Synthesis and Characterization of Triangular Bismuth Nanoplates

Ruiling Fu,† Shu Xu,† Yi-Nong Lu,‡ and Jun-Jie Zhu*,†

Department of Chemistry, Key Lab of Analytical Chemistry for Life Science, Nanjing University, Nanjing 210093, China, and College of Materials Science and Engineering, Nanjing University of Technology, Nanjing 210009, China

Received September 11, 2004; Revised Manuscript Received November 2, 2004

ABSTRACT: Monodispersed bismuth was successfully prepared as triangular nanoplates via a simple thermal process. Refluxing provided the driving force to facilitate the Ostwald ripening process growth of the platelike materials. All the nanoplates were highly oriented single crystals with the (001) planes as the basal planes. The crystal growth process and the influence of pH value, complexing agent, and surfactant were investigated. The characterization of mid-infrared showed that the as-prepared sample transferred from a semimetal to a semiconductor.

Introduction

Over the past decade, there has been a dramatic interest in both the preparation and the properties of nanocrystalline materials. Such materials possess several advantages compared with the bulk materials, which can be used for efficient transport of electrons and optical excitations and are expected to be critical to function and integration of nanoscale devices. So they have great potential in electronics, catalysis biological labeling and so on. Meanwhile, they can provide an ideal testing system to measure the surveying properties under the various physical limitations. Currently, the majority of this field has focused on semiconductor particles, transition metal, silver, and II–VI composite compounds. However, little work has been directed toward the formation and fundamental properties of nanocrystalline main-group metals.

Bismuth, in bulk form, is a semimetal with a small band overlap (38 meV at 5 K) and a very anisotropic electron effective-mass tensor. 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 even at larger diameter. Theoretical calculations predicted that nanostructured semimetal of bismuth might have an enhanced thermoelectric figure of merit. On the other hand, the bismuth also holds promise for optical applications. For example, quantum wells, quantum dots, and quantum wires usually have to be doped to populate the lowest subband and to allow for optical excitation of the electrons to a higher subband. 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.

A few techniques have been developed to fabricate the nanosized metal or semimetal materials. Different from the gas-phase approach that can only generate nanostructured materials with well-defined shapes in low fields, solution-phase methods have the potential to synthesize many materials into nanostructures with a range of well-defined morphologies and in bulk quantities. However, the solution-phase routes for the synthesis of nanostructured bismuth were not well developed. Recently, there were some groups fabricating bismuth nanotubes by using a low-temperature hydrothermal reduction method with bismuth nitrate and different reducing agents. Some references reported on the synthesis of nanostructured bismuth using electrochemical deposition, vacuum melting, and pressure injection process in a certain anodic alumina template. The decomposition of Bi[N(SiMe 3)2] 3 to fabricate bismuth nanoparticles and nanowires was also reported. However, the preparation of nanostructured Bi by some simple methods still needs exploration because of the wide applications.

In this paper, we reported a simple thermal process to fabricate bismuth nanoplates. The products were characterized by techniques such as X-ray powder diffraction (XRD), transmission electron microscopy (TEM), electron diffraction (ED), thermal gravimetric analysis (TGA), inductively coupled plasma (ICP), CHN element analysis and infrared spectroscopy (IR). The TEM observation described a clear process of Ostwald ripening. In the initial stage, bismuth nanoparticles of about 5 nm were formed as the seeds through a reduction reaction, and then a rapid dissolution and growth process made seeds grow to the uniform B nanoparticles. Structural characterizations indicated that these platelike crystals were highly oriented single crystals with (001) planes as the basal planes. Infrared spectroscopy measurements indicated that the band gap of the final products increased compared with the common bulk bismuth.

Experimental Section

All the reagents including bismuth nitrate (Bi(NO 3) 3), ascorbic acid (AA), ethylenediaminetetraacetic acid disodium salt (Na 2EDTA), poly(vinyl pyrrolidone) (PVP-K30, M w 40 000), and sodium hydroxide (NaOH) were analytical pure grade purchased from Huakang Co. Chemical Reagent Factory.

10.1021/cg049686n CCC: $30.25 © 2005 American Chemical Society
Published on Web 04/26/2005
weight of the final product began to increase. We

265.00 °C, which was higher than Bi melting point, the

loss indicated that the polymer content in final product

600.00 °C at 20.00 °C/min. In the range of 20.00

Figure 2 showed the TGA result, heating from 20.00 to

determine the polymer content of the final product.

Figure 1. A typical XRD pattern of the obtained bismuth

product.

(China) and were used without further purification. Distilled

water was used in our experiments.

In a typical procedure, 0.002 mol/L Bi(NO₃)₃ was added into

0.01 mol/L Na₂EDTA aqueous solution, and then some 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, a certain amount of PVP (about

0.0016 mol/L) was added into the solution. The solution was

refluxed at the boiling point about 12 h to get the black

precipitate. The products were purified by centrifugation. In

this case, the mixture was centrifuged at 9000 rpm for 10

minutes, and the products were washed with distilled water

and ethanol three times. The products were characterized by

XRD, TEM, high-resolution (HR)/TEM, TGA (Pyris 1 TGA,

PerKin Elmer), ICP (ICP, J-A 1100, USA Jarrell-Ash), CHN

element analysis (CHN-O-Rapid, Germany Foss Heraeus), and

IR.

The samples were characterized by powder X-ray diffraction
(XRD) at a scanning rate of 2°/min in the 2θ range from 10°
to 80°, using Cu Kα radiation (λ = 1.5418 Å) on Philips ARL
XTRA diffractometer. The morphology of the samples was
studied on a JEM-200CX transmission electron microscope
(TEM) using an accelerating voltage of 200 kV and high-
resolution TEM (HRTEM, using a JEOL JEM 2010, 200 kV).
The infrared optical transmission was measured as a function
of frequency at room temperature using a BRUKER VECTOR
22 IR spectrophotometer.

Results and Discussion

Component and Morphology Characterization

of Bismuth Nanoplates. XRD measurements were

used to determine the crystalline phase of the as-

prepared powders. The XRD pattern of the product is

shown in Figure 1. All the diffraction peaks can be

indexed to be hexagonal rhomb-centered phase bismuth

(JCPDS card no. 05-0519) [space group, R̅3m (166)] with

cell parameters of a = 4.545 Å and c = 11.83 Å, which

are in good agreement with the literature values (a =

4.546 Å, c = 11.852 Å). The intensities and positions of

the peaks match those data reported in the literature

very well. No peaks of any other phases are detected,

indicating the high purity of the product.

Thermal gravimetric analysis (TGA) was used to
determine the polymer content of the final product.

Figure 2 showed the TGA result, heating from 20.00 to
600.00 °C at 20.00 °C/min. In the range of 20.00–265.00
°C, the weight loss was caused by the disappearance
of polymer coated on the surface of the particles. The
loss indicated that the polymer content in final product
was about 1.39%. When the temperature was above
265.00 °C, which was higher than Bi melting point, the
weight of the final product began to increase. We

supposed that the increase might be caused by the
reaction between Bi and N₂ to form BiN. At the same
time, we used ICP and CHN element analysis to
examine the purity of the as-prepared sample. Table 1
presents the element analysis of the sample, which
shows little nitrogen, carbon, and hydrogen in the final
sample. The result of the ICP showed that the percent-
age of bismuth in the sample was 102.43%, which was
in the range of experimental and instrumental error.

All these measurements indicated the high purity of as-
prepared sample.

The dimension and morphology of the product were
examined by TEM measurements. A representative
TEM image is shown in Figure 3a. Statistical analysis
of the sample showed that the triangle edge length
varied from 130 to 200 nm or so. Although some other
shapes were observed, the main morphology of the
product was triangles according to the observation from
the TEM images. In Figure 3b, we could observe the
typical triangle bismuth nanoparticle with a little higher
resolution. The electron-diffraction pattern (inset of
Figure 3b) recorded on individual triangular faces with
a convergent electron beam indicated that the triangular
Bi exhibited a single-crystalline structure. The
hexagonal symmetry of these diffracted spots suggested
that each bismuth nanotriangle was a single crystal
bounded by (001) facets. Three sets of spots could be
identified through the diffraction pattern: the set with
the strongest intensity could be indexed to the (110)
planes of rhombohedral with a corresponding lattice
spacing of 2.290 Å. The outer set with weaker intensity
was caused by reflections from (214) planes with a
lattice spacing of 1.347 Å. The outer set with the
weakest intensity corresponded to the formally forbid-
den (220) reflection with a lattice spacing of 1.145 Å.

As-Prepared Sample

Table 1. The C, H, N Element Analysis of the

<table>
<thead>
<tr>
<th>weight of sample, mg</th>
<th>percentage weight of sample, mg</th>
<th>N</th>
<th>C</th>
<th>H</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5650</td>
<td>0.048</td>
<td>0.514</td>
<td>1.355</td>
<td></td>
</tr>
<tr>
<td>1.4150</td>
<td>0.034</td>
<td>0.331</td>
<td>0.975</td>
<td></td>
</tr>
<tr>
<td>average</td>
<td>0.041</td>
<td>0.422</td>
<td>1.165</td>
<td></td>
</tr>
</tbody>
</table>

The dimension and morphology of the product were
examined by TEM measurements. A representative
TEM image is shown in Figure 3a. Statistical analysis
of the sample showed that the triangle edge length
varied from 130 to 200 nm or so. Although some other
shapes were observed, the main morphology of the
product was triangles according to the observation from
the TEM images. In Figure 3b, we could observe the
typical triangle bismuth nanoparticle with a little higher
resolution. The electron-diffraction pattern (inset of
Figure 3b) recorded on individual triangular faces with
a convergent electron beam indicated that the triangular
Bi exhibited a single-crystalline structure. The
hexagonal symmetry of these diffracted spots suggested
that each bismuth nanotriangle was a single crystal
bounded by (001) facets. Three sets of spots could be
identified through the diffraction pattern: the set with
the strongest intensity could be indexed to the (110)
planes of rhombohedral with a corresponding lattice
spacing of 2.290 Å. The outer set with weaker intensity
was caused by reflections from (214) planes with a
lattice spacing of 1.347 Å. The outer set with the
weakest intensity corresponded to the formally forbid-
den (220) reflection with a lattice spacing of 1.145 Å.

Meanwhile, in the HRTEM image (Figure 3d), it was
obviously observed that the surface of the bismuth
nanoplate was not well-crystallized and showed amor-
phous structure, which was expected due to the oxidation of the bismuth surface. To our knowledge, because bismuth has a low melting point (271.3 °C), the bismuth nanoplate could be gradually oxidized when exposed to air. On the other hand, the nanostructured bismuth was sensitive to the beam irradiation during the TEM examinations. The convergent beam electron diffraction pattern showed some changes from regular to irregular and finally to polycrystalline diffraction rings, displaying the sensitive characteristic of metal bismuth to electron beam radiation.

Microscopic Monitoring of the Possible Growing Process. The formation of bismuth crystal was a slow process. Through the time-dependent experiments, we could clearly observe the whole process of the reaction. At first, the whole solution was light yellow; with the increase of reaction time, the color of mixed solution darkened gradually and finally became black tint. During the first 6 h, no precipitate appeared. When the reaction was carried out for 6 h, the whole system began to precipitate. We also used the XRD measurements to monitor the whole process. Figure 4 shows the XRD patterns of the as-prepared samples at different reaction times. At the first, when the reaction time reached 6 h, the XRD pattern was not quite well. It only showed some strong peaks of rhomb bismuth. After 8 h, the sample was better crystallized than the one with less reaction time. When the reaction time increased more than 10 hours, all the crystal phases were very clear. It was obvious that the intensity of peaks increased with the reaction time. In the XRD patterns with different reaction stages, we could know the crystallization state of the prepared bismuth, which is a good assistance to observing the growing process of the bismuth nanoplates.

Figure 5 showed the TEM observation of different reaction times. In Figure 5a, it was obvious that the bismuth particles were spheres with ca. 5 nm diameter and aggregated together in the initial reaction mixture. Then with time increase, the bismuth grew into different shapes of polyhedra. When the reaction time reached 8 h, the particles began to grow up and the triangular, quadrangular, and hexagonal bismuth nanoprisms were observed. The size of particles was about 50 ± 10 nm (Figure 5b). Meanwhile, when the reaction time increased, the particle size also increased with the time, and the particles grew into triangular plates gradually. When the reaction time reached 12 h, the triangular nanoplates with mean width about 100 nm (Figure 5d) were observed. After 12 h, the bismuth nanoplates reached a stable state.

The possible growth process could be observed clearly in the TEM images. The initial stage was the formation of seeds. As the reaction proceeded, the amounts of initial particles decreased; meanwhile, the plate-shaped crystals occurred and grew larger and larger. After 6 h, it was mainly a dissolution and prism-shaped seeds formation process. It was likely that the refluxing provided the driving force to facilitate the Ostwald ripening process growth of these platelike seeds at the expense of spherical nanoparticles. In the process of refluxing, the dissolution and crystal growth on the surface of bismuth were the parallel processes. Because of the large surface-to-volume ratio of the nanosized particles, the dissolution was much easier and the growth rate of crystal was comparatively slower. The supersaturated bismuth particles could promote the crystal growth rate at the surface of those seeds. When the reaction time was increased from 6 to 12 h, the growth rate might increase and finally reached the maximum, and then the rate decreased gradually. At last, it was considered that the dissolution and crystal growth reached a balance in the solution to form the final nanoplates.
The Influence of pH Value, Complexing Agent, and Surfactant. We employed ascorbic acid as the reducing agent of Bi$^{3+}$ salt in the reaction system. Ascorbic acid was a mild reducing agent and cannot reduce the bismuth salt in the acidic environment. The pH value in this reaction was very important, which decided whether the reaction could occur and complete. An experiment exhibited that the whole reaction could not be carried out and there was no precipitate formed in the solution of pH lower than 7.0. However, when the pH value was higher than 9.0, it was obvious that the ascorbic acid could reduce the bismuth salt quite well.

The Bi(NO$_3$)$_3$ was different from AgNO$_3$ or other metal salts and easy to hydrolyze to form BiONO$_3$ precipitate in the aqueous solution. On the other hand, Bi$^{3+}$ could form Bi(OH)$_3$ precipitate in the alkaline solution. Therefore, it was necessary to make the Bi$^{3+}$ stable in the pH greater than 9.0 aqueous solution. Na$_2$EDTA could coordinate with Bi$^{3+}$ to form Bi(EDTA)$^-$ and the stabilizing constant $K = -27.8$. Therefore, the Na$_2$EDTA could make the Bi$^{3+}$ stable in the aqueous solution.

Figure 4. The XRD patterns of the as-prepared sample at the different reaction times: (a) 6; (b) 8; (c) 10; (d) 12 h.

Figure 5. The TEM images of different reaction times in the process of refluxing: (a) 6; (b) 8; (c) 10; (d) 12 h.
solution. Because of the formation of the complex Bi(EDTA)\(^{2-}\), the pH value of the mixed solution could be adjusted to about 10–11 to ensure the reaction would proceed.

In this experiment, through adjusting the concentration of Na\(_2\)EDTA, the speed of releasing Bi\(^{3+}\) could be controlled and the speed of the reductive reaction could be reduced to a certain extent. Low reactive speed was a benefit to the growth of nanocrystal, so bismuth nanoplates could grow into a perfect single crystal under the slow reactive speed. When the concentration of the Na\(_2\)EDTA was very low in the molar ratio of Na\(_2\)EDTA/Bi\(^{3+}\) lower than 1:1, the Bi\(^{3+}\) could not dissolve in the aqueous solution. If the molar ratio of Na\(_2\)EDTA/Bi\(^{3+}\) was between 1:1 and 2:1, the final products aggregated together and formed the bulk bismuth (Figure 6a). If the ratio was too high, the reactive speed became very low and the transfer ratio was much lower even after 12 h in the system. However, the sizes and shapes of the bismuth particles had no great change under the high ratio of EDTA vs bismuth salt.

The influence of the surfactant was also investigated. The molar ratio between PVP and Bi(NO\(_3\))\(_3\) in the range of 0.5–1.0 was a benefit to the growth of the triangle bismuth nanoplates. When the ratio was reduced, the as-prepared bismuth nanoplates were nearly spheres, and some particles had polyhedral structures. Figure 6b shows the morphology when the molar ratio was 0.25. In the case of higher molar ratio, the whole system became the bismuth colloid, and we cannot separate the bismuth from the mixture. It was supposed that the final products of bismuth had small mean width. So a large amount of PVP was unfavorable for the growth of bismuth nanoplates. When the molar ratio of PVP and Bi(NO\(_3\))\(_3\) was in the range of 0.5–1.0, the size of the triangular bismuth nanoplates decreased with the increase of PVP amount. Figure 6c,d shows the TEM images of bismuth nanoplates when the ratio was at 0.5 and 0.8. With the increase of the ratio, the plates separated from each other quite well. So a suitable amount of PVP was of great benefit to the formation of dispersed triangular bismuth nanoplates.

The Possible Mechanism for the Growing Process. The Wang group has performed some research on the possible growing mechanism of nanosized silver, palladium, and platinum among others. There are some similarities in our system with their studies. The particle shapes are closely related to the crystallographic surfaces that enclose the particles. The surfaces of hexagonal metal particles are different not only in the surface atom densities, but also in the electronic structure, bonding, and possibly chemical reactivities. Surface energies associated with different crystallographic planes are usually different. 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. Therefore, for those particles with sizes smaller than 10–20 nm, the surface is a polyhedron. With the influence of other factors, the particles could grow toward some selected directions to get the final shapes.

The observed growth patterns suggested that the presence of PVP induced the formation of triangular bismuth particles. El-Sayed carried out some research on the surfactant influence on the growth of crystals. The reasonable explanation in our system was that the relative growth rates of the different faces were quite different; meanwhile, the relative reduction rates on different surfaces competed with the relative rates of polymer capping action. During the preparation of metal nanoplates, some surfactants such as small molecules or polymers were often used to selectively adsorb on certain crystal planes. This method could induce anisotropic growth of different planes, since similar structure was also found in the case of silver, gold, and
nickel\cite{27} triangular or hexagonal plates. In the present paper, PVP was used to kinetically control the growth rates of various faces by interacting with these faces through capping and decapping.

We supposed that the growth at the edges of the nanoplates might be along the (110) or (111) direction since the (001) plane was the basal plane of the prepared bismuth nanoplates. Following Wang’s mechanism, the relatively low growth rate on (001) planes resulted in the formation of triangular plates. It is highly possible that some certain plane may possess the lowest surface tension. In our Bi/PVP system, the adsorption of PVP on this plane could help lower the surface tension and stabilize the plates. At the favorite molar ratio, the plates were elongated along (110) or (111) directions. At the lower molar ratio, due to the less selective adsorption, the equivalent growth rate on different planes induced the formation of polyhedral structure. At a much higher molar ratio, the excessive adsorption could limit the growth rate on all planes, so the speed of growth was much lower, which limited the bismuth crystal growing to the plates.

The Optical Characterization of Bismuth Nanoplates. In addition to the thermoelectric application previously proposed for nanostructured bismuth, it may also hold great interest for optical applications because of its unusual properties. We determined the IR absorption of the as-prepared Bi powder mixed with KBr and compared it with that of pure PVP (because the PVP was not easy to removed from the sample). In the spectrum of Bi (Figure 7a), the intensity of the absorption peak at 1060 cm\(^{-1}\) was almost the same as the peaks at 1655 cm\(^{-1}\), which was quite different from that of PVP (Figure 7c). We also dispersed the bismuth nanoplates into ethanol solution and dropped them onto the KBr plates to get the IR absorption spectrum (Figure 7b). In this case, the increase of the intensity of the peak near \~{}1000 cm\(^{-1}\) was much more obvious and the peak became much sharper.

According to the study of the Black group, the infrared absorption in nanosized bismuth has a strong increase at about 990–1100 cm\(^{-1}\), which also has a very strong polarization dependence.\cite{20,21} This absorption was considered as a result from indirect intersubband transition (indirect transition from the L- to the T-point valence bands). In bulk bismuth, carrier pockets are located at both the L- and the T-points. Near the Fermi level, the L-point has both valence and conduction bands, which are separated by a small energy gap of 36 meV at room temperature. In general, with decreasing size of particles, both the L- and T-point valence bands move down in energy, but the L-point valence bands move down at a faster rate than the T-point valence bands. This is the reason that nanostructured bismuth has a strong absorption peak in the mid-infrared. The qualitative particle size and polarization dependences, as well as the energy (wavenumber) of the absorption peak at \~{}1000 cm\(^{-1}\), also strongly suggested that this absorption was from indirect intersubband transitions. Often indirect transitions are much weaker than direct transitions, since a phonon is required for conservation of momentum. However, since the Debye temperature of bismuth\cite{40} is only 86.5–112 K, many phonons are available at room temperature to contribute to an indirect transition in a phonon absorption process.

Since the nanoplates decreased the size of bismuth in three dimensions, they could increase the quantum effects quite well. The bismuth nanoplates underwent 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. This transition, as well as other quantum effects, occurred in bismuth nanoplates even at larger mean width. However, the decrease of size at (001) direction is much more obvious than the others and offers the main increase of infrared absorption. Since the (001) plane acts as the basal plane, when these bismuth nanoplates were dispersed into ethanol solution and dropped onto the KBr plates, the nanoplates on the KBr surface were highly oriented. It was very similar to Black’s demonstration of the strong polarization dependence of optional absorption.\cite{21} In our experiments, when the light was perpendicular to the (001) planes, the peak get the maximal enhancement. In light of the result, we calculated the direct band gap of the final product to be 131.6 meV (1060 cm\(^{-1}\)), while the direct band gap of bulk bismuth (the L point) is 36 meV.

Conclusion

An effective process has been employed to synthesize bismuth nanoplates. This process was in a common thermal process, which was simple and convenient. The as-prepared bismuth nanoplates were single crystals and highly oriented with the (001) planes as the basal plane. We studied the influences of different experimental conditions and proposed the possible growth mechanism of the bismuth nanoplates. This kind of nanoplate had potential in combination with the extremely small electron effective mass and low thermal conductivity of Bi. These nanostructures of bismuth with unique shape might find use in some areas such as photonics, optoelectronics, and thermal electronics. Further study could focus on preparing highly uniform and excellent structural characteristic bismuth nanocrystals. This method might be applied to other metals and semiconductors for different applications.

Acknowledgment. We thank NSFC (Grant Nos. 20325516 and 90206037) and ”863” Project (No. 2003AA302740) for financial support.

References

Triangular Bismuth Nanoplates


Crystal Growth & Design, Vol. 5, No. 4, 2005 1385