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Large-Scale Synthesis of Carbon Nanotubes by an Ethanol Thermal Reduction Process

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Since discovered by Iijima,[1] there has been much interest in the synthesis and physical properties of carbon nanotubes (CNTs) due to their important applications. For example, carbon nanotubes can be used as electrochemical devices,[2] hydrogen storage,[3] field emission devices,[4] and nanotweezers.[5] Various methods have been developed for the synthesis of carbon nanotubes, including metal-catalyzed chemical vapor deposition (CVD),[6] arc evaporation,[7] laser ablation of carbon, [8] or catalytic decomposition.[9]

Recently, the Fan group applied a nanopore alumina templated-synthesis technique for synthesizing highly ordered carbon nanotube arrays via thermal decomposition of ethylene with iron as the catalyst.[10] Campbell and co-workers reported that small-diameter (1−4 nm) carbon nanotubes were prepared by a catalyst method using the decomposition of ethylene and a Ni−Fe thin film catalyst.[11] To explore other alternatives, considerable effort has been made to use a solvothermal route to fabricate carbon nanotubes, in which hexachorobenzene or tetrachloroethylene was used as the carbon source and alkali metal K was used as the reductant; the yield of carbon nanotubes was 10−15%.[12]

Here, we report a method for synthesizing carbon nanotubes on a large scale using the reaction of ethanol with magnesium in a stainless autoclave at 600 °C. The reaction can be formulated as follows:

$$CH_3CH_2OH + Mg \rightarrow 2C + MgO + 3H_2 \qquad (1)$$

We call this route an ethanol thermal reduction process, in which ethanol is used as the carbon source and Mg is used as the reductant. The bamboo-shaped multiwall carbon nanotubes with the yield of 80% were obtained by this route. In addition, we could also observe some Y-junction nanotubes in the products.

In a typical experiment, the metallic Mg (0.95 g; 99%) and 15 mL of ethanol were mixed in a stainless autoclave of 20 mL capacity. The autoclave was sealed and maintained at 600 °C for 10 h and then allowed to cool to room temperature naturally. The dark precipitate was collected and washed with absolute ethanol, dilute HCl aqueous solution, and distilled water. After that, the obtained sample was dried in a vacuum at 65 °C for 6 h. The yield of carbon nanotubes was estimated through SEM and TEM observations of the as-prepared samples to be about 80%.

The morphologies and structure of the as-prepared products were examined with scanning electron microscopy (SEM, HITACHI X-650 and JEOL JSM-6700F), transmission electron microscopy (TEM, HITACHI 800), and high-resolution transmission electron microscopy (HRTEM, JEOL 2010 using an accelerating voltage of 200 kV).

Figure 1a and b shows SEM images of a typical sample of carbon nanotubes and indicates the large quantity that was achieved using this approach. These carbon nanotubes have diameters ranging from 30 to 100 nm and lengths ranging from hundreds of nanometers to several micrometers. It is also seen from Figure 1b that many of the nanotubes have open ends.

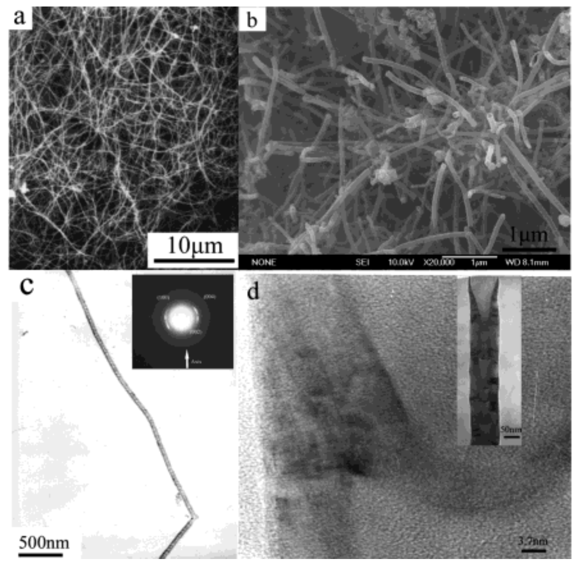

Figure 1. (a) Low-magnification SEM image of carbon nanotubes; (b) field-emission SEM image of CNTs; (c) TEM image of a typical bamboo-shaped carbon nanotube; (inset) SAED pattern of the carbon nanotube; (d) HRTEM image of a tubular structure of a carbon nanotube; (inset) a bamboo-shaped carbon nanotube with an open end.

Figure 1c shows a low magnification TEM image of a typical carbon nanotube with a diameter of ca. 50 nm. We find that the carbon nanotube is bamboo shaped. A bamboo-shaped carbon nanotube with an open end can also be observed from the inset of Figure 1d. Furthermore, we may clearly observe some compartment layers between the walls. The selected area electron diffraction (SAED) pattern (inset Figure 1c) exhibits a pair of small but strong arcs for 002, together with a ring for 100 and a pair of weak arcs for 004 diffractions. The appearance of 002 diffractions as a pair of arcs indicates some orientation of the 002 planes in the carbon tubes.[13]

A further investigation on the tubular structure by high-resolution transmission electron microscopy (HRTEM) (Figure 1d) reveals that the interlayer spacing of carbon nanotube is about 0.34 nm, consistent with the (002) plane lattice parameter of graphited carbon. At the same time, we can also find that graphite sheets combine with compartment layers without any defect as shown in Figure 1d.

In the processing of TEM and HRTEM examinations of as-prepared products, some Y-junction carbon nanotubes were detected. Figure 2 shows the TEM and HRTEM images of Y-junctions. From Figure 2a and b, we can find that the CNTs with closed tips have no encapsulated solid particles and have a bamboo-shaped structure. It is worth noting that a curvature of the

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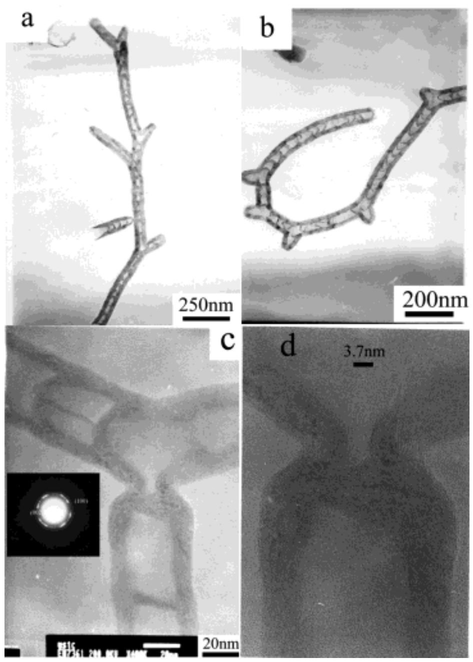

Figure 2. TEM micrographs of Y-junction carbon nanotubes. (a and b) Carbon nanotubes with multiple Y-junctions; (c) a typical Y-junction carbon nanotube; (inset) the junction diffraction pattern; (d) HRTEM image of the junction of a Y-like carbon nanotube.

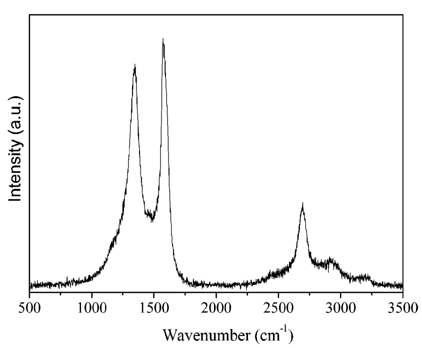

Figure 3. Raman spectrum of the as-prepared sample.

compartment layer in the bamboo-shaped CNTs is directed to the tip. TEM images revealing the presence of multiple Y-junctions are shown in Figure 2a and b. The HRTEM image (Figure 2d) shows that the graphitic layers bend parallel with respect to the junction and absence of impurity. The SAED pattern (inset of Figure 2c) of a junction of Y-like carbon nanotube shows four small but strong arcs for 002, which imply some orientation of the 002 planes in the junction of CNTs. The results suggest that the junction is formed by the curvature caused by different carbon rings. These observations are consistent with those from previous literature.[14]

The Raman spectrum was recorded at ambient temperature on a Spex 1403 Raman spectrometer with an argon-ion laser at an excitation wavelength of 514.5 nm. The representative Raman spectrum (Figure 3) of the sample shows the typical features of MWCNTs.[1] The spectrum demonstrates the peak frequencies of the graphite (G) mode at 1575 cm^{-1} and contains disorder modes at 1343 cm^{-1} (D) along with their overtones at 2691 cm^{-1} ($2 \times$ D). The line at 2922 cm^{-1} is assigned to a combination of the graphitic and a disorder mode (G + D). Hou and co-workers also observed a similar phenomenon.[15]

The experiment results demonstrate that all of carbon nanotubes have a bamboo-shaped structure in which the curvature of compartment layer is directed toward the closed tip. In addition, there is no encapsulated solid particle at the closed tip. Our observations are opposite to that of previous work[16] but consistent with that of Lee and co-workers,[17] who demonstrated that carbons first adsorb on metal particle and then form graphitic sheets as a cap. As the cap lifts off the particle, a closed tip with a hollow inside is produced. While the wall grows upward, the next compartment layer is produced. A detailed study of the growth mechanism of the nanotubes is underway.

In conclusion, we have successfully synthesized bamboo-shaped carbon nanotubes on a large scale through an ethanol thermal reduction process, in which ethanol was used as the carbon source and magnesium was used as the reductant. The toxic or corrosive reagents have been completely avoided. Furthermore, Y-junction carbon nanotubes obtained from our experiment can be used as the building blocks of nanoelectronics.[18] Further studies along this line are in progress. Because of the simplicity and high yield of this route, it may potentially be applied on the scale of industrial production.

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