Photochemical synthesis of Bi$_2$Se$_3$ nanosphere and nanorods

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Abstract

A photochemical reaction route was developed to synthesize bismuth selenide (Bi$_2$Se$_3$) nanoparticles and nanorods. In an aqueous solution, bismuth nitrate (Bi(NO$_3$)$_3$) reacted with sodium selenosulfate in the presence of reducing agent and complexing agent, and the dispersed Bi$_2$Se$_3$ nanoparticles were obtained with the average size of 35 nm. The nanorods were prepared via an alumina template route in the same solution. We carried out experiments to study the formation mechanism in the morphology control of the products and found that series of factors played an effective role including the irradiation time, pH value, the reducing agents and the species of complexing agents. The products were characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM).

Keywords: Photochemical synthesis; Bi$_2$Se$_3$ nanoparticles; Semiconductor

1. Introduction

Synthesis and characterization of nanosized semiconductors have received much intensive research, owing to their potential applications and demonstration devices [1,2]. Main group metal chalcogenides, such as the A$_2$B$_3$VI (A=Sb, Bi, As; B=S, Se, Te) group compounds, have many applications in television cameras with photoconducting targets, thermoelectric devices and electronic and optoelectronic devices and in IR spectroscopy [3].

Bismuth triselenide (Bi$_2$Se$_3$), which belongs to a family of semiconductor materials, has potential applications in modern thermoelectric coolers and thermoelectronic and optical recording materials [4–6]. Thin films of bismuth selenide have been prepared by using various techniques, such as chemical bath deposition [7], solution growth [8], the SILAR [9] and electrodeposition method [10]. But only a few literatures reported on the preparation and characterization of nanocrystalline Bi$_2$Se$_3$ [11].

Here, we report a photochemical reaction route which is used to fabricate nanoparticles and nanowires at room temperature. Compared with the above methods, the present photodeposition technique is more convenient and environmental. The bismuth nitrate (Bi(NO$_3$)$_3$) and sodium selenosulfate were employed as Bi$^3+$ and Se$_2^-$ source, respectively. The sodium selenosulfate decomposed slowly under the ultraviolet irradiation and released Se$_2^-$ ions homogeneously in the presence of complexing agent and reducing agent. It was found that the irradiation time, the pH of the solution, the reducing agents and the species of complexing agents played important roles in the morphology control of the bismuth triselenide (Bi$_2$Se$_3$) nanomaterials.

2. Experimental section

The anode aluminum oxide (AAO) templates with pore sizes of about 80 nm were grown by potentiostatically anodizing aluminum plates (0.17 mm thick, 99.99%) in an aqueous solution of 3% oxalic acid. After the anodization, the remaining aluminum was etched by a 20% HCl–CuCl$_2$ mixed solution. Then the barrier layer was dissolved by using 5% H$_3$PO$_4$ and 20% H$_2$SO$_4$. 

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One gram ethylene diamine tetraacetic acid (EDTA), 0.5 g Bi(NO₃)₃·5H₂O (purchased from Beijing (China) chemical reagents factory) were put into a beaker with 40 ml of distilled water. The pH value was adjusted to 8 by NaOH, and then 1 g of ascorbic acid, 0.2 M Na₂SeSO₃, solution was added to the beaker in turn. After that, the pH value was adjusted to 10 again. 0.2 M Na₂SeSO₃ solution was prepared by stirring 0.2 M Se and 0.5 M Na₂SO₃ at 70 °C for 24 h. An alumina template with pores of 80 nm in diameter was immersed in the above solution. Then the mixture solution was placed in a glass beaker about 10 cm away from a high-pressure mercury lamp (λ≈290 nm) and exposed to ultraviolet irradiation for 3 h at room temperature. When the reaction was finished, black precipitates were obtained. The precipitates were centrifuged, washed several times with distilled water and absolute ethanol. The final product was dried in air at room temperature.

The products were characterized by powder X-ray diffraction (XRD) patterns, with an X’PERT (from Philips company). TEM images were obtained on a JEOL-JEM 200CX TEM at an accelerating voltage of 100 kV.

3. Results and discussion

Powder X-ray diffraction (XRD) was used to characterize the sample. The XRD pattern of the Bi₂Se₃ nanoparticles was shown in Fig. 1. The peaks in the pattern correspond to the reflections of hexagonal phase [12]. The TEM image of nanocrystalline Bi₂Se₃ prepared in the solution was shown in Fig. 2a. This image reveals that the nanocrystalline Bi₂Se₃ consisted of nearly homogenous monodisperse spherical grains. The average size of the particles was about 35 nm. The TEM image of Bi₂Se₃ nanowires synthesized in an alumina template was shown in Fig. 2b. It is shown that all the Bi₂Se₃ nanowires have a diameter of about 70–80 nm, which corresponds closely to the pore diameters. The nanowires are about 40 μm in length.

The effects of reducing agents, reaction time, pH value and complexing agents were investigated. Without the reducing agent ascorbic acid in the solution, Bi(NO₃)₃·5H₂O would hydrolyze to Bi(OH)₃ deposition. Hence, a white product was obtained instead of the expected grains. Appropriate pH value for adding the reducing agent ascorbic acid is 8 or higher, and the pH range of 9–11 is very optimal for the formation of Bi₂Se₃ nanoparticles and nanowires. The decomposition reaction would not happen at pH lower than 7 under the ultraviolet irradiation light for 10 h. When the pH value was higher than 12, the reaction was so fast that the formed particles would congregate in a very short time. Reaction time determined the crystal growth and the phase formation of the particles. The growth of the Bi₂Se₃ particles could be indicated by the color of the solution. When reaction time was less than 2 h, the decomposition reaction would not happen, and the color did not turn to dark. As the time went on, the color of the solution turned deeper and at last, when the reaction time was over 5 h, the color of the solution became dark brown, which showed the formation of crystalline Bi₂Se₃. The complexing agents could reduce the concentration of free Bi³⁺ in the solution and affected the reaction rate. EDTA was chosen as the complexing agent in the experiment. The complexing strength of nitrilotriacetic acid (NTA) with Bi³⁺ is weaker than that of EDTA. Therefore, when NTA is used as the complexing agent, the reaction rate is so fast that large aggregation can be observed. The result is shown in Fig. 3. Initially, in this reaction, the complexing action between Bi³⁺ and EDTA leads to the formation of Bi-EDTA; in the presence of photoirradiation, H₂O can be reduced to H⁻ and OH⁻ radicals. The H⁻ radical can further catalyze the reaction between SeSO₃²⁻ and reducing agents.

Fig. 1. Powder XRD pattern of the Bi₂Se₃ nanocrystals prepared by photosynthesis.

Fig. 2. TEM images of the as-prepared Bi₂Se₃ nanocrystals when EDTA was used as complexing agent. (a) Bi₂Se₃ nanoparticles prepared in the solution and (b) Bi₂Se₃ nanowires prepared in the AAO template.
ascorbic acid and gave rise to the Se$^{2-}$ ions. The Se$^{2-}$ ions could combine with Bi$^{3+}$ ions that were released from the Bi-EDTA complexes to form Bi$_2$Se$_3$. The photoirradiation and complexing agents could confine the release of the Bi$^{3+}$ and Se$^{2-}$ ions in a low rate. In solution, the nascent Bi$_2$Se$_3$ particles would grow into the dispersed particles, and in the present of the AAO template, the nascent particles would be absorbed on the bottom and surface of template wall and continued to grow into the wire-like structure.

The reaction mechanism of photochemical synthesis of Bi$_2$Se$_3$ may be shown as follows:

$$\text{Bi} + \text{EDTA} \rightarrow \text{Bi}$^{3+}$ + EDTA$^{3-}$ (1)

$$\text{H}_2\text{O} \xrightarrow{\text{hv}} \text{H}^+ + \text{OH}^- \quad (2)$$

$$2\text{H}^+ + \text{SeSO}_3^{2-} \xrightarrow{\text{hv} + \text{Vc}} \text{Se}^{2-} + 2\text{H}^+ + \text{SO}_3^{2-} \quad (3)$$

$$2\text{Bi}^{3+} + 3\text{Se}^{2-} \rightarrow \text{Bi}_2\text{Se}_3 \quad (4)$$

$$n \text{Bi}_2\text{Se}_3 \rightarrow (\text{Bi}_2\text{Se}_3)_n \quad (5)$$

4. Conclusion

In summary, Bi$_2$Se$_3$ nanomaterial can be successfully prepared via a photochemical route from an aqueous solution of bismuth nitrate in the presence of complexing agent EDTA and reducing agent ascorbic acid (Vc) at room temperature. In the reaction, the reducing agents, the reaction time and the pH value, the complexing agents play important roles on the formation of Bi$_2$Se$_3$. A possible reaction mechanism is also proposed in this paper. It is found that this is a convenient, mild, efficient and environmentally friendly route for the formation of Bi$_2$Se$_3$. We consider that photodeposition directly in the AAO template is a simple and efficient method to produce II–VI group compound semiconductors nanorods. Next, we will devote to the synthesis of other materials via the same route and the research on the optical properties of the as-prepared materials.

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