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#### Synthesis of Bi<sub>2</sub>O<sub>3</sub> architectures in DMF-H<sub>2</sub>O solution by

#### precipitation method and their photocatalytic activity

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#### ABSTRACT

Well-crystalline flowerlike  $\alpha$ -Bi<sub>2</sub>O<sub>3</sub> hierarchical architectures with pineapple-shaped petals have been synthesized by precipitation method at a volume ratio of DMF/H<sub>2</sub>O of 5, where DMF and H<sub>2</sub>O were used to dissolve Bi(NO<sub>3</sub>)<sub>3</sub> and KOH, respectively. If the DMF/H<sub>2</sub>O ratio was decreased to 2:1, 1:1 and 0:30, flower-, bundle- and dendrite-shaped  $\alpha$ -Bi<sub>2</sub>O<sub>3</sub> microcrystallites aggregated by nanorods were formed, respectively. The simple synthetic route and thus obtained Bi<sub>2</sub>O<sub>3</sub> architectures of various morphologies provide a basis insight for their formation mechanism. The photocatalytic activity of the as-prepared Bi<sub>2</sub>O<sub>3</sub> particles for degradation of Rhodamine B (RhB) under visible-light irradiation was obviously influenced by their morphologies. Bi<sub>2</sub>O<sub>3</sub> of nanorod-based microstructures exhibited higher photodegradation activity than nanobrick-based ones, owing to higher light absorption and carrier separation efficiency in one-dimensional (1D) nanostructured materials.

Keywords: Bi<sub>2</sub>O<sub>3</sub>; Precipitation method; Hierarchical architecture; Photodegradation

#### 1. Introduction

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Bismuth oxide (Bi<sub>2</sub>O<sub>3</sub>), a p-type semiconductor, is widely used as solid electrolyte in gas sensors [1-3], solid fuel cells [4-7], and photocatalysts [8-12]. As comparison to their bulk counterparts, nanostructured Bi<sub>2</sub>O<sub>3</sub> have attracted more research interest due to the high surface area, exposed active lattice facets and thus excellent properties. For example, nanostructured Bi<sub>2</sub>O<sub>3</sub> is considered as a good visible light photocatalyst candidate due to its narrow band gap (about 2.8 eV) and deep valence band comparable to that of TiO<sub>2</sub> [9, 13]. More recently, nanostructured Bi<sub>2</sub>O<sub>3</sub> has been used as composite photocatalysts and co-catalysts because Bi<sub>2</sub>O<sub>3</sub> alone shows a low photocatalytic activity resulting from its more positive potential of the conduction band edge for the single-electron reduction of oxygen ( $E_{cb} = 0.33$  V; O<sub>2</sub> + e<sup>-</sup> = O<sub>2</sub><sup>-</sup>, E = -0.064 V vs SHE) [14-16].

The design and synthesis of the three dimensional (3D) hierarchical architectures by self-assembly of nanostructured building components have received considerable attention in nanoscience and nanotechnology owing to shaped-dependent physical and chemical properties. Various  $Bi_2O_3$  hierarchical architectures have been successfully synthesized. Zhou *et al.* prepared the  $Bi_2O_3$  hierarchitectures composed of 2D sheets via a template-free aqueous method in the presence of  $VO_3^-$  at 60-80 °C, which showed much higher photocatalytic activity over commercial  $Bi_2O_3$  under visible light irradiation [8]. Hierarchical rippled  $Bi_2O_3$  nanobelts were synthesized by an electrodeposition route and possessed higher specific capacitance and electrochemical stability as supercapacitor electrodes than nanobelts with smooth surface [17].  $\alpha$ -Bi<sub>2</sub>O<sub>3</sub> microcrystals and microrods with pyramidal tips have been grown by a vapour-solid method using pure Bi as starting material [18]. Yu *et al* synthesized flower-like  $Bi_2O_3$  superstructures with excellent

visible-light-driven photocatalytic activity for degradation of RhB *via* a hydrothermal process and subsequent calcination [19]. 3D Bi<sub>2</sub>O<sub>3</sub> hierarchical architectures assembled by 2D nanoplates were fabricated from electrodeposited bismuth (Bi) film, which exhibited a strong and wide photoluminescence signal [20]. More recently, Wang *et al* prepared 3D hierarchical flowerlike Bi<sub>2</sub>O<sub>3</sub> microstructures composed of decahedrons and rods using a solution precipitation method with the assistance of glycerin [21]. Bouquet-like hierarchical Bi<sub>2</sub>O<sub>3</sub> photocatalysts with high-density surface oxygen vacancy have been synthesized *via* a hydrothermal method by the synergetic control of NaOH and a polyvinyl alcohol (PVA) stabilizer [22].

Although various methods have been successfully used to synthesize Bi<sub>2</sub>O<sub>3</sub> hierarchical architectures, the challenge has been remained to explore a simple synthetic route and understand formation mechanism to achieve the control. Room-temperature precipitation method is easy and economic for the preparation of Bi<sub>2</sub>O<sub>3</sub> nanoparticles [23, 24]. However, acid (HNO<sub>3</sub> or HCl) was usually used to inhibit hydrolysis of Bi(NO<sub>3</sub>)<sub>3</sub> in order to control uniform precipitation, so extremely excess NaOH was addded to neutralize the acid and obtain pure Bi<sub>2</sub>O<sub>3</sub>. Additionally, to the best of our knowledge, there is little report on the preparation of Bi<sub>2</sub>O<sub>3</sub> hierarchitectures *via* a room precipitation method. Herein, by using DMF as a solvent to dissolve Bi(NO<sub>3</sub>)<sub>3</sub>, pure Bi<sub>2</sub>O<sub>3</sub> microcrystallites in flowerlike shape assembled by nanobrick-based petals with pineapple surface were easily obtained at room temperature after 1 h of reaction. Moreover, the Bi<sub>2</sub>O<sub>3</sub> crystals of different shapes including bundles and dendrites were obtained by varying the ratio of DMF/H<sub>2</sub>O. The corresponding mechanism for the formation of various Bi<sub>2</sub>O<sub>3</sub> architectures was proposed. Finally, the

influence of Bi<sub>2</sub>O<sub>3</sub> in various shapes on the photocatalytic activity for degradation of RhB under visible-light irradiation was investigated.

#### 2. Experimental

A homogeneous solution of  $Bi(NO_3)_3 \cdot 5H_2O(0.97 \text{ g}, 2 \text{ mmol})$  in 25 ml DMF was added into saturated KOH/H<sub>2</sub>O solution (5 ml distilled water, 5.0 g (89 mmol) KOH), and the solution changed pale yellow at once. The mixture was stirred for 3 min, and then left still and aging for about 1 h. The product was collected by filtration, washing several times with deionized water and ethanol, and drying at 60 °C for 12 h. No additional thermal treatment was needed.

The effect of the DMF/H<sub>2</sub>O ratio on Bi<sub>2</sub>O<sub>3</sub> morphologies was investigated. The detailed experimental results are listed in Table 1.

Table	1.	DMF/H <sub>2</sub> O	ratio,	morphologies,	band	gap	energy	and	apparent	rate	constant	k	of	RhB
photoc	legi	radation.												

Sample	DMF/ml	H <sub>2</sub> O/ml	Morphology	Bandgap/eV	$k/h^{-1}$
A1	25	5	brick-based flowers	2.70	0.16
A2	20	10	Rod-based flowers	2.82	0.38
A3	15	15	Rod-based bundles	2.84	0.53
A4	0	30	Rod-based dendrites	2.88	0.63

(\* [KOH]/[Bi] = 89/2)

The X-ray diffraction patterns (XRD) were obtained on a Bruker D8 Advance X-ray diffractometer (Cu K $\alpha$  radiation,  $\lambda = 1.5418$  Å) at a scan rate of 0.05° 20 s<sup>-1</sup>. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) were carried out on a JEM-2100 (JEOL) and FEI Tecnai T20 microscope equipped with an X-ray energy dispersive spectrometer (EDS), respectively. Field-emission scanning electron microscopy (FESEM) was preformed on a HITACHI S-4800 microscope. A Quanta Chrome Nova 1000 analyzer was employed to measure the Brunauer-Emmett-Teller (BET) surface areas of the samples at liquid nitrogen temperature. X-ray photoelectron spectroscopy (XPS) measurements were carried out on a PHI Quantera II SXM X-ray photoelectron spectrometer with monochromatized Al K $\alpha$  as the exciting source, and the results obtained in the XPS analysis were corrected by referencing the C 1s line to 284.8 eV. The UV-Vis diffuse reflectance spectra (DRS) of the products were determined on a shimadzu UV 2550 spectrophotometer equipped with an integrating sphere, using BaSO<sub>4</sub> as a reference.

The photocatalytic activity of the  $Bi_2O_3$  microcrystallites was evaluated by Rhodamine B (RhB) degradation. The  $Bi_2O_3$  powders (0.05 g) were dispersed in 50 ml RhB aqueous solution (5 ppm) under continuous stirring, allowing 1 h in the dark to reach the adsorption-desorption equilibrium between RhB and  $Bi_2O_3$  particles. Visible light irradiation using a xenon lamp (500 W) was applied to the suspension with continuous stirring. At a given time interval, about 5 ml of the suspension was taken out, the catalyst powders were removed by centrifugation, and residual concentration of the dye in the solution was obtained by using a UV-Vis spectrophotometer (BRAIC UV 1201).

#### 3. Results and discussion

C

The purity of the product was strongly dependent on the ratio of [KOH]/[Bi]. When the [KOH]/[Bi] ratio was 89:2, phase pure  $\alpha$ -Bi<sub>2</sub>O<sub>3</sub> was obtained. As displayed in Fig. 1a, XRD pattern of the Bi<sub>2</sub>O<sub>3</sub> microcrystallite obtained at DMF/H<sub>2</sub>O ratio of 5:1 (A1) can be indexed to monoclinic  $\alpha$ -Bi<sub>2</sub>O<sub>3</sub> (JCPDS No. 41-1449). No peaks of impurities were detected, revealing the high purity of the product. The reflection peaks are strong and sharp, which indicates that as-prepared Bi<sub>2</sub>O<sub>3</sub> was well crystalline. The XRD patterns of the samples A2-A4 obtained at various DMF/H<sub>2</sub>O ratios also correspond to pure  $\alpha$ -Bi<sub>2</sub>O<sub>3</sub> phase (Supporting Information Fig. S1). If the [KOH]/[Bi] ratio was decreased to 71:2, the XRD pattern revealed the presence of the impurity BiONO<sub>3</sub> (Fig. 1b), which suggests that sufficiently high ratio of [KOH]/[Bi] was necessary for the formation of phase pure Bi<sub>2</sub>O<sub>3</sub>, different from the result reported by Wu *et al* [23].



**Fig. 1.** XRD patterns of the as-prepared  $Bi_2O_3$  microcrystallites: (a) [KOH]/Bi = 89/2 (A1), (b) [KOH]/[Bi] = 71/2. Vertical sticks below the patterns represent the standard diffraction data from JCPDS

file for bulk Bi<sub>2</sub>O<sub>3</sub> with monoclinic structure (No. 41-1449).

A representative SEM image of the product A1 is shown in Fig. 2a. The flower-like  $Bi_2O_3$  hierarchical architectures contain multi-petals. These petals are aligned perpendicularly to the flower surface with clearly orientation, pointing toward a common center. The surfaces of petals were rough, analogous to pineapples. A high-magnification SEM image indicates that the pineapple-shaped petals were composed of nanobricks attached along certain direction, forming 1D structured petal (Fig. 2b). A TEM image of A1 further confirms that the Bi<sub>2</sub>O<sub>3</sub> microcrystallites were made up of several individual petals with the length of about 5 µm and diameter of 2-3 µm (Fig. 2c), and the edges of the petals look like zigzag stacks of nanobricks (inset in Fig. 2c). These nanobricks were too thick (~ 200 nm) to perform HRTEM studies.

The morphologies of Bi<sub>2</sub>O<sub>3</sub> microcrystallites were obviously influenced by the ratio of DMF/H<sub>2</sub>O. As shown in Fig. 2d, the flower-shaped Bi<sub>2</sub>O<sub>3</sub> crystals (**A2**) made up of microrods with a diameter of about 1  $\mu$ m were formed when the DMF/H<sub>2</sub>O ratio was decreased to 2. With the amount of water increasing further ( $V_{DMF/H2O} = 1$ ), the rod-based Bi<sub>2</sub>O<sub>3</sub> bundles (**A3**) with a rod size of about 200 nm in diameter and 20 to 40  $\mu$ m in length were observed (inset in Fig. 2d). If using pure H<sub>2</sub>O as solvent, typical TEM images indicate that the dendrite-shaped Bi<sub>2</sub>O<sub>3</sub> microstructures (**A4**) consisted of dozens of nanorods with a diameter of about 80 nm extending radially from one root (Fig. 2e and its inset). An HRTEM image of a typical nanorod shows that the obtained Bi<sub>2</sub>O<sub>3</sub> dendrites are highly crystalline (Fig. 2f). The measured lattices distance with *d*-spacings of 0.528, 0.331 and



**Fig. 2.** SEM and TEM images of the as-prepared  $Bi_2O_3$ : (a-c) **A1**, and the inset in (c) is a high-resolution TEM image of an individual petal; (d) **A2**, and the inset is a TEM image of **A3**; (e) **A4**, and the inset showing its nanorod-like building units; (f) An HRTEM image of an individual from **A4**, and the upper

left and lower right insets are its SAED and FFTs patterns, respectively.

0.276 nm corresponds to (011), (111), and ( $\overline{2}$ 11) planes of  $\alpha$ -Bi<sub>2</sub>O<sub>3</sub>, respectively. The selected area electron diffraction (SAED) patterns could be indexed to monoclinic structure with zone axis of [01 $\overline{1}$ ] (upper left inset in Fig. 2f), which is consistent with the hexagonal lattice in the FFT diffractograms (lower right inset in Fig. 2f). The calculated zone axis and the fringes in the HRTEM image indicate that the Bi<sub>2</sub>O<sub>3</sub> nanorods grow along the [001] orientation.

A time-dependent experiment was conducted to track the morphological evolution of the nanobrick-based flowerlike Bi<sub>2</sub>O<sub>3</sub> microcrystallites (A1). When Bi(NO<sub>3</sub>)<sub>3</sub>/DMF solution was mixed with saturated KOH/H<sub>2</sub>O solution, pale yellow Bi<sub>2</sub>O<sub>3</sub> precipitation merged at once, indicating that precipitation reaction was very fast and a large amount of Bi<sub>2</sub>O<sub>3</sub> nuclei were produced in a short time. TEM image of the product with 10 seconds of reaction indicates that Bi<sub>2</sub>O<sub>3</sub> nuclei grew into bricks and a small amount of flower-like structures were formed (Supporting Information Fig. S2a). After 3 min of reaction, a large amount of the Bi<sub>2</sub>O<sub>3</sub> flower buds were observed (Fig. 3a). XRD pattern shows that the flower buds are well crystalline and all the diffraction peaks can be indexed to the monoclinic  $\alpha$ -Bi<sub>2</sub>O<sub>3</sub> (Supporting Information Fig. S3a). When the reaction time was prolonged to 30 min, the flower petals grew longer (Supporting Information Fig. S4a). We proposed that 1D aggregation of nanobricks should be owing to oriented attachment mechanism, in which attachment occurs by sharing the same crystallographic orientation, analogous to the fusion of high active facets, as displayed in Scheme 1A. The shape and



**Fig. 3.** (a)-(d) SEM and TEM images of  $Bi_2O_3$  prepared after 3 min of reaction at various DMF/H<sub>2</sub>O ratio: (a) 5:1; (b) 2:1, and the inset showing the presence of flower-like morphology; (c) 1:1; (d) 0:30, and the inset is a high-magnification TEM image. TEM images of  $Bi_2O_3$  crystals obtained at DMF/H<sub>2</sub>O

ratio of 5: (e) with 1 mmol of  $Bi(NO_3)_3$ , and the inset showing crossed petals; (f) using NaOH instead of KOH.

size of  $Bi_2O_3$  crystals did not show evident changes even when the ageing time was extended to 24 h (Supporting Information Fig. S4b), which suggests that Ostwald ripening did not occur in this case. The absence of Ostwald ripening means that the current precipitation was not a kinetically controlled reaction but a thermodynamically controlled one [23, 25, 26].

The effect of ageing time on morphology of the products (**A2-A4**) has also been studied. After Bi(NO<sub>3</sub>)<sub>3</sub>/DMF solution was mixed with KOH/H<sub>2</sub>O solution at a DMF/H<sub>2</sub>O ratio of 2 and 1 (**A2** and **A3**) for 10 seconds, white BiONO<sub>3</sub> from the hydrolysis of Bi(NO<sub>3</sub>)<sub>3</sub> suspended in the solution except for yellow Bi<sub>2</sub>O<sub>3</sub> precipitates. TEM images of the yellow products show a small amount of rod-based flowers and bundles together with individual rods (Supporting Information Fig. S2b and c). While, yellow precipitates did not appear in one minute without the addition of DMF (**A4**), which suggests that the reaction between BiONO<sub>3</sub> and KOH was a little slower than that of Bi(NO<sub>3</sub>)<sub>3</sub>/DMF and KOH/H<sub>2</sub>O. Some dendritic structures could be observed 1 min later (Supporting Information Fig. S2d). After reacted for 3 min, a considerable amount of rod-based Bi<sub>2</sub>O<sub>3</sub> flowers, bundles and dendrites were formed (Fig. 3b-d). The particles in light yellow together with white revealed that the products were not pure. XRD patterns show that the intensity of diffraction peaks of BiONO<sub>3</sub> was increased with the H<sub>2</sub>O amount increasing (Supporting Information Fig. S3). When the H<sub>2</sub>O amount was increased, some Bi(NO<sub>3</sub>)<sub>3</sub> may strongly hydrolyze into

BiONO<sub>3</sub> except that those reacted directly with KOH to generate  $Bi_2O_3$ . BiONO<sub>3</sub> would dissolve and re-crystallize into  $Bi_2O_3$  due to high KOH concentration. These newly-generated  $Bi_2O_3$  may nucleate heterogeneously attaching to the original  $Bi_2O_3$  nuclei from the reaction of  $Bi(NO_3)_3$ /DMF and KOH, and grew along preferred direction, forming  $Bi_2O_3$  rod-based microstructures due to its strong 1D growth habit [23]. The nucleation and growth processes at the beginning stage are morphology-determinant. The rod-based  $Bi_2O_3$ architectures presented various morphologies including flower (A2), bundle (A3) and dendrite (A4), should be owing to the competition between nucleation and growth rate from various DMF/H<sub>2</sub>O ratios. With the reaction time extending longer, no obvious change in shapes was observed except that the size of the rods became bigger. The possible formation processes of  $Bi_2O_3$  architectures are illustrated in Scheme 1B. The more detailed growth mechanism is not very clear because of rapid precipitation reaction.





Scheme 1. (A): a schematic (a) and SEM image (b) of the sample A1; (B): proposed formation mechanism of  $Bi_2O_3$  architectures.

The effect of the other preparation conditions on the morphology of nanobrick-based flowerlike  $Bi_2O_3$  microcrystallites (A1) has been investigated. If the amount of  $Bi(NO_3)_3 \cdot 5H_2O$  was decreased to 1 mmol keeping other conditions unchanged, TEM observation shows that the crossed flowerlike  $Bi_2O_3$  microcrystallites with an average petal length of 5 µm constituted 60% of all particles except for multi-petal microstructures (Fig. 3e). While the number of petals increased if the amount of  $Bi(NO_3)_3 \cdot 5H_2O$  was increased to 4 mmol (Supporting Information Fig. S4c). The concentration of  $Bi(NO_3)_3 \cdot 5H_2O$ affected the nucleation rate and amount of the  $Bi_2O_3$  nuclei, which controlled the number of the petals. If NaOH was used instead of KOH as OH source, the rod-based bundle-shaped  $Bi_2O_3$  architectures developed (Fig. 3f), possibly because of weaker basic strength of NaOH and thus slower reaction and nucleation rate than growth. When the solvent or bismuth source was changed to DMSO or BiCl<sub>3</sub> and bismuth citrate, the  $Bi_2O_3$  flower-like

morphology could be observed but became poorly uniform (Supporting Information Fig. S4d-f).



Fig. 4. EDS spectra of the  $Bi_2O_3$  microcrystallites: (a) A1 and (b) A3.

The EDS spectra of the  $Bi_2O_3$  microcrystallites (A1 and A3) show that the as-prepared products consisted of O and Bi elements (Fig. 4). C and Cu peaks in the spectra are due to carbon-coated TEM Cu grid [27].



Fig. 5. XPS spectra of the samlpe A1: (a) Bi 4f; (b) O 1s.

The surface composition and chemical state of the product A1 were analyzed by using XPS (Fig. 5). The high-resolution XPS spectrum of Bi 4f shows two peaks at 158.6 and 163.9 eV, corresponding to Bi  $4f_{7/2}$  and  $4f_{5/2}$ , respectively (Fig. 5a). As shown in Fig. 5b, the deconvolution of O 1s spectrum indicates two contributions of lattice oxygen  $O^{2-}$  at 530.5 eV and surface adsorbed oxygen at 531.5 eV [28, 29].



Fig. 6. (a) DRS spectra and (b) the plot of  $(\alpha hv)^2$  as a function of photon energy hv of the samples A1-A4.

The UV-Vis absorption spectrum is one of the important methods for researching the optical properties and band structure of semiconductor nanomaterials. The optical properties of the as-prepared Bi<sub>2</sub>O<sub>3</sub> microcrystallites were measured by using DRS spectra, and the results are shown in Fig. 6. The absorbance edge of the samples **A3** and **A4** located at approximately 450 nm, which are in accordance with their yellowish color. The samples **A1** and **A2** show absorbance throughout the entire visible region. The energy of the band gap ( $E_g$ ) was calculated following Tuac's equation [30]  $\alpha hv = A(hv - E_g)^{n/2}$ , where  $\alpha$ , h, v, and A are the absorption coefficient, Plank's constant, light frequency, and a constant,

respectively. For  $Bi_2O_3$ , the value of *n* is 1 [23]. The band gap energies of the as-prepared  $Bi_2O_3$  samples are found to be about 2.70-2.88 eV (inset in Fig. 6b and Table 1). The band gap energy decreased with increasing rod diameter, whereas the petal-based  $Bi_2O_3$  crystal with the largest thickness and width has the smallest band gap energy, which may be caused by the size effect [4, 23].



**Fig. 7.** (a) Photocatalytic degradation efficiency of RhB and (b) kinetic linear simulation curves of RhB degradation over the samples **A1- A4**.

The photocatalytic activity of the as-prepared  $Bi_2O_3$  microcrystallites were detected by degradation of RhB. Fig. 7a shows the photodegradation efficiency of RhB as a function of irradiation time over different photocatalysts under xenon lamp irradiation, where  $C_0$  is the initial concentration of the RhB after adsorption-desorption equilibration, and *C* is the concentration of RhB at different irradiation time, which was measured by UV-Vis spectra (Supporting Information Fig. S5). After 5 h of irradiation, the photodegradation rate reached 93% and 96% over the rod-based bundle-like (A3) and dendrite-like (A4)  $Bi_2O_3$ , respectively, higher than the nanobrick-based flower-like (A1)  $Bi_2O_3$  (about 53%). On the

other hand, the maximum peak obviously shifted from 554 nm to 500 nm, which can be ascribed to the formation of N-deethylated RhB in the photocatalytic process (Supporting Information Fig. S5). The time-dependent decomposition of RhB follows the first-order kinetics,  $-\ln(C/C_0) = kt$ , where t is the irradiation time and k is the apparent rate constant [29]. The calculated curves tangent values (k) for the samples A1-A4 are 0.16, 0.38, 0.53 and 0.63  $h^{-1}$ , respectively (Fig. 7b), indicating that rod-based Bi<sub>2</sub>O<sub>3</sub> architectures (A2-A4) present higher photocatalytic rate than A1 upon visible-light irradiation. As well known, many factors influence photocatalytic activity including crystallinity, surface area, band gap and so on [31, 32]. BET surface area was also measured and it is found to be 1.28 and 1.24 m<sup>2</sup>/g for the samples A1 and A3, respectively. Therefore, in the present work, the morphology and microstructures of the catalysts are the main factors to influence photodegradation activity. The photocatalytic activity of various Bi<sub>2</sub>O<sub>3</sub> structures or morphology reported by the literatures and this work is listed in Table 2, where 1D needle-like Bi2O3 was reported to exhibit better photocatalytic activity over Bi2O3 polyhedrons and plates [23]. We proposed that the higher photocatalytic efficiency for the nanorod-based Bi<sub>2</sub>O<sub>3</sub> architectures may be attributed to higher light absorption and carrier separation efficiency in 1D nanostructured materials [33]. Additionally, the average diameter of the building units (microrods or nanorods) for the samples A2-A4 is 1  $\mu$ m, 200 nm, and 80 nm, respectively. For a given catalyst amount, a smaller size means a higher specific surface area, and so offers more active reaction centers. The photocatalytic activity of the samples from A2 to A4 increased gradually, which should result from the decrease of the rod diameter and increase of the surface area. As displayed in Fig. 7b, the apparent

rate constant *k* is increased from 0.38 to 0.63  $h^{-1}$  for the samples **A2** to **A4**. A decrease in rod diameter will shorten the route for photogenerated electrons to migrate to the surface and therefore enhance the photodegradation rate [32].

Morphology	Pollutants	Irradiation time (h)	Photodegradation rate
Rod-based flowers [34]	MO <sup>a</sup>	1.5	13.9%
Plates-based flowers [8]	RhB	2.5	87%
Needles [23]	MB <sup>b</sup>	3	28%
Bundles of needles [23]	MB	3	38%
Plates [23]	МВ	3	11%
Polyhedrons [23]	MB	3	14%
Brick-based flowers (A1)	RhB	5	53%
Rod-based flowers (A2)	RhB	5	85%
Rod-based bundles (A3)	RhB	5	93%
Rod-based dendrites (A4)	RhB	5	96%

**Table 2.** Photocatalytic activity of Bi<sub>2</sub>O<sub>3</sub> in various structures or morphology

 $^{a}$  MO = Methyl orange;  $^{b}$  MB = Methyl blue)

#### 4. Conclusions

In summary, by selecting proper DMF/H<sub>2</sub>O ratio, the morphologies of the  $Bi_2O_3$ hierarchical architectures can be easily tuned via precipitation method. The amount of H<sub>2</sub>O

influences the hydrolysis degree of the precursor  $Bi(NO_3)_3$ , thus the amount of initial  $Bi_2O_3$ nuclei, and finally determines the morphology of the building units of the  $Bi_2O_3$ architectures. The facile strategy to fabricate  $Bi_2O_3$  crystals provides a basis for gaining mechanistic insights into shape control of  $Bi_2O_3$  hierarchical architectures.

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#### **Figure Captions:**

**Table 1.** DMF/H<sub>2</sub>O ratio, morphologies, band gap energy and apparent rate constant k of RhB photodegradation.

**Fig. 1.** XRD patterns of the as-prepared  $Bi_2O_3$  microcrystallites: (a) [KOH]/Bi = 89/2 (A1), (b) [KOH]/[Bi] = 71/2. Vertical sticks below the patterns represent the standard diffraction data from JCPDS file for bulk  $Bi_2O_3$  with monoclinic structure (No. 41-1449).

**Fig. 2.** SEM and TEM images of the as-prepared  $Bi_2O_3$ : (a-c) **A1**, and the inset in (c) is a high-resolution TEM image of an individual petal; (d) **A2**, and the inset is a TEM image of **A3**; (e) **A4**, and the inset showing its nanorod-like building units; (f) An HRTEM image of an individual from **A4**, and the upper left and lower right insets are its SAED and FFTs patterns, respectively.

**Fig. 3.** (a)-(d) SEM and TEM images of  $Bi_2O_3$  prepared after 3 min of reaction at various DMF/H<sub>2</sub>O ratio: (a) 5:1; (b) 2:1, and the inset showing the presence of flower-like morphology; (c) 1:1; (d) 0:30, and the inset is a high-magnification TEM image. TEM images of  $Bi_2O_3$  crystals obtained at DMF/H<sub>2</sub>O ratio of 5: (e) with 1 mmol of  $Bi(NO_3)_3$ , and the inset showing crossed petals; (f) using NaOH instead of KOH.

Scheme 1. (A): a schematic (a) and SEM image (b) of the sample A1; (B): proposed formation mechanism of  $Bi_2O_3$  architectures.

Fig. 4. EDS spectra of the Bi<sub>2</sub>O<sub>3</sub> microcrystallites: (a) A1 and (b) A3.

Fig. 5. XPS spectra of the sample A1: (a) Bi 4f; (b) O 1s.

Fig. 6. (a) DRS spectra and (b) the plot of  $(\alpha hv)^2$  as a function of photon energy hv of the samples A1-A4.

Fig. 7. (a) Photocatalytic degradation efficiency of RhB and (b) kinetic linear simulation curves of RhB

degradation over the samples A1- A4.

Acceleration Table 2. Photocatalytic activity of Bi<sub>2</sub>O<sub>3</sub> in various structures or morphology



**Graphic abstract:** 

# Synthesis of Bi<sub>2</sub>O<sub>3</sub> architectures by precipitation method in DMF-H<sub>2</sub>O solution and their photocatalytic activity

#### Li-Li Yang, Qiao-Feng Han, Jin Zhao, Jun-Wu Zhu, Xin Wang, Wei-Hua Ma

Flowerlike  $\alpha$ -Bi<sub>2</sub>O<sub>3</sub> architectures assembled by nanobrick-based petals with pineapple surface were firstly synthesized by precipitation method at room temperature in DMF-H<sub>2</sub>O solution.



#### **Highlights:**

> Nanobrick-based flowerlike  $Bi_2O_3$  crystals with pineapple surface were synthesized by precipitation method.

> Good solubility of  $Bi(NO_3)_3$  in DMF played a crucial role in the growth of flowerlike

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 $Bi_2O_3$ .

> The growth mechanism of Bi<sub>2</sub>O<sub>3</sub> microcrystallites has been explained in detail.

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