A Catalytic-Assembly Solvothermal Route to Multiwall Carbon Nanotubes at a Moderate Temperature

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Herein we report a novel catalytic-assembly benzene-thermal route to multiwall carbon nanotubes using reduction of hexachorobenzene by metallic potassium in the presence of Co/Ni catalyzer at 350 °C.

The discovery of carbon nanotubes in the arc-discharge apparatus was first published by Iijima in 1991, [1] which stimulated a worldwide research effort to improving their synthesis, determining their structure,[2−7] calculating and measuring their physical properties.[8−12] In the following years, other synthesis methods of carbon nanotubes have also been reported: laser evaporation of a metal graphite composite target,[13] carbon monoxide disproportionation on a metal catalyst [14] and hydrocarbon pyrolysis using a metal catalyst.[15]

In our experiment, 15 mL of benzene was placed into a stainless steel autoclave with 30 mL capacity, and then 2 g hexachorobenzene and 3 g potassium were added. After that, 2 mL of benzene was added until about 80% of the autoclave's capacity was filled. Finally, 100 mg of catalyzer precursor was added. The catalyzer precursor was prepared by dissolving 1.0 g of analytical grade $CoCl_2 \cdot 6H_2O$ and $NiCl_2 \cdot 6H_2O$ mixture (Co: Ni molar ratio of 1:1) in 100 mL of absolute alcohol, followed by drying in an oven at 80 °C and calcining in air at 150 °C. The sealed autoclave was heated at 350 °C for 8 h, and then cooled to room temperature in the furnace naturally. The obtained sample was sequentially washed with absolute ethanol, dilute acid, and distilled water to remove residual impurities, such as chlorides and remaining catalyzer, and then vacuum-dried at 70 °C for 6 h.

The morphologies of the sample were observed with Hitachi 800 transmission electron microscope (TEM) performed at 200 kV, and the microstructure of carbon nanotube was analyzed with JEOL 2010 high-resolution transmission electron microscope (HRTEM) performed also at 200 kV. Samples for the electron microscope were prepared by 1 h ultrasonic dispersion of 0.2 g of product with 50 mL of ethanol in a 100 mL conical flask. Then a drop of the solution was placed on a copper microgrid or carbon film and dried in air before performance. Raman spectra were recorded with a Spex 1403 Raman spectrometer at ambient temperature.

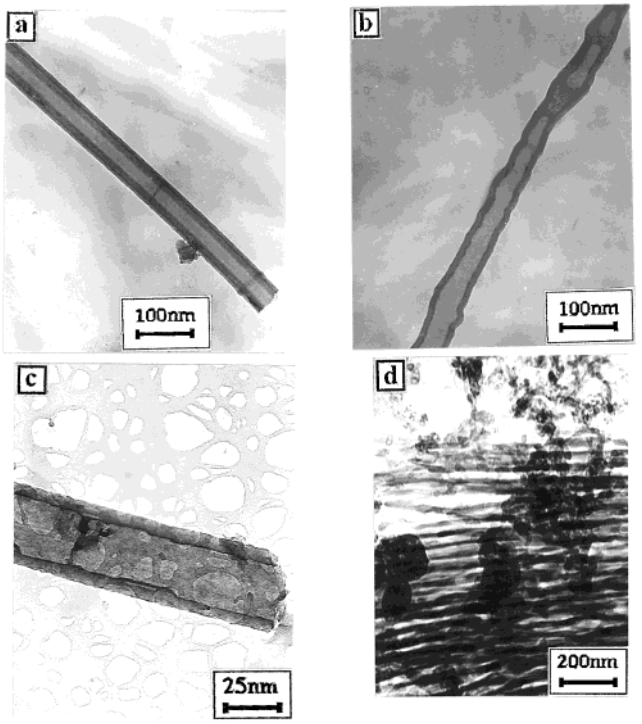

Figure 1. TEM images of multiwall carbon nanotubes (a, b, c, d) obtained. Most nanotubes have straight-line morphology; several nanotubes are shown with a bamboo-like structure (a, b), and some have open ends (a, c).

The micrographs of the nanotube are shown in TEM images (Figure 1a−d). From Figure 1, one can see that the nanotubes are straight with an average length of 1200 nm. The inner diameter of nanotubes is 20 nm and outer diameter 40 nm in average. Most nanotubes have open ends, without amorphous carbon coating. Some carbon nanotubes have a bamboo-like structure (Figure 1a, b). The inner tube is subdivided by single- or multigraphite layers, which may be caused by the surface diffusion of carbon cluster on the large catalytic particle across the nanotube wall.[6]

Another electron micrograph (Figure 1d) also shows the nanotube bundle, shell-like nanoparticles, and amorphous carbon. The HRTEM image of the nanotubes shown in Figure 2a indicates that the carbon nanotube wall is well graphited. The interlayer spacing in the multiwalls is about 0.34 nm, corresponding to the (002) plane lattice parameter of graphite carbon. [1] The Raman spectrum of the product (Figure 3) exhibits two peaks at 1350 and 1580 cm^{-1}, indicating the graphite structure of the nanotubes. According to the analysis of Kasuye et al., the complex structure of 1540−1600 cm^{-1} can be understood by zone-folding of the graphite phonon dispersion relation.[16]

The walls of carbon nanotube, the cylinder stories of multiwall nanotube, and the planar sheet of single wall nanotube, are both built from hexagonal lattice of sp^2 bonded carbon.[17] Apart from arc-discharge and laser evaporation methods, the sources of carbon atoms are small molecules of hydrocarbons, such as CH_4, C_2H_2, and C_2H_4, which can be used to produce carbon nanotubes at a relative high temperature.[18] In our experiments, hexachorobenzene may be reduced to hexagonal carbon clusters by metallic potassium and then assemble into nanotubes in the presence of Co/Ni catalyzer at 350 °C. The reaction process can be represented by Scheme 1 .

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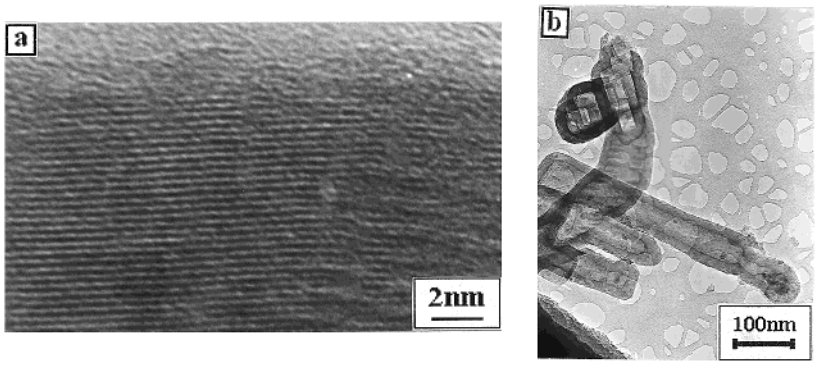


Figure 2. High-resolution TEM images of multiwall carbon nanotubes. Image of nanotube wall (a), spacing between the fringes is about 0.34 nm corresponding to the (002) lattice parameter of graphite. Figure 2b is the low-magnification image of nanotube. Catalytic metal particle exists in the closed end.

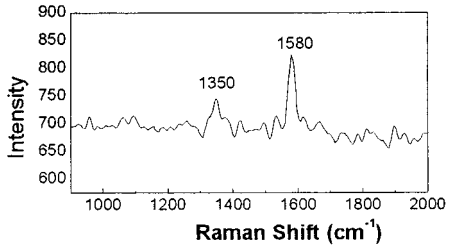
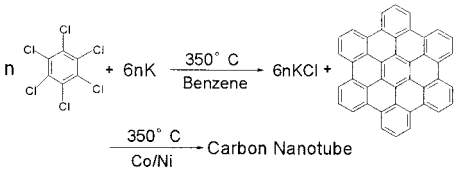


Figure 3. Raman spectra at room temperature of the obtained multiwall carbon nanotube (=514.5 nm).

Scheme 1. Expression of the Catalytic-Assembly Benzene-Thermal Route to Multiwall Carbon Nanotube at a Moderate Temperature



During the above reaction, the chlorides of Co and Ni are reduced to Co/Ni catalyzer particles by metallic potassium, at the same time, hexachorobenzene is also reduced by potassium through deleting chloro to form carbon clusters and KCl. Once the nucleation of carbon nanotube from a freshly reduced metal particle has finished, the hexagonal carbon clusters diffuse to the growth sites through constant surface diffusion, then assemble into nanotubes and cause the axial growth. Meanwhile, because the geometry structure of hexagonal carbon clusters is similar to that of carbon nanotube wall built from hexagonal lattice of sp^2 bonded carbon, the epitaxial growth of newly reduced hexagonal carbon clusters on the nanotube wall is favorable, which results in the formation of multiwall nanotube under such a relatively low temperature benzene-thermal process. In fact, for multiwall carbon nanotube, it is quite likely that the presence of the outer wall stabilizes the inner wall, keeping it open for continuous growth.[19] The absence of single wall carbon nanotube in our observation may also show that the growth mechanism here is different from that of ideal single wall nanotube.[20]

HRTEM images shown in Figure 2b indicates that some carbon nanotubes have bending structure, and at the close end of the tubes, the catalytic metal particles exist clearly, which suggests that the metal particles are responsible for the nucleation of the multiwall carbon nanotubes.

Electron microscope observation of the prepared samples reveals the yield of nanotubes is about 10% from the original reagents, and the other contents of the obtained product are amorphous carbon and some shell-like nanoparticles. Although the yield here is about 10%, we find it is easy to get individual nanotube under electron microscope observation by dispersing the product in ethanol with a ultrasonic bath, which may be useful to utilize and operate single carbon nanotube. We tried to increase the yield by raising the reaction temperature, but due to the decomposition of benzene, a lot of amorphous carbon was produced, which made it nearly impossible to isolate the nanotubes from amorphous carbon.

In summary, a novel catalytic-assembly benzene-thermal route to multiwall carbon nanotubes using reduction of hexachorobenzene by metallic potassium in the presence of Co/Ni catalyzer at 350 °C has been developed. The synthesis temperature is the lowest to our knowledge. The multiwall carbon nanotubes obtained from our experiment are well graphited. The catalytic metal particles may play important role in the nucleation of the nanotube.

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