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

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Abstract

With the assistance of acetic acid (CH_3COOH), a novel 3D flower-like Bi_2O_3 was synthesized via hydrothermal process followed by calcination. For the first time, the role of CH_3COOH as a capping agent in the formation of flower-like structure was investigated. The as-prepared flower-like Bi_2O_3 had a high activity on the degradation of sulfamethoxazole (SMX) under simulated solar light irradiation due to the narrow band gap of 2.69 eV, high percentage of $\beta\text{-Bi}_2\text{O}_3$ as well as high intensity of polar facets (120) and (200). Meanwhile, the photocatalytic degradation followed apparent pseudo-first-order kinetics. The rate constants (k) increased from 0.7×10^{-2} to $3.0 \times 10^{-2} \text{ min}^{-1}$ with the catalyst loading varying from 0.5 to 2.0 g L^{-1} . Increasing pH values 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 be attributed to the electrostatic adsorption between SMX molecules and Bi_2O_3 . The radical quenching experiments show both direct (h^+) and indirect oxidation ($\bullet\text{OH}$ and $\bullet\text{O}_2^-$) happen in this process.

Key words: Flower-like Bi_2O_3 , Acetic Acid, Growth Mechanism, Photocatalytic Activity, Degradation Mechanism

1. Introduction

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

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

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

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

2. Experimental

2.1 Chemicals

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

2.2 Preparation of Bi_2O_3 particles

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

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

2.3 Characterization of Bi₂O₃ particles

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

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

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

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

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

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

2.4 Optical properties

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

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

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

3. Results and discussion

3.1 Effect of acetic acid

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

Fig. 1 here

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

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

Fig. 2 here

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

Fig. 3 here

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

3.2 Effect of P-123 addition

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

Fig. 4 here

BET gas sorptometry measurements were conducted to examine the porous property of the Bi_2O_3 particles. Fig 4 a shows the N_2 adsorption-desorption isotherm and the calculated surface areas (Inset of Fig 4 a) of the Bi_2O_3 samples with P-123 amounts changing from 2-20 wt%. According to BDDT classification, all samples display a type III isotherm which shows a the weak interaction between adsorbate and adsorbent [37]. Moreover, the hysteresis loop shifts to higher P/P_0 , indicating the existence of macropores [38]. It was found that the increase of P-123 concentration could result in a larger surface area. The surface area increased by 41% from 3.4 to $4.8 \text{ m}^2 \text{ g}^{-1}$ with the P-123 concentration increased from 2-10 wt% (much higher than that of the commercial one with the surface area of $0.4 \text{ m}^2 \text{ g}^{-1}$ [19]). Higher P-123 concentration caused more pore coalescence and multi-micellar interactions during heat treatment which would result in relatively large pores and high porosity [39]. However, with the addition of 20 wt% P-123, the surface area decreased again, which might be caused by the collapse of Bi_2O_3 structure. This change could be further evidenced by SEM images of the Bi_2O_3 with different P-123 additions (Fig S4). From the SEM images, it could be seen with the addition of 2-10% P-123, the particles show a sheet structure with pores on the sheet surface (Figs S4 and S5), while with a higher P-123 addition, the particles would stick with each other to form a larger 2-D piece (Fig S4 d). Compared with the Bi_2O_3 precursor and Bi_2O_3 particle, both of which were prepared with 5 wt% P-123, the surface area difference should be caused by the removal of P-123 as well as the transformation from precursor to Bi_2O_3 in the calcination process, which could be evidenced by TGA/DSC results (Fig 4 b). Meanwhile, as a comparison, the surface area of needle-like Bi_2O_3 was also tested as $2.8 \text{ m}^2 \text{ g}^{-1}$. The higher surface area of flower-like Bi_2O_3 could be a benefit for the photocatalysis process.

3.3 Effect of calcination temperature

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

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

Fig. 5 here

3.4 Flower-like Bi_2O_3 structure evolution and phase transformation

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

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

Fig. 6 here

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

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

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

 Fig. 7 here

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

3.5 Optical properties and catalytic performance

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

calculated by the Tauc equation [47,48]:

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

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

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

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

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

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

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

Fig. 8 here

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

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

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

3.6 Photocatalytic degradation of SMX on flower-like Bi_2O_3

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

the small absorption constant (K) [55].

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

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

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

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

Fig. 9 here

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

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

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

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

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

Fig. 10 here

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

4. Conclusion

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

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

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