

Acetic acid-assisted fabrication of hierarchical flower-like Bi₂O₃ for photocatalytic degradation of sulfamethoxazole and rhodamine B under solar irradiation

Bao, Yueping; Lim, Teik-Thye; Zhong, Ziyi; Wang, Rong; Hu, Xiao

2017

Bao, Y., Lim, T.-T., Zhong, Z., Wang, R., & Hu, X. (2017). Acetic acid-assisted fabrication of hierarchical flower-like Bi₂O₃ for photocatalytic degradation of sulfamethoxazole and rhodamine B under solar irradiation. *Journal of Colloid and Interface Science*, 505, 489–499. doi:10.1016/j.jcis.2017.05.070

<https://hdl.handle.net/10356/143832>

<https://doi.org/10.1016/j.jcis.2017.05.070>

© 2017 Elsevier Inc. All rights reserved. This paper was published in *Journal of colloid and interface science* and is made available with permission of Elsevier Inc.

Downloaded on 03 Feb 2023 18:33:08 SGT

1 Acetic acid-assisted fabrication of hierarchical flower-like Bi₂O₃ for
2 photocatalytic degradation of sulfamethoxazole and rhodamine B under
3 solar irradiation

4

5 Yueping Bao ^{1,2}, Teik-Thye Lim ^{2,3}, Ziyi Zhong ², Rong Wang ^{2,3}, Xiao Hu ^{2,4*}

6

7

8 ¹ *Interdisciplinary Graduate School, Nanyang Technological University, 637141, Singapore*

9 ² *Nanyang Environment and Water Research Institute, Nanyang Technological University,*
10 *637141, Singapore*

11 ³ *School of Civil and Environmental and Engineering, Nanyang Technological University,*
12 *639798, Singapore*

13 ⁴ *School of Materials Science and Engineering, Nanyang Technological University, 639798,*
14 *Singapore*

15

16

17

18

19

20

21 * Corresponding author at: School of Materials Science and Engineering, Nanyang
22 Technological University, Block N4.1, 50 Nanyang Avenue, Singapore 639798, Singapore.

23 Tel.: + 65 6790 4610

24 E-mail address: ASXHU@ntu.edu.sg.

25

26

27

28

29

30

31

32

33

34 **Abstract**

35 With the assistance of acetic acid (CH₃COOH), a novel 3D flower-like Bi₂O₃
36 was synthesized via hydrothermal process followed by calcination. For the first time,
37 the role of CH₃COOH as a capping agent in the formation of flower-like structure was
38 investigated. The as-prepared flower-like Bi₂O₃ had a high activity on the degradation
39 of sulfamethoxazole (SMX) under simulated solar light irradiation due to the narrow
40 band gap of 2.69 eV, high percentage of β-Bi₂O₃ as well as high intensity of polar
41 facets (120) and (200). Meanwhile, the photocatalytic degradation followed apparent
42 pseudo-first-order kinetics. The rate constants (*k*) increased from 0.7×10^{-2} to $3.0 \times$
43 10^{-2} min^{-1} with the catalyst loading varying from 0.5 to 2.0 g L⁻¹. Increasing pH values
44 from 3 to 11 led to the decrease of *k* from 2.2×10^{-2} to $0.2 \times 10^{-2} \text{ min}^{-1}$, which could
45 be attributed to the electrostatic adsorption between SMX molecules and Bi₂O₃. **The**
46 **radical quenching experiments show both direct (h⁺) and indirect oxidation (•OH and**
47 **•O₂⁻) happen in this process.**

48

49

50 Key words: Flower-like Bi₂O₃, Acetic Acid, Growth Mechanism, Photocatalytic
51 Activity, **Degradation Mechanism**

52

53

54

55

56

57

58

59

60

61

62

63

64 1. Introduction

65 As one of the attractive materials, bismuth oxide (Bi_2O_3) possesses excellent
66 properties such as high refractive index of 2.9, high dielectric permittivity of 190,
67 high oxygen conductivity of 1.0 S cm^{-1} as well as remarkable photoluminescence
68 properties [1–5], leading to extensive applications in gas sensing [6], fuel cell [7],
69 photo and photo-electro application [8,9] and water treatment [10]. Additionally,
70 Bi_2O_3 has also been proved to be a safe, nontoxic and non-carcinogenic photocatalyst
71 [11] and could be used for oxygen evolution reaction and pollutants decomposing
72 under visible light irradiation [12,13], owing to its narrower band gap of $\sim 2.8 \text{ eV}$
73 compared with TiO_2 ($\sim 3.2 \text{ eV}$) [14], which needs to be modified to enhance the
74 visible light activity [15]. Another way to improve the visible light absorption of
75 catalyst is to prepare nanocomposites, which could be observed in literature [16,17].
76 Since the photocatalytic process is a surface phenomenon and limited to mass-transfer
77 effect, the activity of photocatalyst is strongly affected by the crystal phase, specific
78 surface area, morphology and microstructures. Therefore, Bi_2O_3 with hierarchical
79 microstructures, well-defined morphologies and high crystallinity is highly desirable.

80 Hydrothermal process has been used to prepare hierarchical Bi_2O_3 in recent years
81 due to its simple operation and capability of large-scale production. In previous study,
82 Zhang et al prepared spherical flower-like Bi_2O_3 via a citric acid assisted
83 hydrothermal process followed by calcination [18]. With the assistance of citric acid,
84 the flower-like structure could be obtained when the hydrothermal temperature
85 reached 200°C . However, there was no further investigation on its photocatalytic
86 performance [18]. Meanwhile, because of the surface phenomena of photocatalysis,
87 the surface area of catalysts is a critical parameter for the catalysts. Many researchers
88 have been working on enhancing the surface area of Bi_2O_3 , which is around $0.4 \text{ m}^2 \text{ g}^{-1}$
89 for the commercial one [19]. In Wang's study, the addition of ethanol and
90 dimethylformamide (DMF) in the hydrothermal process was proved to enhance the
91 surface area of monoclinic- Bi_2O_3 to $4.8 \text{ m}^2 \text{ g}^{-1}$, which showed a removal of
92 Rhodamine B (RhB) at 60% after 4 h irradiation under visible light irradiation [19].
93 L-asparagine was also used to prepare flower-like Bi_2O_3 with the surface area of 3.6

94 $\text{m}^2 \text{g}^{-1}$ in previous study [20]. Until now, developing a facile method to synthesize
95 hierarchical Bi_2O_3 with a comparable surface area is still needed.

96 Here, we report a novel and facile approach to synthesize Bi_2O_3 spherical flower
97 structure via an acetic acid assisted process. The dual functional roles of acetic acid as
98 pH adjustor and capping agent were firstly discussed. In this process, poly(propylene
99 glycol)-block poly(ethylene glycol)-block poly(propylene glycol) (PPG-PEG-PPG,
100 Pluronic[®] P-123, P-123), which is a tri-block copolymer, was chosen as the structure
101 directing agent (SDA) to control the Bi_2O_3 surface area as well as the product yield
102 [21]. Furthermore, the growth mechanism and optical properties of the as-prepared
103 flower-like Bi_2O_3 crystals were also examined.

104 **2. Experimental**

105 *2.1 Chemicals*

106 Bismuth (III) nitrate pentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$), nitric acid (HNO_3), glacial
107 acetic acid (CH_3COOH) and poly(propylene glycol)-block poly(ethylene
108 glycol)-block poly(propylene glycol) (PPG-PEG-PPG, Pluronic[®] P-123, P-123,
109 MW~5800), sodium hydroxide (NaOH), rhodamine B (RhB, $\text{C}_{28}\text{H}_{31}\text{C}_1\text{N}_2\text{O}_3$) and
110 sulfamethoxazole (4-amino-N-(5-methyl-3-isoxazolyl)-benzenesulfonamide, SMX,
111 $\text{C}_{10}\text{H}_{11}\text{N}_3\text{O}_3\text{S}$) were purchased from Sigma-Aldrich Co. Ltd. All the reagents were
112 used as received without further purification. The deionized (DI) water used in
113 experiments was produced by a Milli-Q system (18.2 $\text{M}\Omega \cdot \text{cm}$ at 25°C).

114 *2.2 Preparation of Bi_2O_3 particles*

115 The Bi_2O_3 samples were synthesized by the self-assembly (SA) method using
116 P-123 as a SDA followed by hydrothermal and calcination process. As shown in Fig
117 S1, in a typical experimental procedure, $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ with a predetermined amount
118 was dissolved into acetic acid solution, then P-123 with the amount ranging from 0 -
119 20 wt% were added into the solution under stirring. The mixture was aged with
120 stirring for several hours and then transferred into a Teflon-lined stainless steel
121 autoclave. The autoclave was heated up to 150°C and held for 2-24 h for the crystals
122 growth. After that, the autoclave was cooled down to room temperature and the
123 precipitate (Bi_2O_3 precursor) was washed and dried at room temperature. The Bi_2O_3

124 precursor was then calcinated at 350 - 650°C for 3 h to obtain Bi₂O₃ sample. To
125 investigate the role of CH₃COOH, the control experiment was conducted in which
126 acetic acid was replaced by nitric acid (HNO₃). Meanwhile, the effect of solution pH
127 was investigated by changing the ratio of CH₃COOH and Bi(NO₃)₃·5H₂O (Table S1).

128 *2.3 Characterization of Bi₂O₃ particles*

129 To understand the thermal decomposition and phase transformation behaviors of
130 as-prepared Bi₂O₃ precursor to Bi₂O₃ particle, the thermogravimetric analysis (TGA)
131 and differential scanning calorimetry (DSC) measurements were performed at
132 temperatures from 100 to 900 °C using an SDT-Q600 instrument (TA instrument,
133 USA). The sample was heated at a rate of 10 °C min⁻¹ with the air flow of 100 mL
134 min⁻¹. Furthermore, the vibrational absorbance and structural characteristics of the
135 precursor and samples were investigated by Fourier transformed infra-red spectra
136 (FTIR, FT-IR/NIR spectrometer Frontier, Perkin Elmer, USA). The FTIR spectra were
137 collected between 4000 to 400 cm⁻¹ with the interval of 1 cm⁻¹ and the total number of
138 scan was 16 with the resolution of 4 cm⁻¹.

139 Nitrogen (N₂) adsorption/desorption isotherms for the porosimetry analysis of
140 Bi₂O₃ particles were measured using Quantachrome Autosorb -1 Analyzer at liquid N₂
141 temperature of 77 K. The pulverized Bi₂O₃ powders were degassed at 150 °C for 5
142 hours prior to the actual measurement. The Brunauer-Emmett-Teller surface area
143 (*S*_{BET}) was calculated based on BET model [22].

144 The surface morphologies and particle size were obtained by field emission
145 scanning electron microscope (FESEM, JSM-6340F, JEOL, Japan) with the resolution
146 of 3.0 nm. Prior to the analysis, the samples were coated with platinum using Auto
147 Fine Coater (JEC-300FC, JEOL, Japan) to reduce the effect of surface charging. The
148 mineralogy and crystal structures of Bi₂O₃ particles were analyzed using X-rays
149 diffractometer (XRD, Bruker D8 Advance) with a monochromated high intensity
150 Cu-K_α (λ = 1.54 Å) radiation over a 2θ range of 15-75° at a step size of 0.02 combined
151 with a rotation speed of 15 rpm. The minimum crystallite size of Bi₂O₃ was estimated
152 by Scherrer's equation [23] as follows:

$$153 \quad D = R \lambda / \beta \cos \theta \quad (1)$$

154 where D is the diameter of the particles (nm), R is Scherrer's constant (0.89), λ is the
155 incident wavelength (0.154 nm), β (rad) is the peak width at half height and θ ($^{\circ}$) is
156 the diffraction angle. Meanwhile, the percentage of different crystal phases was
157 calculated via rietveld refinement by TOPAS (Version of 4.1).

158 To further detect the chemical states of the elements in Bi_2O_3 , X-ray
159 photoelectron spectroscopy (XPS) measurement was conducted on a Kratos Axis
160 Supra spectrophotometer (Shimadzu, Japan) equipped with a dual anode
161 monochromatic K_{α} excitation source ($h\nu = 1486.7$ eV). All binding energies for
162 elements of interest were corrected against an adventitious carbon C 1s core level at
163 284.8 eV. All XPS peaks were fitted using Shirley background together with
164 Gaussian-Lorentzian function.

165 *2.4 Optical properties*

166 The diffuse reflectance spectroscopy (DRS) study of the Bi_2O_3 samples was
167 carried out on a UV/Vis/NIR spectrometer (Lambda 950, Perkin Elmer, USA) in the
168 wavelength range for from 250 to 700 nm at the data interval of 1 nm. The
169 photoluminescence spectra (PL) were obtained using a Cary Eclipse Fluorescence
170 Spectrophotometer (Agilent Technologies, USA) with the excitation wavelength of
171 260 nm.

172 Photochemical degradation experiments were performed in a Quartz reactor with
173 different target pollutants. All the reaction mixture (50 mL of 10 mg L^{-1} RhB/SMX)
174 containing 50 mg Bi_2O_3 was irradiated with a solar simulator of 300 W supplied by
175 Newport under continuous magnetic stirring. The experiment setup is shown in Fig S1
176 with the light intensity of 1 Sun (~ 1000 W m^{-2}). The control experiments were
177 conducted under the same condition but without catalysts. Before the photochemical
178 reactions, all solutions were put in dark for 20 min to achieve the adsorption -
179 desorption equilibrium. The spectra of RhB visible light absorption (from 600-450 nm)
180 over the duration of the photocatalytic degradation were collected using UV-1800
181 spectrophotometer (Shimadzu, Japan). The concentration of SMX was determined
182 using a high-performance liquid chromatography system (PerkinElmer Series 200)
183 equipped with a C-18 column. The mobile phases were methanol and water (v/v,

184 60/40) at a flow rate of 0.6 mL min⁻¹. The UV detector was operated at a wavelength
185 of 256 nm and the injection volume is 100 uL.

186 **3. Results and discussion**

187 *3.1 Effect of acetic acid*

188 In this study, acetic acid was used to synthesize the flower-like structure of Bi₂O₃
189 in a facile method and the role of acetic acid was discussed for the first time. To
190 investigate the role of CH₃COOH, control experiment was carried out by replacing
191 CH₃COOH with HNO₃ while keeping the other conditions unchanged. As shown in
192 Fig 1, needle-like structure could be achieved with the addition of HNO₃, while
193 flower-like structure could be prepared with the addition of CH₃COOH, which shows
194 the critical role of CH₃COOH in the formation of flower-like hierarchal structure.
195 Both of the as-prepared precursors were identified as Bi(C₂O₄)(OH) (04-015-6948)
196 (Fig S2), **which indicates that [C₂O₄] group was provide by P-123**, but the difference
197 of peak intensities on specific crystal faces shows the preferential growth of the
198 crystals. In the following calcination process, both precursors transferred to Bi₂O₃ (a
199 mixture of α- and β-phases) corresponding to card numbers 04-003-2034 and
200 01-074-1374 in the database of PDF-4+2015 RDB (Fig 2). The crystal structures with
201 phase parameters for both phases are shown in Fig S3.

202 -----

203 Fig. 1 here

204 -----

205 The crystal morphology is determined by its growth habit, which could be
206 affected by external conditions including hydrothermal temperature and pH of
207 solution [24]. α-Bi₂O₃ is supposed to be a polar crystal with space group of 2/m and
208 polar surface of [001] [25], thus, its crystal often appears in needle-like morphology
209 with an elongation of crystal shape along the preferential direction. The existence of
210 NO₃⁻ in solution induced the preferential one-dimensional crystal growth of Bi₂O₃ in
211 the [001] direction and favored the formation of long needle-like Bi₂O₃ crystals [25],
212 which is shown in Fig 1 (a and b). However, when acetic acid was introduced, the

213 coupling of -OH in acetic acid molecules on certain crystal faces can provides
214 shielding effect [26], suppressing the crystal growth rate in the preferential direction.
215 Therefore, the Bi₂O₃ crystal shortened and changed from needle-like to flake-like
216 structure (Figs 1c and d). Meanwhile, in hydrothermal process, CH₃COOH molecules
217 are more favorable to be adsorbed on the tip of the petals to form a hierarchical
218 structure accompanied with Ostwald ripening due to the surface energy difference
219 [27]. In this work, CH₃COOH works as a capping agent to confine the growth rate of
220 crystal in certain crystal faces as well as a pH adjustor to avoid the hydrolysis of
221 Bi(NO₃)₃·5H₂O.

222 -----

223 Fig. 2 here

224 -----

225 The diffraction patterns of Bi₂O₃ samples have shown difference in the range of
226 24°-39° (Inset of Fig 2), with the peak positions at 24.8°, 25.8°, 27.1°, 27.6°, 28.2°,
227 32.0°, 32.8°, 33.5°, 35.3°, 36.1° and 37.8°. The peaks at 24.8°, 25.8°, 27.1°, 27.6°,
228 33.5°, 35.3°, 36.1° and 37.8° are identified as monoclinic α-Bi₂O₃ (04-003-2034 in
229 the database of PDF-4+2015 RDB), corresponding to (-102), (002), (111), (120), (200)
230 (210), (102) and (112) [28]. While other peaks at 28.2°, 32.0°, 32.8° are characteristic
231 of tetragonal β-Bi₂O₃ (01-074-1374 in the database of PDF-4+2015 RDB) with the
232 crystal plane of (221), (002) and (400) [29]. Meanwhile, XRD measurements show
233 α-Bi₂O₃ is present as the major phase in both samples. But in the needle-like sample,
234 Bi₂O₃ contains a more predominant α phase (more than 80%) and only several small
235 peaks could be assigned to the β phase (Fig 2). With the addition of acetic acid, the
236 flower-like structure was composed by around 74% α-Bi₂O₃, resulting a higher
237 percentage of β phase. From these results, it could be proposed that the addition of
238 acetic acid could achieve the transformation of Bi₂O₃ from α to β phase, which might
239 enhance its photoactivity [30–32].

240 -----

241 Fig. 3 here

242 -----

243 To further investigate the effect of acetic acid, different amounts of acetic acid
244 were added (Table S1). Since $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ can be hydrolyzed easily in water to
245 produce slightly soluble irregular shaped BiONO_3 [33,34], acetic acid was added to
246 prepare a more uniform and transparent solution. When the pH of solution is higher
247 than 0.80 (with the acetic acid addition of 0 and 1 mL), the hydrolysis process of
248 $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ cannot be inhibited totally and the solutions became non-transparent
249 along with the formation of a white precipitate. A large amount of precipitates with
250 irregular shape was formed, resulting in the inhomogeneous distribution of particles
251 (Figs 3 a and b). The white precipitate was completely dissolved as the amount of
252 acetic acid was increased to 3 mL, and the solution became transparent. After the
253 hydrothermal reaction and calcination, Bi_2O_3 with a uniform flower structure was
254 obtained (Fig 3c). Interestingly, with the further addition of acetic acid, the flower
255 structure was destabilized and all flakes grew bigger and Ostwald ripening process
256 was depressed, resulting in the formation of 2D flakes structures (Fig 3d).

257 *3.2 Effect of P-123 addition*

258 As reported in the literature, crystal nucleation and growth could be dramatically
259 influenced by foreign molecules which would attach onto specific crystal planes to
260 decrease the surface energy, leading to altered crystal orientation and preferential
261 growth [35]. In this work, the foreign molecules of P-123 were chosen because of
262 their mesostructured ordering properties, amphiphilic character, low-cost commercial
263 availability and biodegradability [36]. The addition of P-123 allows fine-tuning the
264 porosity and porous structure of the resulting samples [36]. It was also found that a
265 turbid solution was formed from the transparent $\text{Bi}(\text{NO}_3)_3/\text{CH}_3\text{COOH}$ solution when
266 the addition of P-123 reached to 10 wt%. These tiny precipitate particles may act as
267 the heterogeneous nuclei for growth of the as-prepared particle crystals. P-123 plays a
268 key role in the successful precipitation of tiny crystals and the yield of product is
269 nearly 0% without the addition of P-123.

270

Fig. 4 here

272

273 BET gas sorptometry measurements were conducted to examine the porous
274 property of the Bi₂O₃ particles. Fig 4 a shows the N₂ adsorption-desorption isotherm
275 and the calculated surface areas (Inset of Fig 4 a) of the Bi₂O₃ samples with P-123
276 amounts changing from 2-20 wt%. According to BDDT classification, all samples
277 display a type III isotherm which shows a the weak interaction between adsorbate and
278 adsorbent [37]. Moreover, the hysteresis loop shifts to higher P/P₀, indicating the
279 existence of macropores [38]. It was found that the increase of P-123 concentration
280 could result in a larger surface area. The surface area increased by 41% from 3.4 to
281 4.8 m² g⁻¹ with the P-123 concentration increased from 2-10 wt% (much higher than
282 that of the commercial one with the surface area of 0.4 m² g⁻¹ [19]). Higher P-123
283 concentration caused more pore coalescence and multi-micellar interactions during
284 heat treatment which would result in relatively large pores and high porosity [39].
285 However, with the addition of 20 wt% P-123, the surface area decreased again, which
286 might be caused by the collapse of Bi₂O₃ structure. This change could be further
287 evidenced by SEM images of the Bi₂O₃ with different P-123 additions (Fig S4). From
288 the SEM images, it could be seen with the addition of 2-10% P-123, the particles
289 show a sheet structure with pores on the sheet surface (Figs S4 and S5), while with a
290 higher P-123 addition, the particles would stick with each other to form a larger 2-D
291 piece (Fig S4 d). Compared with the Bi₂O₃ precursor and Bi₂O₃ particle, both of
292 which were prepared with 5 wt% P-123, the surface area difference should be caused
293 by the removal of P-123 as well as the transformation from precursor to Bi₂O₃ in the
294 calcination process, which could be evidenced by TGA/DSC results (Fig 4 b).
295 Meanwhile, as a comparison, the surface area of needle-like Bi₂O₃ was also tested as
296 2.8 m² g⁻¹. The higher surface area of flower-like Bi₂O₃ could be a benefit for the
297 photocatalysis process.

298 *3.3 Effect of calcination temperature*

299 TGA/DSC was employed to investigate transformation of $\text{Bi}(\text{C}_2\text{O}_4)(\text{OH})$ to Bi_2O_3
300 (Fig 4 b). Fig 4 b shows an endothermic peak around 330°C and the weight loss is
301 located in the temperature range of $250\text{-}350^\circ\text{C}$, which is attributed to the removal of
302 organic residue and the mass loss of phase transformation. The calcination
303 temperature was set from $350\text{-}650^\circ\text{C}$ to investigate the effect and the results are
304 shown in Fig 5. All samples are composed of flakes with a dimension of hundreds of
305 nanometers, which is in accordance with crystallite size obtained from Scherrer's
306 equation (Eq. 1). The nano-sheet structure with a nearly non-porous structure could
307 result the hysteresis in the N_2 adsorption-desorption isotherm (Fig 4 a) [38].

308 The diffractogram of Bi_2O_3 samples under different calcination temperatures is
309 shown in Fig 5 e. The Bi_2O_3 precursor without calcination showed the crystalline
310 peaks at Bragg angle (2θ) of 15.49° , 22.38° , 31.26° , 31.55° , 33.30° , 45.03° , 47.67° ,
311 60.71° and 65.19° , which is corresponding to $\text{Bi}(\text{C}_2\text{O}_4)(\text{OH})$ with the card number of
312 04-015-6948 in the database of PDF-4+2015 RDB (Fig S2). The crystal structure of
313 $\text{Bi}(\text{C}_2\text{O}_4)(\text{OH})$ is mainly composed of BiO_6 polyhedra and $[\text{C}_2\text{O}_4]$ groups, which
314 alternatively connected through two bridging O atoms along $[010]$ direction to form
315 the 3D structure (Fig S6 a). After the calcination process, the precursor transferred to
316 Bi_2O_3 (Fig S6 b). When the calcination temperature was increased from 350 to 650°C ,
317 both the percentage of monoclinic $\alpha\text{-Bi}_2\text{O}_3$ (Fig 5 e) and crystal size (Fig 5 f)
318 increased. Further observation indicates that with the increase in calcination
319 temperature, the widths of the XRD appear to be sharper, indicating the enhanced
320 crystallization and crystal growth of the Bi_2O_3 (Fig 5 e).

321 -----

322 Fig. 5 here

323 -----

324 *3.4 Flower-like Bi_2O_3 structure evolution and phase transformation*

325 The formation of flower-like structure is a self-assembly process which involves
326 a combination of electrostatic and hydrogen-bonding interaction [36]. In the system,
327 the hydrolysis of $\text{Bi}(\text{NO}_3)_3$ is inhibited by the addition of acetic acid, producing Bi^{3+}

328 in the solution which could associate preferentially with the hydrophilic poly
329 (ethylene oxide) moieties of P-123. At a low P-123 concentration, there is no
330 assembly of the P-123 molecules, resulting in a low yield of product. In aqueous
331 solution where the concentration of P-123 is higher than its critical micelle
332 concentration (CMC), P-123 could assemble to form micelles, spherical or cylindrical
333 structures by maintaining the hydrophilic parts of the surfactant in contact with water
334 while shielding the hydrophobic parts within the micellar interior. Attractive forces
335 between Bi^{3+} and P-123 led to the assembly of Bi^{3+} species on the micelle surface,
336 and after the calcination steps, the template was removed, leaving behind an ordered
337 porous structure (Fig 6 g).

338 -----

339 Fig. 6 here

340 -----

341 To investigate the growth mechanism of the Bi_2O_3 hierarchical structure, the
342 hydrothermal growth process was systematically studied by analyzing SEM images of
343 the samples obtained at different growth stages (Figs 6 a-f). Clearly, the evolution of
344 flower-like structure is related to the hydrothermal treatment time (2-24 h). As shown
345 in Fig 6 a, only nanosheets with dimension of around 100 nm were obtained at
346 hydrothermal time of 2 h. The size of Bi_2O_3 flakes increases with the increasing of the
347 hydrothermal time (Fig 6 b). When the hydrothermal time reached 8 hours, Bi_2O_3
348 nanosheets with the size of ca. 1 μm were obtained and these structures were
349 uniformly formed and distributed (Fig 6 c). Further prolonging the reaction time, the
350 nanosheets showed a self-assembly tendency of building-up-shaped 3D hierarchical
351 structures (Fig 6 d). The product obtained after 24 h contains a mixture of flower
352 structures and sheets aggregates (Fig 6 f). The flowery structures are constructed by
353 lots of small nanosheets intercrossed with each other via Ostwald ripening [27].

354 FTIR analysis was further carried out to verify the conversion of Bi_2O_3 in the
355 calcination process. As shown in Fig S7, after the calcination process, several peaks
356 disappeared in the spectrum compared with that of the precursor which contains

357 carbon (Fig S2). The peak at around 1733 cm^{-1} could be ascribed to the stretching
358 vibration of C=O while the peak at around 1300 cm^{-1} could be assigned to the
359 stretching vibration of C-C bond [40]. For Bi_2O_3 sample, the bands observed at 431
360 and 507 cm^{-1} could be due to stretching vibrations of Bi-O bonds in distorted BiO_6
361 coordination polyhedron in monoclinic Bi_2O_3 crystals [41–43], while the band
362 identified at 800 cm^{-1} could be caused by the symmetrical stretching vibration of Bi-O
363 bonds of BiO_3 pyramidal units.

364 -----

365 Fig. 7 here

366 -----

367 XPS was used to characterize the Bi oxidation state and the coexistence of Bi
368 connected with different O atoms is evidenced by a shoulder observed on the main
369 peaks of 158.7 and 164 eV for Bi 4f_{7/2} and Bi 4f_{5/2}, respectively. From Fig 7 (b), Bi
370 4f_{7/2} in Bi_2O_3 shows the binding energies of 158.7 and 161.5 eV [44,45] and the
371 peaks with binding energies of around 164 and 166.5 are identified as Bi 4f_{5/2} in
372 Bi_2O_3 [46]. **The shoulders at 161.5 and 166.5 eV could be caused by higher oxidation**
373 **state of bismuth (Bi^{3+x}) and the existence of multiple oxidation states in Bi_2O_3 could**
374 **enhance its photocatalytic ability.** Before calcination, the precursor shows the higher
375 binding energies of 159 and 164.3 eV, indicating the higher electronegativity in
376 $\text{Bi}(\text{C}_2\text{O}_4)(\text{OH})$ in which all Bi atoms are connected with 6 O atoms (Fig S6 a).
377 Meanwhile, the peak intensity of C1s decreased significantly after calcination,
378 showing the transformation of precursor to Bi_2O_3 is accompanied with the removal of
379 carbon, which is in accordance with the TGA results (Fig 4b).

380 *3.5 Optical properties and catalytic performance*

381 The photocatalytic activity of Bi_2O_3 partly depends on the absorbance of light.
382 The UV-Visible DRS spectra of Bi_2O_3 with needle and flower-like structures are
383 shown in Fig 8 a. Both structures exhibit a visible light absorption, while red shift of
384 light absorbance was observed in the flower-like structure. The band gaps (E_g) of the
385 samples, which are determined by the optical absorption near the band edge, can be

386 calculated by the Tauc equation [47,48]:

$$387 \quad \alpha h\nu = A (h\nu - E_g)^n \quad (2)$$

388 where α is the absorption coefficient, $h\nu$ is the photo energy, A is a constant and n is
389 $1/2$ for Bi_2O_3 , which is a direct transition. The plots of $(\alpha h\nu)^2$ versus $h\nu$ in Fig 8a
390 (Inset) give the extrapolated intercept corresponding to the absorption band gap
391 energy of both needle and flower-like Bi_2O_3 .

392 The corresponding VB and CB positions of the samples can be calculated through
393 the following equations [47,49]:

$$394 \quad E_{\text{VB}} = \chi - E^{\text{c}} + 0.5 E_g \quad (3)$$

$$395 \quad E_{\text{CB}} = E_{\text{VB}} - E_g \quad (4)$$

396 where χ is the absolute electronegativity of semiconductors, which is 6.12 eV for
397 Bi_2O_3 . E^{c} is the energy of free electrons on the hydrogen scale (~ 4.5 eV), E_g is the
398 band gap energy. The calculated VB and CB positions for flower and needle-like
399 Bi_2O_3 are shown in Fig 8 a. **The intense absorption in the visible-light region implies**
400 **that the flower-like Bi_2O_3 produce more electron-hole pairs, resulting a photocatalytic**
401 **activity under visible-light irradiation [16,17].** The calculated results predict a high
402 photocatalytic activity of the Bi_2O_3 under solar light irradiation. **The reason for the**
403 **extension of the absorption to visible region could be attributed to the diversity of**
404 **morphology, similar results could be observed in literatures [50,51] as well as the**
405 **different crystal phases and polar facets.**

406 Furthermore, PL emission spectra was applied to analyze the separation
407 efficiency of electron-hole pairs in the prepared samples (Fig S8). The PL emission
408 can be mainly attributed to Bi^{3+} and Bi^{2+} intra-ionic transitions as well as complex
409 defects involving oxygen vacancies [26]. The emission band at around 440 nm (2.81
410 eV) could be assigned to the direct transitions from conduction band to valence band
411 since the band gap energy of as-prepared samples estimated from the DRS are 2.69
412 eV and 2.88 eV for flower-like Bi_2O_3 and needle-like Bi_2O_3 , respectively.

413

414

415 -----

416 Fig. 8 here

417 -----

418 Fig 8 b shows the photocatalytic activities of the Bi_2O_3 with different
419 morphologies in photo-degradation of RhB under simulated solar light irradiation.
420 The degradation of RhB follows pseudo-first-order kinetics with a reaction rate
421 constant k of 0.005 and 0.008 min^{-1} for needle and flower-like structure, respectively.
422 The higher degradation rate of the flower-like structure could be attributed to the
423 hierarchical structure with a high fraction of β phase as well as the narrower band gap
424 [30]. For the novel flower-like structure, 86% of RhB at the initial concentration of 10
425 mg L^{-1} could be removed in 4 h under a simulated sunlight irradiation. The
426 deethylation process of RhB is evidenced by the shift of maximum absorption peak
427 which is shown in Fig S9 [52]. The electrical efficiency per log order (EE/O) of RhB
428 destruction at 50% degradation was calculated as $2.88 \times 10^4 \text{ kW h m}^{-3}$ based on the
429 following equation:

$$430 \quad EE/O = P \times t / (V \times \log (C_i/C_f)) \quad (5)$$

431 where P is the lamp power output (kW), t is the irradiation time (h), V means the
432 reactor volume (m^3), C_i is the initial concentration of RhB (mg L^{-1}), and C_f is the
433 final concentration of RhB (mg L^{-1}).

434 3.6 Photocatalytic degradation of SMX on flower-like Bi_2O_3

435 As a typical antibiotic, SMX has been used widely to treat bronchitis and urinary
436 tract infections and the release of SMX has caused environmental pollution as well as
437 human diseases [53,54]. In this study, SMX was chosen as a target pollutant to further
438 investigate the catalytic performance of flower-like Bi_2O_3 . SMX photodegradation in
439 aqueous solution is similar to that of conventional heterogeneous photocatalytic
440 reactions, in which the interaction of radicals with SMX is thought to be a
441 rate-limiting step. Langmuir-Hinshelwood model which is shown in Eq. 6 could be
442 used to describe this process, from which pseudo-first-order reaction kinetics can be
443 assumed (Eq.7) on the condition of a low SMX concentration of 10 mg L^{-1} as well as

444 the small absorption constant (K) [55].

$$445 \quad r = k (KC/(1+KC)) \quad (6)$$

$$446 \quad r = k KC = k_{ap}C \quad (KC \ll 1) \quad (7)$$

447 where r is the reaction rate, k means the intrinsic reaction rate constant, K represents
448 the Langmuir adsorption equilibrium constant, k_{ap} is the apparent reaction rate
449 constant and C means the concentration of SMX.

450 In this study, the effects of initial pH (3-11) and catalyst loading amount (0.5-2 g
451 L^{-1}) on the photocatalytic degradation kinetics of SMX under simulated solar light
452 irradiation were examined. Under these conditions, all the decomposition processes of
453 SMX followed pseudo-first-order kinetic ($R^2 > 0.92$) and the parameters including
454 removal rate, apparent reaction rate constant, half-lives and EE/O is summarized in
455 **Table S2**.

456 -----

457 **Fig. 9 here**

458 -----

459 The pK_a values of SMX are $pK_{a1} = 1.8$ and $pK_{a2} = 5.6$, implying that the pH value
460 has an impact on the diffusivity of SMX in solution by affecting the species and
461 hydration of molecules. SMX can be modeled as a typical diprotic acid [56] and the
462 relationship curve of cationic SMX ($[SMX^+]$), neutral SMX ($[SMX]$), and anionic
463 SMX ($[SMX^-]$) distribution coefficient with the solution pH is shown in Fig **S10**.
464 When the SMX solution pH is lower than 1.8 or higher than 5.6, SMX mainly exists
465 in $[SMX^+]$ and $[SMX^-]$ for low pH values and high pH values, respectively. On the
466 contrary, SMX is primarily in the neutral SMX form when the solution pH is set
467 between 1.8 and 5.6, which might make SMX less charged and reduce the
468 intramolecular electrical repulsion, thus increasing the mass transfer coefficient.
469 Therefore, it predominantly exists as SMX at pH = 3 and 5 and SMX^- at pH 7, 9 and
470 11, respectively. Meanwhile, Bi_2O_3 is positively charged at pH 3, while negatively
471 charged at pH 5, 7, 9 and 11 because of the point of zero charge (PZC) of 3.2 [57].
472 The adsorption of SMX on Bi_2O_3 may be inhibited by the electrostatic repulsion

473 between negatively charged SMX^- and Bi_2O_3 at high pH values, while at low pH
474 value of 3, the neutral SMX molecule seemed to be attracted to the positively charged
475 Bi_2O_3 surface. As shown in Table S2, the k value at initial pH value of 3 (2.2×10^{-2}
476 min^{-1}) was about 11 times higher than that at pH value of 11 ($0.2 \times 10^{-2} \text{ min}^{-1}$),
477 suggesting that the apparent mass transfer coefficient of SMX increased 11 times as
478 the pH value decreased from 11 to 3. The degradation of SMX was also affected by
479 the addition of catalyst in this study. The direct photolysis of SMX under simulated
480 solar light is negligible and the photocatalytic degradation of SMX is enhanced with
481 the addition of Bi_2O_3 (Fig 9 b). The k value increased from 0.7×10^{-2} to 3.0×10^{-2}
482 min^{-1} when the catalyst concentration changed from 0.5 to 2 g L^{-1} , which could be
483 caused by the increasing light absorption by the photocatalyst as well as the
484 generation of radicals [58].

485 As a visible-light driven material, the photocatalytic performance of flower-like
486 Bi_2O_3 was investigated on the degradation of SMX under visible light irradiation ($\lambda \geq$
487 420 nm). As a comparison, the photocatalytic activity of P25 under same condition
488 was also investigated (Fig 9 c). The results show that flower-like Bi_2O_3 exhibits a
489 much higher photocatalytic activity (38% removal of SMX in 60 min) compared with
490 P25 (9% removal), which could be attributed to its narrower band gap. As mentioned
491 in section 3.3, the calcination temperature has an effect on crystal size as well as the
492 percentages of crystal phases, which would further affect their photocatalytic
493 performance. The photodegradation of SMX on catalysts prepared under different
494 calcination temperatures is shown in Fig 9 d. The results show that higher percentage
495 of $\alpha\text{-Bi}_2\text{O}_3$ as well as larger crystal size would be an adverse factor for photocatalytic
496 process.

497 The degradation of SMX on Bi_2O_3 could be achieved by direct oxidation via
498 holes and indirect oxidation via the generation of reactive oxygen species (ROS),
499 which is shown in Fig 10 a. When irradiated by solar light, the electrons e^- from CB
500 of Bi_2O_3 can be excited and transfer to VB, leaving the holes h^+ behind. The
501 photogenerated electrons will be scavenged by dissolved oxygen (O_2) in water to
502 produce superoxide radical $\bullet\text{O}_2^-$ [59]. These $\bullet\text{O}_2^-$ can turn to H_2O_2 with the trapped

503 electrons and holes, which could produce hydroxyl radical $\bullet\text{OH}$ [60]. Meanwhile, the
504 $\bullet\text{O}_2^-$ can react with h^+ to produce singlet oxygen $^1\text{O}_2$, which is also known as one of
505 the highly reactive oxygen species [61]. Simultaneously, the holes left on the VB of
506 Bi_2O_3 can react with water to form hydroxyl radicals $\bullet\text{OH}$. All these radicals can
507 attack SMX molecular, making the degradation process happen. To study the role of
508 various radicals during the photocatalytic process, different scavengers were used. In
509 this study, oxalate was chosen as h^+ scavenger [62] while dimethyl sulfoxide (DMSO)
510 was used as a chemical probe to trap $\bullet\text{OH}$ because it is highly reactive with the
511 hydroxyl radicals [63]. Benzoquinone (BQ) and NaN_3 were added as quenchers of
512 $\bullet\text{O}_2^-$ and $^1\text{O}_2$ [64,65]. As shown in Fig 10 b, the presence of DMSO, BQ and oxalate
513 remarkably inhibited the degradation of SMX under solar light while the inhibition
514 effect caused by NaN_3 was less significant (Fig 10 b). Such results illustrate that $\bullet\text{O}_2^-$
515 and $\bullet\text{OH}$ were the two primary radicals generated in this process while $^1\text{O}_2$ played a
516 minor role. Meanwhile, the direct oxidation via the valence band holes played a vital
517 role as well.

518 -----

519 Fig. 10 here

520 -----

521 To investigate the stability of catalyst, the XRD pattern of the catalyst after four
522 degradation cycles is given in Fig S11. The results show no significant changes on the
523 structure of Bi_2O_3 , except a small part impurities were detected after 4 times recycles
524 (Fig S11) which could be caused by the reaction of Bi_2O_3 with CO_2 dissolved in
525 solution [35].

526

527 4. Conclusion

528 A novel flower-like Bi_2O_3 was successfully prepared with the assistance of acetic
529 acid. The presence of acetic acid impacts both morphology (needle-like to flower-like)
530 and the phase composition (α - to β - phase) of the Bi_2O_3 samples, and the addition of
531 P-123 increases both yield and surface area of Bi_2O_3 samples. The formation of the

532 flowery structure as a function of hydrothermal time involves the initial formation of
533 particles followed by their self-assembly to microspheres and final transformation into
534 the hierarchical flower-like structure by Ostwald ripening. The novel structure
535 exhibited a high catalytic activity on the degradation of RhB and SMX under
536 simulated solar light irradiation, which could be attributed to the narrower band gap,
537 higher surface areas and the existence of more β phase in the flower-like Bi_2O_3
538 sample. Also, the high intensity of some polar facets like (120) and (200) in the
539 flower-like structure could enhance the degradation rate because of higher production
540 of $\cdot\text{OH}$ radicals [66,67]. In the future study, the impact of some other organic acids
541 ($-\text{OH}$) on the final Bi_2O_3 structure as well as the relationship between the crystal
542 facets and catalytic performance should be investigated. Further, the flower-like Bi_2O_3
543 shows high performance on the photodecomposition of sulfamethoxazole (SMX)
544 under simulated solar light irradiation, **in which both direct and indirect oxidation**
545 **process exist. The indirect oxidation was dominated by ($\cdot\text{OH}$ and $\cdot\text{O}_2^-$), while IO_2^-**
546 **played a minor role in the photocatalytic process.** The degradation of SMX followed
547 pseudo-first-order kinetic and the k value increased with the decreasing of pH values
548 (11-3) and increasing of catalyst loading ($0-2 \text{ g L}^{-1}$).

549

550

551

552 **Acknowledgement**

553 The sample characterization (FESEM and XRD) work were performed at the
554 Facility for Analysis, Characterization, Testing and Simulation (FACTS) in Nanyang
555 Technological University, Singapore. Also, the author is grateful for the support and
556 help from Environmental Chemistry and Materials Centre (ECMC) under Nanyang
557 Environment and Water Research Institute (NEWRI), especially for the XPS test by
558 Dr. Ronn Goei.

559

560

561

562 **References**

- 563 [1] Z. Adamian, H. Abovian, V. Aroutiounian, Smoke sensor on the base of Bi₂O₃
564 sesquioxide, *Sens. Actuators B Chem.* 35 (1996) 241–243.
- 565 [2] L. Leontie, M. Caraman, M. Delibaş, G. Rusu, Optical properties of bismuth trioxide thin
566 films, *Mater. Res. Bull.* 36 (2001) 1629–1637.
- 567 [3] L. Leontie, M. Caraman, A. Visinoiu, G. Rusu, On the optical properties of bismuth oxide
568 thin films prepared by pulsed laser deposition, *Thin Solid Films.* 473 (2005) 230–235.
- 569 [4] H. Fan, X. Teng, S. Pan, C. Ye, G. Li, L. Zhang, Optical properties of δ-Bi₂O₃ thin films
570 grown by reactive sputtering, *Appl. Phys. Lett.* 87 (2005) 231916.
- 571 [5] R. Thayer, C. Randall, S. Trolier-McKinstry, Medium permittivity bismuth zinc niobate
572 thin film capacitors, *J. Appl. Phys.* 94 (2003) 1941–1947.
- 573 [6] S. Park, H. Ko, S. Lee, H. Kim, C. Lee, Light-activated gas sensing of Bi₂O₃
574 -core/ZnO-shell nanobelt gas sensors, *Thin Solid Films.* 570 (2014) 298–302.
- 575 [7] R. Li, D. Wang, L. Ge, S. He, H. Chen, L. Guo, Effect of Bi₂O₃ on the electrochemical
576 performance of LaBaCo₂O_{5+δ} cathode for intermediate-temperature solid oxide fuel cells,
577 *Ceram. Int.* 40 (2014) 2599–2603.
- 578 [8] Y. Azizian-Kalandaragh, F. Sedaghatdoust-Bodagh, A. Habibi-Yangjeh,
579 Ultrasound-assisted preparation and characterization of β-Bi₂O₃ nanostructures:
580 Exploring the photocatalytic activity against rhodamine B, *Superlattices Microstruct.* 81
581 (2015) 151–160.
- 582 [9] D. Maruthamani, S. Vadivel, M. Kumaravel, B. Saravanakumar, B. Paul, S.S. Dhar, A.
583 Habibi-Yangjeh, A. Manikandan, G. Ramadoss, Fine cutting edge shaped Bi₂O₃
584 rods/reduced graphene oxide (RGO) composite for supercapacitor and visible-light
585 photocatalytic applications, *J. Colloid Interface Sci.* 498 (2017) 449–459.
- 586 [10] F. Qin, H. Zhao, G. Li, H. Yang, J. Li, R. Wang, Y. Liu, J. Hu, H. Sun, R. Chen,
587 Size-tunable fabrication of multifunctional Bi₂O₃ porous nanospheres for photocatalysis,
588 bacteria inactivation and template-synthesis, *Nanoscale.* 6 (2014) 5402–5409.
- 589 [11] K. Brezesinski, R. Ostermann, P. Hartmann, J. Perlich, T. Brezesinski, Exceptional
590 photocatalytic activity of ordered mesoporous β-Bi₂O₃ thin films and electrospun
591 nanofiber mats, *Chem. Mater.* 22 (2010) 3079–3085.
- 592 [12] P. Hajra, S. Shyamal, H. Mandal, P. Fageria, S. Pande, C. Bhattacharya, Photocatalytic
593 activity of Bi₂O₃ Nanocrystalline Semiconductor developed via Chemical-bath
594 Synthesis, *Electrochimica Acta.* 123 (2014) 494–500.
- 595 [13] N.S. Azhar, M.F.M. Taib, O.H. Hassan, M.Z.A. Yahya, A.M.M. Ali, Structural, electronic
596 and optical properties of Bi₂O₃ polymorphs by first-principles calculations for
597 photocatalytic water splitting, *Mater. Res. Express.* 4 (2017) 034002.
- 598 [14] Y. Xu, M.A. Schoonen, The absolute energy positions of conduction and valence bands of
599 selected semiconducting minerals, *Am. Mineral.* 85 (2000) 543–556.

- 600 [15] S. Feizpoor, A. Habibi-Yangjeh, S. Vadivel, Novel $\text{TiO}_2/\text{Ag}_2\text{CrO}_4$ nanocomposites:
601 Efficient visible-light-driven photocatalysts with n-n heterojunctions, *J. Photochem.*
602 *Photobiol. Chem.* 341 (2017) 57–68.
- 603 [16] M. Shekofteh-Gohari, A. Habibi-Yangjeh, $\text{Fe}_3\text{O}_4/\text{ZnO}/\text{CoWO}_4$ nanocomposites: Novel
604 magnetically separable visible-light-driven photocatalysts with enhanced activity in
605 degradation of different dye pollutants, *Ceram. Int.* 43 (2017) 3063–3071.
- 606 [17] M. Pirhashemi, A. Habibi-Yangjeh, Photosensitization of ZnO by AgBr and Ag_2CO_3 :
607 Nanocomposites with tandem nn heterojunctions and highly enhanced visible-light
608 photocatalytic activity, *J. Colloid Interface Sci.* 474 (2016) 103–113.
- 609 [18] L. Zhang, Y. Hashimoto, T. Taishi, I. Nakamura, Q.-Q. Ni, Fabrication of flower-shaped
610 Bi_2O_3 superstructure by a facile template-free process, *Appl. Surf. Sci.* 257 (2011)
611 6577–6582.
- 612 [19] J. Wang, X. Yang, K. Zhao, P. Xu, L. Zong, R. Yu, D. Wang, J. Deng, J. Chen, X. Xing,
613 Precursor-induced fabrication of $\beta\text{-Bi}_2\text{O}_3$ microspheres and their performance as
614 visible-light-driven photocatalysts, *J. Mater. Chem. A.* 1 (2013) 9069–9074.
- 615 [20] X. Xiao, S. Tu, C. Zheng, H. Zhong, X. Zuo, J. Nan, l-Asparagine-assisted synthesis of
616 flower-like $\beta\text{-Bi}_2\text{O}_3$ and its photocatalytic performance for the degradation of
617 4-phenylphenol under visible-light irradiation, *RSC Adv.* 5 (2015) 74977–74985.
- 618 [21] C.J. Brinker, Y. Lu, A. Sellinger, H. Fan, Evaporation-induced self-assembly:
619 nanostructures made easy, *Adv. Mater.* 11 (1999) 579–585.
- 620 [22] S. Brunauer, P.H. Emmett, E. Teller, Adsorption of gases in multimolecular layers, *J. Am.*
621 *Chem. Soc.* 60 (1938) 309–319.
- 622 [23] P. Scherrer, Bestimmung der inneren Struktur und der Größe von Kolloidteilchen mittels
623 Röntgenstrahlen, Springer, 1912.
- 624 [24] W.-J. Li, E.-W. Shi, W.-Z. Zhong, Z.-W. Yin, Growth mechanism and growth habit of
625 oxide crystals, *J. Cryst. Growth.* 203 (1999) 186–196.
- 626 [25] Y.-C. Wu, Y.-C. Chaing, C.-Y. Huang, S.-F. Wang, H.-Y. Yang, Morphology-controllable
627 Bi_2O_3 crystals through an aqueous precipitation method and their photocatalytic
628 performance, *Dyes Pigments.* 98 (2013) 25–30.
- 629 [26] Y. Wang, J. Zhao, B. Zhou, X. Zhao, Z. Wang, Y. Zhu, Three-dimensional hierarchical
630 flowerlike microstructures of $\alpha\text{-Bi}_2\text{O}_3$ constructed of decahedrons and rods, *J. Alloys*
631 *Compd.* 592 (2014) 296–300.
- 632 [27] T. Sugimoto, Kinetics of reaction-controlled Ostwald ripening of precipitates in the
633 steady state, *J. Colloid Interface Sci.* 63 (1978) 369–377.
- 634 [28] H. Cheng, B. Huang, J. Lu, Z. Wang, B. Xu, X. Qin, X. Zhang, Y. Dai, Synergistic effect
635 of crystal and electronic structures on the visible-light-driven photocatalytic
636 performances of Bi_2O_3 polymorphs, *Phys. Chem. Chem. Phys.* 12 (2010) 15468–15475.
- 637 [29] W.-N. Shen, B. Dunn, C.D. Moore, M.S. Goorsky, T. Radetic, R. Gronsky, Synthesis of
638 nanoporous bismuth films by liquid-phase deposition, *J. Mater. Chem.* 10 (2000) 657–

- 639 662.
- 640 [30]R. Chen, Z.-R. Shen, H. Wang, H.-J. Zhou, Y.-P. Liu, D.-T. Ding, T.-H. Chen, Fabrication
641 of mesh-like bismuth oxide single crystalline nanoflakes and their visible light
642 photocatalytic activity, *J. Alloys Compd.* 509 (2011) 2588–2596.
- 643 [31]H. Weidong, Q. Wei, W. Xiaohong, D. Xianbo, C. Long, J. Zhaohua, The photocatalytic
644 properties of bismuth oxide films prepared through the sol–gel method, *Thin Solid*
645 *Films.* 515 (2007) 5362–5365.
- 646 [32]Q. Huang, S. Zhang, C. Cai, B. Zhou, β - and α - Bi_2O_3 nanoparticles synthesized via
647 microwave-assisted method and their photocatalytic activity towards the degradation of
648 rhodamine B, *Mater. Lett.* 65 (2011) 988–990.
- 649 [33]A. Kudo, K. Omori, H. Kato, A novel aqueous process for preparation of crystal
650 form-controlled and highly crystalline BiVO_4 powder from layered vanadates at room
651 temperature and its photocatalytic and photophysical properties, *J. Am. Chem. Soc.* 121
652 (1999) 11459–11467.
- 653 [34]Y. Yu, C.H. Jin, R.H. Wang, Q. Chen, L.-M. Peng, High-quality ultralong Bi_2S_3
654 nanowires: structure, growth, and properties, *J. Phys. Chem. B.* 109 (2005) 18772–
655 18776.
- 656 [35]Y. Lu, Y. Zhao, J. Zhao, Y. Song, Z. Huang, F. Gao, N. Li, Y. Li, Induced Aqueous
657 Synthesis of Metastable β - Bi_2O_3 Microcrystals for Visible-Light Photocatalyst Study,
658 *Cryst. Growth Des.* 15 (2015) 1031–1042.
- 659 [36]D. Zhao, J. Feng, Q. Huo, N. Melosh, G.H. Fredrickson, B.F. Chmelka, G.D. Stucky,
660 Triblock copolymer syntheses of mesoporous silica with periodic 50 to 300 angstrom
661 pores, *Science.* 279 (1998) 548–552.
- 662 [37]S. Brunauer, L.S. Deming, W.E. Deming, E. Teller, On a Theory of the van der Waals
663 Adsorption of Gases, *J. Am. Chem. Soc.* 62 (1940) 1723–1732.
- 664 [38]J. Yu, H. Yu, B. Cheng, C. Trapalis, Effects of calcination temperature on the
665 microstructures and photocatalytic activity of titanate nanotubes, *J. Mol. Catal. Chem.*
666 249 (2006) 135–142.
- 667 [39]J. Zhang, *Self-assembled nanostructures*, Springer Science & Business Media, 2003.
- 668 [40]N. Deb, S.D. Baruah, N.N. Dass, Synthesis, characterization and the thermal
669 decomposition of calcium (II) bis (oxalato) calcium (II) dihydrate, *Thermochim. Acta.*
670 285 (1996) 301–308.
- 671 [41]M. Mallahi, A. Shokuhfar, M. Vaezi, A. Esmailirad, V. Mazinani, Synthesis and
672 characterization of Bismuth oxide nanoparticles via sol-gel method, *AJER.* 3 (2014)
673 162–165.
- 674 [42]M. Trivedi, Evaluation of Atomic, Physical, and Thermal Properties of Bismuth Oxide
675 Powder: An Impact of Energy Treatment, *Am. J. Nano Res. Appl.* 3 (2015).
- 676 [43]Z. Ai, Y. Huang, S. Lee, L. Zhang, Monoclinic α - Bi_2O_3 photocatalyst for efficient
677 removal of gaseous NO and HCHO under visible light irradiation, *J. Alloys Compd.* 509

- 678 (2011) 2044–2049.
- 679 [44]L. zhong Zhao, J. biao Zhang, Bi and O valences in Ba-K-Bi-O, Ba-KM-Bi-O (M=Rb, La,
680 Eu, In, Tland Pb) and the related compounds, *Solid State Commun.* 90 (1994) 709–712.
- 681 [45]V. Nefedov, D. Gati, B. Dzhurinskii, N. Sergushin, Y.V. Salyn, X-ray electron study of
682 oxides of elements, *Zhurnal Neorganicheskoi Khimii.* 20 (1975) 2307–2314.
- 683 [46]B. Afsin, M. Roberts, Formation of an oxy-chloride overlayer at a Bi (0001) surface,
684 *Spectrosc. Lett.* 27 (1994) 139–146.
- 685 [47]H. Huang, Y. He, Z. Lin, L. Kang, Y. Zhang, Two novel Bi-based borate photocatalysts:
686 crystal structure, electronic structure, photoelectrochemical properties, and
687 photocatalytic activity under simulated solar light irradiation, *J. Phys. Chem. C.* 117
688 (2013) 22986–22994.
- 689 [48]Y. Ohko, K. Hashimoto, A. Fujishima, Kinetics of photocatalytic reactions under
690 extremely low-intensity UV illumination on titanium dioxide thin films, *J. Phys. Chem.*
691 *A.* 101 (1997) 8057–8062.
- 692 [49]P. Madhusudan, J. Ran, J. Zhang, J. Yu, G. Liu, Novel urea assisted hydrothermal
693 synthesis of hierarchical BiVO₄/Bi₂O₂CO₃ nanocomposites with enhanced visible-light
694 photocatalytic activity, *Appl. Catal. B Environ.* 110 (2011) 286–295.
- 695 [50]M. Yang, J. He, Fine tuning of the morphology of copper oxide nanostructures and their
696 application in ambient degradation of methylene blue, *J. Colloid Interface Sci.* 355
697 (2011) 15–22.
- 698 [51]N. Talebian, S.M. Amininezhad, M. Doudi, Controllable synthesis of ZnO nanoparticles
699 and their morphology-dependent antibacterial and optical properties, *J. Photochem.*
700 *Photobiol. B.* 120 (2013) 66–73.
- 701 [52]P. Lei, C. Chen, J. Yang, W. Ma, J. Zhao, L. Zang, Degradation of dye pollutants by
702 immobilized polyoxometalate with H₂O₂ under visible-light irradiation, *Environ. Sci.*
703 *Technol.* 39 (2005) 8466–8474.
- 704 [53]A.G. Trovó, R.F. Nogueira, A. Agüera, C. Sirtori, A.R. Fernández-Alba,
705 Photodegradation of sulfamethoxazole in various aqueous media: persistence, toxicity
706 and photoproducts assessment, *Chemosphere.* 77 (2009) 1292–1298.
- 707 [54]P.C. Walker, L.H. Karnell, C. Ziebold, D.S. Kacmarynski, Changing microbiology of
708 pediatric neck abscesses in Iowa 2000–2010, *The Laryngoscope.* 123 (2013) 249–252.
- 709 [55]X. Wang, T.-T. Lim, Solvothermal synthesis of C–N codoped TiO₂ and photocatalytic
710 evaluation for bisphenol A degradation using a visible-light irradiated LED photoreactor,
711 *Appl. Catal. B Environ.* 100 (2010) 355–364.
- 712 [56]M.C. Dodd, C.-H. Huang, Transformation of the antibacterial agent sulfamethoxazole in
713 reactions with chlorine: kinetics, mechanisms, and pathways, *Environ. Sci. Technol.* 38
714 (2004) 5607–5615.
- 715 [57]Y.-W. Lai, W.-C. Wei, Synthesis and Study on Ionic Conductive (Bi_{1-x}V_x)O_{1.5-δ} Materials
716 with a Dual-Phase Microstructure, *Materials.* 9 (2016) 863.

717 [58]L. Hu, P.M. Flanders, P.L. Miller, T.J. Strathmann, Oxidation of sulfamethoxazole and
718 related antimicrobial agents by TiO₂ photocatalysis, *Water Res.* 41 (2007) 2612–2626.

719 [59]W.Y. Teoh, J.A. Scott, R. Amal, Progress in heterogeneous photocatalysis: from classical
720 radical chemistry to engineering nanomaterials and solar reactors, *J. Phys. Chem. Lett.* 3
721 (2012) 629–639.

722 [60]T. Wu, G. Liu, J. Zhao, H. Hidaka, N. Serpone, Photoassisted degradation of dye
723 pollutants. V. Self-photosensitized oxidative transformation of rhodamine B under
724 visible light irradiation in aqueous TiO₂ dispersions, *J. Phys. Chem. B.* 102 (1998)
725 5845–5851.

726 [61]T. Daimon, T. Hirakawa, M. Kitazawa, J. Suetake, Y. Nosaka, Formation of singlet
727 molecular oxygen associated with the formation of superoxide radicals in aqueous
728 suspensions of TiO₂ photocatalysts, *Appl. Catal. Gen.* 340 (2008) 169–175.

729 [62]J. Lee, W. Choi, J. Yoon, Photocatalytic degradation of N-nitrosodimethylamine:
730 mechanism, product distribution, and TiO₂ surface modification, *Environ. Sci. Technol.*
731 39 (2005) 6800–6807.

732 [63]M.N. Abellán, R. Dillert, J. Giménez, D. Bahnemann, Evaluation of two types of TiO₂
733 -based catalysts by photodegradation of DMSO in aqueous suspension, *J. Photochem.*
734 *Photobiol. Chem.* 202 (2009) 164–171.

735 [64]M. Styliadi, D.I. Kondarides, X.E. Verykios, Visible light-induced photocatalytic
736 degradation of Acid Orange 7 in aqueous TiO₂ suspensions, *Appl. Catal. B Environ.* 47
737 (2004) 189–201.

738 [65]X. Wang, T.-T. Lim, Effect of hexamethylenetetramine on the visible-light photocatalytic
739 activity of C–N codoped TiO₂ for bisphenol A degradation: evaluation of photocatalytic
740 mechanism and solution toxicity, *Appl. Catal. Gen.* 399 (2011) 233–241.

741 [66]A. McLaren, T. Valdes-Solis, G. Li, S.C. Tsang, Shape and size effects of ZnO
742 nanocrystals on photocatalytic activity, *J. Am. Chem. Soc.* 131 (2009) 12540–12541.

743 [67]G. Li, T. Hu, G. Pan, T. Yan, X. Gao, H. Zhu, Morphology– function relationship of ZnO:
744 polar planes, oxygen vacancies, and activity, *J. Phys. Chem. C.* 112 (2008) 11859–
745 11864.

746
747