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Preparation of Fe–Ni alloy nanoparticles inside carbon nanotubes *via* wet chemistry

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The filling of carbon nanotubes with Fe–Ni alloy *via* wet chemistry is presented. Crystalline Fe–Ni alloy nanoparticles consisting of Fe (75 at%) and Ni (25 at%), with diameters in the range of 5–10 nm and lengths of 10–50 nm, have been successfully introduced into carbon nanotubes. We anticipate that this method will lead to extensive study of the chemistry and physics of alloys inside nanotubes, which might find applications in catalysis, the fabrication of magnetic storage devices and nanoscale thermostats.

The study of metal-filled carbon nanotubes is now becoming a promising and challenging area of research owing to their unique electronic, magnetic and nonlinear optical properties,[1] as well as to a variety of industrial applications as catalysts, electronic devices, biosensors,[2–6] as an improved magnetic tape, and in magnetic data storage, xerography and magnetic resonance imaging.[7] Two advantages are given when carbon nanotubes are filled with metal: (1) although the metal nanoparticles show quantum effects, the carbon shells isolate the metal particles from each other, and from the outside environment, also preventing the oxidation of the metallic particles, and (2) the lubricating properties of the graphite coating might be helpful in magnetic recording applications and reinforce the material's durability.[8] As is well known, there have been various approaches[9] to inserting metal into carbon nanotubes, such as arc discharge,[10–12] pyrolysis,[13–19] the template technique,[20–22] CVD,[23,24] capillary action,[25–28] electrolysis,[29] plasma discharge[30] and the wet chemical method.[31–35] The wet chemical method can be applied to a greater variety of materials and has relative higher yields than other methods.

As for bimetallic systems or alloys inside carbon nanotubes, there are few reports. Only the electrolytic formation of a carbon-sheathed Sn–Pb nanowire,[29] the template carbonisation synthesis of Pt–Ru nanoparticle-filled carbon nanotubes[22] and the pyrolysis introducing Invar ($Fe_{65}Ni_{35}$) into carbon nanotubes[19] have been reported. Since Fe–Ni alloys are interesting for their low thermal expansion, their remarkable magnetic properties,[19,36–38] and their saturation magnetization, which increases with an increase in the iron content,[39] we are interested in the encapsulation of Fe–Ni alloy nanoparticles in carbon nanotubes by wet chemistry. Here we describe the generation of carbon nanotubes filled with crystalline Fe–Ni alloy nanoparticles containing relatively high iron content, with diameters in the range of 5–10 nm and lengths of 10–50 nm, by wet chemistry.

Experimental

The multi-walled carbon nanotubes (MWNTs), prepared by the thermal catalytic decomposition of hydrocarbons, were gifts from the Chengdu Institute of Organic Chemistry (P R China). The procedure employed by us for preparing Fe –Ni alloy nanoparticles inside carbon nanotubes is as follows. In a typical synthesis, MWNTs (200 mg) were treated with boiling HNO_3 (68%, 50 mL) for 24 h, then washed with water and dried in an oven at 60 °C for 24 h. The acid-treated carbon nanotubes (150 mg) were stirred with 50 mL of saturated mixed ferric nitrate and nickel nitrate solution (Fe : Ni = 7 : 3 atom ratio) for 24 h, filtered and washed with water, then dried at 60 °C for 10 h. The sample was then heated under an argon atmosphere at a rate of 8 $^\circ C\ min^{-1}$ from room temperature to 100 °C and kept at this temperature for 1 h before ramping at 4 $^\circ C\ min^{-1}$ to 450 °C. The sample was then calcined at 450 °C for 6 h. The calcined samples were then heated at 450 °C under H_2 for 6 h to reduce the metal oxide.

Transmission electron microscopy (TEM) micrographs were taken using a Hitachi Model H-800 transmission electron microscope, with an accelerating voltage of 200 kV. High-resolution transmission electron microscopy (HRTEM) was performed using JEOL 2010 microscopes operated at optimum defocus with accelerating voltages of 200 kV. Energy-dispersive X-ray (EDX) spectrometry was carried out with spectroscope (Oxford, Link ISIS) attached to HRTEM.

Results and discussion

The carbon nanotubes used had an inner diameter in the range 5–20 nm and an outer diameter in the range of 10–50 nm (with lengths of up to a few microns), which were checked by HRTEM. The nanotubes are almost open after being treated with nitric acid for 24 h. The calcined and reduced samples of ferric nitrate- and nickel nitrate-coated carbon nanotubes were shown to have been satisfactorily filled with metal from the typical TEM images presented in Fig. 1. About 50% of the open nanotubes ($\sim$22% of the volume, on average) contained metallic material inside. Some metal-containing material was observed on the exterior of the nanotubes. Close examination of the metallic material inside the tubes [Fig. 2(a)] showed lattice fringes with an observed fringe separation of 2.83 Å, consistent with the interlayer separation of the (211) crystal plane of Fe–Ni alloy. The selected area electron diffraction (SAED) pattern shows the presence of diffraction spots due to the (210) and (211) planes, as shown in Fig. 2(b), signifying

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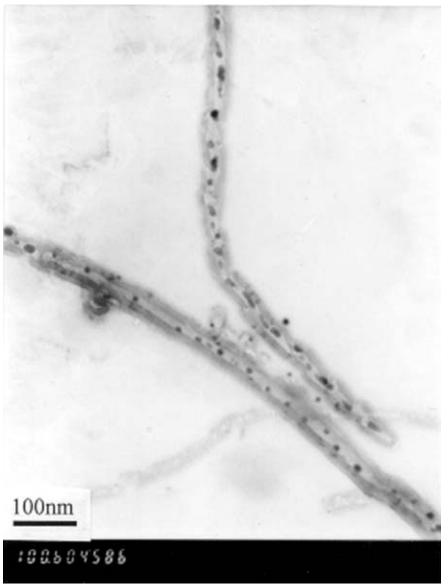

Fig. 1 TEM images of carbon nanotubes filled with Fe–Ni alloy.

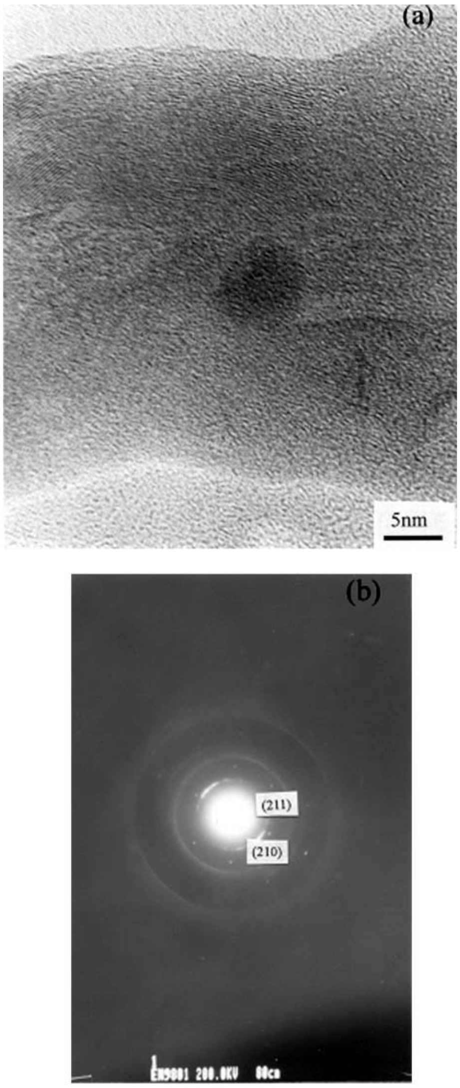

Fig. 2 (a) HRTEM images and (b) selected area electron diffraction pattern of carbon nanotubes filled with Fe–Ni alloy.

the crystalline nature of Fe–Ni (JCPDS 18-877). It is interesting to note that the (211) Fe–Ni plane is always aligned at 50–60° to the graphite layer (002) of the tube. Most of the Fe–Ni crystallites have diameters less than the internal cross-section of the tubes. These crystallites can also be observed at a considerable distance from the opened ends of the tubes. It can be envisaged that the mixed nitrate solution could be sucked into the tubes as they were opened and metal oxides were formed during calcination, and crystalline Fe–Ni was formed during reduction. The growth of the Fe–Ni crystallites may be influenced by the surface structure of the inner tube and the elongated shape of the Fe–Ni crystallites may reflect their surface-wetting properties.

The chemical composition of the alloy nanoparticles in the carbon nanotubes was analyzed using an energy-dispersive X-ray spectrometer attached to a high-resolution electron microscope. The EDX spectrum (Fig. 3) of an individual nanoparticle shows the presence of iron, nickel, carbon and copper. It is obvious that the copper peak is caused by the copper grid used to clamp the nanoparticles. The carbon comes from the carbon nanotube. EDX quantitative microanalysis indicates a predominance of Fe (74.63 at%) and Ni (25.37 at%). This sample consisted of a relatively higher content of iron than that found for Invar in CNTs[19] or in BN tubes.[40] It was also noted that the proportion of mixed metals inside the nanotubes formed from their mixed nitrate solutions was different from the original composition of nitrates.[33]

It has been reported that Cu,[41] Co,[42] Pd, Pt, Ag and Au nanoparticles[43] were prepared by solid-state reaction between carbon nanotubes and the corresponding metal salts. The preparation process includes the following steps: addition of a soluble metal salt to a suspension of the carbon nanotubes in distilled water or acetone, with vigorous stirring at 100 °C until all the solvent has evaporated, followed by decomposition and reduction of the above mixture under H_2. Satishkumar *et al.*[44] also reported the modification of carbon nanotubes with metal (Au, Pt, Ag) nanoparticles by employing an appropriate reducing agent in mixtures of carbon nanotubes and a metal complex. In these situations most of the metal particles are deposited on the outside of the nanotubes. However, under our experimental conditions the majority of metal particles is present inside the nanotubes, which is similar to Green's results.[31] It should be mentioned that the calcination process was carried out slowly, lest the metal nitrate be forced out of the tube by the rapid expulsion of the solution molecules present in the nanotube cavities. It may be that the nature of the filling material also affects the outcome of the filling process, a factor which needs to be investigated further.

The formation of crystalline nanoparticles of Fe–Ni in the present study is noteworthy. One possible mechanism of formation of the nanoparticles may be as follows. It is possible that the decomposition of the oxide precursor (nitrate salts) in the hot combustion zone of the nanotubes gives rise to the metal oxide crystals *in situ*.[45] The crystals could become elongated as a result of the evolution of gases (NO_2, H_2O) during the transformation. Then, the metal oxides would be

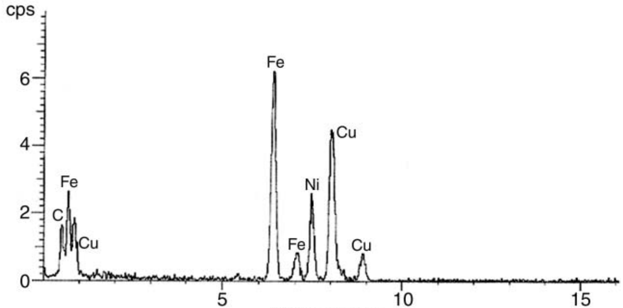

Fig. 3 EDX spectrum taken from the tube filling, displaying Fe and Ni X-ray peaks.

reduced by hydrogen to the native metals,[31] thus forming the crystalline alloy particles.

Summary

The present study establishes that carbon nanotubes can be readily filled with nanoparticles of Fe–Ni alloy *via* wet chemistry. The crystalline Fe–Ni alloy nanoparticles have diameters in the range of 5–10 nm and lengths of 10–50 nm. The method offers certain advantages, such as providing crystalline nanoparticles in good yields, and also opens the way to filling the inner volume of nanotubes with a wide variety of alloys using solutions of their precursors. Fe–Ni alloy inside carbon nanotubes could have important applications in nanoelectronics, nanoscale thermostats and magnetic storage devices.

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