A RAPID PREPARATION OF BISMUTH NANOWIRES VIA A MICROWAVE-ASSISTED POLYOL METHOD

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Bismuth nanowires with width of 10–20 nm, and length of ~200 nm were rapidly prepared from the reduction of Bi(NO₃)₃·5H₂O by ethylene glycol (EG) in alkaline solution under microwave irradiation for 5 minutes. The product was characterized by XRD, TEM and SAED. The effects of the microwave irradiation, the alkaline solution, and the solvent on the formation of bismuth nanowires were also investigated.

Keywords: Bismuth nanowires; polyol method; microwave-assisted.

1 Introduction

One-dimensional (1D) nanostructures and nanomaterials (including nanorods, nanowhiskers, nanowires, nanobelts and nanotubes) have recently attracted great attention because of their potential value in both theoretical and practical areas. Considerable efforts have been placed on the synthesis of these 1D nanostructures and nanomaterials. Among various methods for the preparation of 1D nanostructures, liquid-phase chemical methods are more promising in terms of low cost, low processing temperature, simplicity and potential for large-scale production. Sovothermal process, sonochemical method, and microwave-assisted route are among the promising “solution routes” to nanostructures.

Bismuth is of great interest in terms of both theory and application. Its small effective mass (~0.001 m0) and large mean free path (~0.4 mm at 4 K) make nanosized Bi an interesting system for studying quantum confinement effects. And the bismuth materials have recently been suggested to have enhanced thermoelectric properties at room temperature. However, the synthesis of nanosized Bi is somewhat difficult, as the relatively low melting point of Bi (271.3 °C) makes most of the existing high-temperature approaches inappropriate.

The low-temperature (100~200°C) sovothermal synthesis method for the preparation

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of Bi nanowires and nanotubes has been reported. However, these methods need relatively long time in the preparation of Bi materials.

Herein we report a rapid microwave-assisted polyol method to bismuth nanowires. Polyol method, in which a polyol (for example, EG) acted as both the solvent and the reducing reagent, was employed to prepare nanoparticles. Some of these reactions were achieved by the conventional heating, but, very recently, microwave heating was used. Microwave heating has unique effects compared with the conventional heating, such as rapid volumetric heating, selective heating and energy saving. These effects make microwave heating a promising technology that can increase reaction rates, shorten reaction time, and enhance reaction selectivity. In addition, some researchers think that microwave irradiation may have some “non-heating effects”. The microwave irradiation makes the polyol process rapid and simple, and greatly expands its applications. Nanoparticles of Pt and Ag, CdSe, Cd1-xZnxSe, TiO2, Se and Bi2Se3, etc. were prepared using this microwave-assisted polyol method. However, most of these nanoparticles prepared were spherical in shape and were not 1D nanostructures. Here, we report the preparation of Bi nanowires by this method, without using any template or surfactant. It is a simple, fast and low-cost method for the fabrication of 1D Bi nanostructures.

2 Experimental

All reagents were commercially available and used without further purification. The microwave-assisted reaction was carried out in a domestic microwave oven (National) equipped with a refluxing system (operate frequency, 2.45GHz; power, 365W).

In a typical procedure, bismuth nitrate (Bi(NO3)3·5H2O, 1 g) and potassium hydroxide (KOH, 2 g) were dissolved in 30mL of EG. And then the system was heated in the microwave oven for 5 minutes under refluxing. It was observed that a great amount of black precipitate occurred during the reaction. After cooling to room temperature, the precipitates were centrifuged, washed with water and absolute ethanol in sequence, and dried under vacuum.

The crystal structures and compositions of the products were analyzed by powder X-ray diffraction (XRD). The obtained samples were mounted on glass substrates and the XRD pattern was recorded using a Philip X'pert X-ray diffractometer with Cu-Kα radiation (λ = 1.5418Å). The morphology and size of the products were characterized by transmission electron microscope (TEM) and selected area electron diffraction (SAED), using a JEM-200CX (JEOL, 200 kV) transmission electron microscope.

3 Results and Discussions

Figure 1A shows the TEM and SAED (the inset) images of as-prepared bismuth nanowires with width of 10~20 nm, and length of ~200 nm. The SAED image indicates that these nanowires were crystalline. Due to the relatively low melting point of Bi, the prepared samples were highly sensitive to electron beam irradiation during the TEM examination. After several seconds of intensive electron beam irradiation, some bismuth
nanowires had melted into small droplets (as shown in Figure 1B). Similar phenomena were also reported previously.  

Figure 1. A) TEM image and SAED pattern (inset) of bismuth nanowires. B) TEM image of bismuth nanowires after several seconds of intensive electron beam irradiation.

To study the crystalline structure of the product, XRD measurement was carried out at room temperature. The XRD pattern shown in Figure 2 reveals that all of the reflection peaks can be readily indexed as rhomb-centered hexagonal phase Bi (JCPDS Card No. 44-1246). In the figure, no peaks of any other phases were detected, indicating the high purity of the product.

Figure 2. XRD pattern of the as-prepared Bi nanowires

Some factors, such as microwave irradiation, alkaline solution, and solvent, have effects on the formation of bismuth nanowires.

Microwave irradiation is crucial in this rapid polyol process. In a comparing experiment, almost no bismuth precipitate was produced after the system was conventionally heated (without microwave irradiation) in an oil-bath at 180°C for 46 h and then at ~197°C (the boiling point of EG) for 6 h. This indicates that the conventional heating is not the critical factor in the formation of bismuth nanowires. Microwave is a
high-frequency electromagnetic wave, containing both electric and magnetic field components. In the case of a liquid-phase microwave reaction, a coupling between the oscillating electric field (2.45 GHz) and the permanent dipole moment of the molecules results in molecular rotations, which leads to rapid volumetric heating of the liquid phase. Such dielectric heating is capable of promoting the reaction to produce Bi nuclei. Compared with conventional heating methods, microwave dielectric heating presents a much more rapid and simultaneous nucleation due to the fast and homogeneous heating effects of microwaves. With microwave irradiation of reactants in polar solvents, temperature and concentration gradients can be effectively avoided, providing a uniform environment for the nucleation, which is very important to the final formation of uniform and regular wires. Microwave irradiation is also capable of inducing the preferential 1D growth of the Bi crystals. One possible hypothesis of microwave-induced effects is the generation of localized high temperatures and pressures at the reaction sites to enhance the reaction rate in a manner analogous to that of ultrasound waves, where both localized transient high pressures and temperatures are produced during reactions, which is favorable for the 1D growth of Bi.\(^{39}\)

In another comparing experiment, when the reaction was carried out under sonication (using a sonicator (JY 92-2D, Ningbo Scientz Biotechnology Co., LTD) with an immersion ultrasonic probe, the power used was 600W) instead of microwave irradiation, precipitate began to occur only after 3 h, and irregular bismuth nanoparticles were obtained at last. Obviously, microwave irradiation is superior to conventional heating and sonication in this reaction.

Alkaline solution played an important role for the formation of the Bi nanowires. Without alkali, white precipitate was observed firstly during the reaction. Then the precipitate began to turn into black after 0.5 h, and almost pure bismuth was obtained after 1 h. However, in alkaline solution, black precipitate occurred rapidly (~1 min), and no white precipitate was observed during the reaction. This suggests that the addition of KOH may change the reaction mechanism and result in the rapid formation of bismuth.

Solvent is another important factor. When water was added into EG, the reaction was greatly slowed down, and longer time was need for the formation of bismuth. This can be attributed to the reducing of the boiling point in the system and the decrease of the reducing potential of EG. In view of the promoting effect of the temperature on the polyol reduction, we tried to replace EG by glycerol, the boiling point of which is much higher (~290°C). Indeed the reaction was carried out faster and more vigorously. The system boiled vigorously and gave out large amount of black precipitate almost immediately. However, the as-prepared bismuth was found to be a mixture of spherical particles and blocks with size of hundreds of nanometers, because of the higher boiling point of glycerol than the melting point of bismuth.

In addition, reaction time should be controlled strictly. Longer reaction time will lead to agglomeration. After microwave irradiation for 30 min, spherical and hexagonal blocks of bismuth were observed (Figure 3).
Preparation of Bismuth Nanowires

Figure 3. TEM image of the bismuth obtained after microwave irradiation for 30 min.

4 Conclusions
In summary, we have prepared bismuth nanowires via a microwave-assisted polyol process. The outstanding advantage of our method is its simplicity and rapidity. Bismuth nanowires with the width of 10–20 nm and the length of ~200 nm were obtained within 5 min. The microwave irradiation is crucial in this process. The alkaline solution and the solvent have effects on the reaction mechanism, the reaction speed, and the morphology of the products. This method provides a convenient and rapid route to the fabrication of one-dimension structural metallic materials and hopes to be a generic approach.

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References