Fabrication of bismuth telluride nanotubes via a simple solvothermal process

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Abstract

The unique Bi2Te3 tubes were obtained via a simple solvothermal reaction in the presence of ethylenediaminetetraacetic acid disodium salt. The product was characterized by X-ray diffraction, scanning electron microscopy and transmission electron microscopy. Bi2Te3 nanosheets are vertically grown off the tube wall to form Bi2Te3 tubes. A possible formation mechanism is proposed.

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1. Introduction

The performance of thermoelectric materials (TE) depends on the figure of merit \( ZT \) of the material \( (ZT = \alpha^2 T / \rho k) \), where \( \alpha \) is the Seebeck coefficient, \( \rho \) is the electrical resistivity, \( k \) is the thermal conductivity, \( T \) is the absolute temperature). Excellent TE materials require a perfect combination of electrical and thermal properties, which needs achieve simultaneously high power factor (\( \alpha^2/\rho \)) and low thermal conductivity. Interests are then focused on searching for novel and more efficient thermoelectric materials for cooling and power generation applications. Hicks and Dresselhaus [1,2] pointed out that, it may be possible to increase \( Z \) of certain materials by a factor of several times of their bulk values if they have a 1D or 2D nanostructure. Thermoelectric properties of low-dimensional structures started to attract attention in the 1990s. Impressive \( ZT \) values have been reported in some low-dimensional structures [3–7].

Currently, the bulk material with the highest thermoelectric figure of merit at room temperature (300 K) is Bi2Te3 with \( Z=0.003 \), but an improvement by about a factor of 2 is necessary for thermoelectric devices to be competitive with vapor-compression technology. Bismuth telluride based alloys have many important applications, for example, used as thermopiles, thermal sensors, or thermoelectric cooler for laser diodes [8]. A few methods have been developed to prepare Bi2Te3 nanomaterials by hard templates approach, kinetic control solution growth, and self-assembly process [9–16]. However, the preparation of Bi2Te3 nanotubes is seldom reported [5]. The hollow tube channels have a strong phonon scattering effect like the cages in a holey compound, so one-dimensional nanotubes reduce the lattice thermal conductivity further due to the phonon blocking effect of their low-dimensional nature. It is promising to enhance the overall TE properties by preparing Bi2Te3 materials in the shape of nanotube. The challenges in this field are still the development of synthetic methods, control of morphology, and assembly of desired nanostructures. Herein, we reported that Bi2Te3 nanotubes can be easily obtained using tubular precursor Te tubes as sacrificial template in the presence of ethylenediaminetetraacetic acid disodium salt (EDTA). Bi2Te3 nanocrystals show unique tubular structure we call ‘sheet-tube’. Bi2Te3 nanosheets grows off the wall of the Te tubes by packing them perpendicular to the axis of the Te tubes, and the content of tube wall change from Te to Bi2Te3.

2. Experimental

All chemicals were purchased from Beijing Chemical Co. Limited. A mixture of BiCl3 (0.315 g, 1 mmol), tellurium powder (99.99%, 0.191 g, 1.5 mmol) and EDTA (0.744 g, 2 mmol) was put into a 50 ml Teflon-lined autoclave. The autoclave was then filled with \( N,N \)-dimethylformamide (DMF) up to 80% of its capacity, and stirred for 1 h at room
temperature. Next KOH (2.225 g, 40 mmol) was added slowly into the autoclave and stirred for 0.5 h at room temperature. The autoclave was maintained at 140 °C for 10–36 h, followed by cooling to room temperature naturally. The products were filtered and washed with distilled water and absolute ethanol in sequence. Finally, the dark products were dried at 80 °C.

Powder XRD data were collected on a Rigaku D/MAX 2200 PC automatic X-ray diffractometer with Cu Kα radiation (λ = 0.154056 nm). The grain morphology and size were observed by SEM (FEI Siron 200) and TEM (HITACHI H-8100). Further structural and elemental analyses were performed using HRTEM (FEI Company, Tecnai G2 F20 S-Twin FEG TEM at 300 kV) and selected area electron diffraction (SEDX).

3. Results and discussion

Fig. 1 shows the XRD patterns of the final product obtained at 140 °C for 36 h. It is identified as a rhombohedral of Bi₂Te₃. The obtained lattice parameters for Bi₂Te₃ are a = 4.384 Å and c = 30.49 Å, which are in agreement with the reported values a = 4.385 Å, c = 30.46 Å (JCPDS 15-0863). Some Te was present in the products when the reaction time was less than 16 h.

Under our solvothermal treatment, the reaction of Te powders with BiCl₃ yields about 30% Bi₂Te₃ tube-like materials and Bi₂Te₃ sheets. The SEM images of the sheet-rod-like materials are shown in Fig. 2. The tubes, consisted of orientation attachment of Bi₂Te₃ rings, have not been achieved so far (Fig. 2(a) and (c)). The hexagonal or triangle channel of the sheet-tubes is clearly observed in the Fig. 2(b) and (c), with the same shape as that of Te tube [17]. The thickness of the hexagonal plates ranges from more than 20 to 50 nm. Energy dispersive X-ray (EDX) analysis of the sheets and the tube wall indicates that the atomic composition is almost the same in whole sheet-tubes, with ratio of Bi/Te about 2.0:3.0, which is in good agreement with that of the stoichiometric composition of Bi₂Te₃. Size control of the Bi₂Te₃ sheet-tubes was achieved by adjusting the growth temperature and the growth time.

The microstructure of the product was further examined using TEM and HRTEM. TEM image as shown in Fig. 3(a) presents that Bi₂Te₃ sheet-tubes are made up of the lamellar sheets but with ordered and aligned arrangement relationship, which suggests a possible crystallographic orientation relationship among them. A close examination of the sheet-tubes (Fig. 3(b)) indicates that the sheets grow off a tube and they are mostly attached to the edge of tube wall. The measured wall thickness of the nanotubes is about 10 nm. The selected area electron diffraction (SAED) pattern (inset in Fig. 3(a)) taken from a single sheet-tube indicates that the sheet-tubes are single crystals.

Fig. 3(c) and (d) are representative HRTEM images of a single-crystalline Bi₂Te₃ sheet-tubes shown in Fig. 3(b), which were taken from the area A and B, respectively. An interesting phenomenon was observed in Fig. 3(c) that the lattice planes in the Bi₂Te₃ sheets have almost the same direction with the tube
wall, implying that Bi$_2$Te$_3$ sheets epitaxially grow off the tube wall. It is possible to have a long distance epitaxial growth of Bi$_2$Te$_3$ sheets on tube wall, and result in the formation of Bi$_2$Te$_3$ sheet-tube. A close examination reveals that there is a slight mis-orientation of the lattice fringes between the Bi$_2$Te$_3$ sheets and the tube wall (about 1°). The observed fringe pattern of Bi$_2$Te$_3$ sheets and tube wall, with spacing of 1.02 nm, is nicely indexed to the (003) plane of the rhombohedral Bi$_2$Te$_3$, which indicates that the Bi$_2$Te$_3$ sheets grow along the [003] direction. The image shown in Fig. 3(d) indicates the sheets on the tube are a single crystal with a preference growth direction.

The series of starting materials fed, solvent and reaction temperature play a key role in the formation of Bi$_2$Te$_3$ sheet-tubes. It is necessary to first mix BiCl$_3$ with EDTA at room temperature for some time to stabilize Bi ions. The sheet-tubes formed only at the temperature range of 120–160 °C. In our reaction process, Te tubes could be prepared under the same solvothermal condition without the using of Bi salts at 140 °C for 24 h, while Te rods would dominate occurred at higher temperature above 180 °C. Typical SEM micrograph of as-prepared Te tubes is shown in Fig. 2(d), the hexagonal pores of the Te tubes indicate that the Te tubes may work as sacrificial template in the formation of Bi$_2$Te$_3$ sheet-tubes. The present of Te tubes at the early stage of the reaction might be the key to synthesize Bi$_2$Te$_3$ sheet-tubes.

Thus, Bi$_2$Te$_3$ sheet-tubes may also be prepared via a two-step process using Te tubes as parent templates. When the Te powders were heated in DMF with KOH at 140 °C, the Te tubes appear to form in the initial heating step, and then Bi$_2$Te$_3$ appears to grow epitaxially off the surface of the tube wall to give Bi$_2$Te$_3$ sheet-tubes (shown in Fig. 3(e)) after they were cooled, added by BiCl$_3$ and EDTA and were heated again at 140 °C. Those results further confirm that tubular precursor Te tubes work as sacrificial template to form Bi$_2$Te$_3$ tubes in our solvothermal process.

According to the analysis above, the Bi$_2$Te$_3$ sheet-tubes in this solvothermal process occur mainly by the following route as a Dissolution–Precipitation–In-site reaction–Growth process to result in such a novel nanostructure. The whole reaction process can be expressed as follow (shown in Fig. 4): When BiCl$_3$, Te powder and EDTA were stirred at room temperature, bismuth ions were first stabilized by the coordination of organic ligand EDTA. Te powders would slowly dissolve into solution after the addition of KOH. Then Te nuclei precipitate from the saturated solution and some nuclei quickly grow into Te crystalline tubes. During the next solvothermal treatment at 140 ºC, Te tubes are easy to undergo an in-site reaction with Bi$^{3+}$ or [Bi(EDTA)]$^{3+}$ to give Bi$_2$Te$_3$ seeds on Te tube wall. The epitaxial orientation relationship of the growth direction between Bi$_2$Te$_3$ and Te is preserved to reduce the lattice mismatch energy. The intrinsic crystal properties dominate the shape of the primary Bi$_2$Te$_3$ particles. Due to the anisotropic bonding environment, the crystalline facets tend to develop on the low-index planes to minimize the surface energy, and the Bi$_2$Te$_3$ nuclei forming from the solution are tiny thin crystals. Further epitaxial growth of the Bi$_2$Te$_3$ seeds perpendicular to the axial direction of Te tubes occurred in the next growth step, in which the consumed Te came from tube wall and solution. Finally, Bi$_2$Te$_3$ sheet-tubes formed due to the completely growth of the Te tube wall.

4. Conclusions

In conclusion, single-crystal Bi$_2$Te$_3$ sheet-tubes have been synthesized by a simple ligands-assisted solvothermal method at 140 ºC. Of interest to note is the formation of the Bi$_2$Te$_3$ sheet-tubes is due to in-site reaction of Te tube wall to Bi$_2$Te$_3$ sheets. Te tubes are intentionally formed in the first step and epitaxial growth of Bi$_2$Te$_3$ nanosheets occurred by packing them perpendicular to the axis of the central Te tubes in the second step. We believe that these well-built structures are desired low-dimensional thermoelectric building-blocks for possibly achieving a high thermoelectric figure of merit. And this facile solvothermal route might make a new generation of sophisticated nanostructures such as Bi$_2$Te$_3$–Te sheet-tube possible.

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References