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Controlled growth, characterization and thermodynamic behavior of bismuth–tin nanostructures sheathed in carbon nanotubes

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ABSTRACT

We report the controlled synthesis of bismuth–tin (Bi–Sn) nanostructures sheathed in graphitic shells that resemble carbon nanotubes (CNTs). Our approach is based on a simple catalytic chemical vapor deposition over a mixture of Bi_2O_3 and SnO_2 supplied as starting materials. Shape control of the nanostructures strongly relies on the weight ratio of Bi_2O_3 and SnO_2 . Sheathed nanoparticles and nanorods are formed at SnO_2 to Bi_2O_3 weight ratios of less than 4:1. They are composed of two separate crystals: rhombohedral Bi and tetragonal Sn_{19}Bi crystals. On the other hand, the sheathed nanowires are formed at SnO_2 to Bi_2O_3 weight ratios above 4:1. The nanowires have only tetragonal Sn_{19}Bi structure with a diameter of approximately 100 nm. Elementary analyses support the core/shell heterostructure of the resulting products. A favorable temperature for the Sn-rich Sn_{19}Bi nanowires is in the range of 700–800 °C, more specifically around 750 °C. Thermodynamic analysis reveals that the CNTs play a significant role in the protection of the Bi–Sn nanostructures during phase transition by temperature change. This simple and reproducible method may be extended to the fabrication of similar binary or ternary nanostructures.

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1. Introduction

Carbon nanotube (CNT) is a good candidate for the nano-encapsulation of various materials [1–4]. These CNT-based encapsulations are of great importance because of the fact that such unique structures can offer significant advantages of being able to induce enhanced properties and unique behaviors, and particularly protect core materials from harsh environments [5–9]. The CNT-encapsulation has been accomplished by two techniques. First, various materials are filled in the cavity of pre-existing CNTs through capillary action, wet chemical technique and nano-filling reaction [1,10,11]. Sec-

ond, the formation of core materials and graphitic shells occurs simultaneously during growth process involving an arc-discharge and chemical vapor deposition (CVD) [12,13]. The latter processes are a more controllable synthesis route compared with the former methods. Transition metals such as Ni, Fe, and Co and their alloys have been widely used for such formations [14–17]. Recently, several efforts have been devoting to achieving the growth of the filled CNT from metals such as Cu and Pd with poor catalytic activity [18,19].

On the other hand, metals and their alloys with low melting point can be very useful for the potential applications such as thermal nanodevices and heat storage because of

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unique thermodynamic behaviors during phase transition by temperature change [20]. However, they can undergo serious morphological deformation and be easily exposed to chemical attack such as oxidation during the phase change [21]. Therefore, the CNT-based encapsulation can become a powerful technique capable of providing these meltable metals and their alloys with a protective barrier. Hsu et al. showed an electrolyte formation of the Sn, Pb and Sn–Pb nanowires sheathed in an amorphous carbon shell [22]. Some studies reported that the CNT-encapsulated Sn nanowires were fabricated through a catalytic CVD [23,24]. These findings showed the likelihood of success in the high-yield preparation of the fusible metal-filled CNTs as well as a significant advance in the related applications. However, the correlation between the composition and catalytic activity of the fusible alloys as well as their growth mechanism, which affects the morphological configuration of the final products, still remains to be clarified.

In this paper, we report the in-situ formation of CNT-sheathed Bi–Sn nanostructures via the catalytic decomposition of C_2H_2 over a mixture of Bi_2O_3 and SnO_2 . Their shape was changed to nanoparticles, nanorods, or nanowires by controlling the SnO_2 to Bi_2O_3 weight ratio ($M_{SnO_2}/M_{Bi_2O_3}$). EDX analysis was performed to compare the composition of Bi and Sn in the nanostructures. Microscopic and spectroscopic analyses were carried out in order to confirm the core/shell configuration of the CNT-sheathed Bi–Sn nanostructures and prove their growth mechanism. Understanding of this mechanism would serve the successful encapsulation of a variety of fusible alloys in CNTs through similar scenario. In addition, thermodynamic analysis was performed to observe the morphological changes and thermal stability of the Bi–Sn nanostructures inside the CNT as temperature increases and decreases.

2. Experimental

2.1. Synthesis of CNT Sheathed Bi–Sn Nanostructures

For synthesis of the CNT-sheathed Bi–Sn nanostructures, Bi_2O_3 (99.999%) and SnO_2 (99.99%) were used as starting materials (Sigma-Aldrich). The oxides were soaked in deionized water, and then stirred for 30 min. The SnO_2 to Bi_2O_3 weight ratio was controlled in the range of 1–6. The mixed solution was filtered out and dried at 100 °C for 1 h. Although perfect mixing of SnO_2 and Bi_2O_3 is practically difficult, the prepared mixture looks relatively uniform and the oxide particles are in good contact with each other after the filtration. Argon (Ar: 99.999%) and a mixture of hydrogen/argon gas (H_2/Ar with 5 vol.% H_2) were used as carrier gases. Acetylene (C_2H_2 : 99.9%) was supplied as a reactant for the growth of the core/shell nanostructures. 1.0 gram oxide mixture was placed at the center of a quartz tube reactor with dimensions of $20 \times 500 \text{ mm}^2$ ($D_{in} \times L$). The reactor was installed vertically and heated using an electric heater. The flow rate of the carrier gas was controlled at $\sim 1000 \text{ mL/min}$ and C_2H_2 at $\sim 50 \text{ mL/min}$. Synthesis was carried out in the range of 650–800 °C for 1 h. The reactor was first evacuated to 5×10^{-3} Torr at room temperature, purged with Ar, and then

heated to the synthesis temperature at a rate of 10 °C/min in Ar. When the temperature of the reactor reached the desired point, the carrier gas was converted from Ar to H_2/Ar with 5 vol.% H_2 , after which C_2H_2 was then introduced. Finally, the reactor was cooled down to room temperature in Ar.

2.2. Characterizations

Scanning electron microscopy (SEM) analysis was carried out using a field emission SEM (FE-SEM: S-4700, HITACHI) operated at an accelerating voltage of 10–15 keV. X-ray diffraction (XRD) patterns were obtained using a Rigaku DMAX-2500 operated under 40 kV and 100 mA. The scanning range was controlled in the range of 20–70 (2 θ). Transmission electron microscopy (TEM) analysis was conducted using a field emission TEM (FE-TEM: FEI, Tecnai F30 Super-twin) operated at an accelerating voltage of 200–300 keV with a Gatan imaging filter (GIF) model 2002 and a JEM-2100F operated at an accelerating voltage of 200 keV with a Cs corrector (JEOL/CEOS). In order to observe crystal structures of Bi–Sn hetero-nanostructures with low eutectic temperature, low temperature in-situ TEM (JEM-3011 (HR), JEOL) operated at an accelerating voltage of 200 keV with a cryotransfer holder ($-175 \text{ }^\circ\text{C}$) was used. For TEM analysis, the sample was sonicated in an ethanol solution and then placed on TEM grids (a carbon-coated Cu grid with 1.2 μm holes and a Lacey carbon type-A-300 mesh). Electron energy loss spectroscopy (EELS: Gatan, Enia 1000) and energy dispersive X-ray spectroscopy (EDX: Genesis) were carried out to confirm the composition and core/shell configuration of the CNT-sheathed Bi–Sn nanostructures. For characterization of as-formed graphitic layers, Raman measurements were performed with a JY LabRam HR filtered with a liquid nitrogen cooled CCD detector. The spectrum was collected under ambient conditions using the 514.5 nm line of an argon-ion laser. In order to study the surface chemistry of the core/shell nanostructures, X-ray photoelectron spectroscopy (XPS) was conducted using an AXIS-NOVA (Kratos Inc.) with an X-ray source of monochromatic Al- $K\alpha$ radiation. The analytic area was $1 \times 2 \text{ mm}^2$ and the base pressure was 5.0×10^{-9} Torr. To investigate morphological changes of the Bi–Sn nanowire inside the CNTs during temperature change, thermodynamic analysis was performed using a specimen heating and tilting holder (25–800 °C).

3. Results and Discussion

FE-SEM micrographs show nanostructures synthesized at different $M_{SnO_2}/M_{Bi_2O_3}$ (Fig. 1(a)–(d)). Synthesis was carried out at 750 °C. Elliptical nanoparticles predominate in the sample obtained at a $M_{SnO_2}/M_{Bi_2O_3}$ of 1 (Fig. 1(a)). Some spherical particles were observed. Corresponding XRD pattern reveals that the nanoparticles are composed of rhombohedral Bi and tetragonal Sn crystals (Fig. 1(e)). When the $M_{SnO_2}/M_{Bi_2O_3}$ is 2, the nanoparticles started to elongate along the axial direction, resulting in the formation of nanorods with a length of approximately 500 nm (Fig. 1(b)). Nanowires with diameters of approximately 100 nm and a length of 2 μm were observed at a $M_{SnO_2}/M_{Bi_2O_3}$ of 4 (Fig. 1(c)). Increasing the $M_{SnO_2}/M_{Bi_2O_3}$ to 6, as-synthesized nanowires showed a regular morphology with an increased length up to 5 μm

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