研究简报

热化学法合成金属铋纳米棒

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Synthesis of Bismuth Nanorod *via* Thermal Process

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Abstract: Bismuth with rod-like shape was prepared by refluxing an aqueous dispersion of spherical colloids. The spherical colloids of bismuth were generated by reducing bismuth nitrate with ascorbic acid in the presence of cethyltrimethylammonium bromide (CTAB) and ethylene diamine tetraacetic (EDTA). The mixed solution was refluxed at temperature of 60~70 ℃ for about 5 hours to get bismuth nanorods with a diameter about 10~30 nm. Experimental results showed that this method could facilitate the growth of these rod-like nanomaterials. Various techniques such as transmission electron microscopy (TEM), selected-area-electron diffraction (SAED), and x-ray diffraction (XRD) have been used to characterize the nanorods.

Key words: bismuth; nanoparticles; cethyltrimethylammonium bromide

0 Introduction

Low-dimensional systems represent the important frontiers in advanced material research. Quantum confinement of electrons in low-dimensional systems provides a powerful tool for manipulating their optical, electrical and thermoelectric properties[1,2]. It is generally accepted that one dimensional (1D) nanostructure provides a good system to investigate the dependence of electrical and thermal transport or mechanical properties on dimensionality and size reduction (or quantum confinement). There were many reports about the fabrication of 1D nanostructured materials. Xia group[3] synthesized the silver nanowires based on the polyol process. Murphy group[4-6] used the same strategy in the presence of a rod-shaped micelle for template-mediated shape control to synthesize metallic nanorods. Martin group[7] also reported synthesis of 1D gold or silver nanowires using the electrochemical deposition or vacuum melting and pressure injection process in the certain anodic alumina template. Although the 1D nanomaterials could be synthesized using a number of advanced nanolithographic techniques, such as electron-beam (e-beam) or focused-ion-beam (FIB) writing, proximal probe patterning, and X-ray or extreme-UV lithography, further development of 1D nanostructures from a diversified range of materials, rapidly, and at reasonably low costs, still requires great ingenuity. In contrast, unconventional routes based on chemical synthesis might provide an inter-

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esting method for preparing 1D nanostructures in terms of material diversity and high volume production.

Theoretical calculations predict that the nanostructured semimetal bismuth should have an enhanced thermoelectric figure of merit[8~11]. Bismuth has the smallest electron effective mass among all known materials. Quantum confinement effects in bismuth are more pronounced and can be observed in nanostructures of larger diameter than for any other nanostructural systems. Bismuth with small enough diameter undergoes a transition from a semimetal with a small band overlap to a semiconductor with a small indirect band gap, thus allowing the unusual properties of bismuth to be available as a semiconducting material as well as a semimetal.

There were some reports on synthesizing nanosized bismuth through the methods of low-temperature hydrothermal reduction, electrochemical deposition, and vacuum melting etc[12~18]. In the present work we report a simple method to synthesize bismuth nanorods via thermal process with a surfactant cethyltrimethylammonium bromide (CTAB) and complexing agent (EDTA). The ascorbic acid (AA) was employed to reduce the $Bi(NO_3)_3$ in the reaction. The effect of complexing agents and capping agents on the reaction was also investigated. The experimental results showed that the product could be prepared in mild conditions and could be stable for several weeks.

1 Experimental

All reagents including bismuth nitrate ($Bi(NO_3)_3$), ascorbic acid (AA), ethylene diamine tetraacetic acid (EDTA), hexadecyltrimethylammonium bromide (CTAB), and sodium hydroxide (NaOH) were analytical pure grade, purchased from Huakang Co. Chemical Reagent Factory (China), and were used without further purification. Distilled water was used in the experiments.

In a typical procedure, 5 $g \cdot L^{-1}$ $Bi(NO_3)_3$ was added into 10 $g \cdot L^{-1}$ EDTA aqueous solution, and then 10 $g \cdot L^{-1}$ ascorbic acid (AA) was added. The pH value of the resulting solution was adjusted to the range of 10 ~ 11 by addition of NaOH aqueous solution. At last, 20 $g \cdot L^{-1}$ of CTAB was added into the solution. The mixture was refluxed and stirred for about 5~6 hours at 60~70 ℃ to get the bismuth colloid. The colloid was separated by high-speed centrifugation for 5 minutes and washed with distill water twice.

The samples were characterized by powder X-ray diffraction (XRD) at a scanning rate of 4°·min^{-1} in the 2θ range from 10° to 80°, using Cu $K\alpha$ radiation (λ = 0.154 18 nm) and a nickel filter on Philips X′pert X-ray diffractometer. The morphology of the samples was studied on a JEM-200CX transmission electron microscope (TEM) using an accelerating voltage of 200 kV.

2 Results and discussion

XRD pattern revealed that all of the reflection peaks were indexed as hexagonal rhomb centered phase bismuth (JCPDS Card No. 05-0519) [space group: $R\bar{3}m$ (166)], as shown in Fig.1. Lattice constants calculated from the diffraction data corresponded to the literature values (a=0.454 6 nm, c=1.185 2 nm). These data indicated that the reduction of Bi^{3+} was completed under the present conditions, and the final product had little impurity. Fig.2 was the typical TEM image of the final product. It was obvious that the bismuth nanorods had uniform width and the mean diameter was about 20 nm. According to the TEM image the length of the rods was calculated to be about 120 nm and the aspect ratio to be about 6. Although there were some other shapes of bismuth existed in the product, main shapes were nanorods. The corresponding electron diffraction (ED) pattern (inset of Fig.2) clearly shows three diffused diffraction rings, which can be characterized as (101), (012) and (110) plane from inner to outer, respectively, through calculating the ratio of the corresponding radii. This also indicates the crystalline nature of the as-prepared

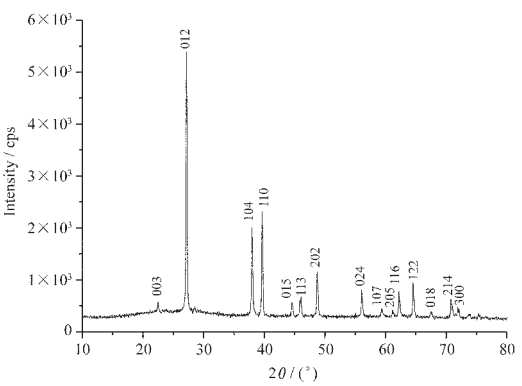


Fig.1 A typical XRD pattern of the as prepared bismuth sample

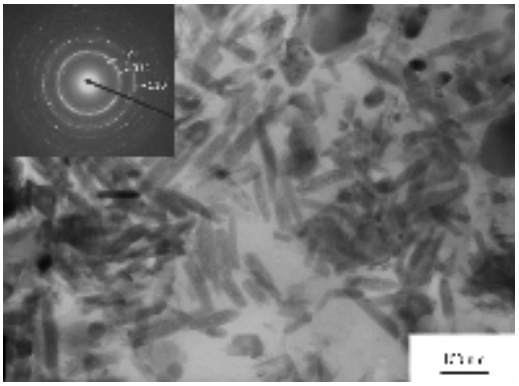
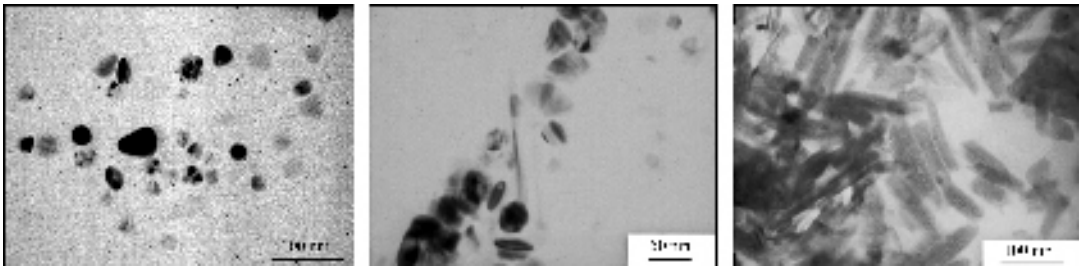


Fig.2　TEM image of the bismuth nanorods, together with their selected-area-electron-diffraction pattern (shown as the inset)

samples.

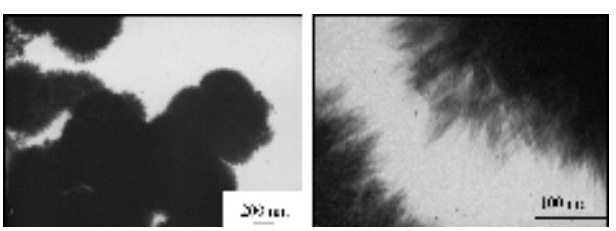
Li and Qian groups[11,12] used the low-temperature controlled hydrothermal reduction method to prepare bismuth nanotubes since metallic bismuth had the pseudolayered structure similar to that of rhombohedral graphite. This structure indicated the phosphorus nanotubes were stable, so they used the hydrothermal reduction to make the layered bismuth curl to form the tube-like bismuth. In the experiment, the effect of reaction time on the shapes of the product was studied. Initially, the bismuth tended to form spherical particles. With the increase of reaction time, the bismuth grew into the rod-like shapes gradually (Fig.3).



(a)　(b)　(c)

Fig.3　TEM images of different bismuth products at different reactive time
(a) 2 hours, (b) 4 hours, (c) 6 hours

Different from previous report, the synthesis of bismuth nanorods, somewhat similar to shape-controlled synthesis of spheroidal and rodlike gold or PbO_2[5,20], herein we used the same growth strategy in the presence of a rod-shaped soft template for shape control. The CTAB played an important role in determining the morphology of the final product. This process involved two steps: first, the formation of small size spherical bismuth nanoparticles, and second, growth of the prepared spherical particle in rod-like micellar environment. Initially, the growth rates of different crystal facets were quite different, and also there were some competition between the reduction rates and the rates of polymer capping agent. For a spherical single-crystalline particle, its surface must contain high-index crystallography planes, which possibly results in a higher surface energy. Facets tend to form on the particle surface to increase the portion of the low-index planes. With the influence of other factors, the particles could grow towards some selected directions to get the final shapes. In this work, the CTAB was possibly adsorbed on certain crystal planes to induce the growth of some different plane facets. This could make the bismuth particles grow into some preferred directions to form the rod-like shapes. When the reaction time reached 12 hours, the morphology of sample was shown in Fig.4. It seemed that when the reaction time was increased, the rods tended to aggregate together to form a large sphere. At the edge of these spheres, needle-like samples were observed. The possible mechanism about this growth direction is still an open question.



(a)　(b)

Fig.4　TEM image of the sample reacted for 12 hours (a), and the higher resolution image of the product (b)

The different experimental conditions also had a great influence on the reductive reaction. The ascorbic acid was employed as the reducing agent for Bi^{3+} salt in the reaction system. It was a mild reducing agent and cannot reduce the bismuth salt in the acidic en-

vironment. Therefore, the pH value in this reaction was very important for the reaction to occur and complete. The $Bi(NO_3)_3$ was easy to hydrolyze to become $BiONO_3$ precipitate in the aqueous solution. Meanwhile, Bi^{3+} could form the $Bi(OH)_3$ precipitate in the alkaline solution. Therefore, it was necessary to make the Bi^{3+} stable in the pH > 9.0 aqueous solution. EDTA could coordinate with Bi^{3+} to form $Bi(EDTA)^+$ and the stabilizing constant $K=10^{27.8}$. Therefore, the EDTA could make the Bi^{3+} stabilize in the aqueous solution quite well. Because of the complex $Bi(EDTA)^+$, the pH value of the mixed solution could be adjusted to about 11~12 to ensure the reaction to go towards the right direction. However, if the pH value was above 12, the Bi^{3+} would form $Bi(OH)_3$ which was difficult to transfer to other form, and thus obstructing the reductive reaction. In this experiment, through adjusting the concentration of EDTA, the speed of releasing Bi^{3+} could be controlled and the speed of the reductive reaction could be lowered to a certain extent. Low reactive speed was beneficial to the growth of nanocrystal. When the concentration of the EDTA was very low, the Bi^{3+} could not dissolve in the aqueous solution. The extremely high molar ratio resulted in the sluggish reaction and the transfer ratio remained in a very low level even after 5~6 hours in the system. However, the sizes and shapes of the bismuth particles remained almost unchanged under the high ratio of EDTA vs bismuth salt.

3 Conclusions

A simple chemical method was suggested to prepare the bismuth nanorods. The experimental conditions were mild and easy to achieve uniform shape samples. The nanorods had narrow size distribution and the mean width was about 20 nm which was lower than the Bohr radius of bismuth. This kind of structure was beneficial to the combination of the small electron effective mass with low thermal conductivity of bismuth. Further work would focus on synthesizing the more uniform bismuth nanorods and studying the transport properties of one-dimensional system.

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