Synthesis and Formation Mechanism of Bi(Se,S) Nanowires via a Solvothermal Template Process

Huilan Su, Yi Xie,* Peng Gao, Hong Lu, Yujie Xiong, and Yitai Qian
Structure Research Laboratory and Laboratory of Nanochemistry and Nanomaterials, University of Science and Technology of China, Hefei, Anhui 230026, P. R. China

Hexagonal Bi(Se,S) nanowires (20 nm × 1.5 μm) were prepared for the first time via a mild solvothermal template reaction of $BiCl_3$ with triphenylphosphine sulfide (TPPS) and elemental Se in ethylenediamine (en) at 120 °C for 20 h. In this process, the sulfur source TPPS as a template, the solvent ethylenediamine, and reaction temperature were critical factors of forming hexagonal Bi(Se,S) nanowires.

One-dimensional (1-D) nanostructures as building blocks for many novel functional materials are currently the focus of considerable interests.[1–4] The fabrication of desirable nanocrystallites is an ultimate challenge of modern material researches. The study of reaction mechanisms will help us to understand the chemical control of nanocrystallite nucleation and growth process at the atomic level. The general principle in constructing nanocomposites involves the intimate mixing of nanocrystals with processing matrices, which include polymers, glasses, or ceramics.[5,6]

Chalcogenides of group 15 have important applications. For example, bismuth chalcogenides are important semiconductor materials in temperature-control devices.[7,8] We are mainly interested in the S–Bi–Se system, which is seldom found in the mixed chalcogenide nanocomposites. Given that binary sulfides and selenides commonly have similar crystalline modification, Bi–S and Bi–Se have similar properties, so it will not be difficult to achieve the coexistence of Bi–S and Bi–Se in the same system S–Bi–Se. In previous researches, we noticed that ethylenediamine was an active solvent, which always played important roles in some solvothermal processes.[9–11] In addition, it was critical to select suitable reactants in the chemical synthesis of desirable materials. In this letter, with ethylenediamine as the solvent, $BiCl_3$, triphenylphosphine sulfide (TPPS),[12] and elemental Se as the reactants, a mild solvothermal technique was developed to prepare Bi(Se,S) nanowires. This process is described as follows.
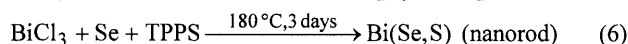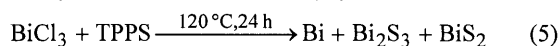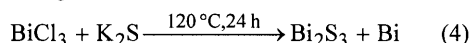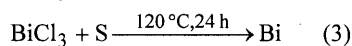
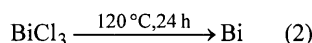$$BiCl_3 + xSe + (1 - x)TPPS \xrightarrow{\text{en, 120 °C(20 h)}} Bi(Se,S) \text{ (nanowire)} \quad (1)$$
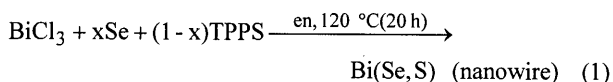
$BiCl_3$ (99.95%, 5 mmol), excessive elemental Se (99.99%, 3 mmol), and TPPS (3 mmol) were put into an autoclave filled with ethylenediamine up to 90% of the volume (50 mL). The autoclave was kept at 120 °C for 20 h, then cooled to room temperature naturally. A dark gray precipitate was collected and washed with ethylenediamine, absolute ethanol and distilled water, respectively, then dried in a vacuum at 50 °C for 2 h.

Figure 1a shows the X-ray diffraction (XRD) pattern[12] of Bi(Se,S) nanowires. The peaks can be indexed as hexagonal

Bi(Se,S) with the cell constants a = 4.190 Å, c = 23.21 Å. The broadening of these diffraction peaks indicates that the sample is nanosized. The (104) diffraction peak is unusually narrow and strong, indicating a preferential growth along the c axis in the crystal. There is a small peak marked with an asterisk, which can be indexed as (102) diffraction peak of hexagonal elemental Bi, indicating that probably there is trace elemental Bi in the sample. Transmission electron microscopy (TEM) images[12] (Figure 2a) reveal that the powders are some nanowires (20 nm × 1.5 μm) adhering small particles which may be elemental Bi. IR spectroscopy was carried out to examine the purity of the product, and indicated the absence of both ethylenediamine and TPPS. Elemental analysis showed a ratio of Bi : Se : S as 1.05 : 0.48 : 0.52, indicating that the composition of the nanowires is close to the formula Bi_2SeS.

To demonstrate the influence of different sulfur sources and reaction temperatures on the final products, and to investigate the formation mechanism of Bi(Se,S) nanowires, a series of relevant experiments were carried out in ethylenediamine through similar solvothermal processes. The main experimental conditions and results are summarized in the following equations.

$$BiCl_3 \xrightarrow{\text{120 °C, 24 h}} Bi \quad (2)$$

$$BiCl_3 + S \xrightarrow{\text{120 °C, 24 h}} Bi \quad (3)$$

$$BiCl_3 + K_2S \xrightarrow{\text{120 °C, 24 h}} Bi_2S_3 + Bi \quad (4)$$

$$BiCl_3 + TPPS \xrightarrow{\text{120 °C, 24 h}} Bi + Bi_2S_3 + BiS_2 \quad (5)$$

$$BiCl_3 + Se + TPPS \xrightarrow{\text{180 °C, 3 days}} Bi(Se,S) \text{ (nanorod)} \quad (6)$$

It is obvious that ethylenediamine was an interesting solvent, and selecting suitable reactants was also very important. Ethylenediamine had reducing power, could reduce Bi^{3+} to Bi. The XRD pattern and TEM image of produced elemental Bi are shown in Figure 1(b) and Figure 2(b), respectively. Ethylenediamine could dissolve by-product triphenylphosphine (TPP) and unreacted elemental Se, which are not present in the final products. In addition, ethylenediamine could dissolve elemental sulfur and probably formed a stable complex, so the reaction (3) could not produce bismuth sulfides.

The reaction temperature also played a critical role in both affecting reaction activity of the system and further controlling the formation and growth of crystallites. Lower temperature than 120 °C could not initiate the reactions. At 120 °C for 20 h, hexagonal Bi(Se,S) nanowires were obtained. At higher temperature, the formation and the growth of crystallites were rapid, there was not enough predominance for epitaxial growth of
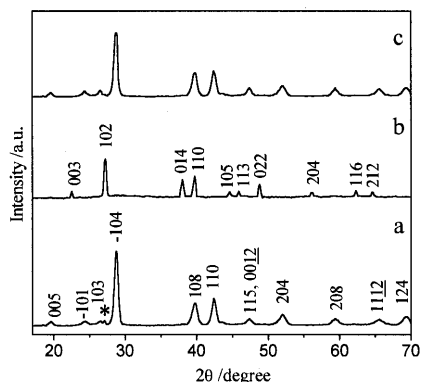
Figure 1. XRD patterns of (a) Bi(Se,S) nanowires obtained by experiment (1), (b) elemental Bi obtained by experiment (2), (c) Bi(Se,S) nanorods obtained by experiment (6).

nanocrystallites, so short nanorods were preferential to long nanowires. For example, Bi(Se,S) nanorods were obtained at 180 °C for 3 days, the corresponding XRD pattern and TEM image are shown in Figure 1c and Figure 2c, respectively.
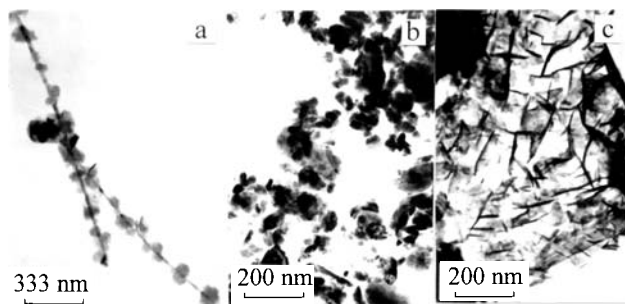

Figure 2. TEM images of (a) Bi(Se,S) nanowires obtained by experiment (1), (b) elemental Bi obtained by experiment (2), (c) Bi(Se,S) nanorods obtained by experiment (6).

Based on the above experiments, the formation of Bi(Se,S) nanowires can be described as following processes: under the solvothermal condition, ethylenediamine reduced Bi^{3+} to atomic Bi; and the linkage of Bi–S was formed with the deviation of S from TPPS. It is obvious that Bi competed with P from the TPPS for S, so the bond Bi–S was weaker than the usual linkage of Bi–S, but close to the normal bond Bi–Se. Thus Bi–S and Bi–Se could form synchronously and coexist in the system S–Bi–Se to construct crystalline Bi(S,Se) together. On the other hand, due to the steric hindrance in TPPS, the bond Bi–S formed along certain direction, which brought about the orientation of the bond Bi–Se in constructing crystalline Bi(Se,S), finally Bi(Se,S) crystallites formed and grew epitaxially hexagonal Bi(Se,S) nanowires. So TPPS was an excellent template to grow Bi(Se,S) nanowires.

In summary, a solvothermal template synthetic route has been developed to obtain Bi(Se,S) semiconductor nanowires. The solvent ethylenediamine, suitable sulfur sources, and reaction temperature played important roles in the formation of Bi(Se,S) nanowires. A solvothermal template mechanism for the growth of 1-D nanostructure is proposed and may be applicable to prepare other desirable nanostructural materials.

References and Notes
1   H. Dai, E. W. Wong, Y. Z. Lu, and C. M. Lieber, *Nature*, **375**, 769 (1995).
2   T. J. Trentler, K. M. Hickman, S. C. Goel, A. M. Viano, P. C. Gibbons, and W. E. Buhro, *Science*, **270**, 1791 (1995).
3   P. D. Yang and C. M. Lieber, *Science*, **273**, 1836 (1996).
4   P. V. Braum, P. Osenar, and S. I. Stupp, *Nature*, **380**, 325 (1996).
5   G. A. Ozin, *Adv. Mater.*, **4**, 612 (1992).
6   C. H. M. Hofman-Caris, *New J. Chem.*, **18**, 1082 (1994).
7   C. Shafa and M. J. Brett, *Can. J. Phys.*, **74**, S139 (1996).
8   S. K. Mishra, S. Satpathy, and O. Jepsen, *J. Phys.: Condens. Matter*, **9**, 461 (1993).
9   S. H. Yu, Y. T. Qian, L. Shu, Y. Xie, L. Yang, and C. S. Wang, *Mater. Lett.*, **35**, 116 (1998).
10 W. Wang, Y. Geng, P. Yan, F. Liu, Y. Xie, and Y. Qian, *J. Am. Chem. Soc.*, **121**, 4062 (1999).
11 Y. D. Li, H. W. Liao, Y. Ding, Y. Fan, Y. Zhang, and Y. T. Qian, *Inorg. Chem.*, **38**, 1382 (1999).
12 TPPS is prepared by a solvothermal reaction of elemental S with stoichiometric triphenylphosphine in diethylamine at 160 °C for 10 h. XRD patterns were obtained on a Japan Rigaku D/Max-γA rotation anode X-ray diffractometer, with the Ni-filtered Cu Kα radiation (λ = 1.54178 Å). TEM images were taken with a Hitachi Model H-800 transmission electron microscope, using an accelerating voltage of 200 kV.