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Filling of multi-walled carbon nanotubes with tin(IV) oxide

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Multi-walled carbon nanotubes (MWNTs) have attracted much interest since their discovery owing to their high mechanical strength and electrical properties [1,2]. Another fascinating aspect of carbon nanotubes is their cavities. Only a few nanometers in diameter and a few micrometers in length, such a cavity should allow for interesting nanoscale experiments, if it can be filled with other materials in a systematic way. Theoretical studies suggest that the introduction of foreign material into the inner cavities of MWNTs may enhance or modify the properties of the resulting composite materials [3,4].

The procedure to fill carbon nanotubes can be classified in two groups: (a) the chemical method [5–7], and (b) the physical method [8–10]. In the physical method, no solvent is used in the process and opened tubes are directly immersed in the molten material whereby the liquid is driven into the tube by capillary forces [7,10,11]. Thus, the physical method is more restrictive in the material choice and the ability of such materials to be so incorporated depends on three characteristics [12]: (i) they must ‘wet’ the capillaries and have surface tensions below a threshold value in the range 100–200 $\mathrm{mN\,m^{-1}}$ [13]; (ii) their overall melting temperature must be low enough to preclude thermal damage to the MWNT; and (iii) they must not attack MWNTs chemically. The wet chemical method consists of the opening of nanotube ends and the inclusion of salt solution into the opened tubes. The main advantage of the wet chemical approach is its flexibility and the level of experimental control, so that a wider variety of materials can be introduced into carbon nanotubes than the physical method.

SnO_2 is one of the most important and useful semiconductor materials with a large band gap, which has been extensively used for gas sensors [14], transparent conducting electrodes [15], transistors, and solar cells [16]. Sloan et al. [17] reported a two-step wet chemical method using $SnCl_2$ as a precursor for the filling of MWNTs with SnO nanoparticles in high yield, involving (a) opening and (b) filling. Unfortunately, they still need to dissolve $SnCl_2$ in hot concentrated HCl solution first and the solid-state SnO is thermodynamically unstable with respect to β-Sn and SnO_2. The decomposition reaction of $2SnO \rightarrow SnO_2 + Sn$ was reported to occur starting at a temperature as low as 370 °C [18]. Here we use a weak acidic $SnCl_2$ solution as precursor for the filling of MWNTs with SnO_2 nanocrystals. The addition of a small amount of acid is only for reducing the hydrolysis of $SnCl_2$.

MWNTs prepared by the catalytic decomposition of CH_4 were kindly provided by Shenzhen Nanotech Port Ltd. Co. (Shengzhen, China) and used as received. The inner and outer diameters of the MWNTs measured by transmission electron microscopy (TEM,

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JEM-200CX, operated at 200 kV) were 6–20 nm and 15–45 nm, respectively. A typical experimental procedure was described as follows. Firstly, the MWNTs were opened by oxidation with nitric acid solution (20 wt.%) at 140 °C for 3 h, and the treated MWNTs were then rinsed and dried at 60 °C. Secondly, 2 g of $SnCl_2$ was put into 200 ml of distilled water, followed by adding 2 ml of HCl (38 wt.%). 150 mg of the pre-opened MWNTs were immersed in the above solution. The mixture was stirred 12 h at room temperature as an immersion procedure and then treated at 140 °C for 3 h in air. After cooling to the ambient temperature, the resulting products were washed and dried at 60 °C (denoted as sample A); and then a part of sample A was calcined by annealing in a stream of argon at 600 °C for 2 h (denoted as sample B).

The samples were characterized using X-ray diffraction (XRD) with Cu Kα radiation (Rigaku D/max 2550V) and TEM using a JEM-2010 microscope equipped with an energy dispersive spectrometer (EDS).

Fig. 1 shows X-ray patterns of the pristine MWNTs (a) and hybrid MWNTs of sample A (b). The diffraction angles at $2\theta = 26.70°$, 34.05 °, 51.51°, 65.45°, (Fig. 1b), can be assigned to 1 1 0, 1 0 1, 2 1 1, 3 0 1 planes of the cassiterite structure of SnO_2, respectively. No other crystalline peaks corresponding to $SnCl_2$ or other tin products, such as SnO, were observed in the powder pattern. The broad peaks in the XRD pattern indicate that the SnO_2 nanoparticles are very small. The mean particle size of SnO_2 calculated by Scherrer equation is about 3 nm. It is hard to elicit the characteristic peaks of MWNTs from the spectrum of sample A, mainly because of the overlap of cassiterite SnO_2 1 1 0 with the main peak of MWNTs 0 0 2. In addition, the crystal structure of MWNTs may suffer some damage during the refluxing process in nitric acid. Elemental analysis by EDS indicates the atomic ratio of O to Sn is close to 2.

Fig. 2 shows one of the low-magnification TEM images of sample A, which reveal that the hollow cavities of MWNTs are filled with SnO_2 nanoparticles at the entire length in a high yield (~80%). They are most noticeable because of the striking contrast from the filling material to the empty cavity of MWNTs, which is consistent with the presence of SnO_2 nanoparticles. It can be clearly seen that the fine SnO_2 nanoparticles attach to one another densely and continuously, and form an almost continuous dark line in the cavity of the MWNTs. The average size of the SnO_2 nanoparticle is about 3 nm, in accordance with the results calculated using the Scherrer equation. It can be envisaged that tin(II) chloride solution is sucked into the opened tubes [5] and then crystalline SnO_2 are formed during the treatment at 140 °C in air. The formation of SnO_2 is represented as [19]: $2Sn^{2+} + 2H_2O + O_2 \rightarrow 2SnO_2 + 4H^+$. At the same time, the outer surface of MWNTs is fully coated with a thin SnO_2 layer (~6 nm in thickness). We propose a tentative mechanism for the coating of SnO_2 on the outer surface of MWNTs. Firstly, negatively charged functionalities such as –COOH and –OH are introduced to the surface of MWNTs after oxidation [8]. Then, the tin ions in the solution are adsorbed to the surfaces due to the electrostatic attraction. Finally, SnO_2 nanocrystals are in-situ formed on the outer surface of MWNTs.

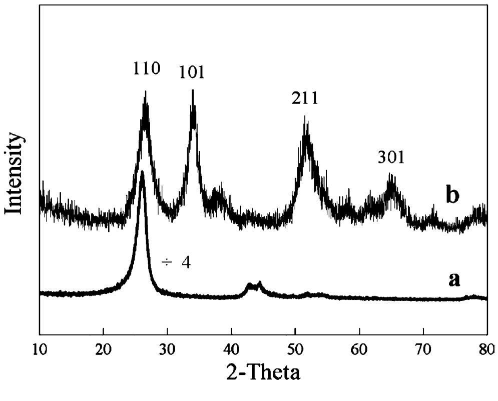

Fig. 1. XRD patterns of (a) pristine MWNTs and (b) sample A.

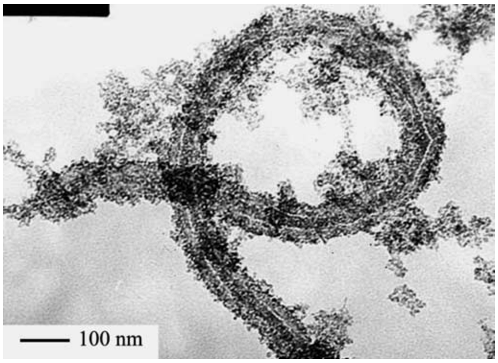

Fig. 2. TEM micrograph of sample A.

We have also found that the immersion duration before heat treatment is an important factor for the filling of MWNTs with SnO_2. In a controlling experiment to fill SnO_2 into MWNTs, the pre-opened MWNTs were stirred in a mixture of $SnCl_2$ and HCl for only 30 min and then directly treated at 140 °C for 3 h. As shown in Fig. 3, only the outer surface of MWNTs is coated with a thin SnO_2 layer and there is no obvious filling material to the empty cavity of MWNTs. It can be concluded that there is no $SnCl_2$ solution being sucked into the inner cavity of opened tubes in a short mixing duration of 30 min. During the treatment at 140 °C, crystalline SnO_2 are formed only at the outer surface because of the functionalities on the surface.

After calcined at 600 °C in a stream of argon (sample B), particles coated on the outer surface disappear (Fig. 4a). The particles in the inner cavity still exist and yield a discontinuous filling formed by a series of spherical nanoparticles. The filling occurs at the entire length in

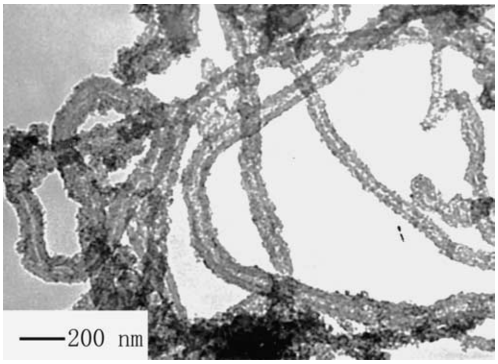

Fig. 3. TEM micrograph of the sample obtained without the procedure of soakage.

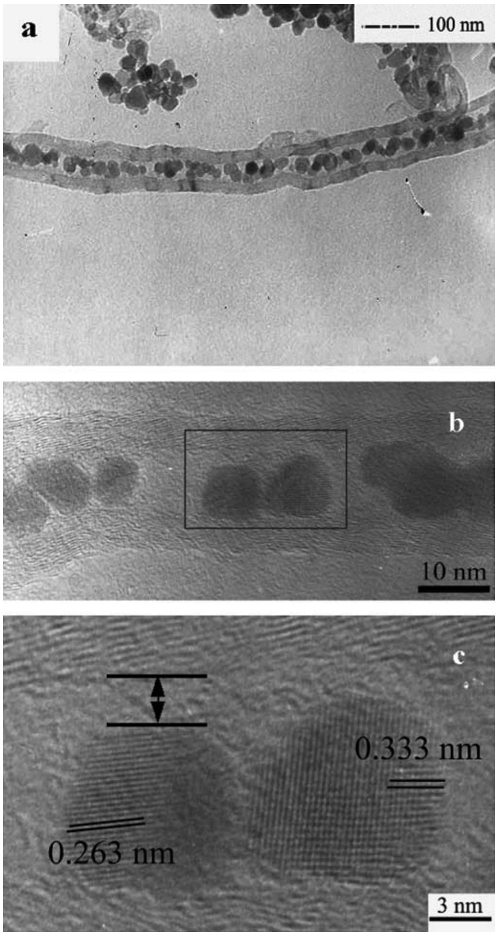

Fig. 4. TEM (a) and HRTEM (b) images of sample B; (c) shows an enlarged view of the boxed region of (b).

the hollow cavity, which is irrespective with the length of the MWNTs. The high resolution transmission electron microscopy (HRTEM) image shows that most of the nanoparticles appear to fill the entire internal cavity of the MWNTs (Fig. 4b). These particles fit tightly in the nanotube, and the tube is intact at the tube–particle interface. The spherical nanoparticles, which are considerably smaller than the cross-section of the inner diameter of MWNTs, are also observed (arrow indicated in Fig. 4c). The SnO_2 nanoparticles filling the MWNTs present either 1 1 0 or 1 0 1 lattice fringes, which are in accordance with the cassiterite SnO_2 lattice fringe spacing given in the literature as 0.333 nm and 0.263 nm, respectively. During the annealed procedure, the inner nanoparticles crystallize further and grow to be larger particles. The growth of SnO_2 particles is restricted by the size of the inner cavity and the final particle has a mean size of 10 nm. Calcining the sample A in a stream of argon slowly to 600 °C can result in the removal of these functional groups on the surface of MWNTs [7]. Thus, the SnO_2 nanocrystals, adsorbed to the surface of the functionalized MWNTs with the carboxyl groups due to electrostatic attraction, then fall off from the outer surface of MWNTs for sample B.

Just as illustrated in Fig. 5, three distinct stages maybe exist during the filling of SnO_2 into MWNTs based on our observation. In the first stage of immersion, $SnCl_2$ solution was soaked into the empty cavity of MWNTs. In the second stage of the treatment at 140 °C, the $SnCl_2$ solution was then nucleated to be SnO_2 nanocrystals. The inner cavity acted as a reactor with sucked $SnCl_2$ solution. In the third stage of the calcination at 600 °C in a stream of argon, the SnO_2 nanocrystals in the inner cavity further grew up and yield a discontinuous filling formed by a series of spherical nanoparticles. According to the conservation of mass, the amount of SnO_2 nanocrystals filled in the cavity is consistent with the concentration of $SnCl_2$ solution. So, the amount of SnO_2 nanocrystals filled in the MWNTs can be controlled by changing the concentration of $SnCl_2$ solution.

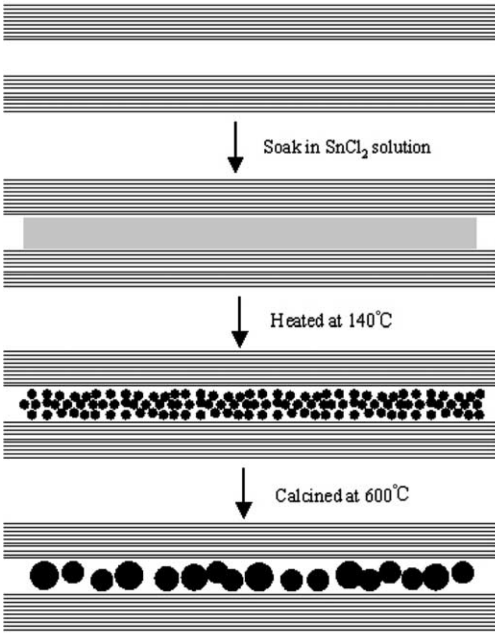

Fig. 5. Three distinct stages during the filling of SnO_2 into MWNT.

In conclusion, we have demonstrated a simple and reproducible wet chemical method using a weak acidic $SnCl_2$ solution as precursor for the filling of the MWNTs in high yield with SnO_2 nanoparticles. After the filling is finished, the fine SnO_2 nanoparticles both fill the entire internal cavity and coat the outer surface of MWNTs. After annealed in a stream of argon, particles filled the internal cavity grow larger, and then yield a discontinuous filling formed by a series of spherical nanoparticles at the entire length. Using this method one can obtain different amount of SnO_2 nanocrystals filled MWNTs only by changing the concentration of precursor. Optimizing the filling process should allow one to fill the internal volume of MWNTs with different materials using solutions of their precursors, whose novel properties will be important to future nanotechnology.

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