Glucose-assisted continuous flow synthesis of Bi₂Te₃ nanoparticles in supercritical/near-critical water

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ABSTRACT

Nanostructuring of materials is an effective way to lower the thermal conductivity. A novel supercritical/near-critical water approach was developed for the fabrication of Bi₂Te₃ nanoparticles. The method provides a rapid, “green” and large scale synthesis of nanoparticles with uniform particle sizes, and the production can be scaled up for commercial production. The synthesis temperature and the pH condition were studied for the synthesis of Bi₂Te₃. It is found the formation mechanisms are different when the NaOH concentration is changed in the solution. The method may be applied for preparing nanoparticles of other metals and intermetallic compounds.

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1. Introduction

Recent progress in thermoelectric materials has primarily involved nanostructuring of materials to dramatically lower the thermal conductivity [1–7]. The thermoelectric figure of merit (zT) is enhanced through controlling the transport of phonons and electrons in the superlattices or quantum dots, and high zT values of about 2.4 and 1.6 were reported at room temperature for Bi₂Te₃/Sb₂Te₃ superlattices [5] and PbSeTe based quantum dots [6], respectively. Enhancement of zT is also possible in bulk nanostructured materials such as nanocomposite, and a zT value of 1.4 was reported in the nanocrystalline bulk BiSbTe alloy [7]. Bi₂Te₃ based alloys are industrially applied materials for thermoelectric cooling application. Many chemical routes have been used for preparing nanostructured Bi₂Te₃ based alloys. However, common chemical routes for the preparation of nanostructured Bi₂Te₃ based compounds rely on organic solvents and toxic reductants such as NaBH₄ and hydrazine [8–11]. The use of “green” methods for production of engineered nanomaterials in both industrial application and scientific research has gained an enormous amount of attention in recent years [12]. Utilization of environmentally benign solvents and nontoxic chemicals are some of the key issues in green synthesis strategy considerations [13]. Recently, we have successfully synthesized Bi₂Te₃ nanoparticles by a green biomolecule-assisted hydrothermal method [14,15].

The synthesis method plays an important role on the effective utilizations of nanoparticles. Conventional chemical methods for the fabrication of nanoparticles are time consuming and have high manufacturing cost. Over the past decades, supercritical/near-critical fluid technology has received considerable attention in materials science [16]. The particle size and size distribution of the nanoparticles are controlled by the large changes in reaction rates and solubilities around the critical point of the solvent. The main advantage of supercritical/near-critical fluids lies in the particularly attractive physicochemical properties such as gas-like transport properties in diffusivity, viscosity, and surface tension, while maintaining liquid-like properties such as high solvation capability and high density [16,17]. Supercritical fluids have been used as reaction media to synthesize a number of materials with sizes ranging from micrometer down to nanometer scale [16–20]. Supercritical fluid reactions can be carried out in two types of reactors: batch type and flow type (continuous flow reactor) [20]. Continuous flow supercritical reactors have the advantage that nanoparticles can be synthesized in considerable quantities, that phase space can be probed in a short time, and that the effect of the heating period on the synthesis is eliminated by the rapid heating. Moreover, compared with other time consuming methods for preparation of nanoparticles such as high-energy ball milling, the manufacturing costs of continuous flow synthesis are relatively low and the production can be easily scaled up. The present study reports a continuous flow synthesis of an important thermoelectric alloy Bi₂Te₃ in supercritical or near-critical water using glucose as reductant, and contributes a promising “green” and fast method for preparing nanoparticles of a wide range of other metals and alloys in large quantities.

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Fig. 1. Sketch of the continuous flow equipment for supercritical/near-critical synthesis.

2. Experimental

For the preparation of bismuth precursor the following steps were taken: (1) 5 mmol BiCl_3 was dissolved in 50 ml of 2 M HCl solution and 3 g ethylenediamine-tetra-acetic acid sodium (EDTA) was dissolved in 400 ml of distilled water. (2) The two solutions were then mixed and diluted with water to a volume of 500 ml. Tellurium precursor was prepared by: (1) dissolving 7.5 mmol $\text{Te}(\text{OH})_6$ and a proper amount of NaOH in distilled water. (2) Glucose 6 g was added as reductant to the Te solution and it was finally diluted with distilled water to a volume of 500 ml. The NaOH concentrations of the Te precursors were adjusted to 0.1, 1 and 6 M for different experiments. Note that excess of 100 mmol NaOH was further added to each Te precursor to counteract the HCl from the Bi precursors. Both Bi and Te precursors are clear solutions. In the used continuous flow setup (shown in Fig. 1), the reactor is first pressurized with water and the correct intended working temperature is set. The reactants and solvent (water) are pumped into the reactor using air-driven liquid pumps. The solvent is preheated to the desired temperature and pressure before it meets the two precursors. The reaction takes place immediately upon mixing as well as during the flow through the reactor. For a typical synthesis, both precursors were pumped continuously at the same rate of 5 ml/min, and the preheated distilled water was pumped at a rate of 10 ml/min. The samples are named as “Lx”, “Mx” and “Hx” in the present study, where “L”, “M” and “H” denote low, medium, and high NaOH concentrations of 0.1, 1 and 6 M in the Te precursors, respectively, while “x” is the temperature.

The products were analyzed by X-ray diffraction (XRD) on a STOE powder diffractometer using $\text{Cu K}\alpha_1$ radiation ($\lambda = 1.5406 \text{ \AA}$). The morphology and particle size of Bi_2Te_3 nanoparticles were observed on a NOVA600 field-emission scanning electron microscope (SEM). Differential scanning calorimetry (DSC) measurements were done with a NETZSCH STA 449 thermoanalyzer in helium atmosphere with a heating rate of 10 K/h.

3. Results and discussion

In our previous work [14,15], we studied the formation and growth of Bi_2Te_3 under hydrothermal condition using conventional batch type autoclaves, and it was found that the concentrations of pH controlling additives play a crucial role on the formation of Bi_2Te_3 , as well as on the morphology and crystal size of the Bi_2Te_3 nanostructure. Since continuous flow synthesis is a promising method for potential commercial production, it is of interest

Fig. 2. XRD patterns of sample L250, L300 and L350, respectively.

to extend batch studies of Bi_2Te_3 to a continuous flow reactor. Our *in situ* synchrotron radiation studies showed that it takes several minutes for the phase transformation from the precursors to Bi_2Te_3 , but typically the residence time in the heater after the mixing point of a continuous flow reactor is less than 1 min. This means that other reaction parameters such as reaction temperature and the concentration of pH additives are crucial in a continuous flow synthesis. In addition, the concentration of Bi and Te precursors also plays an important role on the products. As an example the *in situ* found that it is possible to form Bi_2Te_3 at 3 M NaOH condition, but when an experiment is performed at 3 M NaOH with a ten times diluted Bi and Te precursors, only Bi_4Te_5 is obtained. In the *in situ* studies the concentration of the precursors is often decided by the fact that high concentrations are needed to get good diffraction data. For a continuous flow synthesis, a lower concentration of the precursors is often necessary to avoid that the products block the reactor. This is one reason why it may be difficult to directly convert insight from *in situ* studies to laboratory scale reactors. Furthermore, when comparing with conventional autoclave synthesis, it is preferred to have stable and clear solutions of the precursors for the flow synthesis. Instead of using strong or toxic reductants, reducing sugars and various biomolecules can act as mild reducing agents. In the present study we simply use glucose as reductant, while the precursors are clear and stable solutions of Bi and Te.

Fig. 2 shows the XRD patterns of sample L250, L300 and L350, which were prepared at low NaOH concentration of 0.1 M NaOH in the Te precursor. The major phase of sample L250 is Te and only traces of Bi_2Te_3 can be detected. When the reaction temperature is increased to 300 or 350 °C, almost single phase of Bi_2Te_3 can be achieved, as shown by the XRD patterns of L300 and L350. At low NaOH concentration, $\text{Te}(\text{OH})_6$ can be easily reduced to Te due to the high redox potential. Therefore, the following formation mechanism is suggested. Te is formed from $\text{Te}(\text{OH})_6$ in a fast reaction using glucose as reducing agent. Bi_2Te_3 is then formed by the combination of elemental Te and Bi^{3+} (or $[\text{Bi}(\text{EDTA})]^{+}$) ions. The formation mechanism has been established by other chemical synthesis studies where Te is used as templates to form Bi_2Te_3 [14,15,21].

Fig. 3a shows the XRD patterns of sample M200, M250, M300, M350, M375 and M400, respectively, which were prepared at medium concentration of NaOH. Different products were obtained at the different reaction temperatures. At the reaction temperature of 200 °C, single phase Bi was obtained. When increasing the reaction temperatures to 250 and 300 °C the observed majority phases were Bi_2Te_3 and Bi_4Te_5 , respectively. Traces of Bi_2Te_3 phase were detected at the reaction temperature of 300 °C. With the reaction temperature further increased, the content of Bi_4Te_5

Fig. 3. (a) XRD patterns of sample M200, M250, M300, M350, M375 and M400, respectively, (b) the zoom view of the XRD patterns, (c) DSC curves of M200, M250, M300 and M400. All curves are shown with an off-set for clarity.

decreased while that of Bi_2Te_3 increased. Almost single phase of Bi_2Te_3 was obtained at 400°C . One can clearly see the different peak positions of the different products in the enhanced view of the XRD patterns (Fig. 3b). The different products can be further verified, through determination of their melting point, this was done by DSC analysis. Sample M400 shows an endothermic peak at 583°C , which is the melting point of Bi_2Te_3 , while M200, M250 and M300 have no endothermic peak around the Bi_2Te_3 melting point (see Fig. 3c). Samples M200, M250 and M300 show rather weak endothermic peaks around 265 , 420 and 520°C , respectively, indicating the melting points of the main phases for each sample. From the above results, the Te incorporation in the products increases with the increase of the reaction temperature. Compared with the

reaction at low NaOH concentration, medium NaOH concentration enhances the reductive ability of glucose due to the reaction between the oxidation products of glucose and OH^- . Under this condition, therefore, Bi^{3+} is much easier reduce to Bi than at low NaOH concentration, and the reduction product of $\text{Te}(\text{OH})_6$ is probably Te^{2-} ions rather than elemental Te. This is also the reason that most of the products are deficient in Te since excessive Te exists as divalent ions in solution. As a result, the bismuth tellurides formed in medium NaOH concentration probably result from the reaction between elemental Bi and Te^{2-} ions.

Upon further increasing the NaOH concentration to 6M in the Te precursor, not the Bi_2Te_3 phase, can be obtained even at the

Fig. 4. XRD patterns of sample H200, H250, H300, H350 and H375, respectively.

Fig. 5. XRD patterns of sample M350* and H350* prepared under nonstoichiometric amounts of Bi and Te with Bi:Te of 1.7:3, and 1.3:3 at medium and high NaOH concentrations, respectively, at the reaction temperature of 350°C .

Fig. 6. (a–c) SEM images of sample L350, M350* and H350*, respectively, (d) enlarged SEM image of L350, (e) size distribution derived from the particles of (d).

reaction temperature of 375 °C. Fig. 4 shows the XRD patterns of sample H200, H250, H300, H350 and H375, respectively. At reaction temperature of 200 and 250 °C, the products have white colors, and are likely to be an oxide (or hydroxide). X-ray fluorescence (XRF) analysis on a SPECTRO.XEPOS shows that the oxide contains both Bi and Te. The XRD pattern of the oxide can be fit quite well by a cubic structure with cell parameter of about 8.2 Å. However, we have not been able to fully identify the phase. When the reaction temperature was enhanced to 300 °C or above, the XRD patterns show that the products of sample H300, H350 and H375 were BiTe. It is difficult to propose the reaction process of BiTe at supercritical/near-critical condition due to the rapid reaction. Based on the above results from the different reaction temperatures, the oxide might be an intermediate product during the synthesis of bismuth telluride at high NaOH concentration. Unlike the above two formation mechanisms of

different bismuth tellurides at low and medium concentrations of NaOH, the BiTe formed at high NaOH concentration can possibly take place by the co-reduction of the oxide containing both Bi and Te.

At the conditions of medium or high concentration of NaOH, the products always have deficiency of Te compared with the stoichiometric ratio of Bi:Te = 2:3 in the precursors. This is because the rest of the Te exists as Te^{2-} ions in the NaOH solution. One can further improve or obtain phase purity of Bi_2Te_3 by either reducing the concentration of Bi in the precursor or by slowing down the pump rate of Bi precursor, instead of pumping the stoichiometric amounts of Bi and Te in the reactor. For example, if at medium and high NaOH concentrations and a temperature of 350 °C (sample M350* and H350*) then if the stoichiometry is adjusted to Bi:Te = 1.7:3 and 1.3:3, respectively, single phase of Bi_2Te_3 can be obtained as shown by the XRD patterns in Fig. 5.

The different products and formation mechanisms at different NaOH concentration presumably is due to the changing reductive ability of glucose. The aldehyde group in the glucose can be oxidized to form a carboxylic acid group and it can further form a carboxylate ion in the presence of NaOH. As a result, excess of NaOH will promote the reducing reaction. With respect to electrochemistry, the reduction potential decreases as pH increases [22], and therefore the reduction of Bi and Te precursors increases with NaOH concentration. However, the processes during the synthesis are complex. As an example, glucose can be converted into lactic acid due to the alkaline catalytic activity [23], and this will result in other products such as in sample H200 and H250.

The differences in morphology and particle size of Bi_2Te_3 between samples L350, M350* and H350* were analyzed by scanning electron microscopy (SEM). Fig. 6a–c is the typical SEM images of sample L350, M350* and H350*. All the samples show almost single morphology and are composed of particles with granular forms. With increasing NaOH concentration, the particle size increases from sample L350 to H350*, which is in good agreement with the *in situ* synchrotron radiation study of the formation and growth of Bi_2Te_3 [15]. The morphology and particle size of Bi_2Te_3 are quite uniform for each sample suggesting a good control of nucleation and growth kinetics under the supercritical or near-critical condition. Fig. 6d is an enlarged SEM image of sample L350 and Fig. 6e is a histogram of the size distribution derived from the particles in random directions of Fig. 6d. The irregular granular morphology and the size distribution histogram indicate that the anisotropic crystallographic growth of Bi_2Te_3 crystals is not so evident in the supercritical/near-critical reaction. The average particle size is about 75 nm for sample L350.

4. Conclusions

For the first time, Bi_2Te_3 nanoparticles have been successfully prepared by a “green” and rapid continuous flow synthesis method in supercritical or near-critical water using glucose as reductant. The NaOH concentration plays an important role on the synthesis of Bi_2Te_3 in the continuous flow method. The study of the formation under different NaOH concentrations reveals the different formation mechanisms of bismuth tellurides mainly due to the fact that the reductive ability of glucose increases with NaOH concentration. Proper adjustment of all synthesis parameters is crucial for formation of bismuth telluride since the continuous flow method has limited residence time during the synthesis. In general, synthesis of intermetallic materials is a great challenge for continuous flow methods due to the required simultaneous reduction of the metals, but the present results provide a clear example that by proper tuning of process parameters it is possible to obtain robust results.

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