

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

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1	Differences of characteristics and performance with Bi <sup>3+</sup> and			
2	<b>Bi<sub>2</sub>O<sub>3</sub> doping over TiO<sub>2</sub> for photocatalytic oxidation under</b>			
3	visible light			
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# Differences of characteristics and performance with Bi<sup>3+</sup> and Bi<sub>2</sub>O<sub>3</sub> doping over TiO<sub>2</sub> for photocatalytic oxidation under visible light

32

Abstracts: Bi-doped TiO<sub>2</sub> 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 TiO<sub>2</sub> could be transformed into 36 the distinctive crystals phase of Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub>, which was crucial for improving activity. 37 The excess Bi<sub>2</sub>O<sub>3</sub> doping into TiO<sub>2</sub>, such as Bi<sub>2</sub>O<sub>3</sub>-N/TiO<sub>2</sub> and Bi<sub>2</sub>O<sub>3</sub>-C/TiO<sub>2</sub>, generated 38 a mixed oxides with Bi<sub>2</sub>O<sub>3</sub> and Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub>, 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 Bi<sup>3+</sup>/TiO<sub>2</sub> 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 TiO<sub>2</sub> and Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub>, attributing to create superoxide radical anion 44  $(^{\circ}O_2^{-})$  and hydroxyl radical ( $^{\circ}OH$ ). The present results of Bi<sup>3+</sup>/TiO<sub>2</sub> indicated that HCHO 45 could be effectively oxidized from 1.094 to 0.058 mg/m<sup>3</sup> (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 TiO<sub>2</sub>. 48

49 Keywords: TiO<sub>2</sub>; Bi-doped; Photocatalytic oxidation; Formaldehyde; Visible light

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- 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<sup>[8]</sup>. 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 <sup>[9]</sup>. 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 <sup>[10]</sup>, photocatalysis <sup>[11, 12]</sup>, low 64 temperature plasma<sup>[13]</sup>, and catalytic oxidation at ambient temperature<sup>[14]</sup>. Considering 65 efficiency and practicality, photocatalytic oxidation using TiO<sub>2</sub> semiconductors is one 66 of advanced technologies and it is still receiving attentions from many researches <sup>[15, 16]</sup>. 67 Up to now, TiO<sub>2</sub> is still the most frequently used photocatalyst due to the high solar 68 sensitivity, chemical stability and low toxicity <sup>[17]</sup>. In addition, its high density of states 69 in bands enables the efficient photo to current conversion, and this makes TiO<sub>2</sub> more 70 active than other semiconductors, such as ZnO, SnO<sub>2</sub>, ZrO<sub>2</sub>, CdS and g-C<sub>3</sub>N<sub>4</sub> <sup>[18]</sup>. 71 Therefore, TiO<sub>2</sub> has been widely applied in various photocatalytic fields, such as water 72 and gas stream treatment, and organic contaminant decomposition <sup>[19, 20]</sup>. However, 73 owing to its large band gap energy of 3.2 eV ( $\lambda$ <380nm), TiO<sub>2</sub> absorbs only ultraviolet 74 light rather than more visible light that including a large part of solar irradiation <sup>[21, 22]</sup>. 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 TiO<sub>2</sub> with electronic, for example, the noble metal deposition <sup>[22]</sup>, the other 79 semiconductor coupling <sup>[23]</sup>, and metal cations or non-metal anions doping <sup>[24-27]</sup>. 80 Coupling of TiO<sub>2</sub> with Bi<sub>2</sub>O<sub>3</sub><sup>[28]</sup>, 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 <sup>[29]</sup>. Bi<sub>2</sub>O<sub>3</sub> 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 TiO<sub>2</sub>. Some studies about the Bi<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> composite or Bi-doped TiO<sub>2</sub> found 85 better performance of VOCs photocatalytic oxidation under the excitation of visible 86 light <sup>[30]</sup>. However, it is still unclear about the existence state of bismuth to improve the 87 oxidation activity over Bi-doped TiO<sub>2</sub>, especially for Bi<sup>3+</sup> or Bi<sub>2</sub>O<sub>3</sub>, which donate as 88 composite oxides (Bi<sub>x</sub>TiO<sub>y</sub>), or mixed oxides (Bi<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub>), separately. Murcia-Lopez 89 et al. <sup>[31]</sup> synthesized a series of Bi<sup>3+</sup>-doped TiO<sub>2</sub> 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 Bi<sup>3+</sup> in TiO<sub>2</sub> was the main reason for the increase in the 92 photocatalytic activity. Bentouami et al. <sup>[32]</sup> also found that the binding energy of Bi 93 detected by XPS wasn't the same as the one of Bi in Bi<sub>2</sub>O<sub>3</sub>, and the shift in binding 94 energies of XPS could be ascribed to some valence states higher than Bi<sup>3+</sup>. Bouattour 95 et al. <sup>[33]</sup> and Xu et al. <sup>[34]</sup> 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<sub>1-x</sub>Bi<sub>x</sub>Ti<sub>1-x</sub>Fe<sub>x</sub>O<sub>3</sub>, and BiFeO<sub>3</sub>, according to the results of XRD and XPS. Kang et al <sup>[35]</sup> found that Bi ions 98 inserted into TiO<sub>2</sub> could markedly improve CO<sub>2</sub> reduction to CH<sub>4</sub> due to the inhibited 99 recombination of photogenerated electron-hole. However, some scholars had a different 100 opinion that Bi<sub>2</sub>O<sub>3</sub> rather than Bi<sup>3+</sup> played an important role in the photocatalytic 101 oxidation over Bi-doped TiO<sub>2</sub>. For instance, Li et al. <sup>[36]</sup> found that the flower-like 102 Bi<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> with enrichment Bi<sub>2</sub>O<sub>3</sub> quantum dots on the surface of photocatalyst 103 exhibited higher activity due to the strong interaction between Bi<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>. Leung 104 <sup>[37]</sup> and Wang <sup>[38]</sup> et al. hold that heterojunction structures with mixed semiconductors, 105 such as TiO<sub>2</sub>/ZnO/Bi<sub>2</sub>O<sub>3</sub>, 3D BiOCl<sub>x</sub>Br<sub>1-x</sub>/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 Bi<sup>3+</sup> and Bi<sub>2</sub>O<sub>3</sub> over Bi-doped TiO<sub>2</sub> photocatalysts. Li et al. <sup>[39]</sup> 109 reported an ordinary approach, doping Bi<sub>2</sub>O<sub>3</sub> powder into TiO<sub>2</sub> sol, to synthesis Bi-110 doped TiO<sub>2</sub> photocatalyst. When the loading of Bi<sub>2</sub>O<sub>3</sub> exceed 5mol%, Bi<sub>2</sub>Ti<sub>4</sub>O<sub>11</sub> 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<sub>x</sub>TiO<sub>y</sub> and TiO<sub>2</sub>, the photocatalytic activity over 114 Bi-doped TiO<sub>2</sub> could be improved. Gao et al. <sup>[30]</sup> found that Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> and Fe-doped 115 Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> nanosheets, described with a formula of  $(Bi_2O_2)^{2+}(Bi_2Ti_3O_{10})^{2-}$ , which was 116 constructed with a TiO<sub>6</sub> 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 Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> composite photocatalysts. According to the XPS analysis, XPS signals of 119 Bi<sub>2</sub>O<sub>3</sub> powders could also be found. Prabhakaran et al. <sup>[40]</sup> reported that Bi-doped and Bi-120 N co-doped TiO<sub>2</sub> 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 Bi<sub>2</sub>O<sub>3</sub>, while the positive shift 123 of XPS peaks corresponding to Bi4f<sub>7/2</sub> and Bi4f<sub>5/2</sub> 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 TiO<sub>2</sub> photocatalysts. I t is still necessary to investigate the state of Bi in-depth and find the rules between bismuth and 128 TiO<sub>2</sub> in Bi-doped TiO<sub>2</sub> 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 Bi<sub>2</sub>O<sub>3</sub> with TiO<sub>2</sub> in the form of heterojunction structure. Different 132 133 from previous studies that some simple approaches have been developed to synthesize Bi-doped TiO<sub>2</sub> photocatalysts with the formation of Bi<sub>x</sub>TiO<sub>y</sub> or Bi<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub>, 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 TiO<sub>2</sub> 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 TiO<sub>2</sub> photocatalysts were prepared.

The first one was for Bi<sup>3+</sup>/TiO<sub>2</sub> 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(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O) and 0.4 g 147 ammonium carbonate ((NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>) 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 Bi<sub>2</sub>O<sub>3</sub>-C/TiO<sub>2</sub> and Bi<sub>2</sub>O<sub>3</sub>-N/TiO<sub>2</sub> as composite/mixed oxides. 3.2 155 g bismuth nitrate (Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O) 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 Bi<sub>2</sub>O<sub>3</sub>-C powders, or not calcined at 450 °C for 4h, denoted 160 as Bi<sub>2</sub>O<sub>3</sub>-N powders, to obtain two different powders (Bi<sub>2</sub>O<sub>3</sub>-C and Bi<sub>2</sub>O<sub>3</sub>-N). After that, 161 another solution was prepared with the same way as Bi<sup>3+</sup>/TiO<sub>2</sub> without bismuth nitrate, 162 and then these Bi<sub>2</sub>O<sub>3</sub>-C or Bi<sub>2</sub>O<sub>3</sub>-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 Bi<sub>2</sub>O<sub>3</sub>-C/TiO<sub>2</sub> and Bi<sub>2</sub>O<sub>3</sub>-N/TiO<sub>2</sub>. 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 Bi<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub>.

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 $\alpha$  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 BaSO<sub>4</sub> 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<sup>-1</sup>. 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<sup>-1</sup>. 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 TiO<sub>2</sub> 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  $24.56 \text{ mg/m}^3$  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 TiO<sub>2</sub> for HCHO oxidation

Fig. 1 shows the conversion of HCHO and stability under visible light irradiation over 221 different types of Bi-doped TiO<sub>2</sub> 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 TiO<sub>2</sub>, Bi<sub>2</sub>O<sub>3</sub> and Bi<sup>3+</sup>/TiO<sub>2</sub> catalysts under dark, the 225 concentration of HCHO decreased from 1.052 to 0.923 mg/m<sup>3</sup> 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 TiO<sub>2</sub> and Bi<sub>2</sub>O<sub>3</sub>, 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 TiO<sub>2</sub> catalysts, the photocatalytic activity and stability of Bi<sup>3+</sup>/TiO<sub>2</sub> were significantly higher than other 231

three kinds of Bi-doped TiO<sub>2</sub> catalysts due to the composition and structure (Fig. 1(B) 232 and (C)). The HCHO concentration decreased from 1.094 to 0.058 mg/m<sup>3</sup> at 36h, even 233 below the limits value of standard (0.08 mg/m<sup>3</sup>). Moreover, the catalyst demonstrated 234 good stability with four consecutive tests. However, Bi<sub>2</sub>O<sub>3</sub>-N/TiO<sub>2</sub>, Bi<sub>2</sub>O<sub>3</sub>-C/TiO<sub>2</sub>, and 235 Bi<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> catalysts showed the same activity for HCHO degradation and the 236 conversion was about 50% at 48h. Meanwhile, the stability of Bi<sub>2</sub>O<sub>3</sub>-N/TiO<sub>2</sub> was as bad 237 as its oxidation activity, without improving. Owing to the rapid recombination of 238 photogenerated electrons and holes, although Bi<sub>2</sub>O<sub>3</sub> owned lower band gap energy (2.9 239 eV) than TiO<sub>2</sub> (3.2 eV), it exhibited the lowest activity for HCHO oxidation. 240









Fig. 1. Photocatalytic degradation of HCHO and stability over Bi-doped TiO<sub>2</sub> catalysts (A: blank
 and adsorption experiments under dark; B: photocatalytic oxidation of HCHO over Bi-doped TiO<sub>2</sub>
 catalysts; C: stability experiments over Bi<sup>3+</sup>/TiO<sub>2</sub> and Bi<sub>2</sub>O<sub>3</sub>-N/TiO<sub>2</sub> with four times )

247 *3.2 XRD analysis* 

Fig. 2 shows the XRD patterns of Bi-doped TiO<sub>2</sub> catalysts with different preparation methods calcinated at 450 °C for 8.5 h. For comparison, the XRD patterns of the asprepared pure Bi<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> were also provided. The XRD patterns of TiO<sub>2</sub> and Bi<sub>2</sub>O<sub>3</sub> were corresponded to the anatase phase of TiO<sub>2</sub> (PDF # 21-1272) and the monoclinic phase of  $\alpha$ -Bi<sub>2</sub>O<sub>3</sub> (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 TiO<sub>2</sub> catalysts, 255 except for Bi<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> mixed oxides, the XRD patterns of Bi<sup>3+</sup>/TiO<sub>2</sub> were assigned to 256 anatase TiO<sub>2</sub> 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  $\alpha$ -Bi<sub>2</sub>O<sub>3</sub> and the composite oxide of Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub>, implying that Bi<sub>2</sub>O<sub>3</sub> with calcining or not had no effect on the crystal structure. This is due to that these two 261 kinds of Bi-doped TiO<sub>2</sub> catalysts composed of Bi<sub>2</sub>O<sub>3</sub> and Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> led to a lower 262 activity than Bi<sup>3+</sup>/TiO<sub>2</sub>. In terms of Bi<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> mixed oxide catalyst, the diffraction 263 peaks in the patterns were ascribed to the TiO<sub>2</sub> and α-Bi<sub>2</sub>O<sub>3</sub>, respectively. Therefore, 264 the above results indicated that the heterojunction structure with TiO<sub>2</sub> and Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> 265 was the critical factor to obtain a high activity for HCHO oxidation, rather than the 266 incorporation of Bi<sub>2</sub>O<sub>3</sub> and Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub>, even with Bi<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>. 267



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Fig. 2. XRD patterns of TiO<sub>2</sub>, Bi<sub>2</sub>O<sub>3</sub>, and Bi-doped TiO<sub>2</sub> catalysts

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

273 Table 1. Textural properties of TiO<sub>2</sub>, Bi<sub>2</sub>O<sub>3</sub>, and Bi-doped TiO<sub>2</sub> catalysts



Fig. 3. Nitrogen adsorption-desorption isotherms and pore-size distribution curves of TiO<sub>2</sub>, Bi<sub>2</sub>O<sub>3</sub>,
and Bi-doped TiO<sub>2</sub> 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 N<sub>2</sub> adsorption-desorption isotherms and the appropriate pore size distribution curves of different types of Bi-doped TiO<sub>2</sub> catalysts. The 280 isotherms of TiO<sub>2</sub> 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 TiO<sub>2</sub> catalysts, except 284 for Bi<sup>3+</sup>/TiO<sub>2</sub>, 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, Bi<sup>3+</sup>/TiO<sub>2</sub> 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 Bi<sup>3+</sup>/TiO<sub>2</sub> had larger channels, 291 which was also confirmed by the pore size distribution and the improved HCHO 292 adsorption. Bi<sup>3+</sup>/TiO<sub>2</sub> ( $S_{BET}$ =52.39 m<sup>2</sup>/g) exhibited the largest surface areas and pore 293 sizes among these different types of Bi-doped TiO<sub>2</sub> catalysts. In addition, the surface 294 areas of TiO<sub>2</sub> and Bi<sub>2</sub>O<sub>3</sub> were calculated to be 59.53 m<sup>2</sup>/g and 37.96 m<sup>2</sup>/g, respectively. 295 Bi<sub>2</sub>O<sub>3</sub> and Bi<sub>2</sub>O<sub>3</sub>-N/TiO<sub>2</sub> 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 TiO<sub>2</sub> catalysts



of anatase  $TiO_2$ <sup>[39]</sup>, indicating that the  $TiO_2$  was one of the main phase structures in the 307 sample of Bi<sup>3+</sup>/TiO<sub>2</sub> and Bi<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub>, which was consistent with the XRD results. While 308 for Bi<sub>2</sub>O<sub>3</sub>-N/TiO<sub>2</sub> and Bi<sub>2</sub>O<sub>3</sub>-C/TiO<sub>2</sub>, it was difficult to detect the presence of anatase 309 TiO<sub>2</sub> by Raman spectra. More importantly, the Raman peak at 481 cm<sup>-1</sup> could be 310 assigned to the characteristic band of Bi<sub>2</sub>O<sub>3</sub>. Among these samples, the Bi<sub>2</sub>O<sub>3</sub>-C/TiO<sub>2</sub> 311 exhibited the strongest intensity due to Bi<sub>2</sub>O<sub>3</sub> powder calcined at 450 °C for 4h. While 312 for Bi<sub>2</sub>O<sub>3</sub>-N/TiO<sub>2</sub>, Bi<sub>2</sub>O<sub>3</sub>-C/TiO<sub>2</sub> and Bi<sup>3+</sup>/TiO<sub>2</sub>, it was easy to find the presence of 313 Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub>, not Bi<sub>2</sub>O<sub>3</sub>, by the XRD measurement, which was not corroborate well with 314 Raman spectra. That was because the composite oxides of Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> contained the 315 characteristic band of Bi<sub>2</sub>O<sub>3</sub>. 316

#### 317 *3.5 Morphology measurement*

The morphology structure of TiO<sub>2</sub>, Bi<sub>2</sub>O<sub>3</sub>, and Bi-doped TiO<sub>2</sub> catalysts were 318 investigated by using SEM and TEM. TiO<sub>2</sub> showed an aggregated of lumpy particles 319 with a smooth surface, while Bi<sub>2</sub>O<sub>3</sub> displayed some aggregated and smaller particles 320 with a rough surface attributed to nano-sized spherical Bi<sub>2</sub>O<sub>3</sub> (Fig. 5(B)). Bi<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> 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 TiO<sub>2</sub> 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 Bi<sub>2</sub>O<sub>3</sub>-N/TiO<sub>2</sub> and Bi<sub>2</sub>O<sub>3</sub>-C/TiO<sub>2</sub> 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 Bi<sub>4</sub>Ti<sub>3</sub>O<sub>4</sub>, 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 TiO<sub>2</sub>, respectively. However, the images 332 of Bi<sub>2</sub>O<sub>3</sub>-N/TiO<sub>2</sub> and Bi<sub>2</sub>O<sub>3</sub>-C/TiO<sub>2</sub> catalysts exhibited that these particles aggregated 333 together and produced a large number of lumps with a smooth surface due to roasted 334 Bi<sub>2</sub>O<sub>3</sub> without doping into TiO<sub>2</sub>. 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.







Fig. 5 SEM and TEM images of photocatalysts: (A) TiO<sub>2</sub>, (B) Bi<sub>2</sub>O<sub>3</sub>, (C) Bi<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub>, (D, G) Bi<sup>3+</sup>/TiO<sub>2</sub>, (E, H) Bi<sub>2</sub>O<sub>3</sub>-N/TiO<sub>2</sub>, and (F) Bi<sub>2</sub>O<sub>3</sub>-C/TiO<sub>2</sub>

#### 345 *3.6 Optical absorption properties*

The corresponding UV-vis DRS and PL spectra of TiO<sub>2</sub>, Bi<sub>2</sub>O<sub>3</sub> and Bi-doped TiO<sub>2</sub> 346 catalysts are presented in Fig. 6. The absorption peak of pure TiO<sub>2</sub> at 380–780 nm could 347 be found as anatase TiO<sub>2</sub> 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 Bi<sub>2</sub>O<sub>3</sub> 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. Bi<sub>2</sub>O<sub>3</sub> 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<sup>-</sup> and h<sup>+</sup>. Therefore, Bi<sub>2</sub>O<sub>3</sub> couldn't be used independently as an oxide catalyst for HCHO 354 oxidation and it needed to be combined with other semiconductors, such as TiO<sub>2</sub>, to 355 form heterojunctions structure or others to improve the oxidation activity. In terms of 356 Bi-doped TiO<sub>2</sub> 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<sup>-</sup> and h<sup>+</sup> with Bi<sub>2</sub>O<sub>3</sub>. Therefore, the samples of Bi<sub>2</sub>O<sub>3</sub>-N/TiO<sub>2</sub> and 361 Bi<sub>2</sub>O<sub>3</sub>-C/TiO<sub>2</sub> displayed poor activities for HCHO oxidation. The above results were all 362 consistent with the activity of Bi-doped TiO<sub>2</sub> 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 Bi<sub>2</sub>O<sub>3</sub>-N/TiO<sub>2</sub>, Bi<sub>2</sub>O<sub>3</sub>-C/TiO<sub>2</sub>, 367 Bi<sup>3+</sup>/TiO<sub>2</sub> and Bi<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub>. Among these four samples, Bi<sub>2</sub>O<sub>3</sub>-C/TiO<sub>2</sub> exhibited the 368 highest PL intensity, indicating that Bi<sub>2</sub>O<sub>3</sub>-C/TiO<sub>2</sub> showed a high recombination rate of 369 photoinduced e<sup>-</sup> and h<sup>+</sup>, which was not beneficial to increase the activity for 370 photocatalytic oxidation of HCHO. While, compared with Bi<sub>2</sub>O<sub>3</sub>-N/TiO<sub>2</sub>, Bi<sup>3+</sup>/TiO<sub>2</sub> 371 displayed a lower PL intensity, implying that Bi<sup>3+</sup>/TiO<sub>2</sub> could improve charge 372 separation with a low recombination rate of e<sup>-</sup> and h<sup>+</sup>. This was mainly due to the Bi<sup>3+</sup> 373 doping on TiO<sub>2</sub>, which can capture photogenerated e<sup>-</sup> from the surface of Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> to 374 reduce charge recombination. This result indicates that Bi<sup>3+</sup>/TiO<sub>2</sub> can exhibit a higher 375 photocatalytic activity due to that Bi<sup>3+</sup> doping TiO<sub>2</sub> hinders free carriers from 376 recombination under irradiation. Although Bi<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> showed the lowest PL intensity, 377 the photocatalysts of Bi<sub>2</sub>O<sub>3</sub> 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 Bi<sup>3+</sup>/TiO<sub>2</sub> that was composed of TiO<sub>2</sub> and Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub>, confirmed by 380 XRD. 381





Fig. 6. Diffuse reflectance UV-vis and PL spectra of TiO<sub>2</sub>, Bi<sub>2</sub>O<sub>3</sub>, and Bi-doped TiO<sub>2</sub> catalysts













Fig. 7. XPS spectra of different types of TiO<sub>2</sub>, Bi<sub>2</sub>O<sub>3</sub>, and Bi-doped TiO<sub>2</sub> catalysts

The chemical states of TiO<sub>2</sub>, Bi<sub>2</sub>O<sub>3</sub>, and Bi-doped TiO<sub>2</sub> 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<sub>3/2</sub> and T 2p<sub>1/2</sub> for TiO<sub>2</sub> and Bi<sup>3+</sup>/TiO<sub>2</sub> were situated at a binding energy (BE) of 458.5 eV and 464.2 eV, respectively. However, the BE of T 2p<sub>1/2</sub> for Bi<sub>2</sub>O<sub>3</sub>-N/TiO<sub>2</sub> was shifted to high binding energy due to the influence of Bi<sub>2</sub>O<sub>3</sub><sup>[39]</sup>. The results implied that Bi<sup>3+</sup>/TiO<sub>2</sub> and Bi<sub>2</sub>O<sub>3</sub>-N/TiO<sub>2</sub> consisted of TiO<sub>2</sub> and Bi<sub>2</sub>O<sub>3</sub>, 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

Fig. 8. In-situ DRIFTS and IR spectrum for (A, C) Bi<sup>3+</sup>/TiO<sub>2</sub>, and (B, D) Bi<sub>2</sub>O<sub>3</sub>-N/TiO<sub>2</sub> catalysts with the different reaction time

Base on the In-situ DRIFTS spectra of Bi<sup>3+</sup>/TiO<sub>2</sub> and Bi<sub>2</sub>O<sub>3</sub>-N/TiO<sub>2</sub>, as shown in Fig. 419 8A) and Fig. 8(B), upon exposure to a mixed flow of HCHO/O<sub>2</sub> ( $1.05 \pm 0.05 \text{ mg/m}^3$ ) 420 with different reaction time (0, 3, 6, 12, 24, and 36h) and different bands, such as 591, 421 1063, 1160, 1237, 1315 cm<sup>-1</sup> and others could be observed. According to references <sup>[1,</sup> 422  $^{2,8,9,14,42]}$ , as for Bi<sup>3+</sup>/TiO<sub>2</sub>, the bands at 591 and 1315 cm<sup>-1</sup> of Bi<sup>3+</sup>/TiO<sub>2</sub> can be assigned 423 to the asymmetric stretching vibration of Ti-O-Ti and stretching vibration of Ti-O, 424 respectively <sup>[42]</sup>. The bending vibration of water at ca. 1611 cm<sup>-1</sup> and the characteristic 425 bands of molecularly adsorbed HCHO at 1063 cm<sup>-1</sup> were found in the Bi<sup>3+</sup>/TiO<sub>2</sub> <sup>[14]</sup>. 426 The band at 1348 and weak bands at 2822 and 2975 cm<sup>-1</sup> were attributed to the 427 symmetric  $v_s(COO)$  and  $v_s(CH)$  stretching of formate <sup>[1]</sup>. In addition, a broad negative 428 band at ca. 1237 and 1452 cm<sup>-1</sup> were ascribed to  $v_s(CH_2)$  and  $\delta(CH_2)$  vibration of 429 dioxymethylene (DOM)<sup>[2]</sup>. The results implied that formate and DOM species were the 430 main intermediates for photocatalytic oxidation of HCHO. As for Bi<sub>2</sub>O<sub>3</sub>-N/TiO<sub>2</sub> (Fig. 431 8(B)), the characteristic bands with different reaction time were almost the same as 432 Bi<sub>2</sub>O<sub>3</sub>-N/TiO<sub>2</sub>(0h) without significant changing. The bending vibration of H<sub>2</sub>O at 1618 433 cm<sup>-1</sup> and the characteristic bands of molecularly adsorbed HCHO at 1058 cm<sup>-1</sup> were 434 also discovered. Meanwhile, the bands at 1386, 2848 and 2985 cm<sup>-1</sup> 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<sup>-1</sup> corresponding to the bending vibration of OH<sup>-</sup> in water adsorbed decreased and the band at 1710 cm<sup>-1</sup> 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<sup>-1</sup> corresponded to the hydroxyl group and the 443 bending vibration at ca. 1616  $\text{cm}^{-1}$  was attributed to OH- from the adsorption of H<sub>2</sub>O. 444 However, Bi<sup>3+</sup>/TiO<sub>2</sub> exhibited markedly higher H<sub>2</sub>O adsorption than Bi<sub>2</sub>O<sub>3</sub>-N/TiO<sub>2</sub>. 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<sup>-1</sup> and 448 2906 cm<sup>-1</sup> suited to the symmetric or other C-H orientations stretching vibration of 449 formate ( $V_{\rm s}$  (COO<sup>-</sup>)) were detected. Furthermore, the bands appearing at around 2334 450 cm<sup>-1</sup>, 1386 cm<sup>-1</sup>, and 1446 cm<sup>-1</sup> can be assigned to the stretching or bending vibration 451 of C-O ( $V_s$  (HCO<sub>3</sub><sup>-</sup>)) and  $\delta$ (CH<sub>2</sub>) vibration of dioxymethylene (DOM) due to the 452 photocatalytic oxidation reaction. The above results confirmed the presence of surface 453 hydroxyls (OH<sup>-</sup>) in the structure of these two samples and revealed that the importance 454 of surface hydroxyls on HCHO degradation, especially for Bi<sup>3+</sup>/TiO<sub>2</sub>. These adsorbed 455 H<sub>2</sub>O and OH<sup>-</sup> 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 <sup>[1, 2, 8, 9,</sup> 458 <sup>14, 42, 43, 44]</sup>, HCHO was degraded into dioxymethylene (DOM) at first, and then further 459 into formate and carbonate, then finally desorbs as CO<sub>2</sub>. 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  $O_2^-$  <sup>[45]</sup>, and the value of paramagnetic

characteristic could be increased by Bi3+ doping with TiO2. Bi3+/TiO2 displayed the 466 highest amount of 'O<sub>2</sub>', followed by TiO<sub>2</sub>, Bi<sub>2</sub>O<sub>3</sub>-N/TiO<sub>2</sub>, and Bi<sub>2</sub>O<sub>3</sub>. 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 Bi<sub>2</sub>O<sub>3</sub> doped in TiO<sub>2</sub>, some of Bi<sub>2</sub>O<sub>3</sub> exposed as an electrically 469 charged composite centre, which prevented some e<sup>-</sup> 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 TiO<sub>2</sub>, Bi<sub>2</sub>O<sub>3</sub>, and Bi-doped TiO<sub>2</sub> catalysts

477 *3.10 Mechanisms for photocatalytic oxidation of HCHO* 

Depending on the structure of Bi-doped TiO<sub>2</sub>, particularly for Bi<sup>3+</sup>/TiO<sub>2</sub>, the structure 478 479 of heterojunction, identified as Bi<sub>4</sub>Ti<sub>3</sub>O<sub>4</sub> and TiO<sub>2</sub>, could promote efficient charge separation, with the consequence of reducing the recombination of photogenerated e<sup>-</sup> 480 and  $h^+$  (Fig. 10). Gan et al. found UV-vis DRS, the  $E_{bg}$  for Bi<sub>4</sub>Ti<sub>3</sub>O<sub>4</sub> and TiO<sub>2</sub> were 481 about 2.91 eV and 3.1 eV <sup>[46]</sup>. Therefore, the  $E_{cb}$  and  $E_{vb}$  for Bi<sub>4</sub>Ti<sub>3</sub>O<sub>4</sub> and TiO<sub>2</sub> were 482 calculated as -0.41 eV, -0.12 eV, 2.50 eV and 2.98 eV, respectively. Because the  $E_{cb}$  of 483 TiO<sub>2</sub> was lower than Bi<sub>4</sub>Ti<sub>3</sub>O<sub>4</sub>, the photogenerated e<sup>-</sup> could be moved easily from 484 Bi<sub>4</sub>Ti<sub>3</sub>O<sub>4</sub> to TiO<sub>2</sub>. 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<sup>-1</sup>) and dioxymethylene (1237 and 1452 cm<sup>-1</sup>), ascribed to the results of in-situ 487 DRIFTS spectra, could be found clearly in the Bi<sup>3+</sup>/TiO<sub>2</sub>. 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<sup>-1</sup> 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<sup>-1</sup> 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. Bi<sup>3+</sup>/TiO<sub>2</sub> was activated by the visible light and the 495 photogenerated  $e^{-}$  and  $h^{+}$  could be transferred by the heterojunction structure. Then, 496 these e<sup>-</sup> can react with O<sub>2</sub> to generate superoxide radical anion ('O<sub>2</sub><sup>-</sup>), 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  $CO_2$ <sup>[2, 47]</sup>. Another possible pathway is 499 that these photogenerated holes can be combined with OH<sup>-</sup> or H<sub>2</sub>O to generate hydroxyl 500 501 radical (•OH), which could directly oxidize HCHO or formate into CO<sub>2</sub> and H<sub>2</sub>O and tackle the environmental pollution [48, 49]. 502



Fig. 10. Proposed electron-hole pair separation in the Bi<sup>3+</sup>/TiO<sub>2</sub> composites under visible

irradiation

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- 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 TiO<sub>2</sub> and 509 Bi<sub>2</sub>O<sub>3</sub>, photocatalytic oxidation of HCHO can be further improved by the Bi-doped 510 TiO<sub>2</sub> catalysts, especially Bi<sup>3+</sup>/TiO<sub>2</sub>. According to the investigation of characterization, 511 it could be observed that the excess Bi<sub>2</sub>O<sub>3</sub> doping into TiO<sub>2</sub> catalysts, such as Bi<sub>2</sub>O<sub>3</sub>-512 N/TiO<sub>2</sub> and Bi<sub>2</sub>O<sub>3</sub>-C/TiO<sub>2</sub>, formed a mixed oxides with Bi<sub>2</sub>O<sub>3</sub> and Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub>, and they 513 were disadvantage to enhance the activity. However, Bi<sup>3+</sup>/TiO<sub>2</sub> composed of TiO<sub>2</sub> and 514 Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> displayed a higher activity and remained good stability for HCHO oxidation. 515 It was worth mention that Bi<sup>3+</sup>/TiO<sub>2</sub> 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 TiO<sub>2</sub> and Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> 518 via charge transfer. 519

In summary, this study demonstrated that HCHO can be effectively oxidized to 0.058 mg/m<sup>3</sup> (94.7%) at visible light excitation within 36 h. The heterogeneous catalysts with TiO<sub>2</sub> and Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> 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 TiO<sub>2</sub> crystal.

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#### 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.