating that Bi₂O₃-C/TiO₂ showed a high recombination rate of 369 photoinduced e⁻ and h⁺, which was not beneficial to increase the activity for 370 photocatalytic oxidation of HCHO. While, compared with Bi₂O₃-N/TiO₂, Bi³⁺/TiO₂ 371 displayed a lower PL intensity, implying that Bi³⁺/TiO₂ could improve charge 372 separation with a low recombination rate of e⁻ and h⁺. This was mainly due to the Bi³⁺ 373 doping on TiO₂, which can capture photogenerated e⁻ from the surface of Bi₄Ti₃O₁₂ to 374 reduce charge recombination. This result indicates that Bi³⁺/TiO₂ can exhibit a higher 375 photocatalytic activity due to that Bi³⁺ doping TiO₂ hinders free carriers from 376 recombination under irradiation. Although Bi₂O₃-TiO₂ showed the lowest PL intensity, 377 the photocatalysts of Bi₂O₃ composite was not conducive to photocatalytic oxidation of 378 379 HCHO. The above results show that the critical factor to determine the activity of these photocatalysts was Bi³⁺/TiO₂ that was composed of TiO₂ and Bi₄Ti₃O₁₂, confirmed by 380 XRD. 381





Fig. 6. Diffuse reflectance UV-vis and PL spectra of TiO₂, Bi₂O₃, and Bi-doped TiO₂ catalysts













Fig. 7. XPS spectra of different types of TiO₂, Bi₂O₃, and Bi-doped TiO₂ catalysts

The chemical states of TiO₂, Bi₂O₃, and Bi-doped TiO₂ catalysts were detected by using XPS analysis. Ti, Bi, O, C and N elements could be observed on the surface of samples (Fig. 7). The Ti 2p_{3/2} and T 2p_{1/2} for TiO₂ and Bi³⁺/TiO₂ were situated at a binding energy (BE) of 458.5 eV and 464.2 eV, respectively. However, the BE of T 2p_{1/2} for Bi₂O₃-N/TiO₂ was shifted to high binding energy due to the influence of Bi₂O₃^[39]. The results implied that Bi³⁺/TiO₂ and Bi₂O₃-N/TiO₂ consisted of TiO₂ and Bi₂O₃, and these were all consistent with XRD analysis. Interestingly, the Bi 4f photoelectron peaks of



3.8 In-situ DRIFTS and IR spectral characteristics











416 417

with the different reaction time

Base on the In-situ DRIFTS spectra of Bi³⁺/TiO₂ and Bi₂O₃-N/TiO₂, as shown in Fig. 419 8A) and Fig. 8(B), upon exposure to a mixed flow of HCHO/O₂ ($1.05 \pm 0.05 \text{ mg/m}^3$) 420 with different reaction time (0, 3, 6, 12, 24, and 36h) and different bands, such as 591, 421 1063, 1160, 1237, 1315 cm⁻¹ and others could be observed. According to references ^{[1,} 422 $^{2, 8, 9, 14, 42]}$, as for Bi³⁺/TiO₂, the bands at 591 and 1315 cm⁻¹ of Bi³⁺/TiO₂ can be assigned 423 to the asymmetric stretching vibration of Ti-O-Ti and stretching vibration of Ti-O, 424 respectively ^[42]. The bending vibration of water at ca. 1611 cm⁻¹ and the characteristic 425 bands of molecularly adsorbed HCHO at 1063 cm⁻¹ were found in the Bi³⁺/TiO₂ ^[14]. 426 The band at 1348 and weak bands at 2822 and 2975 cm⁻¹ were attributed to the 427 symmetric $v_s(COO)$ and $v_s(CH)$ stretching of formate ^[1]. In addition, a broad negative 428 band at ca. 1237 and 1452 cm⁻¹ were ascribed to $v_s(CH_2)$ and $\delta(CH_2)$ vibration of 429 dioxymethylene (DOM)^[2]. The results implied that formate and DOM species were the 430 main intermediates for photocatalytic oxidation of HCHO. As for Bi₂O₃-N/TiO₂ (Fig. 431 8(B)), the characteristic bands with different reaction time were almost the same as 432 Bi₂O₃-N/TiO₂(0h) without significant changing. The bending vibration of H₂O at 1618 433 cm⁻¹ and the characteristic bands of molecularly adsorbed HCHO at 1058 cm⁻¹ were 434 also discovered. Meanwhile, the bands at 1386, 2848 and 2985 cm⁻¹ were also ascribed 435

to the symmetric $v_s(COO)$ and $v_s(CH)$ stretching of formate. With the prolonging reaction time, the band at 1618 cm⁻¹ corresponding to the bending vibration of OH⁻ in water adsorbed decreased and the band at 1710 cm⁻¹ assigned to the v(CO) vibration mode of HCHO emerged.

The analysis of water absorption and surface hydroxyl showed the IR spectrum of 440 Bi3+/TiO2 and Bi2O3-N/TiO2 (Fig. 8(C) and Fig. 8(D)). The results seemed to no 441 significant of water absorption and surface hydroxyl change with the reaction time. The 442 stretching vibration at ca. 3423 cm⁻¹ corresponded to the hydroxyl group and the 443 bending vibration at ca. 1616 cm^{-1} was attributed to OH- from the adsorption of H₂O. 444 However, Bi³⁺/TiO₂ exhibited markedly higher H₂O adsorption than Bi₂O₃-N/TiO₂. In 445 addition, the performance of H2O adsorption could be increased with reaction time, and 446 thus it displayed a higher activity for HCHO oxidation. Due to the inadequate 447 photocatalytic oxidation of HCHO at 3-36h, two absorption bands at ca. 1413 cm⁻¹ and 448 2906 cm⁻¹ suited to the symmetric or other C-H orientations stretching vibration of 449 formate ($V_{\rm s}$ (COO⁻)) were detected. Furthermore, the bands appearing at around 2334 450 cm⁻¹, 1386 cm⁻¹, and 1446 cm⁻¹ can be assigned to the stretching or bending vibration 451 of C-O (V_s (HCO₃⁻)) and δ (CH₂) vibration of dioxymethylene (DOM) due to the 452 photocatalytic oxidation reaction. The above results confirmed the presence of surface 453 hydroxyls (OH⁻) in the structure of these two samples and revealed that the importance 454 of surface hydroxyls on HCHO degradation, especially for Bi³⁺/TiO₂. These adsorbed 455 H₂O and OH⁻ are crucial to improve the activity for HCHO oxidation due to their 456 reaction with the photogenerated hole on the surface and the formation of hydroxyl 457 radicals. As the above data of In-situ DRIFTS and IR and reported in literatures ^{[1, 2, 8, 9,} 458 ^{14, 42, 43, 44]}, HCHO was degraded into dioxymethylene (DOM) at first, and then further 459 into formate and carbonate, then finally desorbs as CO₂. 460

461 *3.9 EPR spectroscopy*

To understand the roles of reactive oxygen species such as O_2^- and OH in the photocatalytic process, EPR technique was used to detect the characteristics and active radicals in the samples. As shown in Fig. 9, the value of g=2.003 was ascribed to the paramagnetic characteristic value of O_2^- ^[45], and the value of paramagnetic

characteristic could be increased by Bi3+ doping with TiO2. Bi3+/TiO2 displayed the 466 highest amount of 'O₂', followed by TiO₂, Bi₂O₃-N/TiO₂, and Bi₂O₃. The results showed 467 that the types and amount of Bi doping played an important role in the change of O_2^- 468 concentration. When Bi₂O₃ doped in TiO₂, some of Bi₂O₃ exposed as an electrically 469 charged composite centre, which prevented some e⁻ from being trapped by oxygen 470 vacancies. The reduce of charged oxygen vacancies resulted in the reduction of the 471 amount of O_2^{-129} . Therefore, when the amount of O_2^{-1} decreased, the peak strength on 472 the paramagnetic characteristic of O_2^- and the activity decreased, which was consistent 473 with the results of photocatalytic oxidation of HCHO. 474







Fig. 9. EPR spectra of different types of TiO₂, Bi₂O₃, and Bi-doped TiO₂ catalysts

477 *3.10 Mechanisms for photocatalytic oxidation of HCHO*

Depending on the structure of Bi-doped TiO₂, particularly for Bi³⁺/TiO₂, the structure 478 479 of heterojunction, identified as Bi₄Ti₃O₄ and TiO₂, could promote efficient charge separation, with the consequence of reducing the recombination of photogenerated e⁻ 480 and h^+ (Fig. 10). Gan et al. found UV-vis DRS, the E_{bg} for Bi₄Ti₃O₄ and TiO₂ were 481 about 2.91 eV and 3.1 eV ^[46]. Therefore, the E_{cb} and E_{vb} for Bi₄Ti₃O₄ and TiO₂ were 482 calculated as -0.41 eV, -0.12 eV, 2.50 eV and 2.98 eV, respectively. Because the E_{cb} of 483 TiO₂ was lower than Bi₄Ti₃O₄, the photogenerated e⁻ could be moved easily from 484 Bi₄Ti₃O₄ to TiO₂. The holes transferred in the opposite direction and thus depressed the 485

recombination of e^{-} and h^{+} . Moreover, the formation of formate species (2822 and 2975) 486 cm⁻¹) and dioxymethylene (1237 and 1452 cm⁻¹), ascribed to the results of in-situ 487 DRIFTS spectra, could be found clearly in the Bi³⁺/TiO₂. These two kinds of species, 488 identified as by-products of photocatalytic oxidation, could also be observed by IR 489 spectrum. On the other hand, the weak band at 1710 cm⁻¹ corresponding to the v(CO)490 vibration of HCHO could be observed on the surface of catalysts. More importantly, 491 the intensity of stretching vibration at ca. 3423 cm⁻¹ assigned to the hydroxyl group 492 493 decreased with the extension of reaction time.

According to the above investigations, the adsorption of HCHO on the surface was the 494 first step in the catalytic reaction. Bi³⁺/TiO₂ was activated by the visible light and the 495 photogenerated e^{-} and h^{+} could be transferred by the heterojunction structure. Then, 496 these e⁻ can react with O₂ to generate superoxide radical anion ('O₂⁻), which can oxidize 497 HCHO into the DOM and formate species. The formate can further break up into CO 498 and H_2O , and CO could be further oxidized to CO_2 ^[2, 47]. Another possible pathway is 499 that these photogenerated holes can be combined with OH⁻ or H₂O to generate hydroxyl 500 501 radical (•OH), which could directly oxidize HCHO or formate into CO₂ and H₂O and tackle the environmental pollution [48, 49]. 502



Fig. 10. Proposed electron-hole pair separation in the Bi³⁺/TiO₂ composites under visible

irradiation

- 503
- 504 505

506 **4. Conclusions**

507 In this study, a serious of Bi-doped TiO_2 catalysts were synthesized by sol using the 508 hydrothermal method, and then promoted for the photocatalytic degradation of HCHO

under visible light irradiation and ambient temperature. Compared with pure TiO₂ and 509 Bi₂O₃, photocatalytic oxidation of HCHO can be further improved by the Bi-doped 510 TiO₂ catalysts, especially Bi³⁺/TiO₂. According to the investigation of characterization, 511 it could be observed that the excess Bi₂O₃ doping into TiO₂ catalysts, such as Bi₂O₃-512 N/TiO₂ and Bi₂O₃-C/TiO₂, formed a mixed oxides with Bi₂O₃ and Bi₄Ti₃O₁₂, and they 513 were disadvantage to enhance the activity. However, Bi³⁺/TiO₂ composed of TiO₂ and 514 Bi₄Ti₃O₁₂ displayed a higher activity and remained good stability for HCHO oxidation. 515 It was worth mention that Bi³⁺/TiO₂ didn't have the lowest binding energy, but it 516 displayed a lower PL intensity. The highest activity mainly depends on the uniform 517 particulates, high surface areas, and the great interaction between TiO₂ and Bi₄Ti₃O₁₂ 518 via charge transfer. 519

In summary, this study demonstrated that HCHO can be effectively oxidized to 0.058 mg/m³ (94.7%) at visible light excitation within 36 h. The heterogeneous catalysts with TiO₂ and Bi₄Ti₃O₁₂ were the main critical factor to degrade gaseous organic pollutants. The results made new contribution for a better understanding of the existing state of Bi in the TiO₂ crystal.

525

526 Acknowledgements

This work was financially supported by the Natural Science Foundation of Jiangsu 527 Province (Nos. BK20170954 and BK20150890), the National Natural Science 528 Foundation of China (Nos. 21501097), the Qing Lan Project of the Jiangsu Higher 529 Education Institutions of China, the Priority Academic Program Development of 530 Jiangsu Higher Education Institutions (PAPD), the Top-notch Academic Programs 531 Project of Jiangsu Higher Education Institutions (PPZY2015C222), the Jiangsu 532 Engineering Technology Research Centre of Environmental Cleaning Materials and 533 Open Research Fund Program of Jiangsu Key Laboratory of Atmospheric Environment 534 Monitoring & Pollution Control (KHK1806), A projected funded by the Priority 535 Academic Program Development of Jiangsu Higher Education Institutions (PAPD). 536

538 **References**

- 539 [1] F. Liu, S.P. Rong, P.Y. Zhang, L.L. Gao. Appl. Catal. B 235 (2018) 158.
- 540 [2] D. Sun, S. Wageh, A.A. Al-Ghamdi, Y. Le, J.G. Yu, C.J. Jiang. Appl. Surf. Sci. 466 (2019) 301.
- 541 [3]V. Binas, V. Stefanopoulos, G. Kiriakidis, P. Papagiannakopoulos. J. Mater. 5 (2019) 56.
- 542 [4] A. Okawa, R. Yoshida, T. Isozaki, Y. Shigesato, Y. Matsushita, T. Suzuki. Catal. Commun. 100
 543 (2017) 1.
- [5] X.A. Dong, W. Cui, H. Wang, J.Y. Li, Y.J. Sun, H.Q. Wang, Y.X. Zhang, H.W. Huang, F. Dong.
 Sci. Bull. 64 (2019) 669.
- 546 [6] J.Y. Li, X.A. Dong, G. Zhang, W. Cui, W.L. Cen, Z.B. Wu, S. C. Lee, F. Dong. J. Mater. Chem.
 547 A 7 (2019) 3366.
- 548 [7] Z. Zhang, J. Huang, H.Q. Xia, Q.G. Dai, Y.F. Gu, Y.J. Lao, X.Y. Wang. J. Catal. 360 (2018) 277.
- 549 [8] Z.X. Yan, Z.H. Xu, Z.H. Yang, L. Yue, L.Y. Huang. Appl. Surf. Sci. 467 (2019) 277.
- [9] Y. Zhang, M.X. Chen, Z.X. Zhang, Z. Jiang, W.F. Shangguan, H. Einaga. Catal. Today. 327
 (2019) 323.
- 552 [10] D. Kibanova, M. Sleiman, J. Cervini-Silva, H. Destaillats. J. Hazard. Mater. 211 (2012) 233.
- 553 [11] X.Q. Deng, J.L. Liu, X.S. Li, B. Zhu, X.B. Zhu, A.M. Zhu. Catal. Today. 281 (2017) 630.
- [12] J.Y. Li, W. Cui, P. Chen, X.A. Dong, Y.H. Chu, J.P. Sheng, Y.X. Zhang, Z.M. Wang, F. Dong.
 Appl. Catal. B 260 (2020) 118130.
- 556 [13] X.S. Li, X.Y. Ma, J.L. Liu, Z.G. Sun, B. Zhu, A.M. Zhu. Catal. Today. 337 (2019) 132.
- 557 [14] S.Y. Huang, B. Cheng, J.G. Yu, C.J. Jiang. ACS Sustain. Chem. Eng. 6 (2018) 12481.
- 558 [15] G.K. Zhang, Q. Xiong, W. Xu, S. Guo. Appl. Clay. Sci. 102 (2014) 231.
- 559 [16] M. Malayeri, F. Haghighat, C.S. Lee. Build. Environ. 154 (2019) 309.
- 560 [17] G.X. Zhang, Z.M. Sun, Y.W. Duan, R.X. Ma, S.L. Zheng. Appl. Surf. Sci. 412 (2017) 105.
- 561 [18] X. Li, X.R. Qian, X.H. An, J.W. Huang. Appl. Surf. Sci. 487 (2019) 1262.
- 562 [19] R.F. Liu, W.B. Li, A.Y. Peng. Appl. Surf. Sci. 427 (2018) 608.
- 563 [20] M. He, J. Ji, B.Y. Liu, H.B. Huang. Appl. Surf. Sci. 473 (2019) 934.
- [21] T. Ohno, M. Akiyoshi, T. Umebayashi, K. Asai, T. Mitsui, M. Matsumura. Appl. Catal. A 265
 (2004) 115.
- 566 [22] X.Y. Pan, Y.J Xu. J. Phys. Chem. C. 117 (2013) 17996.
- 567 [23] J. Li, M. Zhang, Q.Y. Li, J.J. Yang. Appl. Surf. Sci. 391 (2017) 184.
- 568 [24] C. Huang, Y. Ding, Y.W. Chen, P. Li, S.B. Shen. J. Environ. Sci. 60 (2017) 61.
- 569 [25] S.H. Liu, W.X. Lin. J. Photoch. Photobio. A 378 (2019) 66.
- 570 [26] W. Low, V. Boonamnuayvitaya. J. Environ. Manage. 127 (2013) 142.
- 571 [27] J.P. Li, D.J. Ren, Z.X. Wu, J. Xu, Y.J. Bao, S. He, Y.H. Chen. J. Colloid. Inter. Sci. 530 (2018)
- 572 78.

- 573 [28] Q. Huang, P. Wang, Y.Z. Fan, Q. Wang. Indoor. Built. Enviro. 26 (2017) 785.
- 574 [29] Y.F. Huang, Y.L. Wei, J. Wang, D. Luo, L.Q. Fan, J.H. Wu. Appl. Surf. Sci. 423 (2017) 119.
- [30] Y.B. Liu, G.Q. Zhu, J.Z. Gao, M. Hojamberdiev, R.L. Zhu, X.M. Wei, Q.M. Guo, P. Liu. Appl.
 Catal. B 200 (2017) 72.
- 577 [31] S. Murcia-López, M. Hidalgo, J.A. Navío. Appl. Catal. A 404 (2011) 59.
- 578 [32] B. Benalioua, M. Mansour, A. Bentouami, B. Boury, E.H. Elandaloussi. J. Hazard. Mater. 288
 579 (2015) 158.
- [33] A. Hamdi, A.M. Ferraria, A.M. Botelho Rego, D.P. Conceicao, L.F. Vieira Ferreira, S.
 Bouattour. J. Mol. Catal. A 380 (2013) 34.
- 582 [34] L.W. Lu, M.L Lv, D. Wang, G.Liu, X.X. Xu. Appl. Catal. B 200 (2017) 412.
- 583 [35] J.H. Lee, H. Lee, M.J. Kang. Mater. Lett. 178 (2016) 316.
- 584 [36] J. Zhu, S.H. Wang, J.G. Wang, D.Q. Zhang. Appl. Catal. B 102 (2011) 120.
- 585 [37] C.C. Pei, W.W.F. Leung. Appl. Catal. B 174 (2015) 515.
- [38] J.Z. Wang, H.L. Li, X.R. Yan, C. Qian, Y.J. Xing, S.T. Yang, Z.K. Kang, J.Y. Han, W.X. Gu,
 H.Y. Yang, F.J. Xiao. J. Alloys. Compounds. 795 (2019) 120.
- [39] Y. Hu, Y.T. Cao, P.X. Wang, D.Z. Li, W. Chen, Y.H. He, X.Z. Fu, Y. Shao, Y. Zhang. Appl.
 Catal. B 125 (2012) 294.
- 590 [40] T.V.L. Thejaswini, D. Prabhakaran, M.A. Maheswari. J. Environ. Chem. Eng. 4 (2016) 1308.
- [41] Q. Huang, Q. Wang, T. Tao, Y.X. Zhao, P. Wang, Z.Y. Ding, M.D. Chen. Environ. Technol. 40
 (2019) 1937.
- 593 [42] H.S. Zuo, J. Sun, K.J. Deng, R. Su. Chem. Eng. Technol. 30 (2007) 577.
- [43]P. Liu, G.L. Wei, H.P. He, X.L. Liang, H.L. Chen, Y.F. Xi, J.X. Zhu. Appl. Surf. Sci. 464 (2019)
 287.
- [44] P. Liu, G.L. Wei, X.L. Liang, D. Chen, H.P. He, T.H. Chen, Y.F. Xi, H.L. Chen, D.H. Han, J.X.
 Zhu. Appl. Clay. Sci. 161 (2018) 265.
- 598 [45] C.P. Kumar, N.O. Gopal, T.C. Wang, M.S. Wong, S.C. Ke. J. Phy. Chem. B 110 (2006) 5223.
- [46] H.H. Gan, F.T. Yi, H.N. Zhang, Y.X. Qian, H.X. Jin, K.F. Zhang. Chinese. J. Chem. Eng. 26
 (2018) 2628.
- 601 [47] Y. Ma, G.K. Zhang. Chem. Eng. J. 288 (2016) 70.
- 602 [48]. H. Yang, X. Huang, J.R. Thompson, R.J. Flower. Science 347 (2015) 834.
- 603 [49]. H. Yang. Nature 509 (2014) 535.