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Simple Template-Free Synthesis of Bi_2O_3 Microflowers Composed of Nanorods

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Abstract

This paper reports that α-Bi_2O_3 microflowers can be synthesized by an extremely simple and easy approach of inducing a reaction through the addition of NaOH aqueous solution to a mixed aqueous solution of $Bi(NO_3)_3 \cdot 5H_2O$ and HNO_3 scanning electron microscopy images of the Bi_2O_3 microflowers indicate that the Bi_2O_3 nanorods grew radially from the centre of the microflower to form the microflower shape. The findings of this study show that control of the reaction temperature, reaction time, and raw material mixture ratio plays an important role in the formation of α-Bi_2O_3 microflowers. It is especially revealed that α-Bi_2O_3 microflowers can be formed at low temperatures with short reaction times. It has thus far been reported that flower-shaped Bi_2O_3 particles or their precursors can be synthesized by the addition of additives such as organic molecules or certain inorganic ions. The present work reports on the discovery of ways to synthesize flower-shaped Bi_2O_3 particles without the use of special additives.

Keywords

Bi_2O_3, Nanorod, Microflower

1. Introduction

Bismuth oxide (Bi_2O_3) particles have attracted attention as candidate materials for helping to solve energy and environmental problems. Practical research is being actively conducted on photocatalysts [1]-[8], supercapacitors [9] [10] [11], and Li-ion and Na-ion battery materials [12] [13]. Such practical research involves implementation of morphological control of Bi_2O_3 particles as a way to improve their properties. Various shapes of Bi_2O_3 particles have been reported, such as nanowires [2], nanorods [5] [10] [11], nanotubes [14], and flowers [1]

[6] [8] [15] [16] [17]; these shapes have been reported to lend excellent properties to the particles. Works such as those outlined next have specifically reported that the flower shape of Bi_2O_3 particles shows potential to lend excellent properties to the particles, on account of the large specific surface area in the case of this shape. Zhou *et al.* [1] succeeded in synthesizing flower-shaped particles of δ-Bi_2O_3 in sheet shape in aqueous solution in the presence of VO_3^-. Tseng *et al.* [15] succeeded in synthesizing flower-shaped γ-Bi_2O_3 particles from petals produced by the self-organization of nanosized triangular and pyramidal structures formed by a reaction in aqueous solution by using polyethylene glycol as a capping agent. Wang *et al.* [16] synthesized flower-shaped α-Bi_2O_3 by using a mixture of glycerine and oleic acid in an ethanol-water medium as a capping agent. Zhang *et al.* [17] synthesized flower-shaped $Bi_2(CO_3)O_2$ particles consisting of nanosheet petals in the presence of citric acid. By calcining the particles, they succeeded in converting them to flower-shaped α-Bi_2O_3 while retaining the morphology of the $Bi_2(CO_3)O_2$ particles. After synthesizing flower-shaped $CH_3COO(BiO)$ from nanosheets by using glacial acetic acid, Zhang *et al.* [8] obtained flower-shaped δ-Bi_2O_3 particles via calcination. By performing synthesis in the presence of L-asparagine, Xiao *et al.* [6] further succeeded in synthesizing bismuth-asparagine complex microspheres and subsequently converting them to flower-shaped α-Bi_2O_3 particles via calcination. Therefore, it is clear that studies conducted thus far have obtained different flower-shaped Bi_2O_3 or Bi_2O_3 precursor particles according to the type of additives such as the inorganic ions or organic molecules added in the reaction solution.

The present paper reports that α-Bi_2O_3 microflowers composed of nanometre-sized rod-shaped particles can be synthesized by an extremely easy and simple approach of inducing a reaction at a suitable reaction temperature and for a suitable reaction time through the addition of NaOH aqueous solution to mixed aqueous solution of $Bi(NO_3)_3 \cdot 5H_2O$ and HNO_3 without using any particular additive. This paper also reports that the shape of α-Bi_2O_3 particles can be controlled via the addition of an additive such as NaF or Na_2CO_3 to the reaction solution.

2. Material and Methods

Transparent reaction solution was obtained by mixing $Bi(NO_3)_3 \cdot 5H_2O$ (Wako Pure Chemical Industries, Ltd.) (0.001 mol), 20 ml of distilled water, and 7 ml of nitric acid (69 wt%, SIGMA-Aldrich). Then, 20 ml of 10 mol/dm^3 NaOH (Wako Pure Chemical Industries, Ltd.) aqueous solution was added to the reaction solution, and the reaction was induced at certain temperatures (0.2˚C, 20˚C, 40˚C, 80˚C, 120˚C, and 160˚C) and times (0 min [*i.e.* it was recovered immediately after mixing the NaOH aqueous solution], 10 min, 1 h, and 24 h). When the reaction temperature was 80˚C or lower, the reaction was induced in a flask by using a water bath, and when the reaction temperature was 120˚C or higher, the reaction was induced in a hydrothermal reaction vessel (sealed stainless steel container with interior Teflon coating) by using an oil bath. The solid and liquid phases of the obtained product were separated by centrifugation at 3000 rpm for 5 minutes, after which they were washed 5 times with distilled water and then freeze-dried. The use of NaF (SIGMA-Aldrich) or Na_2CO_3 (Wako Pure Chemical Industries, Ltd.) as an additive was also considered. 0.05 mol of NaF or Na_2CO_3 was added to 60 ml of distilled water in order to create an aqueous solution containing the additive. After mixing of the aqueous solution containing the additive with the previously mentioned transparent reaction solution containing $Bi(NO_3)_3 \cdot 5H_2O$ and HNO_3, the reaction was induced via the addition of 10 mol/dm^3 NaOH solution for 1 h at 20˚C. The solid and liquid phases of the obtained product were separated by centrifugation, after which they were washed with distilled water and then freeze-dried. To evaluate the obtained product, crystal structure analysis by powder X-ray diffraction (XRD) measurement (Shimadzu XRD-6100) and shape observation by scanning electron microscopy (SEM; Hitachi S-3000N) and transmission electron microscopy (TEM; JEOL JEM-2100) were performed.

3. Results and Discussion

As a typical example, **Figure 1** shows SEM and TEM images of the product obtained after 1 h of reaction at 20˚C without any additive. The low- and high-magnification SEM photographs in **Figure 1(a)** and **Figure 1(b)** show that microflowers (flower-shaped particles) were formed when rod-shaped particles several micrometres long radiated outwards isotropically. In the TEM image of the rod-shaped particles (**Figure 1(c)**), the edge of the particles was smooth and a black image was observed, suggesting the single-crystal nature of the rods. The width of the rod-shaped particles ranged from several tens of nanometres to several hundreds of nanometres. The average size of the microflowers measured from the SEM image was 11 μm. The largest and smallest parts of the flower-shaped structure were, respectively, about 17 μm and about 5 μm in size. All the diffraction peaks seen in the XRD pattern of the sample (**Figure 2**) are attributable to α-Bi_2O_3 (JCPDS no. 71-2274); the microflowers obtained in this study were found to be α-Bi_2O_3. Although several studies have reported flower-shaped particles, as mentioned in the introduction section, ours is the first study to obtain flower-shaped particles as shown in **Figure 1**.

Next, the process of formation of the microflowers was studied. Block-shaped particles such as those shown in **Figure 3(a)** inset were observed in samples obtained immediately after mixing of $Bi(NO_3)_3$ and NaOH aqueous solutions.

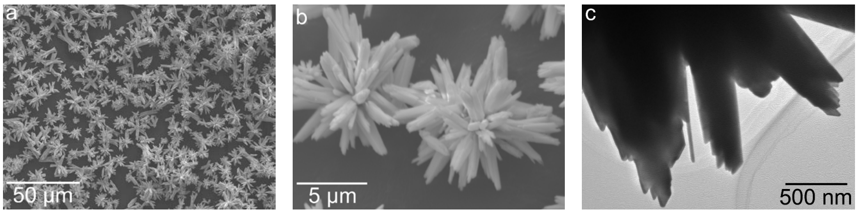

Figure 1. SEM ((a), (b)) and TEM (c) images of microflowers formed after 1 h of reaction at a reaction temperature of 20˚C.

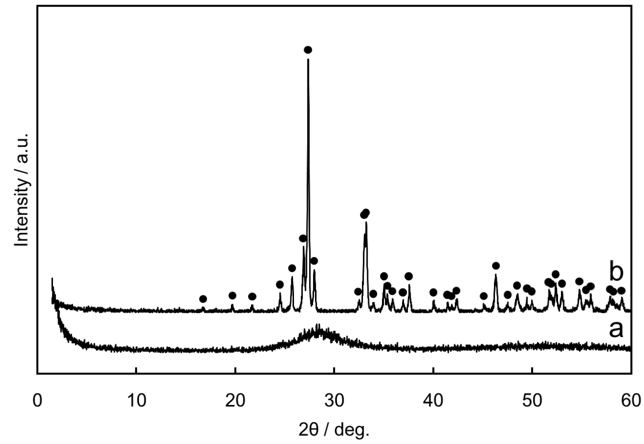

Figure 2. XRD patterns of samples obtained under various reaction times: (a) immediately after mixing of NaOH solution; (b) 1 h. Peak assignment: ●, α-Bi_2O_3.

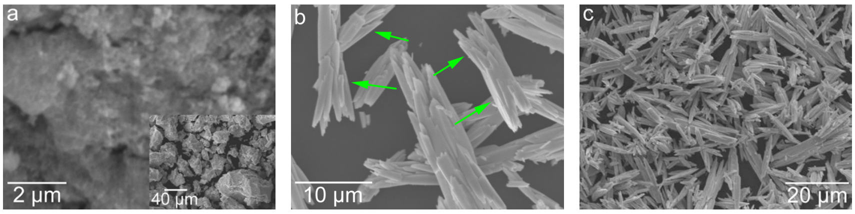

Figure 3. SEM images of samples obtained under various reaction times: (a) immediately after mixing of NaOH solution; (b) 10 min; (c) 24 h.

These particles are fine particles (**Figure 3(a)**) that clumped upon drying, and they are thought to be produced by the formation of secondary particles. No sharp diffraction peaks were observed in the XRD pattern (**Figure 2**) of this sample, which reveals that an amorphous substance was generated. When the reaction time reached 10 min, rod-shaped particles were observed to assemble and grow regularly as shown in **Figure 3(b)**; that is, rod-shaped particles were observed to radiate outwards symmetrically on the right and left sides as indicated by green arrows. Through progression of this kind of growth, when the reaction time reached 1 h, the rod-shaped particles radiating outwards isotropically were thought to have produced microflowers such as those shown in **Figure 1**. The factors that contribute to the formation of the flower shape are currently unknown, but the reaction mechanism is currently surmised to be as shown in **Figure 4**. It is possible that fine amorphous particles were generated immediately after mixing of $Bi(NO_3)_3$ solution with NaOH aqueous solution and that these particles immediately aggregated, crystallised, and generated rod-shaped particles. A highly reactive crystal surface exists at the tip ends of the rod-shaped particles. It is possible that as a result of the heterogeneous nucleation and its subsequent growth, the rod-shaped particles produced particles that radiated outwards isotropically. NO_3^- could also have been involved in the formation of the rod-shaped particles. As stated in the introduction, in studies thus far, when flower-shaped Bi_2O_3 was synthesized, inorganic ions such as VO_3^- and organic

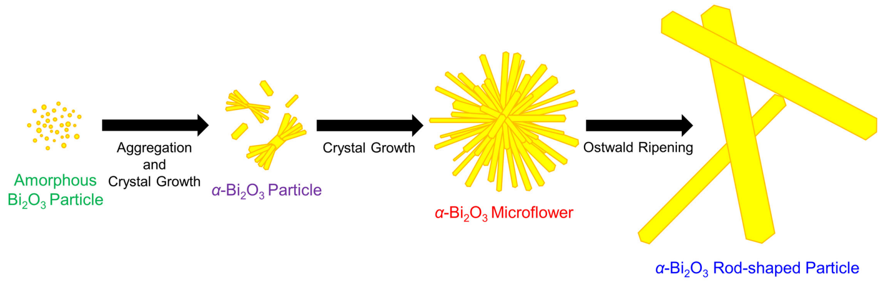

Figure 4. Schematic representation of formation process of α-Bi_2O_3 microflowers.

molecules—which have comparatively stronger affinity towards Bi^{3+} ions—were added [1] [6] [8] [15] [16] [17]. In the present research, because HNO_3 was added to form transparent $Bi(NO_3)_3$ solution, high concentrations of NO_3^- existed in the solution. Zhou *et al.* [1] and Tseng *et al.* [15] also added HNO_3 to obtain transparent $Bi(NO_3)_3$ aqueous solution when synthesizing flower-shaped Bi_2O_3. Under ordinary circumstances, NO_3^- is known to be an ion that have weak affinity towards metal ions; in the present study, NO_3^- existed in high concentrations, even though it does not have any particular strong affinity towards Bi^{3+}; therefore, it could have contributed to the formation of rod-shaped particles by weakly adsorbing to the surface of the particles when the Bi_2O_3 crystals were formed. It is also interesting to note that although a small number of microflowers such as those shown in **Figure 3(c)** were observed after 24 h of reaction, almost all of these particles were rod-shaped; the largest of the rod-shaped particles were several tens of micrometres in size and were significantly larger than those in the samples obtained after 1 h of reaction. Nothing but diffraction peaks attributable to α-Bi_2O_3 was observed in the XRD pattern of this sample. The disappearance of α-Bi_2O_3 microflowers and the increased particle sizes suggest that the dissolution-reprecipitation reaction of α-Bi_2O_3 particles, *i.e.* the Ostwald ripening reaction, tended to occur. In other words, with progress of the Ostwald ripening reaction, small rod-shaped particles that constituted the microflowers disappeared by dissolution and the other large rod-shaped particles grew in size by reprecipitation; as a result, the α-Bi_2O_3 microflowers transformed into a large number of α-Bi_2O_3 rod-shaped particles.

Next, the effect of the reaction temperature on the shape of α-Bi_2O_3 was studied. Synthesis was performed at various reaction temperatures with a reaction time of 1 h. XRD measurement confirmed that only α-Bi_2O_3 was produced at all reaction temperatures. When the reaction temperature was 0.2˚C, as shown in **Figure 5(a)**, microflowers with an average size of 9 μm (approximately 4 - 17 μm in size) were formed. The size distribution of the microflowers obtained at 0.2˚C seems to be broader than that obtained at 20˚C, as shown in **Figure 1(a)**, **Figure 5(a)**, and **Figure 5(b)**. On the other hand, when the reaction temperature reached 40˚C, as shown in **Figure 5(c)**, while some microflowers such as those observed at the reaction temperature of 20˚C were observed, most were rod-shaped particles several tens of micrometres in length. As shown in **Figure 5(d)**, microflowers were not observed at the reaction temperature of 80˚C; only rod-shaped

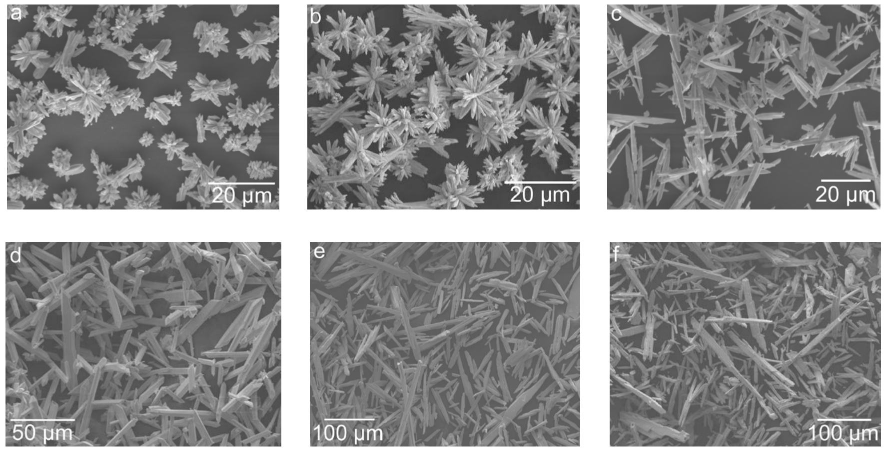

Figure 5. SEM images of samples obtained at various reaction temperatures: (a) 0.2˚C; (b) 20˚C; (c) 40˚C; (d) 80˚C; (e) 120˚C; (f) 160˚C.

particles several tens of micrometres in length were observed at this temperature. These particles were larger than those generated at 40˚C. Rod-shaped particles were also observed in samples obtained at 120˚C and 160˚C as shown in **Figure 5(e)** and **Figure 5(f)**. The length of the particles formed at both these temperatures ranged from several tens of micrometres to several hundreds of micrometres, and these particles were longer and thicker than those formed at 80˚C.

Finally, the effects of additives were studied. The reaction was conducted for 1 h at a temperature of 20˚C. Three types of additives were examined: 60 ml of water solution, a solution of NaF added to 60 ml of water, and a solution of Na_2CO_3 added to 60 ml of water. The reason for using NaF and Na_2CO_3 as additives is that it is well known that F^- or CO_3^{2-} ions strongly coordinate with metal ions to form unique oxides and hydroxides. XRD measurements confirmed that only α-Bi_2O_3 was generated after synthesis with the addition of any of these additives. Microflowers (**Figure 1(a)** and **Figure 1(b)**) such as those observed in particles produced by synthesis without the addition of an additive were not observed in particles produced by synthesis with the addition of the 60 ml of water (see **Figure 6(a)**). Rod-shaped particles clumped to form a shape similar to the feather of a bird (this can also be termed "fan-shaped") were observed. These fan-shaped particles are probably those that were formed when the obtained product was washed and dried, and these fan-shaped particles were probably formed by the crumbling of the aggregate generated by synthesis. These results indicate that the concentration of ions such as Bi^{3+} and NO_3^- has a significant effect on the formation of assemblies of α-Bi_2O_3 rod-shaped particles. More microflowers were observed to be formed from the rod-shaped particles when the solution of NaF added to 60 ml of water was used as the additive (see **Figure 6(b)**) than when 60 ml of water solution was used as the additive; numerous rod-shaped particles that were believed to have been formed when the flower-shaped structure fell apart were observed. On the other hand, although a large number of rod-shaped particle assemblies were observed among the

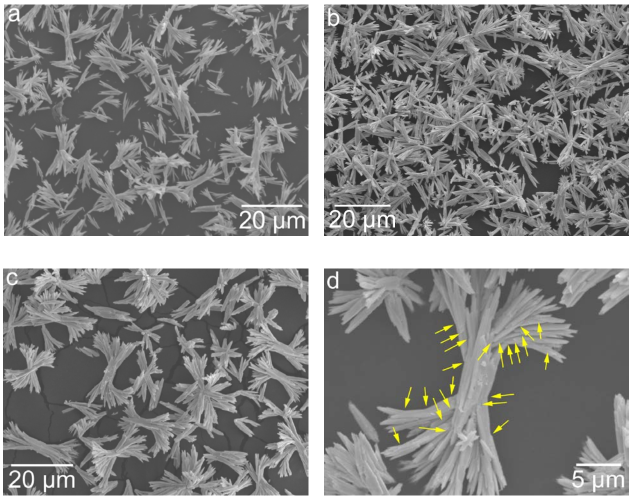

Figure 6. SEM images of samples obtained with the addition of various additives: (a) 60 ml of H_2O; (b) solution of NaF added to 60 ml of H_2O; ((c), (d)) solution of Na_2CO_3 added to 60 ml of H_2O.

particles formed using the solution of Na_2CO_3 added to 60 ml of water (see **Figure 6(c)**), a few microflowers were present that grew out isotropically from rod-shaped particles similar to those observed among the particles formed without any additive; further, numerous butterfly-shaped particles composed of rods radiating outwards in a two-dimensional plane. The length of these particles in the longitudinal direction was approximately 19 μm. Detailed observation of the butterfly-shaped particle (see **Figure 6(d)**) revealed that several rods as indicated by the yellow arrows were connected when the angle changed gradually. As mentioned previously, this image suggests that the tips of the rods are highly reactive, and subsequent nucleation and growth of rods with the tip of the rods as the origin are possible. The difference in the shapes of α-Bi_2O_3 particles resulting from employing these additives is thought to be a result of the difference in the adsorptions to the particle surfaces of F^- or CO_3^{2-}, which are negative ions that coexist in the reaction solution during the growth of the α-Bi_2O_3 crystals. This indicates that size and shape of the flower structure can be controlled by selecting an appropriate additive.

4. Conclusion

This paper has reported that α-Bi_2O_3 microflowers composed of aggregates of nanorods can be synthesized by an extremely simple and easy approach of inducing a reaction through the addition of sodium hydroxide aqueous solution (with a reaction time of 1 h at a temperature of 20˚C) to a mixed aqueous solution of $Bi(NO_3)_3 \cdot 5H_2O$ and HNO_3. The findings of the study have demonstrated that control of the reaction temperature and reaction time plays an important role in the formation of the microflowers; in particular, α-Bi_2O_3 microflowers can be formed easily with a short reaction time and low reaction temperature. The method employed in this study shows promise for synthesizing flower-shaped *α*-Bi_2O_3 from the standpoints of its low cost and low energy consumption. The findings also indicate that the shape of microflowers can be controlled by synthesizing them in the presence of an additive such as NaF or Na_2CO_3. Future study will be aimed at the evaluation of their characteristics of photocatalysts and Li-ion batteries.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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