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Two-step synthesis of Bi_2Te_3–Te nanoarrays with sheet–rod multiple heterostructure

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ABSTRACT

Bi_2Te_3–Te arrays with sheet–rod multiple heterostructure were obtained in large scale, using Te nanorod arrays as the in-situ templates under solvothermal process. The array is formed by the ordered Bi_2Te_3–Te rods where Bi_2Te_3 sheets distribute from the top face to the bottom face along the Te rod vertically. The microstructure of the heterostructure was studied through X-ray diffraction, scanning electron microscopy and transmission electron microscopy. The electrical conductivity and Seebeck coefficient of the arrays were also studied. The course of reaction was monitored so as to propose a possible growth mechanism of such novel heterostructure. The key for the preparation of such heterostructure is to balance the velocity between the dissolution of Te rods and the formation of Bi_2Te_3 sheets. This synthetic approach could be promising to prepare self-assembled low-dimensional nanoarrays of metals and semiconductors with high yield.

1. Introduction

Low-dimensional nanostructured materials such as nanowires, nanorods, nanobelts and nanotubes are especially attractive for nanoscience studies as well as for nanotechnology applications because of their superiority in mesoscopic physics and fabrication of nanoscale devices which are different from those bulky or nanoparticle materials [1,2]. Among all the challenges in well-defined low-dimensional nanomaterials, the most fundamental one should be how to control the growth of nanostructures.

The synthesis of the bismuth–telluride has attracted much interest because of its high thermoelectric figure of merit ZT at room temperature. Low-dimension materials have been proved to be an effective approach to greatly enhance the ZT value [3,4]. The reduction of dimension can result in the increase of density of states (DOS) around Fermi level and the enhancement of phonon scattering, which can heighten the Seebeck coefficient and reduce the thermal conductivity, respectively. Thus, the incorporation of low-dimensional nanostructures into bulk TE materials could effectively enhance TE performance. Pure Bi_2Te_3 materials with different structures have been extensively developed by hard templates approach, kinetic control solution growth, ball milling, melt spinning technique and self-assembly process [5–16]. Some possible mechanisms to explain the formation of Bi_2Te_3 nanocrystals, such as "mono-atom model" and "continuous nucleation model" have subsequently been proposed [17,18]. The nanostructure-contained Bi_2Te_3 based materials exhibit good TE performance due to structural modification induced by low-dimensional nanostructures [11–14]. Besides, Te/Bi and Bi_2Te_3 core/shell heterostructure nanowires have been found with enhanced thermoelectric properties [14]. Among various structures, heterostructure nanowires are predicted to exhibit better thermoelectric performance than conventional nanowires or superlattice films [19]. Thus, the synthesis of Bi_2Te_3 with heterostructure is of much interest for both chemists and materialists.

In our previous work, dispersed Bi_2Te_3–Te sheet–rods were synthesized successfully by a mild and convenient technique [20]. While, from practical application point of view, devices should consist arrays of parallel nanowires in large scale to effectively transfer thermal energy, since a single nanowire is not able to transport enough current to make a device working. It is still a challenge to find a simple and universal strategy with a high degree of control for fabricating the thermoelectric nanowire arrays. Here, we report a simple route for large-scale growth of Bi_2Te_3–Te sheet–rod arrays by using Te nanorod arrays as the in-situ templates through organic-assisted solvothermal method. The advantage of the procedure reported here is the first step to grow Te nanorods on a substrate continuously, compactly and orderly on large scale by physical deposition, instead of individual and discrete Te nanostructures synthesized previously reported by a chemical solvothermal method. This kind of low-dimensional heterostructure could be potential thermoelectric material with

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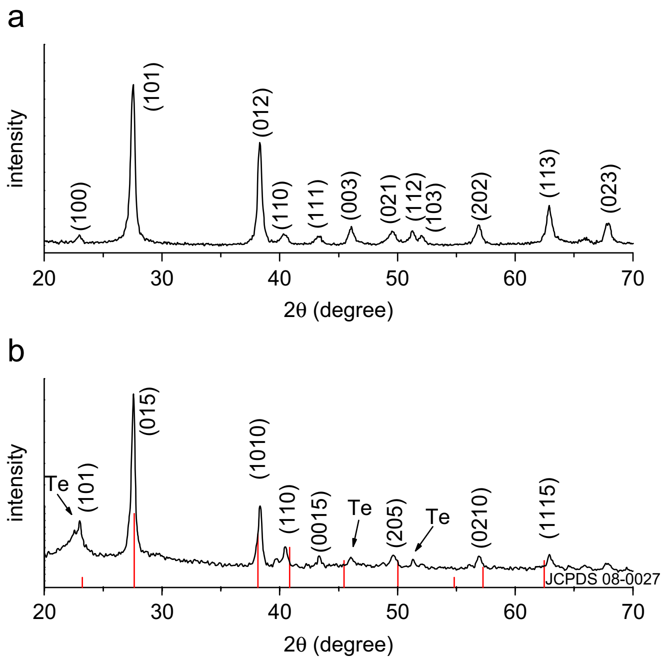

Fig. 1. (a) XRD patterns of Te nanorods. (b) XRD patterns of Bi_2Te_3–Te nanocomposite.

enhanced ZT value considering that it could offer increased phonon scattering to reduce the lattice thermal conductivity while keeping the conduction of carriers.

2. Material and methods

Tellurium (99.99%), KOH (82.0%), $BiCl_3$ (98.0%), EDTA-2Na (99.0%) and *N*,*N*-dimethylformamide (DMF, 99.5%) (all chemicals were from Beijing Chemical Co. Limited) were used directly for synthesis without further purification. First, telluride films in the form of nanorod arrays were prepared (26 mm $\times$ 70 mm) in a simple physical vapor deposition (PVD) system as follows: tellurium powders were mounted on the evaporating dish which is connected to the alternating current (AC) power supplies. Common glass substrates (26 mm $\times$ 70 mm) were cleaned thoroughly by diluted nitric acid and acetone, and dried under the nitrogen airflow. After loading the substrate onto the substrate holder (parallel to the dish), N_2 gas was introduced into the chamber and vacuumized three times to remove oxygen. All the working pressure was maintained at 2×10^{-6} Torr in the deposition process. Then Bi_2Te_3–Te sheet–rod arrays were fabricated by employing the as-deposited Te nanowire arrays as in-situ templates through the organic-assisted solvothermal method. The procedure is as follows: 0.1 mmol (0.060 g) $BiCl_3$, 0.2 mmol (0.140 g) EDTA-2Na, 6 mmol (0.333 g) KOH and 30 ml

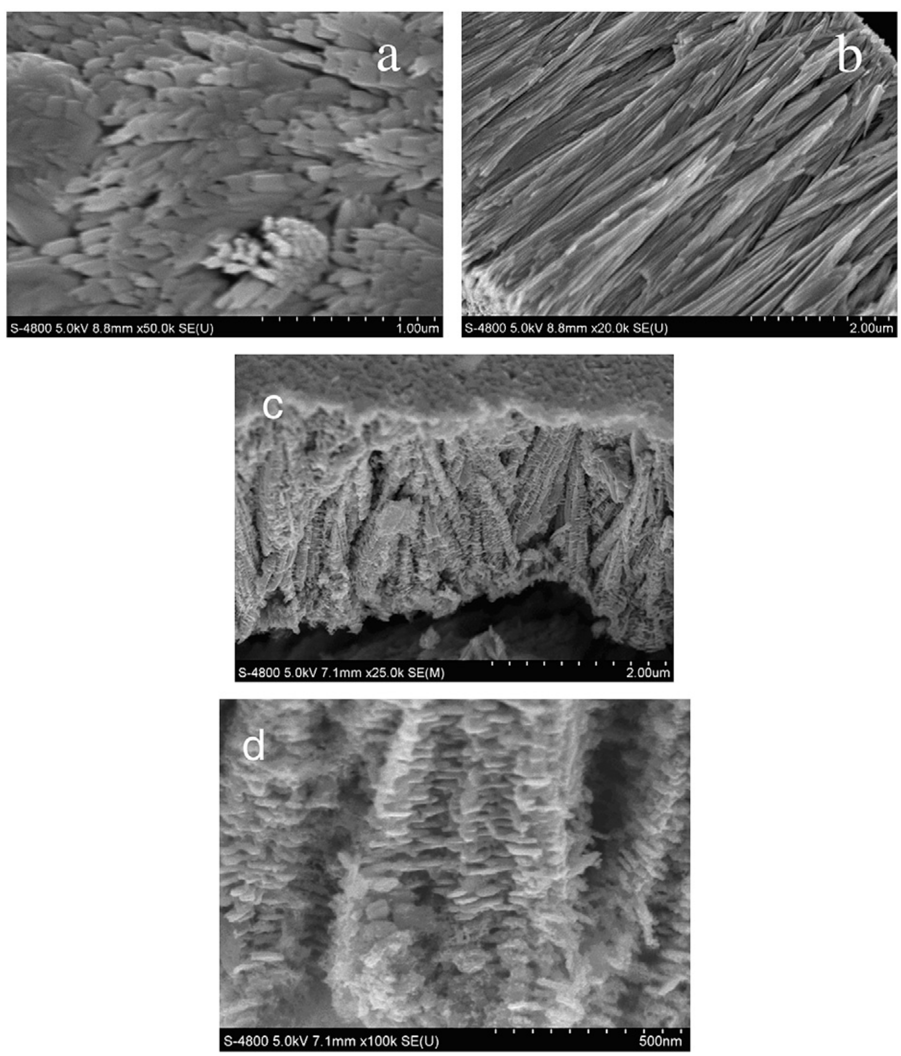

Fig. 2. FE-SEM images of (a) as-deposited Te nanorod arrays, (b) Bi_2Te_3–Te heterostructure array and (c,d) magnified image from (b).