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Research Article

Self-Assembled Bismuth Oxide Microrods Prepared by a Facile Chemical Method

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ABSTRACT

Bismuth oxides (Bi_2O_3) are of interest because of their suitable band gaps for photocatalytic activity. Herein, α-Bi_2O_3 microrods were synthesized by a facile chemical method, and were characterized by X-ray diffraction (XRD), energy dispersive X-ray spectroscopy (EDS), scanning electron microscope (SEM), and UV-Vis diffuse reflectance spectroscopy (UV-Vis DRS). The results showed that the particles were rod-shaped with lengths in the range of 5-10 μm. Crystalline structure of the particles was monoclinic, and the band gap was around 2.88 eV. When citric acid was used in the synthesis, the bismuth oxide microrods can self-assemble into the hierarchical flower-like structures leading to the alteration of band gap. This self-assembled α-Bi_2O_3 microstructure can be employed as a photocatalyst with alterable band gap.

Keywords: Bismuth oxide, Chemical synthesis, Microrod, Microstructure, Optical property

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Introduction

Semiconductor photocatalysis has been employed in many emerging applications, including degradation of organic pollutants, self-cleaning materials, and hydrogen generation [1-2]. Some semiconductor metal oxides have been used as photocatalysts, for examples, TiO_2 [3], ZnO [4], and WO_3 [5]. However, such materials possess wide band gaps, and thus they are inactive under visible light. To increase an efficiency of the photocatalysis, narrower band gap semiconductors have been intensively explored. Among prominent candidates, bismuth oxide (Bi_2O_3) has gained much attention due to its suitable and tunable band gap (e.g., 2.85 eV for α-Bi_2O_3 and 2.58 eV for β-Bi_2O_3 [6]); moreover, it is a non-toxic material, and has high photoluminescence and photoconductivity [2, 7].

Bi_2O_3 can exist in five different polymorphic forms depending on preparation methods and thermal stability. The α-Bi_2O_3 (monoclinic) and δ-Bi_2O_3 (cubic) are stable, whereas β-Bi_2O_3 (tetragonal), γ-Bi_2O_3 (body-centered cubic), and ε-Bi_2O_3 (triclinic) are metastable [8]. Different synthetic procedures could generate micro- or nano- crystalline Bi_2O_3 in various morphologies, including wire [9], fiber [10], flake [11] and rod [2, 8]. The Bi_2O_3 microrods could be prepared by simple heat treatment [8, 12], hydrothermal [13-14], sol-gel [15] and sonochemical [16] methods. However, there was not a work that reported on the optical properties of uniform and self-assembled α-Bi_2O_3 microrods.

In this work, we report a novel and simple route for synthesis of uniform Bi_2O_3 microrods. The obtained microrods could self-assemble into a flower-like structure by using citric acid. Optical properties have been investigated regarding the alteration of particle morphology.

Materials and Methods

Bismuth oxide microrods were prepared by a novel chemical synthesis under aqueous conditions. All chemicals were used as received without further preparation. In a typical synthesis, 0.6 g of citric acid and 5 mmol of $Bi(NO)_3 \cdot 5H_2O$ were dissolved in 20 mL deionized water (DI-water) forming a white suspension. After stirring for 20 min, a solution of 2.5 g NaOH in 20 mL DI-water was added and continued stirring for 10 min. The mixture was then heated to 90 ^oC, and 20 mL of $N_2H_4 \cdot H_2O$ was subsequently injected into the mixture. The reaction was dwelled at 90 ^oC for 2 h. After cooled down to room temperature, the precipitate was separated and re-dispersed in DI-water, and then centrifuged at 3000 rpm for 15 min. The precipitate was collected, and the washing process was repeated with DI-water 2 times and with ethanol 3 times. Final product was dried in an oven at 70 ^oC for 2 h. Four samples were prepared with altered conditions illustrated in Table 1.

Table 1 Synthetic conditions for preparation of the samples.

Sample	Substance (g)			
	$Bi(NO_3) \cdot 5H_2O$	$C_6H_8O_7$	NaOH	PVP
BM01	2.425	-	2.5	-
BM02	2.425	0.6	2.5	-
BM03	2.425	0.6	2.5	1.0
BM04	2.425	0.6	2.5	2.0

A scanning electron microscope (SEM) was used to characterize morphology of the microrods, and the elemental compositions were examined by energy dispersive x-ray spectroscopy (EDS) equipped with the SEM. The crystalline structure was identified by an X-ray diffractometer (XRD) using Cu-Kα radiation and a scanning rate of 0.05 degree/1 second. The optical properties were determined by a UV-Vis diffuse reflectance spectroscopy (DRS) using $BaSO_4$ as a reference and scanned wavelength of 200–600 nm.

Results and Discussion

Figure 1 illustrates the X-ray diffraction patterns of the samples. All samples show the same patterns in which the BM01 reveals the sharpest peaks implying that the sample is most well-crystalline. The apparent peaks in each spectrum can be assigned to that of standard monoclinic α-Bi_2O_3 (JCPDS 41-1449), and no secondary phases have been found in all samples. These results indicate that the samples are high-purity, and the synthetic method is repeatable.

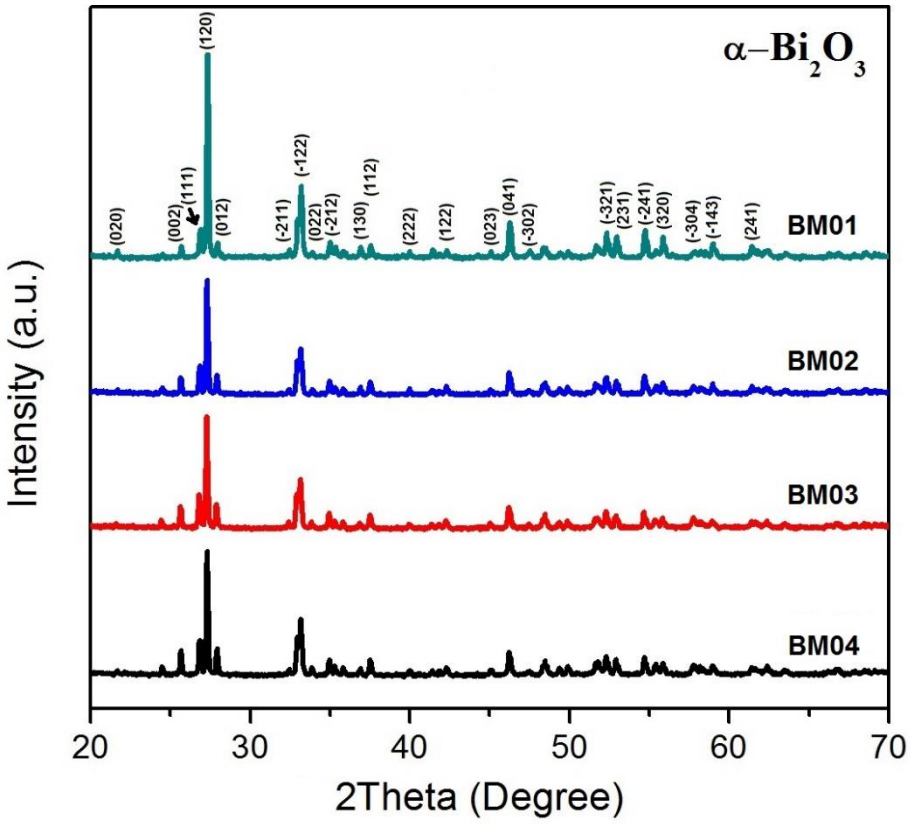

Figure 1 XRD Spectra of samples.

Element composition of the sample BM01 determined by the EDS technique is shown in Figure 2 (other samples also exhibit the same composition). Only Bi and O could be found in the spectrum supporting that the sample is bismuth oxide (C is from a carbon tape that used for sticking the sample). The FT-IR spectrum (Figure 3) also shows the absorption peaks at a wave number of 846 cm^{-1} that could be ascribed to the vibration of Bi-O bonds present in the Bi_2O_3 which is consistent with the

previous literatures [17-18]. The absorption band at around 1383 cm^{-1} indicates the vibrations of NO_3^- ions which are residual in the sample [19].

Morphology of the particles evidently depends on the synthetic conditions as shown in Figure 4. Without citric acid and PVP (BM01), the quite uniform Bi_2O_3 microrods are obtained; their lengths are in the range of 5 – 10 μm while the diameters are smaller than 1 μm (Figure 4(a)). In the presence of citric acid, the microrods tend to self-assemble into the hierarchical flower-like structures with some separated microrods (Figure 4(b)). The effect of PVP on the particle size and shape could be examined on Figure 4(c) (1.0 g PVP, BM03) and Figure 4(d) (2.0 g PVP, BM04). Using PVP in the synthesis shortens the rods, but the flower-like assembly also occurs. Increase of PVP generates the particles with irregular in shape; it is likely that the PVP reduces the growth rate in the elongated direction. According to the previous work, using PVP in the synthesis inhibits the microrod forming, and results in granular grains Bi_2O_3. It is attributed that the PVP adsorbs on the crystal faces and hinders the growth rate in the elongated direction [16].

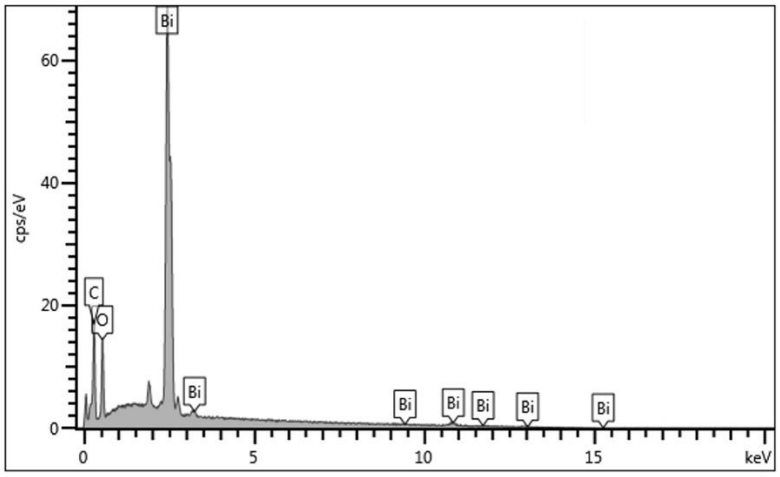

Figure 2 EDS spectrum of the BM01.

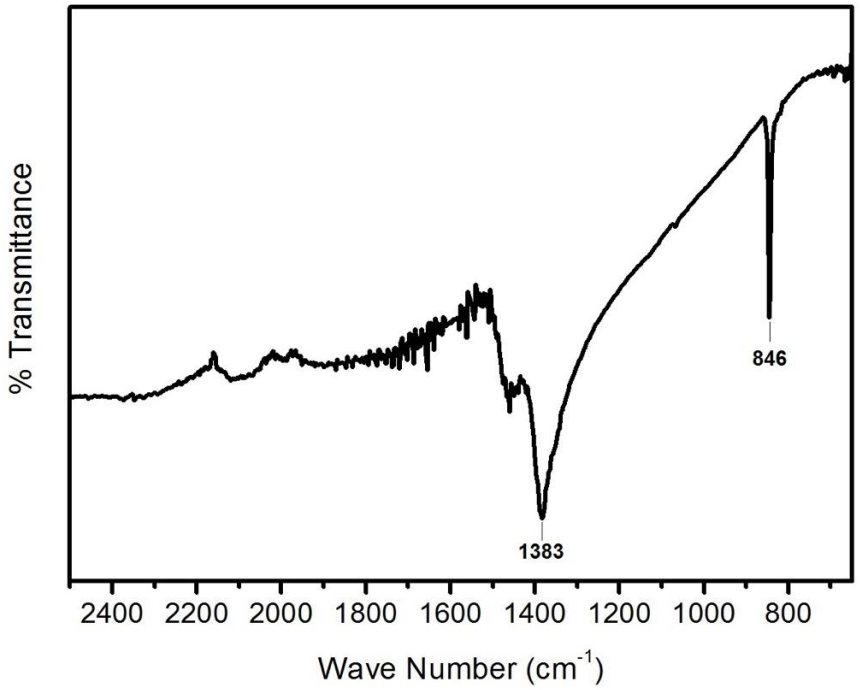

Figure 3 FT-IR spectrum of sample BM01.

To evaluate optical properties of the samples, the UV-Vis DRS spectrometer was performed to determine the absorbance at various wavelengths (Figure 5). The threshold absorption occurs at the wavelength shorter than 440 nm that can be ascribed to the intrinsic band gap absorption [12]. The approximated band gap can be obtained by the Tauc plots (insets in the Figure 5) utilizing the direct band gap transition. The x-intercepts represent that the samples possess the band gap of 2.88 for BM01, 2.81 for BM02, 2.83 for BM03, and 2.83 for BM04. These values are well consistent with the reported values of α-Bi_2O_3 [16, 20]. Interestingly, self-assembled microrods (BM02) can reduce the band gap to be more visible light active which can be used to increase efficiency in photocatalytic applications.

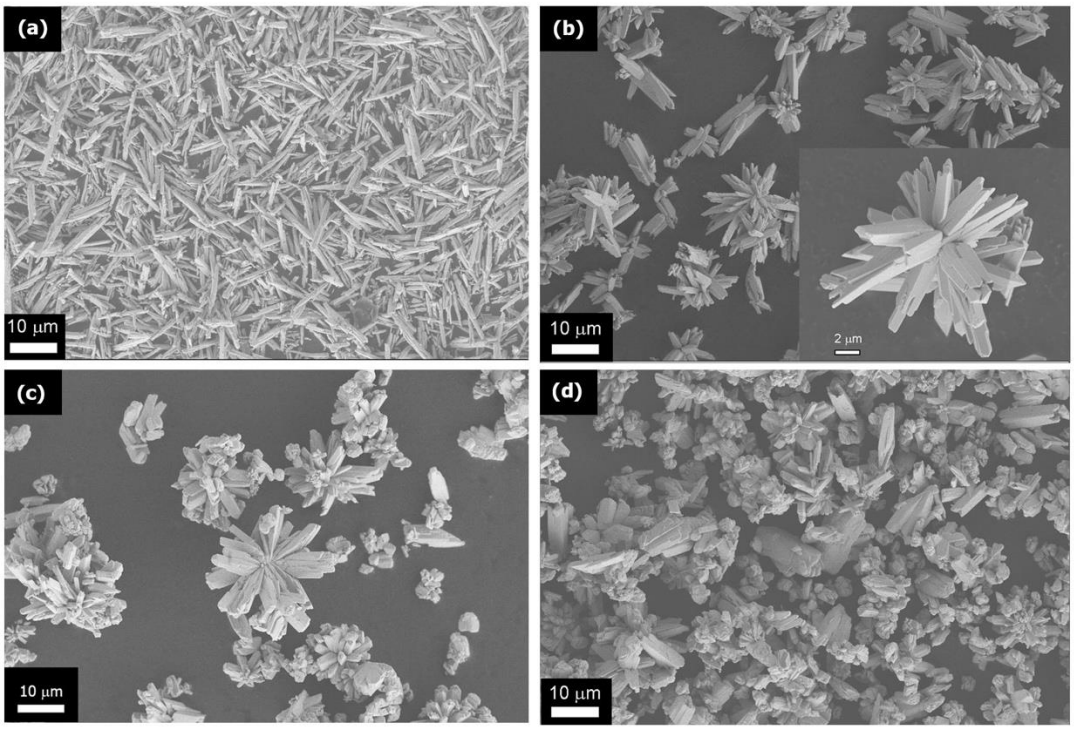

Figure 4 SEM images of the samples (a) BM01, (b) BM02, (c) BM03, and (d) BM04.

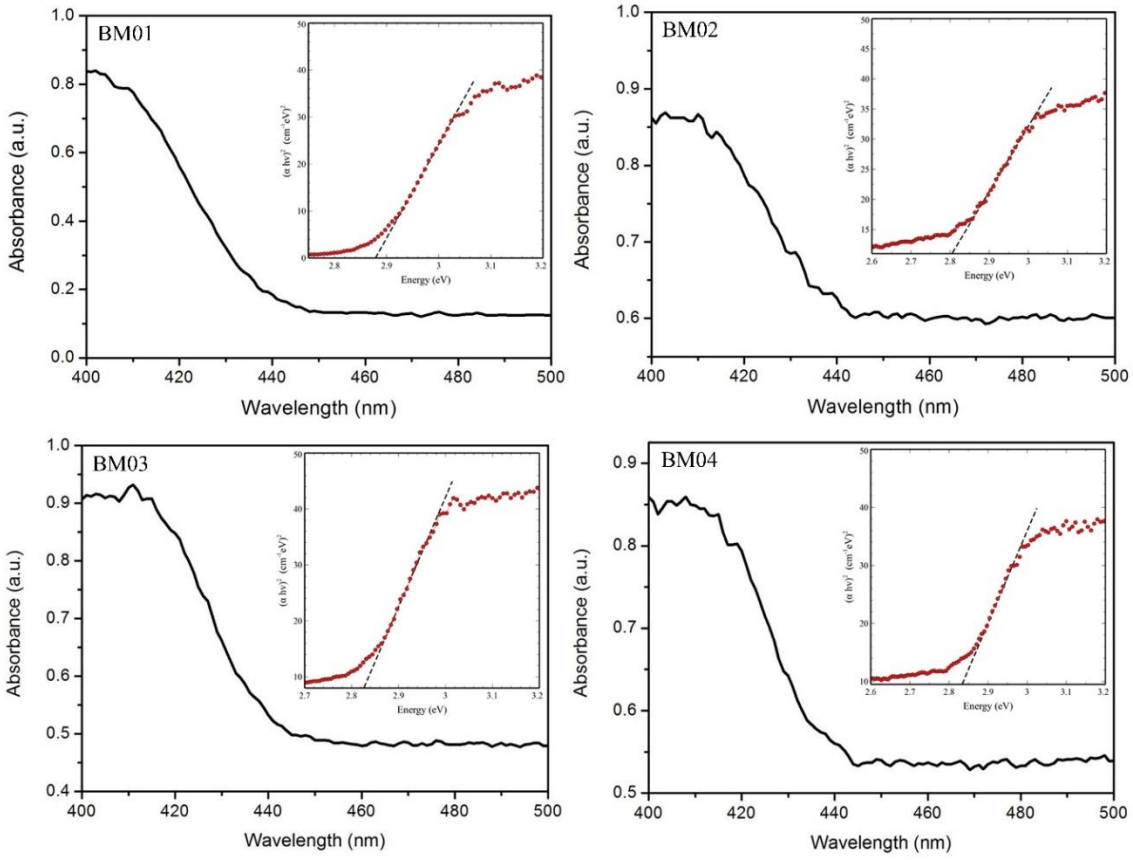

Figure 5 UV-Vis spectra of the samples. Insets are the Tauc plots.

Normally, nitric acid is used in the synthesis of Bi_2O_3 to avoid hydrolyzation of Bi^{3+} ions, and the needle- or rod- like morphologies are obtained because the presence of NO_3^- gives rise to the one-dimensional growth in the [001] direction [21]. However, some works reported the flower-like particles when used citric acid [22] or acetic acid [20]; in the case of acetic acid, the band gap is reduced from 2.88 eV of needle-like shape to 2.69 eV of the flower-like shape which is well comparable with our results. However, the hierarchical flower-like assembled microrods as presented in this work has not been reported yet. The citric acid plays a major role in the self-assembly that may be reasoned to the preferentially adsorption of the citric molecules on the tip of the microrods [23].

Conclusions

Monoclinic Bi_2O_3 microrods have been prepared by the facile chemical process in aqueous solutions. The obtained microrods are quite uniform in shape, but their lengths are in the range of 5 – 10 μm. They can also self-assemble into the hierarchical flower-like structures by using the citric acid. The band gap of the microrods decreases from 2.88 eV to 2.81 eV after the self-assembling process. Using PVP shortens the petals of the self-assembled flowers, however, the band gap does not change significantly. The results indicate that the band gap of Bi_2O_3 can be altered by particle morphology which would be useful in photocatalytic applications. Further study will focus on a control of size and shape of the microrods.

Acknowledgements

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