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Synthesis and characterization of carbon nanotube supported Bi_2Te_3 nanocrystals

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ABSTRACT

Multiwalled carbon nanotube (MWNT) supported Bi_2Te_3 nanoparticle heterostructures were firstly synthesized using a microwave-polyol method assistant with titration. The microwave heating process was adopted to yield nanoscale Bi_2Te_3 by accelerating chemical reaction rate. And the titration of Bi_2Te_3 precursors was conducted to make the nanoparticles grow onto surfaces of MWNTs easily. The general morphology of resulting composites is hexagonal Bi_2Te_3 nanoplates and their aggregates attached on surfaces of MWNTs randomly. When the diameter of MWNT is rather shorter, Bi_2Te_3 crystallites are encapsulated into inner cores of nanotubes.

1. Introduction

Bismuth telluride (Bi_2Te_3) and its alloys are the best thermoelectric (TE) materials near room temperature [1]. Usually, bulk nanostructured Bi_2Te_3 materials [2,3] have a slightly lower ZT (the efficiency of TE materials), when compared with their low dimension system, such as a Bi_2Te_3/Sb_2Te_3 superlattice thin film [4]. But they are much more attractive for the purpose of large-scale commercial application. And their device shows great promise for using as a power generator [5], cooler [6], DNA microchip [7], switch [8], etc. In principle, the preparation of bulk nanostructured Bi_2Te_3 is adding nanoscale Bi_2Te_3 crystals into the bulk solid [9]. Because of an enhanced phonon blocking effect of the small grains, the thermal conductivity κ of the whole composites could remarkably decrease, and thus a high ZT is obtained.

Carbon nanotubes (CNTs) have nanoscale, low dimension, and holey structure features, which are beneficial to high ZT [10,11]. They are promising candidate for TE materials in view of the quantum confinement effect of the charge carriers and the size effect of the heat carriers [12,13]. Specially, the κ of an isolated CNT is more than 3000 W/(m K) at room temperature [14], but recently it is reported that the κ of a packed bed of three-dimensional random networks of CNTs is only about 0.13–0.19 W/(m K) [15]. The dramatic decrease of thermal conductivity, which generates from intertube contact resistance, is greatly helpful to increase ZT [16,17].

In addition to CNTs, CNT-supported nanocrystal heterostructures have interested researchers enormously. They are expected to be important for applications in the range of fuel cells [18], field emission devices [19], chemical sensors [20] and supercapacitors [21]. But there is still no report on the synthesis of CNT-supported TE nanoparticles. For instance, attachment of Bi_2Te_3 nanoparticles onto CNTs would take advantage of considerably low κ of random CNTs in the later bulk materials. This system has the potential to significantly decrease the κ and thus to increase the ZT.

However, there are still two key issues which should be resolved. The first one is to synthesize nanoscale TE particles, while the second one is to attach these particles onto surfaces of CNTs.

Usually, hydrothermal or solvothermal method with conventional heating process is adopted to prepare Bi_2Te_3, with advantages of low cost, less device-dependence and large-scale synthesis [22,23]. But its reaction time is rather long, usually 12–48 h [9], due to the low reaction rate of determinative chemical reaction:

$$2Bi + 3Te \Leftrightarrow Bi_2Te_3 \quad (1)$$

That is also the reason why different morphologies of submicroscale Bi_2Te_3 particles are obtained through this method. These crystals have thermodynamic stability and thus, could not attach to surfaces of MWNTs.

In this paper, a microwave-polyol method assistant with titration is demonstrated to synthesize Bi_2Te_3/CNT nanocompos-

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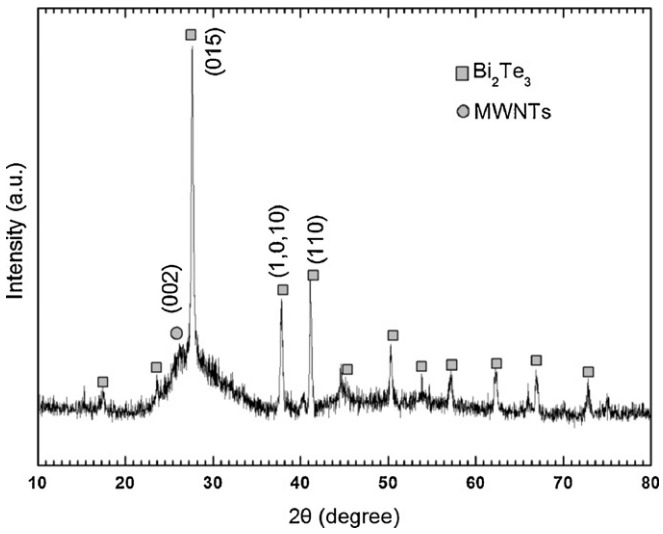

Fig. 1. X-ray diffraction (XRD) pattern of Bi_2Te_3/MWNTs.

ite. Microwave heating process is conducted to help yielding nanoscaled Bi_2Te_3 crystals, because its rapid volumetric and homogenous heating makes it a much more promising progress when compared with conventional heating methods [24,25]. It can accelerate chemical reaction rate, as a result, reaction time is decreased. And titration is also a key process, since it helps coating the nanoparticles easily on surfaces of CNTs.

2. Experimental procedures

Bismuth nitrate pentahydrate ($Bi(NO_3)_3{\cdot}5H_2O$), sodium tellurite (Na_2TeO_3), sodium hydroxide (NaOH), and ethylene glycol (EG) were purchased without further purification. Multiwalled carbon nanotubes (MWNTs) were prepared, purified and functionalized in the laboratory. Their experimental details were shown in the supporting information. In a typical procedure, 4 mL of 0.0005 mol/L $Bi(NO_3)_3{\cdot}5H_2O$ solution in EG and 16 mL of 0.00019 mol/L Na_2TeO_3 solution in EG were mixed. Afterwards, they were magnetically stirred for 10 min. This mixture solution is named A, which was then transferred into a burette connected with the mouth of a 100 mL vessel in the microwave oven. 0.16 g of MWNTs and 1.00 g of NaOH were dispersed into EG. Later, this mixture solution was sonicated for 30 min until MWNTs were dispersed evenly. The obtained black carbon slurry was named B, and then transferred into the vessel. At the beginning of the reaction, B was heated to 150 °C by microwave irradiation. Afterwards, A was titrated into B with rate of approximate 1 mL/min, by adjusting the small hole in glass plug at the end of the burette to an appropriate position. When the titration was finished, the mixture

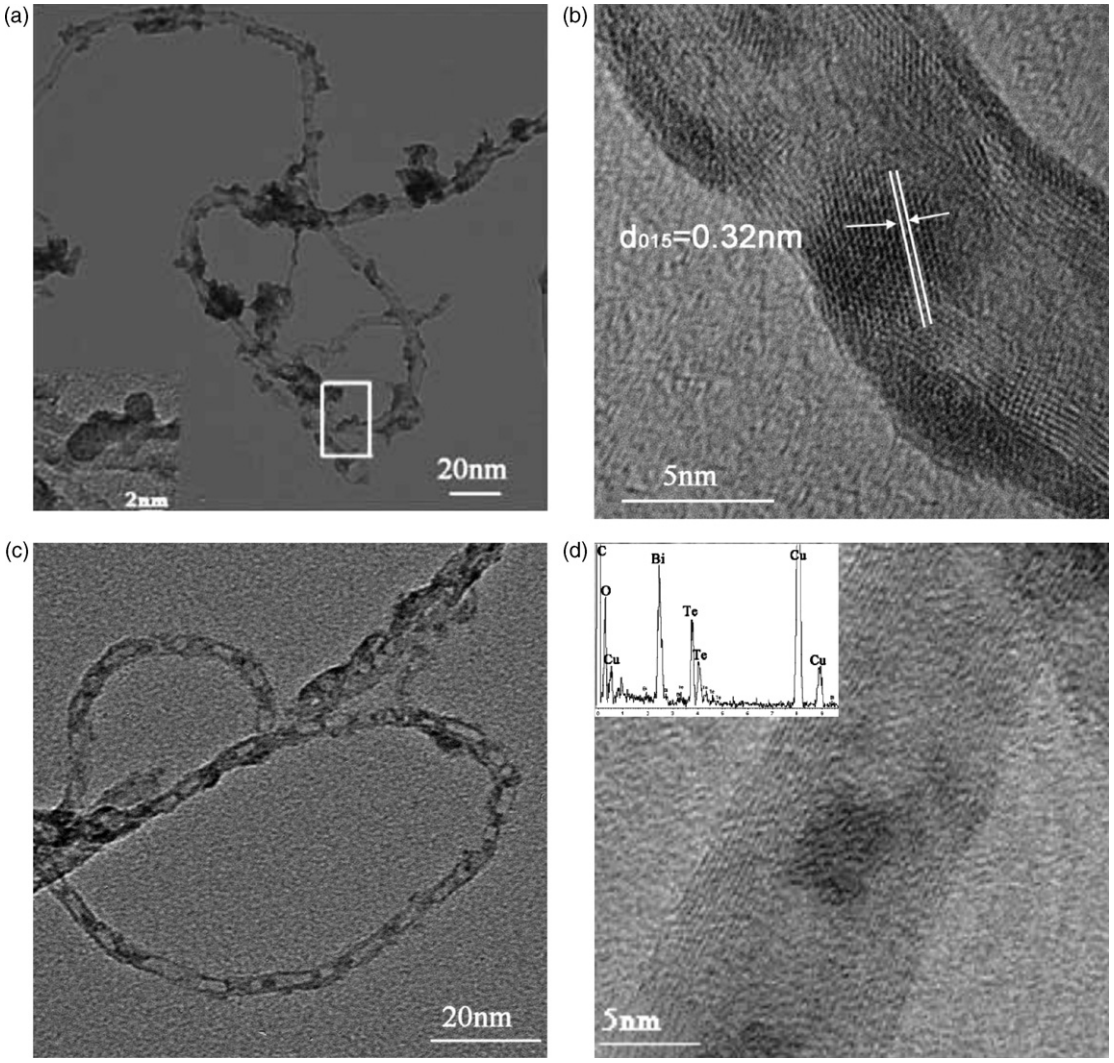

Fig. 2. (a) Typical transmission electron microscopic (TEM) image of Bi_2Te_3/MWNTs and hexagonal nanoplates attached on sidewalls of MWNTs (inset). (b) High-resolution-TEM (HRTEM) image of one hexagonal Bi_2Te_3 nanocrystal on MWNT. Arrows point to the interplanar distance of (0 1 5). Presence of Bi_2Te_3 was confirmed by the value 0.32 nm of the interplanar distance. (c) TEM image of Bi_2Te_3/MWNTs where Bi_2Te_3 encapsulated in the core of MWNTs. (d) HRTEM image of one quantum dot encapsulated in MWNT. Presence of Bi_2Te_3 was confirmed by the energy-dispersive X-ray spectrometer (EDS) signals for Bi and Te (inset).

solution was then heated at 170 °C for 40 min. Furious mechanical stirring was used during all the procedure. Finally, the dark precipitate was collected through centrifugation, washed with ethanol and deionized water, and then dried at 100 °C for 12 h.

Microwave oven was equipped with a temperature monitor and magnetic stirring devices. Its microwave power would be dynamically adjusted between 0 and 1000 W based on reaction temperature. The phase structures of the resulted products were investigated by X-ray diffractions (XRDs) with a Rigaku D/MAX-2550P diffractometer, using Cu Kα radiation (λ = 0.154056 nm). A Philips CM200 transmission electron microscopy (TEM) equipped with energy-dispersive X-ray spectroscopy (EDS) system, was used at an accelerating voltage of 120 kV for low-resolution imaging and 160 kV for high-resolution imaging.

3. Results and discussion

Fig. 1 shows XRD pattern of Bi_2Te_3/MWNTs. The three strongest diffraction peaks at $2\theta = 27.65°$, 37.81° and 41.13° are assigned to the (0 1 5), (1 0 10) and (1 1 0) planes of crystalline Bi_2Te_3, respectively. Other peaks labeled with little square also match with standard Bi_2Te_3 peaks (JCPDS15-0863). The peak at $2\theta = 26°$ corresponds to the (0 0 2) reflection of the graphite structure of MWNTs. Therefore, we conclude that the nanocomposite consists of Bi_2Te_3 and MWNTs.

The Bi_2Te_3/MWNT nanostructures are further characterized by TEM. Fig. 2(a) shows the major morphology of resulting composites. Both nanoplates and their aggregates assemble randomly on surfaces of MWNTs. The inset which is the part pointed by the rectangle in Fig. 2(a), indicates that the particles are hexagonal plates with width 5 nm on average. High-resolution TEM (HRTEM) image (Fig. 2(b)) further demonstrates that the lattice spacing of a hexagonal nanoplate is approximately 0.32 nm, which corresponds to the value of (0 1 5) interplanar distance of the Bi_2Te_3 crystal. When the diameter of MWNTs is rather shorter, for instance, less than 10 nm, some Bi_2Te_3 crystallites are encapsulated into inner cores of nanotubes possibly by capillary action (seen in Fig. 2(c)). Fig. 2(d), the magnified image, also demonstrates above feature. And EDS pattern (in the inset) of one nanoparticle displays that it contains of Bi and Te elements, and the atomicity ratio is about Bi:Te = 36.97:63.03. Therefore, we could safely conclude that it is also Bi_2Te_3. In addition, Cu comes of the copper microgrid where the powder was applied, while C element comes from supporting carbon film on the grid and the MWNT.

When microwave heating method is adopted, the synthesis time of Bi_2Te_3 becomes shorter remarkably, only 40 min, which makes it possible to obtain nanoscale Bi_2Te_3 particles. Microwave heating method also has other two benefits. First, it offers homogenous reaction conditions both of solution's concentration field and of temperature field, which are beneficial for forming particles with a uniform morphology; secondly, microwave heating makes the titration method feasible due to the comparable time between reaction and titration.

Sun et al. [26] notes that platinum nanoparticles could serve as seeds for the heterogeneous nucleation and growth of silver nanowires because of their close match in crystal structure and lattice constants. In this synthesis system, Na_2TeO_3 will be firstly reduced into trigonal Te atoms by EG at high temperature, shown in the following equation:

$$TeO_3^{2-} + 4e^- + 6H^+ = Te + 3H_2O \quad (2)$$

Trigonal Te has a hexagonal lattice [27,28] which is much more similar to a rhombohedral lattice of Bi_2Te_3, when compared with MWNTs. Hence, Te is a better template than MWNTs in solution for the nucleation of Bi_2Te_3. So it is a real challenge to coat Bi_2Te_3 particles onto surfaces of MWNTs rather than Te. Herein, when titration is conducted, Te will be very little in the solution and then Bi_2Te_3 will choose MWNTs as the heterogeneous nucleation points. Therefore, the Bi_2Te_3/MWNT nanocomposites could form, in which MWNTs act as ligands and templates [29].

Well-crystallized submicro-Bi_2Te_3 hexagonal sheets (as shown in supporting information) were produced, when Bi_2Te_3 precursors of considerably higher concentration were mixed directly with the CNTs suspension. However, when the precursor concentration is considerably lower and also the solution is mixed with CNTs suspension without titration, no Bi_2Te_3 were synthesized, even if heat treatment is conducted at the end of the typical procedure. It is proposed that lower concentration of the precursor solution implies not oversaturated solution which is necessary for the formation of the crystal nucleus [30]; also, the probability of the ion impact is decreased. Thus, the chemical reaction to synthesis of Bi_2Te_3 is suspended.

4. Conclusions

In conclusion, Bi_2Te_3/MWNT nanocomposites have been synthesized for the first time using a facile microwave-polyol method assisted with titration. The resulted products are mainly hexagonal Bi_2Te_3 nanoplates attached to surfaces of MWNTs, while some Bi_2Te_3 nanocrystals are encapsulated into cores of relatively small MWNTs. The further work related to the thermoelectric property of these nanocomposite will be performed.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jallcom.2010.01.024.

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