Large scale highly crystalline Bi_2Te_3 nanotubes through solution phase nanoscale Kirkendall effect fabrication†

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We have successfully developed an ethylene glycol mediated solution phase method for synthesizing highly crystalline Bi_2Te_3 nanotubes using Te nanowires as the *in situ* templates; our work demonstrates the generic feature of a solution phase mediated Kirkendall effect for the synthesis of not only hollow nanoparticles but also highly crystalline tubular structures.

Thermoelectric (TE) devices that can directly generate electric power by thermal energy and *vice versa* have been considered as an efficient approach for improving fuel efficiency and relieving the world's energy crisis. Nonetheless, TE materials have long been too inefficient to be cost-effective for fully scalable applications.[1] There has been a resurgence of interest in TE materials since a theoretical prediction suggested that the TE figure of merit (ZT) could be greatly enhanced by reducing the size to nanoscale.[2] Till now, much progress has been made in optimizing TE efficiency through nanostructure engineering,[3] especially in one-dimensional nanowires.[4] More excitingly, it is calculated that compared with solid nanowires, tubular structures will result in a further reduction in thermal conductivity because of the stronger phonon-surface scattering,[5] which could contribute to the enhancement of the ZT value. However, the synthesis of TE nanotubes is relatively undeveloped, and much effort should be devoted to searching for facile and effective routes.

The Kirkendall effect is a classical phenomenon in metallurgy, which refers to a nonreciprocal mutual diffusion process through an interface of two metals, so that vacancy diffusion occurs to compensate for the inequality of the material flow.[6] The application of the Kirkendall effect in a nanoscale system has attracted special attention in various synthetic routes for hollow nanostructures[7] due to its generic feature, which has been applied to synthesize various hollow nanoparticles.[8] In the case of single crystalline tubular structures,[9] Fan *et al.* reported the example of applying the Kirkendall effect for synthesizing single crystalline $ZnAl_2O_4$ nanotubes based on a vapor phase deposition.[9b] Herein, we successfully extended the Kirkendall effect into an ethylene glycol (EG) mediated solution phase method for large scale synthesis of highly crystalline Bi_2Te_3 nanotubes. This work further confirms the generic feature of the Kirkendall effect for synthesizing tubular structures in combination with appropriate fabrication procedures and will contribute to the research on the TE properties of single Bi_2Te_3 nanotubes.

We chose the synthesis of Bi_2Te_3 nanotubes for the following reasons: (i) As one of the best TE materials near room temperature, Bi_2Te_3 holds great potential for scalable applications if further optimization of the ZT value could be achieved. (ii) The current routes for synthesizing Bi_2Te_3 nanotubes, such as a hydrothermal method and a galvanic displacement process,[10] have the limitations of low production yield or polycrystalline nature of the products. Thus, it is still a challenge and very important to develop facile and effective routes for the large scale synthesis of highly crystalline Bi_2Te_3 nanotubes.

In a typical synthesis, single crystalline Te nanowires with $\langle 001 \rangle$ growth direction were firstly obtained by reducing TeO_2 dissolved in EG with $N_2H_4 \cdot H_2O$ at 160 °C, as shown in Fig. S1, ESI.† The as-prepared Te nanowires with diameters of about 50 nm and lengths up to tens of micrometres will act as a faster core diffusion couple in the following Kirkendall effect process for synthesizing Bi_2Te_3 nanotubes. The Bi precursor solution obtained by dissolving $BiCl_3$ into EG solution with appropriate PVP was added to the above Te nanowire containing solution at 160 °C. Highly crystalline Bi_2Te_3 nanotubes can be formed through reacting with the added Bi precursor solution at 160 °C for about 20 min. The detailed synthetic procedure is presented in the ESI.†

Fig. 1 gives the X-ray diffraction (XRD) pattern of the isolated products after injecting the Bi precursor solution and reaction for 20 min at 160 °C, which can be readily indexed to rhombohedral Bi_2Te_3 crystals (Joint Committee on Powder Diffraction Standards (JCPDS) 82-0358). Typical scanning electron microscopy (SEM) images (Fig. 2A and/or Fig. S2

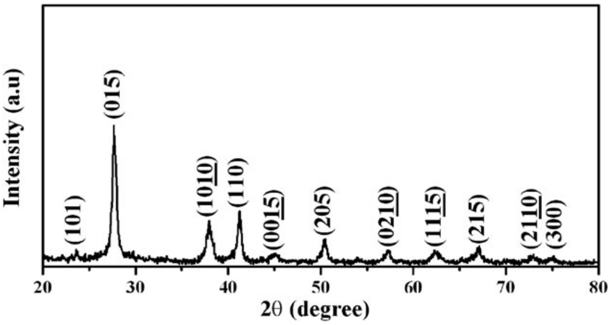

Fig. 1 Typical XRD pattern of the Bi_2Te_3 nanotubes obtained by injecting Bi precursor into Te nanowire solution at 160 °C and reaction for about 20 min.

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† Electronic supplementary information (ESI) available: The detailed synthetic procedure; microstructure analysis of Te nanowires; SEM image of Bi_2Te_3 nanotubes; SAED patterns of the time dependent products during the formation of Bi_2Te_3 nanotubes. See DOI: 10.1039/b822595h

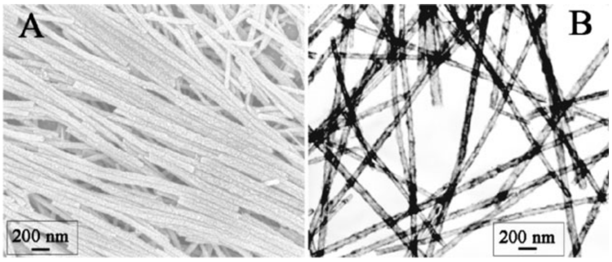

Fig. 2 Typical SEM and TEM images of the as-synthesized Bi_2Te_3 nanotubes at 160 °C for 20 min.

of ESI†) indicate that a large scale one-dimensional structure similar to that of the Te nanowires is conserved, and the transmission electron microscopy (TEM) image shown in Fig. 2B confirms the hollow structure of the obtained Bi_2Te_3. The average diameter and length of the Bi_2Te_3 nanotubes are about 70 nm and tens of micrometres respectively, and the thicknesses of the nanotubes range from 10 to 15 nm estimated from the TEM image. Fig. 3 gives the microstructure and composition analysis of the Bi_2Te_3 nanotubes. Fig. 3B–E show the high-resolution (HR) TEM images and the selected area electron diffraction (SAED) pattern taken from the individual nanotube shown in Fig. 3A, which demonstrates the highly crystalline nature of the products. The measured distances of the neighboring lattice fringes in Fig. 3C and D are 0.323 and 1.008 nm, corresponding well to the (015) and (003) lattice spacings, respectively, for the rhombohedral Bi_2Te_3 phase. The energy dispersive X-ray spectrum (EDS) result (Fig. 3F) reveals that the atomic ratio of Bi and Te is about 41.5 : 58.5, which is close to 2 : 3.

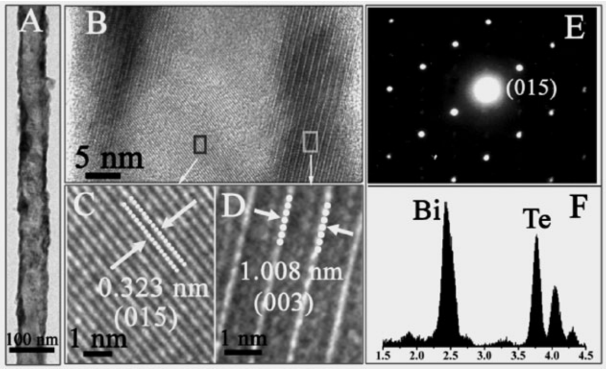

Fig. 3 Microstructure and composition analyses of the as-prepared Bi_2Te_3 nanotubes: (A) TEM micrograph of an individual Bi_2Te_3 nanotube, (B–D) HRTEM images, (E) SAED pattern, (F) EDS spectrum taken from the Bi_2Te_3 nanotube shown in (A).

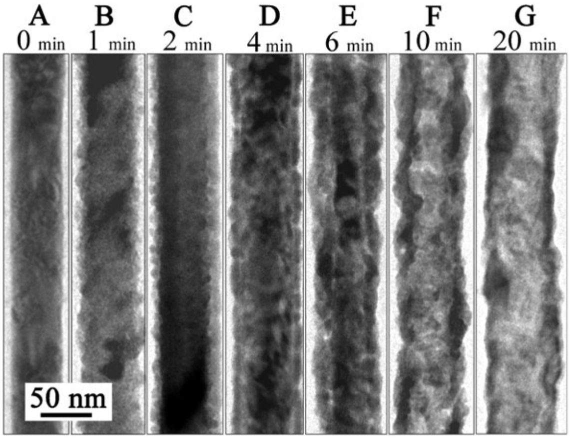

Fig. 4 TEM images of the time-dependent products obtained at 160 °C after the injection of the Bi precursor into Te nanowire solution.

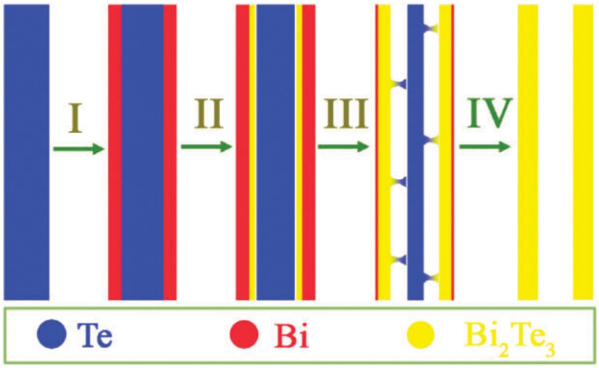

Fig. 5 Schematically illustrated shape evolution process from Te solid nanowire to Bi_2Te_3 nanotube.

To understand the growth process during the shape evolution from Te solid nanowires to Bi_2Te_3 nanotubes, the morphologies of the time-dependent products obtained at 160 °C were carefully observed, as shown in Fig. 4. On the basis of the features in the shape evolution process, it is safe for us to infer that the Kirkendall effect could be the growth mechanism involved. The formation process of the Bi_2Te_3 nanotubes is schematically illustrated in Fig. 5 and can be described as follows: Firstly, the Bi atoms selectively nucleate at the side surfaces of the Te nanowires, which subsequently results in the formation of core–shell nanowires, corresponding to the evolution in Fig. 4A–C and Step I in Fig. 5. After reaction for about 4 min, the formation of a Bi–Te alloy layer can be observed (Fig. 4D and Step II in Fig. 5) and non-reciprocal diffusion between Bi and Te through the Bi–Te alloy layer leads to void formation between the Bi–Te alloy layer and the core Te nanowires, as shown in Fig. 4E and Step III in Fig. 5. The observed shape evolution from Fig. 4C–E provides strong evidence that the nanoscale Kirkendall effect is conducive to nanotube growth in the EG mediated solution phase process. The continuous mass transformation could be maintained through the bridge structure indicated in Step IV of Fig. 5, similar to the formation of hollow nanoparticles by the Kirkendall effect.[8] The Te core nanowire disappears when the reaction time reaches about 10 min (Fig. 4F) and highly crystallized Bi_2Te_3 nanotubes were obtained after reaction for about 20 min (Fig. 4G). In addition, the SAED patterns of the time dependent products obtained after reaction for 1 min, 6 min and 10 min (Fig. S3, ESI†) provide further evidence for the evolution processes from Te nanowire to Bi_2Te_3 nanotube.

In summary, we successfully carried out the large scale synthesis of highly crystalline Bi_2Te_3 nanotubes using Te nanowires as *in situ* templates through an EG mediated solution phase method. The time-dependent products study confirms that the shape evolution from solid Te nanowires to

Bi_2Te_3 nanotubes could be driven by the Kirkendall effect. This work provides an alternative strategy for the synthesis of a one-dimensional tubular structure by applying the Kirkendall effect in a solution phase method.

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