Microwave-assisted Preparation of Bi_2Te_3 Hollow Nanospheres

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Bi_2Te_3 hollow nanospheres with diameters of 50–100 nm have been successfully prepared using TeO_2, $Bi(NO_3)_3$, and HNO_3 in mixed solvents of water and ethylene glycol by a simple microwave heating method at 150 °C for 30 min.

Bi_2Te_3 is a semiconductor with a narrow band gap, which is an efficient thermoelectric material with a variety of applications such as thermoelectric coolers and radioisotope thermoelectric generators.[1] Nanostructured thermoelectric materials exhibit interesting properties that are absent in their bulk counterparts, which can benefit their applications.[2,3] Bi_2Te_3 nanostructures with various morphologies such as nanoparticle,[4–10] nanorod,[11] nanowire,[12–20] nanosheet,[21,22] nanocapsule,[23] and nanotube[24,25] have been prepared.

The application of microwave heating in the synthesis of materials is a fast growing research area owing to its advantages such as rapid volumetric heating, higher reaction rate, selectivity, and shorter reaction time compared to conventional heating methods. There have been only a few reports on the preparation of Bi_2Te_3 nanomaterials by microwave heating method. Harpeness and Gedanken[26] synthesized nanostructured Bi_2Se_3 by a microwave-polyol method, they also tried to prepare Bi_2Te_3, but Bi_3Te_4 was obtained. Zhu et al.[27] prepared Bi_2Te_3 nanorods and nanoflakes by a microwave-assisted polyol method using Te and $Bi(NO_3)_3$. Herein, we report a simple microwave heating method for fast preparation of Bi_2Te_3 hollow nanospheres.

In a typical procedure for synthesis of Bi_2Te_3 (Sample 1), $Bi(NO_3)_3 \cdot 5H_2O$ (0.19 g) was dissolved in 15 mL of ethylene glycol (EG) in a 50-mL flask at room temperature (Solution A). Solution B was prepared by dissolving TeO_2 (0.03 g) in a mixture of 5 M aqueous HNO_3 solution (1.85 mL) and EG (1.85 mL). Solution A was microwave-heated to 150 °C, and then Solution B was rapidly added into Solution A. The mixed solution was maintained at 150 °C for 30 min, then the microwave heating was terminated, and the solution was cooled to room temperature. The microwave oven used was a focused single-mode microwave synthesis system (2.45 GHz, maximum 300 W, Discover, CEM, U.S.A.), which was equipped with a magnetic stirring and a water-cooled condenser. The products were separated by centrifugation, washed with absolute ethanol three times, and dried at 60 °C in a vacuum.

In the synthesis of Sample 2, $Bi(NO_3)_3 \cdot 5H_2O$ (0.045 g) and Sb_2O_3 (0.015 g) were dissolved in a mixture of 5 M aqueous HNO_3 solution (0.2 mL) and EG (22.5 mL) in a 50-mL flask at room temperature (Solution A). Solution B was prepared by dissolving TeO_2 (0.045 g) in a mixture of 5 M aqueous HNO_3 solution (2.75 mL) and EG (2.75 mL). Solution A was microwave-heated to 150 °C, and Solution B was rapidly added into Solution A. The mixed solution was maintained at 150 °C for 30 min.

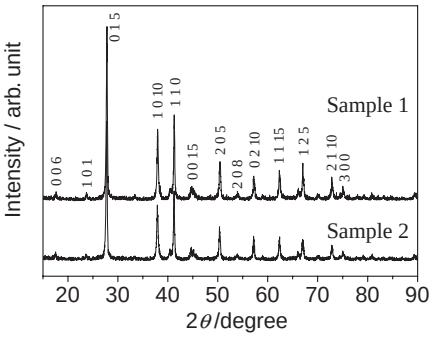

Figure 1. XRD patterns of Samples 1 and 2 synthesized by microwave heating at 150 °C for 30 min.

Figure 1 shows X-ray powder diffraction (XRD, Cu Kα $\lambda = 1.54178$ Å, Rigaku D/max 2550V) patterns of Samples 1 and 2 synthesized by microwave heating at 150 °C for 30 min. Both samples consisted of a single phase of well-crystallized Bi_2Te_3 with a hexagonal structure (JCPDS 82-0358). Although Sb_2O_3 was used in the preparation of Sample 2, no Sb_2Te_3 was detected by XRD in the product. However, only a single phase of elemental Te was obtained under the same condition as Sample 2 except that Sb_2O_3 was used to completely substitute $Bi(NO_3)_3 \cdot 5H_2O$, and no Sb_2Te_3 was obtained in the product.

The morphologies of samples were investigated with transmission electron microscopy (TEM, JEOL JEM-2100F). Figures 2a–2c show the TEM micrographs of Sample 1, from which one can see Bi_2Te_3 hollow nanospheres with diameters ranging from 50 to 100 nm. The shell of hollow nanospheres consisted of very small nanoparticles. The shell thicknesses of the hollow nanospheres ranged from 20 to 35 nm. The majority

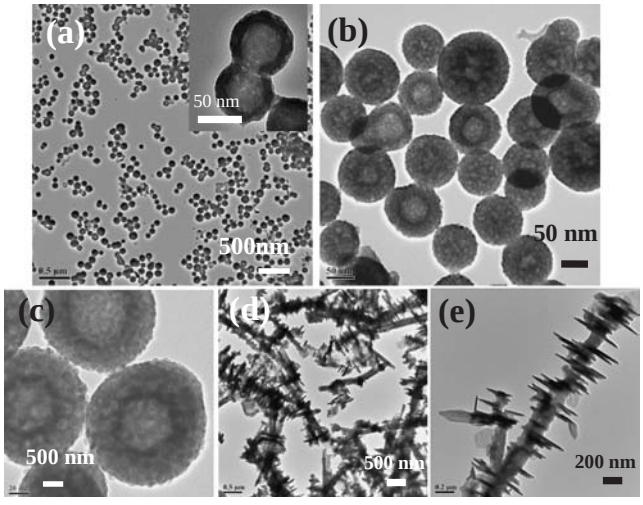

Figure 2. TEM micrographs. (a)–(c) Sample 1; (d) and (e) Sample 2.

were individual hollow nanospheres. However, combined hollow nanospheres were observed in a small numbers, as shown in the inset of Figure 2a. In the presence of Sb_2O_3 (Sample 2), the morphology of Bi_2Te_3 showed organized nanosheet assemblies (Figures 2d and 2e). The widths of main skeletons ranged from 100 to 300 nm and the lengths up to 5 μm. The thicknesses of nanosheet building blocks were less than 30 nm.

There have been reports that Bi_2Te_3 nanostructures were prepared using Te powder, OH^- (basic reagent), Bi^{3+}, and reducing agent (such as $NaBH_4$ and N_2H_4) by a solvothermal method.[6,21,28] OH^- was used to change Te powder into Te^{2-} and the reducing agent was used to reduce Bi^{3+} to elemental Bi. Then, Te^{2-} and Bi^{3+} or Te and Bi could react to form Bi_2Te_3 by heating. In the present work, acidic aqueous HNO_3 solution was used instead of a basic environment reported in the literature, and EG was used as both a reducing reagent and a cosolvent. Our experiments showed that Bi_2Te_3 could not be obtained when using a basic aqueous NaOH solution instead of aqueous HNO_3 solution. Bi^{3+} could not be reduced to elemental Bi in the mixture of EG and HNO_3 at 150 °C by microwave heating. During the preparation process of Sample 1, a white intermediate product (Bi_2TeO_5) was obtained after microwave heating for 10 min at 150 °C, and finally it transformed to black Bi_2Te_3. This white intermediate product could not change to Bi_2Te_3 at temperatures below 130 °C by microwave heating. In comparison, the product prepared by a conventional heating method for 30 min was Bi_2TeO_5 instead of Bi_2Te_3, a mixture of Bi_2Te_3 and Te was obtained when the conventional heating time was increased to 11 h, and a single phase of Bi_2Te_3 was obtained when the conventional heating time was increased to 24 h. The heating time needed to obtain a single phase of Bi_2Te_3 by microwave heating was much shorter than that by a conventional heating method. The similar situation existed in the preparation of Bi_2S_3 and Sb_2S_3 nanostructures.[29] When Sb_2O_3 was used instead of $Bi(NO_3)_3$ in order to synthesize Sb_2Te_3, elemental Te instead of Sb_2Te_3 was obtained after microwave heating for 30 min. Harpeness and Gedanken[26] tried to synthesize Bi_2Te_3 using $BiONO_3$, NaOH, and Te powder as reagents, and ethylene glycol as the solvent by microwave heating method, but Bi_3Te_4 instead of Bi_2Te_3 was yielded. Zhu et al.[27] prepared Bi_2Te_3 nanorods and nanosheets using $Bi(NO_3)_3 \cdot 5H_2O$, Te powder, KOH, EG, and glycerol by microwave-heating, in which elemental Bi was formed by reduction of Bi^{3+}, and then Bi reacted with Te. In the present preparation, we suggest that the intermediate product Bi_2TeO_5 acted as the core for the formation of Bi_2Te_3 hollow nanospheres. Bi_2Te_3 nanoparticles were derived from Bi_2TeO_5 on the Bi_2TeO_5 surface, forming the shell of the hollow nanosphere. When the Bi_2TeO_5 core was completely decomposed, the Bi_2Te_3 hollow nanospheres formed.

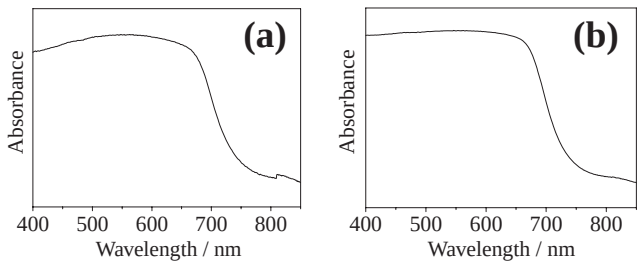

Figure 3. The UV–vis absorption spectra. (a) Sample 1 and (b) Sample 2.

The UV–vis absorption spectra (Lambda 950, Perkin-Elmer) of Samples 1 and 2 are shown in Figure 3. The absorption edge was observed at about 700 nm for both samples. The absorption band gap E_g can be determined by the equation $(\alpha h\nu)^n = B(h\nu - E_g)$, in which α is the absorption coefficient, $h\nu$ is the light energy and B is a constant. For the direct band gap semiconductor Bi_2Te_3, n is 2. The band gaps E_g of Samples 1 and 2 were estimated to be 1.49 and 1.63 eV, respectively. It should be noted that the band gap obtained from the absorption measurement is only an approximately estimated value.

In summary, we have demonstrated a simple microwave-assisted method for the synthesis of Bi_2Te_3 hollow nanospheres in mixed solvents of water and EG. We expect that the microwave-assisted method may also be extended to prepare nanostructures of other VA–VIA compounds.

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