

Sun Ting, Zhu Tiejun, Zhao Xinbing

Nanostructured Bi_2Te_3 synthesized by low temperature aqueous chemical route

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Abstract Chemical and physical reactions during the low temperature aqueous chemical synthesis of nanostructured Bi_2Te_3 powders were investigated in-situ by pH measurement, color observation of the solution and X-ray diffraction analysis of the powders. It was found that Bi_2Te_3 could be synthesized only in a strong alkaline solution. Bi_2Te_3 nanocapsules were synthesized by the aqueous chemical route at 65 °C with the addition of disodium ethylenediaminetetraacetate salt. High-resolution transmission electron microscopy observation indicates that the nanocapsules are hollow-structured with a wall thickness of about 6 nm.

Keywords Bi_2Te_3 , nanocapsule, nanotubes, aqueous chemical synthesis, thermoelectric material

1 Introduction

Thermoelectric (TE) materials can directly convert heat to electricity or the reverse through the charge-carrier transport in a solid. In recent years, TE materials have attracted more and more attention because of their potential applications in power generators and refrigeration devices [1, 2]. Bismuth telluride (Bi_2Te_3) and its alloys are the best TE materials available near room temperature with the highest dimensionless figure of merit, $ZT=(\alpha^2\sigma/\kappa)T$, of about 1 [3], where α is the Seebeck coefficient, σ and κ the electrical and thermal conductivity, respectively, and T the absolute temperature. Nowadays, many attempts have been made to improve the TE properties of the materials [4–6]. Theoretical calculations have predicted that the figure of

merit of TE materials can be significantly improved by dimension downscaling and nanostructuring [7]. Many investigations in these aspects have been focused on superlattice thin films and nanowire arrays [8, 9]. However, these low-dimensional materials merely cater to specific situations. Bulk nanomaterials are usually needed for large-scale commercial applications. Recently, Bi_2Te_3 nanotubes had been successfully synthesized via hydrothermal routes [10]. It was found that the Bi_2Te_3 -based bulk nano-composites with the addition of Bi_2Te_3 nanotubes exhibited enhanced TE properties. A figure of merit of about 1.2 has been obtained [11]

The solvothermal or hydrothermal method, as a simple chemical route to nanoparticle materials, has been successfully used in the synthesis of Bi_2Te_3 nanoparticles [12–15]. However, solvothermal or hydrothermal synthesis is usually performed in a sealed autoclave at a temperature higher than the boiling point of the solvent or water. Here we report a new aqueous chemical route for the synthesis of Bi_2Te_3 nanoparticles at 65 °C in an open system, which makes possible their in-situ observation, as well as both chemical and physical investigations, during the synthesis.

2 Materials and methods

The synthesis was carried out in an 800ml glass beaker. All of the chemical reagents are of analytical grade. Distilled water (400 ml) was put in to the beaker, preheated to 65 °C, and stirred by a magnetic stirrer during the whole synthesis. Then, 30 mmol tellurium (5N, $\leq 30 \mu\text{m}$) was added into the beaker. About 15 min later, 20 mmol BiCl_3 was added into the beaker. For samples A and C, 2 g ethylenediaminetetraacetic disodium salt (EDTA) was added at the same time, while for samples A and B, 3.5 g NaOH was dissolved into the mixture after a 15 min interval. Again after 15 min, 3.5 g NaBH_4 was added into the beaker as the reductant, which sets the starting point of the reaction. During the synthesis, a series of samples

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Sun Ting, Zhu Tiejun, Zhao Xinbing (✉)
Dept. of Materials Science & Engineering, Zhejiang Univ.,
Hangzhou, 310027, P. R. China
E-mail: zhaoxb@zju.edu.cn

containing 10 ml of the mixture solution were taken from the beaker at designated times. Immediately after sampling, the extractions were centrifuged, filtered, washed for several times, and dried at 100 °C in vacuum. The solution pH values were measured with a PHS-25A pH meter during the reaction. The powder structure was characterized by X-ray diffraction (XRD) using a Bede D1 system (Cu K_{α} radiation, $\lambda=0.154056$ nm). The powder morphology was observed using a JEM-2010 transmission electron microscope (TEM), a JEOL-4000EX high-resolution TEM (HRTEM), and an FEI-Siron field emission scan electron microscope (FESEM).

3 Results and discussion

Figure 1 shows the variations of the pH values and the colors of the solution with reaction time of sample A. After putting the Te powders into the distilled water, the pH value shifted to 5.8, which implied that Te could dissolve a little in the water. After the addition of BiCl_3 and EDTA, the solution turned opal and the pH value fell down to 1.15, indicating the hydrolyzation of BiCl_3 . Meanwhile, the replacement reaction between BiCl_3 and EDTA could possibly take place to form the chelate compound of Bi and EDTA. Once NaOH was added into the mixture, the pH value rose promptly to around 13 with no visible change happening to the color of the solution. The dramatic reactions started immediately after the addition of the reductant NaBH_4 , accompanied with the solution color

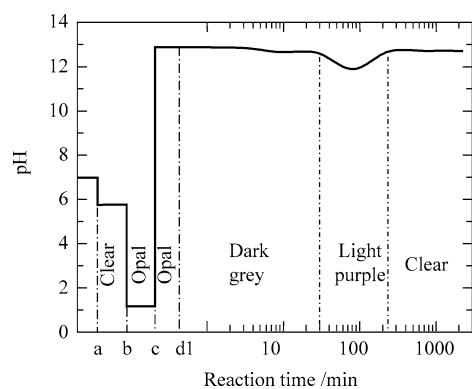


Fig. 1 Changes in pH values and colors of the solution during the synthesis of Bi_2Te_3 .

Points a, b, c, d on the time axis indicate the time when Te, BiCl_3 +EDTA, NaOH, NaBH_4 were added, respectively. The reaction time begins immediately after the addition of NaBH_4

change from opal to dark grey. This indicated the generation of a large amount of solid microparticles insoluble in the water, thought to be the reduced metal Bismuth. It was found that the solution turned from dark grey into purple after about 30 min of reaction, and this color was considered to result from amorphous Te colloids (a-Te) [16]. During this period, the pH values dropped a little. After 4 h reaction, the purple color of the solution gradually disappeared and the pH values returned to about 13. At this

moment, the solution was observed to be completely clear when the stirring was stopped, leaving the black precipitates at the bottom of the beaker. The whole synthesis process was observed until 36.5 h.

Points a, b, c, d on the time axis indicate the time when Te, BiCl_3 +EDTA, NaOH, NaBH_4 were added, respectively. The reaction time begins immediately after the addition of NaBH_4

The XRD patterns of the powders sampled during the synthesis of sample A are given in Fig. 2. Fig. 2a is the XRD pattern of pure Tellurium. The diffraction peaks of BiOCl (Tetragonal, $P4/nmm$) can be seen from the pattern in Fig. 2b after the addition of BiCl_3 and EDTA, while after NaOH addition, the new peaks on XRD pattern 2c could be identified as $\text{Bi}_2\text{O}_{2.33}$ (Tetragonal $I4/mmm$). $\text{Bi}_2\text{O}_{2.33}$ was considered as the dehydrated form of $\text{Bi}(\text{OH})_3$ in the alkaline solution. The synthesis reaction took place immediately after the addition of NaBH_4 as the reductant, and the color of the solution began changing as shown in Fig. 1. However, no remarkable change in XRD patterns could be observed at the beginning (Fig. 2). It can also be seen from Fig. 2 that the intensity of Tellurium peaks at high diffraction angles decrease after 9 min of reaction, and were hardly distinguishable after 27 min. This indicates that the original Tellurium in the system was almost completely dissolved, combining with Bi to form Bi_2Te_3 or becoming amorphous Te colloids. These colloids could re-crystallize during the later drying process, but their XRD intensities could be much lower due to their small sizes. Meanwhile, both BiOCl and $\text{Bi}_2\text{O}_{2.33}$ disappeared in the XRD patterns after 9 min, implying that some Bi_2Te_3 were already synthesized at that moment. Because Te and Bi_2Te_3 are both classified as hexagonal crystal systems, they have similar XRD patterns including the strongest peaks. However, according to the standard XRD data, the distance between the second and the third strongest peaks of Bi_2Te_3 (JCPDS 82-0358, $2\theta_{1010}=37.184^\circ$, $2\theta_{110}=41.040^\circ$) is wider than that of Te (JCPDS 82-0554, $2\theta_{1010}=38.384^\circ$, $2\theta_{110}=40.885^\circ$). Therefore, we could differentiate both phases with the 2θ distance between the second and the third strongest peaks. Observed from the local expanded patterns from $2\theta=38.2^\circ$ to 41.2° (Fig. 2), it is clear that both the peaks near 38° and 41° become wider and wider after 9 min, implying the formation of Bi_2Te_3 crystals. Remarkable Bi_2Te_3 diffraction peaks can be found in the sample at 243 min and these peaks dominated in the 2,187 min sample. Some weak Te peaks remained in the XRD patterns of the 2,187 min sample, indicating the existence of a little tellurium in the final product. The main reason is that the dissolution of Te at the beginning was restricted by its solubility and dissolving rate, and at the terminal, the concentration decrease of bismuth ions depressed the formation rate of Bi_2Te_3 . Another possible reason might be the shortage of bismuth due to the hygroscopic nature of BiCl_3 during the weighing process so that tellurium powder remained relatively excessive.

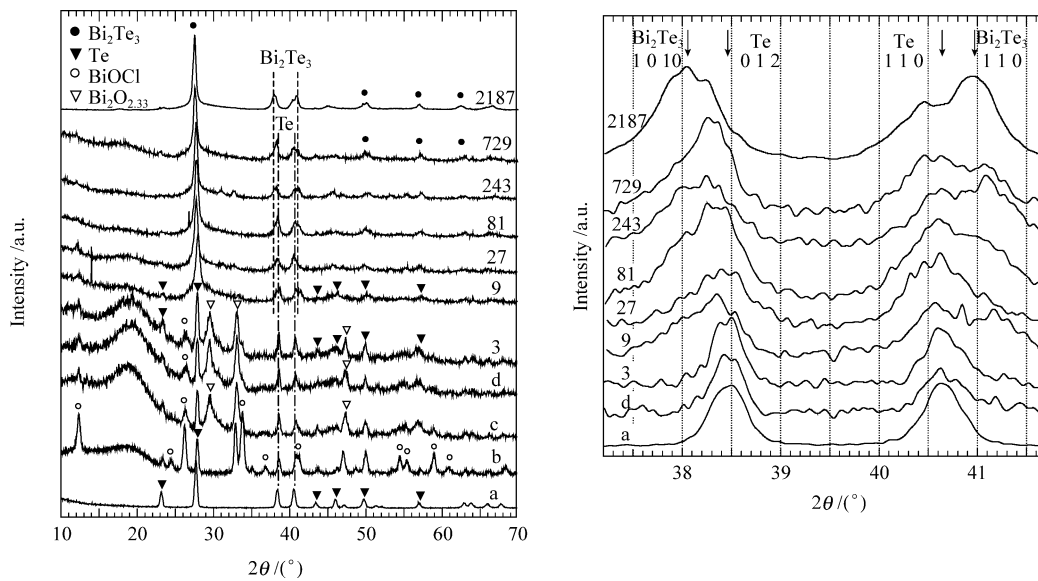
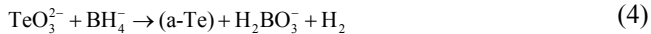
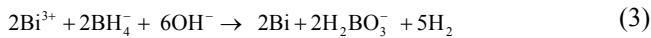
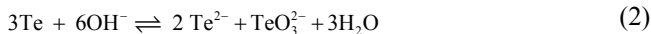


Fig. 2 XRD patterns of the dried powders sampled at 1min after the addition of (a) Te, (b) BiCl₃+EDTA, (c) NaOH, (d) NaBH₄ and at various reaction times after the addition of NaBH₄ indexed minutes.

Possible chemical reactions involved in the synthesis of Bi₂Te₃ could be listed as follow:



Reaction (1) is the hydrolyzation of BiCl₃ and its product BiOCl exists mainly in the early stage. Reversible reaction (2) could take place in a strong alkali solution and (a-Te) colloids would be generated as its reverse reaction product. Reactions (3) and (4) are the reduction process of Bi³⁺ and Te⁴⁺ respectively and should be possible according to the standard redox potential $E^0(\text{Bi}^{3+}/\text{Bi}) = 0.168 \text{ V}$, $E^0(\text{H}_2\text{O}/\text{BH}_4^-) = -1.12 \text{ V}$ and $E^0(\text{Te}^{4+}/\text{Te}) = 0.568 \text{ V}$. The equilibrium between three valence states of Te in the reactions (2) and (4) implies Te atoms will be long-standing along the reaction process, which can be one of the explanations of the remaining Te in the synthesized product. Reactions (5) and (6) respectively represent the ions reaction mechanism and atoms' reaction mechanism in the synthesis of Bi₂Te₃. Therefore, a speculation could be reached from these reactions that OH⁻ is essential for the synthesis of Bi₂Te₃, while EDTA is not.

To further investigate the effects of NaOH and EDTA, two control experiments were performed for sample B (without EDTA) and sample C (without NaOH). XRD analyses results (Fig. 3) also confirmed the above speculation, that is, Bi₂Te₃ could be synthesized under experimental conditions without EDTA, but that the

addition of NaOH is necessary.

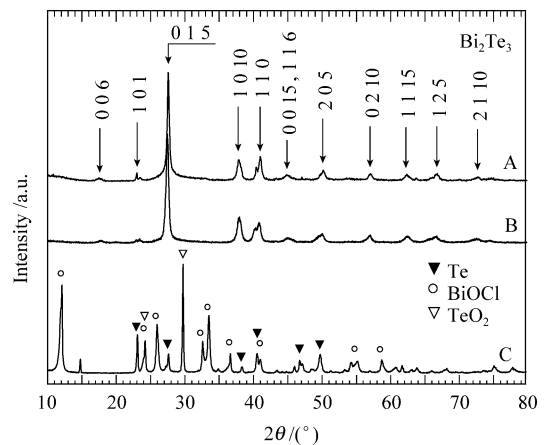


Fig. 3 Influences of EDTA and NaOH on the XRD patterns of the powders synthesized at 65 °C for 2,187 min. (A) with both EDTA and NaOH, (B) NaOH only, (C) EDTA only.

Figure 4 shows the TEM images of samples A and B. Prepared with EDTA, the powders of sample A were mainly hollow tubes with sparse small rags (Fig. 4a, b). The geometric morphologies of the tubes, about 100 nm in diameter and about 500 nm in length, are quite different from those of usual carbon nanotubes and Bi₂Te₃ nanotubes obtained by high-temperature hydrothermal synthesis in a sealed autoclave [10]. We therefore call them *nanocapsules*. The HRTEM image embedded in Fig. 4a indicates that the tube wall is about 6 nm thick, which is about two times the *c*-axis lattice parameter of Bi₂Te₃. The SAED pattern embedded in Fig. 1b taken from an area on the trunk of a nanocapsule shows a typical 6-fold symmetry pattern, which implied the tube wall is vertical to the *c*-axis of the

crystal. Nothing but irregular sheets was observed in the sample obtained without EDTA, which powerfully proves

the controlling effect of EDTA on the microstructure and morphology of Bi_2Te_3 during the synthesis.

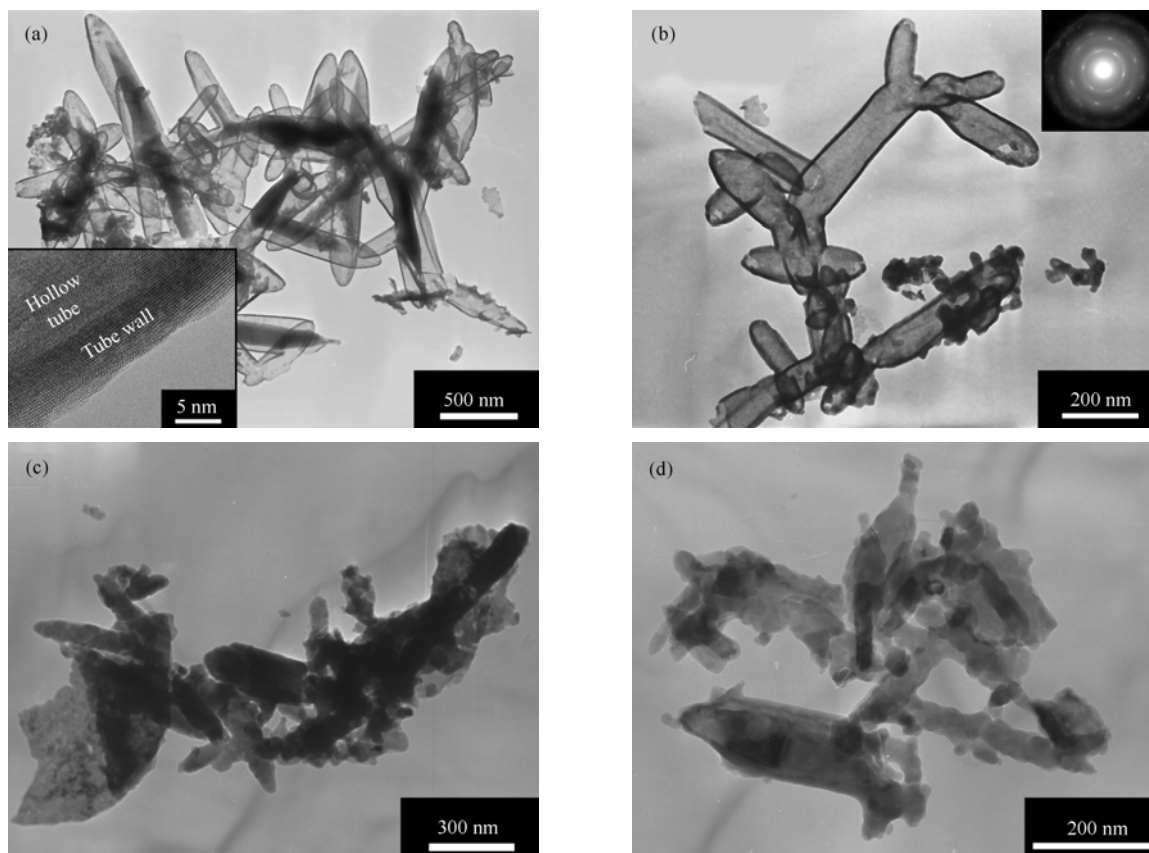


Fig. 4 TEM images of the Bi_2Te_3 powders synthesized with EDTA, (a) and (b), showing forking nanocapsules, and the irregular nanopowders synthesized without EDTA, (c) and (d).

Bi_2Te_3 has a layered anisotropic lattice structure. In every 5 atom layers periodically arranged along the c -axis direction, there are two Te layers combined to neighboring Te layers with van-der-Waals bonds. As shown in Fig. 5, four different positions were available for Te atoms (or ions) from the solution during the growth of Bi_2Te_3 nuclei. Position 1 is the least stable one where combination with the nuclei atoms is based on van-der-Waals bonds. At position 2, on the base plane vertical to the c -axis, an additional broken bond could emerge and the new combined atoms are apt to re-dissolve into the solution. Thus, position 2 is also unstable, although it is a covalent bond position. Positions 3 and 4, at the edges of the nuclei base planes (Fig. 5), are stable ones because Te atoms are able to combine with the nuclei by covalent bonds at these places without increasing broken bonds. Similar analyses could be applied to Bi atoms. Therefore Bi_2Te_3 nuclei would mainly grow along the direction vertical to the c -axis and produce sheet-like crystals in the solution.

The growth process of sheet-like Bi_2Te_3 particles is primarily determined by the formation rate of the nuclei (or the number of nuclei) and the activity of the “free” atom (or ion) in the solution. If there are excessive Bi_2Te_3 nuclei, sheet-like crystals could not grow sufficiently in the solution.

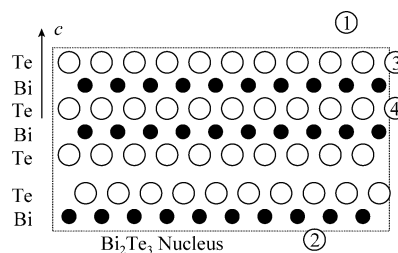


Fig. 5 Schematic drawing of a Bi_2Te_3 nucleus. An atom from the solution is easily attached at position 3 or 4 in the edge of the base plane, but is unstable at position 1 or 2 on the base plane.

Most of tiny crystals (or nuclei) will combine together to decrease the surface broken bonds and reduce the surface energy by surface nucleation [10], stacking or side connection. By these means, the obtained Bi_2Te_3 particles will present irregular shapes, and always congregate to big particles like those synthesized in sample B without EDTA (Fig. 4c, d) and the Bi_2Te_3 particles obtained at above 100 °C by hydrothermal or solvothermal method [13–15]. EDTA, as a multidentate ammoniac carboxylic chelator, could combine with Bi ions in the solution during the synthesis, decrease the activity of Bi ions, and lessen the amount of Bi_2Te_3 nuclei, which would ensure that the Bi_2Te_3

nuclei formed in the beginning will grow sufficiently in the later period. During the growth of Bi_2Te_3 sheets, Bi atoms suffer from the confinement of EDTA and Te atoms in the colloids. Therefore it is more difficult to attach them to the base plane of the sheets, and the Bi_2Te_3 sheets will grow along the base plane. However, due to the difference of the atom arrangement and crystal defect density between both sides, the Bi_2Te_3 sheets are liable to bend up. For a bent sheet, there is tensile force among the atoms on the convex sides as well as compressive force on the concave sides. As a result, the atoms on the concave sides tend to be pushed out of the crystal while “foreign” atoms would insert into the convex sides. These would accelerate the bend process. Meanwhile, the continuous growth along the base plane will bring the two edges of the Bi_2Te_3 sheets closer and closer. Finally, the two edges will combine together, forming a closed loop to decrease the “broken bonds”. Because the cylinder surface is vertical to the c -axis, the crystal will primarily grow along the cylinder axis once the Bi_2Te_3 sheets bend to closed loops. Furthermore, there are many outer factors disturbing the growth of the loops (or the tubes). For example, the growth rate of the inner sides incomparable to that of the outer ones will cause the shrinking of the tubes and consequently, the closing at the ends. The local block to the tube growth and/or the breaking up at the defects will result in the forking of the tubes, and so on. That is why the nanocapsules are short, fat and forked as shown in Fig. 4a, b.

The low temperature aqueous chemical route developed in this work has many advantages, including the relatively low synthesis temperature, the simple preparation equipment, the convenience for in-situ investigation during the process and the applicability for mass synthesis of materials. Moreover, compared to the nanotubes obtained by high-temperature hydrothermal synthesis in the high-pressure autoclave [10–11], the tube wall of these nanocapsules prepared under low temperature aqueous chemical method is around 6 nm thick, about two times the lattice parameter of Bi_2Te_3 in c -axis and obviously thinner than those of the nanotubes (20–30 nm). The tube-like hollow structure with thin walls may possibly have more remarkable nano effects, and be likely applied to new TE materials and other research fields.

4 Conclusions

(1) Bi_2Te_3 nanopowders could be synthesized at 65 °C by the aqueous chemical route, using BiCl_3 and pure Te powders as reactants, NaOH as alkaline adjustor and NaBH_4 as reductant.

(2) Compared to the usual hydrothermal or solvothermal method, aqueous chemical synthesis could be performed in an open system and is convenient for in-situ investigation and observation during the synthesis process.

(3) The addition of EDTA to the system could decrease the activity of Bi ions in the solution, reduce the rate of Bi_2Te_3 nucleation, and thus favor the synthesis of Bi_2Te_3 nanocrystals with hollow capsule-like microstructures.

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