Rapid and Facile Synthesis of Monodisperse α-Bi_2O_3 Nanowires by Solution Precipitation Method

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Abstract. Monodisperse α-Bi_2O_3 nanowires with the diameter of 50–100 nm and the length-diameter ratio of 60–100, were synthesized successfully by solution precipitation method, an efficient and convenient route, with the assistance of oleic acid. X-ray diffraction (XRD) and field-emission scanning electron microscope (FE-SEM) were employed to characterize the obtained products. By analyzing the influential factors, it was found that the size and morphology of α-Bi_2O_3 nanowires were affected mainly by temperature, reagent concentration, drip feed speed, and reaction time. It was found that oleic acid played a crucial role in the formation process of nanowires. And the optimum synthesis conditions were identified to prepare the final products to meet the needs of application.

1. Introduction

Bi_2O_3 nanomaterials, especially nanowires, have attracted great attention recently, because of its physical properties, such as high refractive index[1], dielectric permittivity and oxygen ionic conductivity, as well as a remarkable photoconductivity and photoluminescence response[2]. So far, Bi_2O_3 nanowires have been successfully prepared by various methods including metal organic chemical vapor deposition (MOCVD)[3, 4], hydrothermal method[5, 6], and oxidative metal vapor transport deposition[7, 8], magnetron sputtering[9]. These techniques need expensive and specialized devices. And operation processes are tedious and inefficient.

In this paper, we prepared monodisperse α-Bi_2O_3 nanowires by solution precipitation method successfully at room temperature and atmospheric pressure, and studied critical influences on the size and morphology of Bi_2O_3 nanowires, such as temperature, reagent concentration, drip feed speed, and reaction time.

2. Materials and Methods

2.1. Materials

All chemicals were analytical grade reagents. Bismuth nitrate pentahydrate (Bi $(NO_3)_3 \cdot 5H_2O$), and nitric acid (HNO_3) were purchased from Beijing Chemical Reagent Company, China. Sodium hydroxide (NaOH) and heptane (C_7H_{16}) were purchased from Xilong Chemical Reagent Company, China. Oleic acid ($C_{18}H_{34}O_2$) and acetone (C_3H_6O) were purchased from Tianjin Fuchen Chemical Reagent Company. Deionized water was used throughout the experiments.

2.2. Preparation Method

A typical experiment process is as follows. 5 mmol $Bi(NO_3)_3 \cdot 5H_2O$ dissolved in 50 mL dilute nitric acid solution, and the concentration of solvent HNO_3 was 1.0 mol/L. 15 mL oleic acid, 15 mL heptane, and 50 mL acetone were sequentially added into the solution with continuous stirring. After stirring for 15 min, 40 mL 5 mol/L NaOH solution was added drop-wise into the above solution. And the mixture was kept stirring for another 8 h at room temperature. Subsequently, the resulting yellow precipitate was separated from the solution by centrifugation, and washed alternately with ethanol and deionized water for 3 times, then dried in a vacuum under 80 °C for 10

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h. Finally, the canary yellow powder of α-Bi_2O_3 was obtained.

2.3. Characterization

Surface morphologies of as-prepared Bi_2O_3 nanowires were studied using Hitachi S-4800 field-emission scanning electron microscopy (FE-SEM), operated on 15 kV. The crystal structure and phase purity of the products were determined by a Germany Bruker D8 Advance diffractometer using Ni-filtered Cu/Kα radiation (λ=1.5406 nm) by a scanning rate of 0.02^o s^{-1} in a range from 10^o to 70^o.

3. Results and Discussion

Fig.1 shows a typical XRD pattern of the final Bi_2O_3 nanowires. The peaks (2θ=27.47^o, 33.38^o, 46.46^o), marked by their indices (–121), (–202) and (041), were observed and in good agreement with the standard values of bulk α-Bi_2O_3 (JCPDS 65-2336). No other impurities, such as $Bi(OH)_3$, BiOOH, or organic compounds related to the reactants.

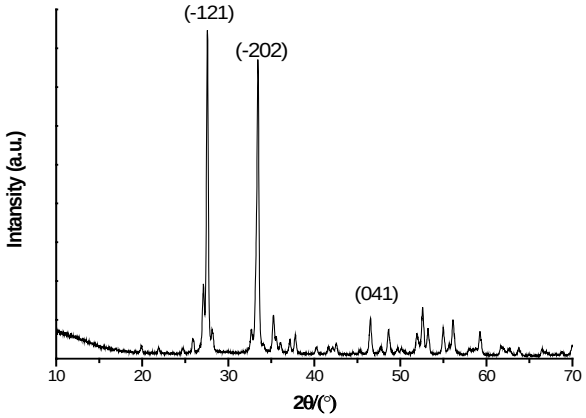

Fig.1. XRD pattern of the sample synthesized at room temperature.

Fig.2 shows typical SEM images of the α-Bi_2O_3 sample. There are long and straight nanowires with a diameter of about 100 nm and a length of about ten micrometers. The length-diameter ratio is more than 100, with uniform shape and smooth surface. Most of the nanowires aggregated together to bunch, side by side.

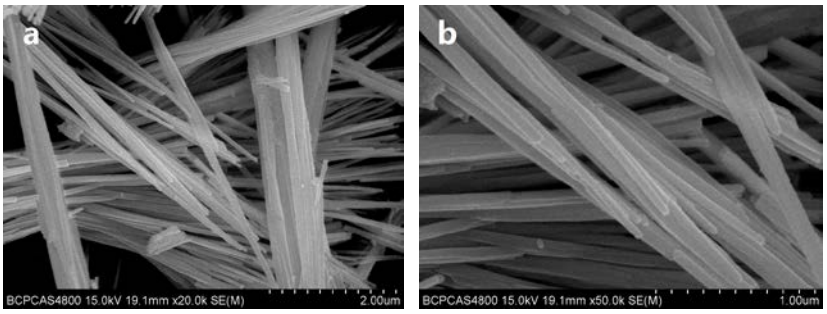

Fig.2. SEM images of the sample.

Further experiments show that the reaction time, temperature, reagent concentration, and drip feed speed have great influences on the size and morphology of the final Bi_2O_3 products. Fig.3 shows the effect of reaction time on the diameter of Bi_2O_3 products. It was found that nanowires possess the more uniform morphology and the small diameter, when reaction time ranged from 4 h to 6 h.

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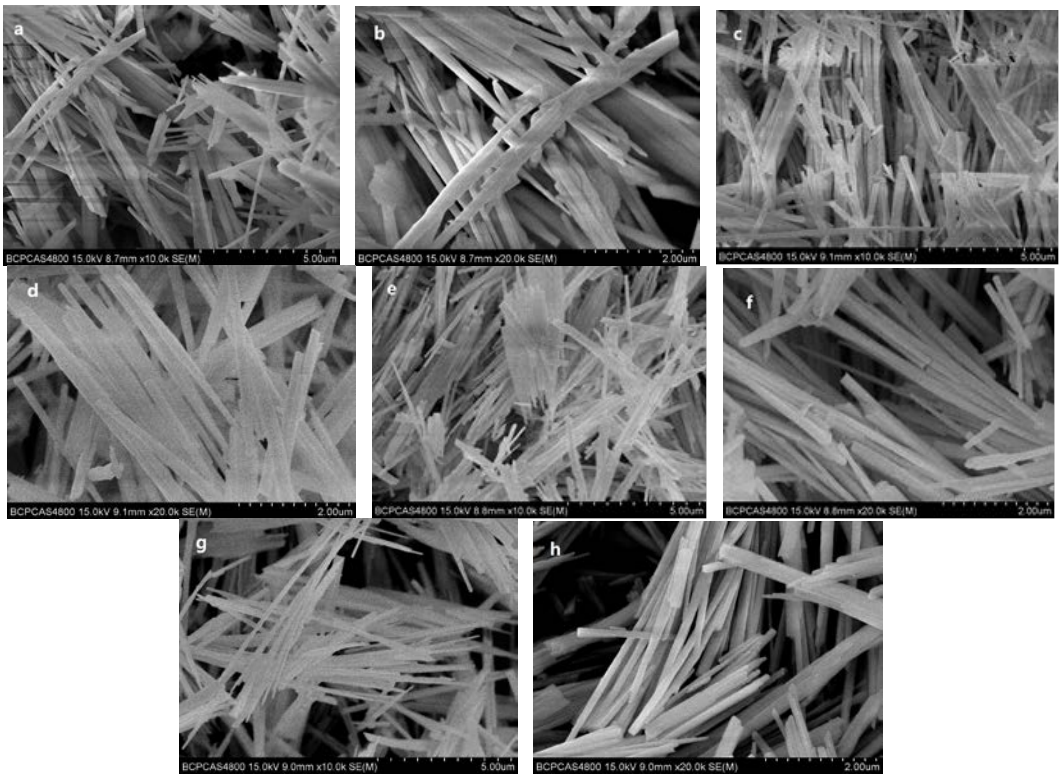

Fig.3. The effect of reaction time on the diameter and morphology of Bi_2O_3 products. (a) and (b) 0.5 h; (c) and (d) 2 h; (e) and (f) 4 h; (g) and (h) 6h.

The effect of drip feed speed on the diameter and morphology of Bi_2O_3 products was crucial, as shown in Fig.4. The results show that the diameter of α-Bi_2O_3 nanowires increased with the increase of drip feed speed. It was clear that the nanowires with better appearance were obtained when the drip feed speed was at 3.0 mL/min.

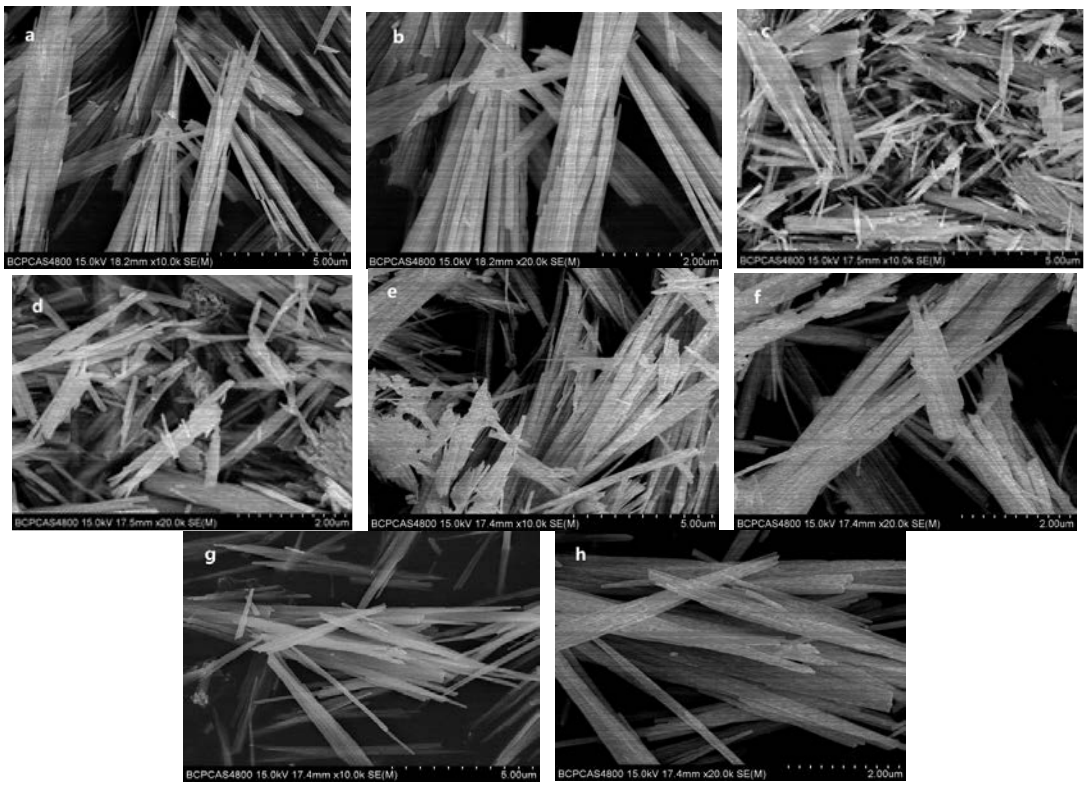

Fig.4. The effect of drip feed speed on the diameter and morphology of Bi_2O_3 products. (a) and (b) 3.0 mL/min; (c) and (d) 6.0 mL/min; (e) and (f) 9.0 mL/min; (g) and (h) 12.0 mL/min.

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The systhesis process of α-Bi_2O_3 nanowires was conducted at room temperature. However, when the reaction was carried on at 50 °C and 60 °C, it was found that formation mechanisim of nanowires was changed so that no nanowires were obtained, as shown in Fig.5.

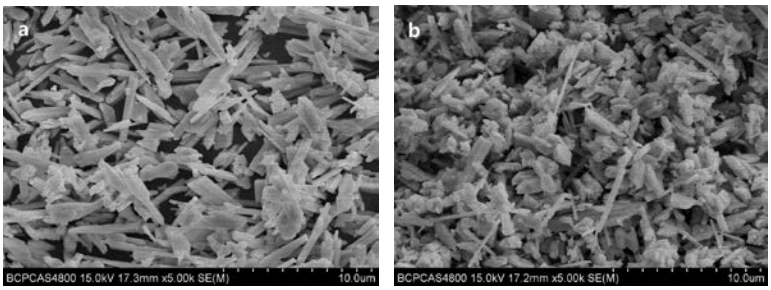

Fig.5. The effect of reaction temperature on the morphology of Bi_2O_3 products. (a) 60 °C; (b) 50 °C.

Further experiments show that Bi^{3+} concentration has a great influence on the morphology of Bi_2O_3 products. It was found that low concentration was not helpful to forming nanowires. And at lower concentration, flaky nanorods were obtained and tended to align themselves in parallel just like α-Bi_2O_3 nanowires did, and as-prepared Bi_2O_3 products had the tendency to grow into nanowires, as shown in Fig.6. So when $c(Bi^{3+})$ was 0.2 mol/L, nanowires with good morphology could be obtained.

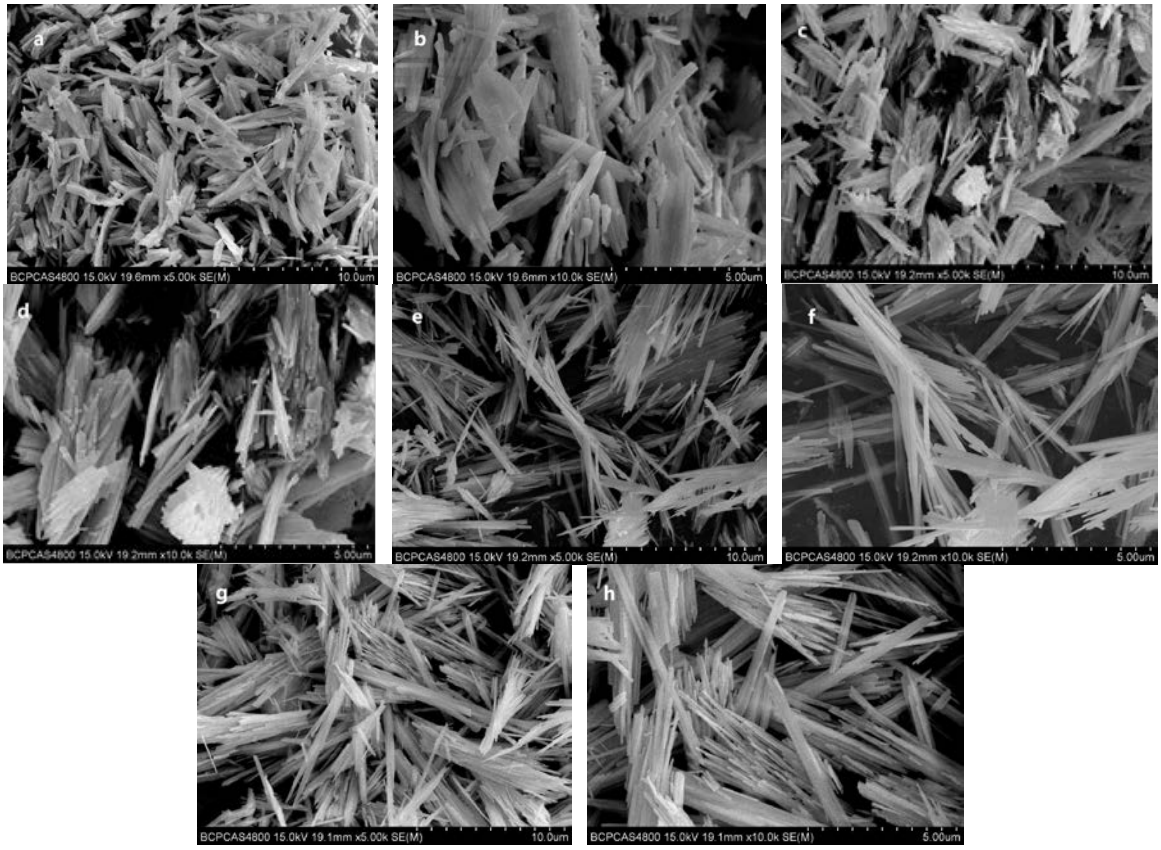

Fig.6. The effect of Bi^{3+} concentration on the diameter and morphology of Bi_2O_3 products. (a) and (b) 0.025 mol/L; (c) and (d) 0.05 mol/L; (e) and (f) 0.2 mol/L; (g) and (h) 0.4 mol/L.

The influence of OH^- concentration was also studied. These experimental results in Fig.7 indicate that the diameter of α-Bi_2O_3 nanowires increased, the length decreased and the length-to-width aspect ratio decreased with the increase of OH^- concentration. Also, it was found that both ends of as-prepared products became sharp, with the toothpick-like shape. When kept OH^- concentration at

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5.0 mol/L, the Bi_2O_3 nanowires with the diameter of about 50 nm and the length-diameter ratio of more than 100 were obtained.

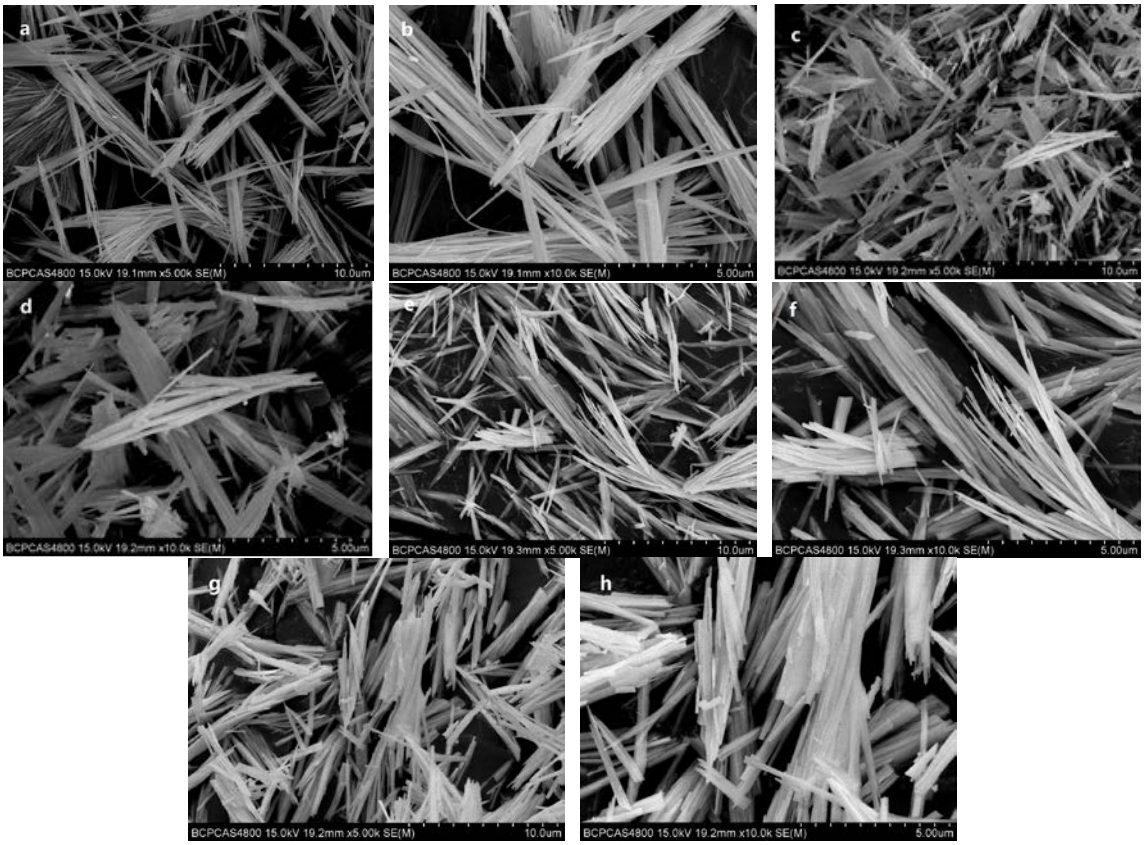

Fig.7. The effect of OH^- concentration on the diameter and morphology of Bi_2O_3 products. (a) and (b) 5.0 mol/L; (c) and (d) 7.0 mol/L; (e) and (f) 13.0 mol/L; (g) and (h) 15.0 mol/L.

4. Conclusion

In summary, we adopted a facile and mile solution synthesis route to obtain high quality α-Bi_2O_3 nanowires. The method has many advantages in comparison with other technologies, such as convenient, high yield, and low cost, because of the simple operation only at room temperature and ambient atmospheric pressure. It was found that oleic acid as capping agent plays an important role in the growth control of nanowires.

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References:

[1] H.T. Fan, X.M. Teng, S.S. Pan, C. Ye, G.H. Li, L.D. Zhang, Optical properties of δ-Bi_2O_3 thin films grown by reactive sputtering, Appl. Phys. Lett. 87 (2005) 231916.

[2] Y. Greenberg, E. Yahel, E.N. Caspi, C. Benmore, B. Beuneu, M.P. Dariel, G. Makov, Evidence for a temperature-driven structural transformation in liquid bismuth, Europhys. Lett. 86 (2009) 36004.

[3] H.W. Kim, J.W. Lee, C. Lee, Temperature-Controlled Fabrication of Crystalline beta-Bi_2O_3 Nanowires through an MOCVD Process, J. Korean Phys. Soc. 50 (2007) 1308-1311.

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[4] L.C. Tien, Y.C. Lai, Nucleation control and growth mechanism of pure alpha-Bi_2O_3 nanowires, Appl. Surf. Sci. 290 (2014) 131-136.

[5] L. Liu, J. Jiang, S. Jin, Z. Xia, M. Tang, Hydrothermal synthesis of β-bismuth oxide nanowires from particles, Cryst. Eng. Comm. 13 (2011) 2529-2532.

[6] C. Wu, L. Shen, Q. Huang, Y. Zhang, Hydrothermal synthesis and characterization of Bi_2O_3 nanowires, Mater. Lett. 65 (2011) 1134-1136.

[7] C.C. Huang, I.C. Leu, K.Z. Fung, Fabrication of delta-Bi_2O_3 nanowires, Electrochem. Solid-State Lett. 8 (2005) A204-A206.

[8] H.W. Kim, H.G. Na, J.C. Yang, H.S. Kim, J.H. Lee, K.H. Yoo, Fabrication and Characteristics of beta-Bi_2O_3 Nanowires Prepared by Heating a Mixture of In and Bi Powders, Electrochem. Solid-State Lett. 13 (2010) K67-K71.

[9] Sirota, Ben, Synthesis and Characterization of ZnO and Bi_2O_3 Nanowires Grown by Magnetron Sputtering, Carbondale: Southern Illinois University, 2011.

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