



# Electron irradiation induced dimensional change in bismuth filled carbon nanotubes

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## Abstract

We have produced bismuth-filled carbon nanotubes by heating solid bismuth nanoparticles with single-walled carbon nanotubes. Most of the filled nanotubes are one-dimensional nanowires with high aspect ratios. Some of the nanotubes have a second layer formed during the filling process. We have also observed nanotube structure change due to atom loss upon electron irradiation. This effect may help us understand the filling mechanism. © 2000 Elsevier Science Ltd. All rights reserved.

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## 1. Introduction

Single-walled carbon nanotubes [1–6] have shown great promise for a future generation of nanoscale devices [7–12], and filled single-walled carbon nanotubes are expected to lead to an even more diverse range of applications [13–18]. We filled single-walled carbon nanotubes with bismuth metal and studied the effect of heat on these materials, which has an important implication of the diffusion process in single-walled carbon nanotubes.

## 2. Synthesis

We synthesized single-walled carbon nanotubes with an electric arc running at a 95 A DC current under 300 Torr helium buffer gas at a flow rate of 700 cm<sup>3</sup>/min [19]. The anode is a 6 mm diameter graphite rod containing mixtures of, in atomic percentage, graphite powder (93%), cobalt catalyst (2%), and bismuth promoter (5%) [19–21]. Soot samples collected from the chamber walls were sonicated in ethanol for 1 min and a drop of the solution was put on a lacey carbon grid for High-resolution transmission electron microscopy (HRTEM) studies. Microscopy was done on Phillips CM200 and CM300 microscopes each equipped with a Gatan slow-scan camera, an image filter, and an energy dispersive X-ray spectrometer.

The soot produced with Bi promoter contains high percentage of large diameter single-walled carbon nanotubes, as illustrated in Fig. 1. A histogram of the

diameter distribution is displayed in Fig. 2. As shown in the histogram, more than 50% of the single-walled carbon nanotubes have diameter greater than 1.5 nm, with signifi-

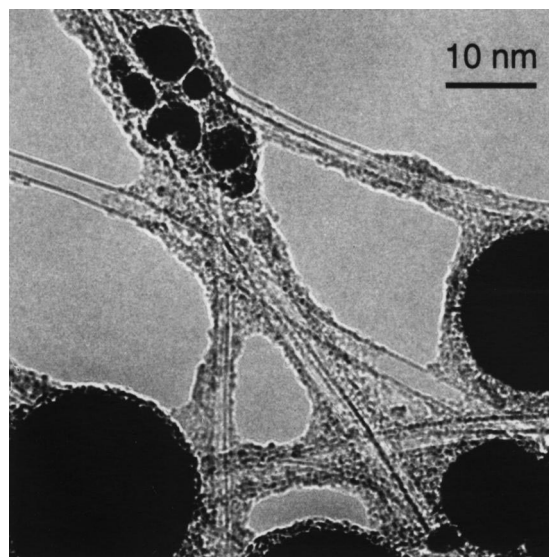


Fig. 1. Transmission electron micrograph of single-walled carbon nanotubes produced with Co + Bi. The yield is high with abundant large diameter single-walled carbon nanotubes. The large dark particles are Bi nanoparticles to be used for sub-sequence filling.

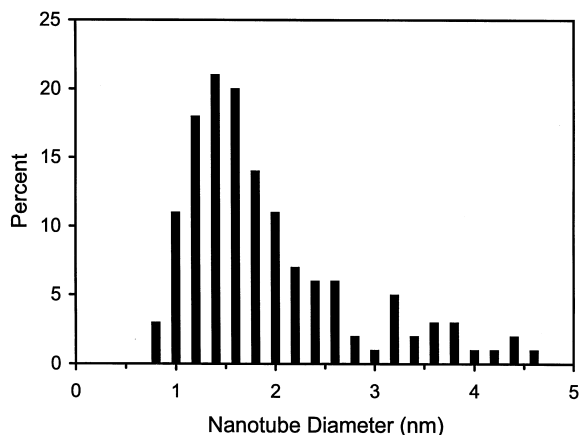


Fig. 2. Diameter distribution of single-walled carbon nanotubes produced with an arc using cobalt catalyst and bismuth promoter. Significant amounts of single-walled carbon nanotube diameters larger than 2 nm.

### 3. Filling

In order to fill the single-walled carbon nanotubes with metal, we heated the soot containing Bi nanoparticles in air at a rate of 20°C/min to raise the temperature to 400°C and kept them at 400°C for 30 min. About 10% of the nanotubes were filled with this technique [22]. Most of the filled single-walled carbon nanotubes are of relatively large diameters (see Fig. 3), whose stability plays an important role in surviving the heating process.

### 4. Irradiation

The mechanism of atomic and molecular transport in and out of nanotubes will shed light on the diffusion process, which is crucial in optimizing the filling of

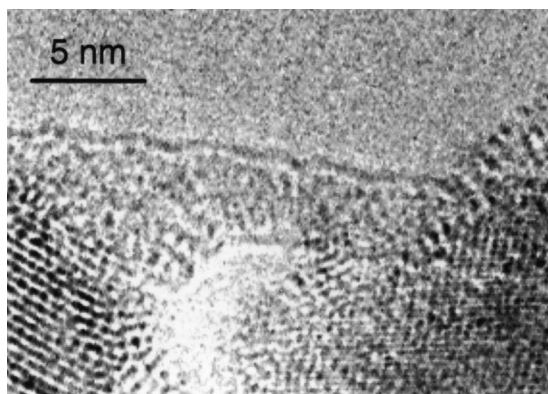


Fig. 3. A filled single-walled carbon nanotube with 3.5 nm diameter.

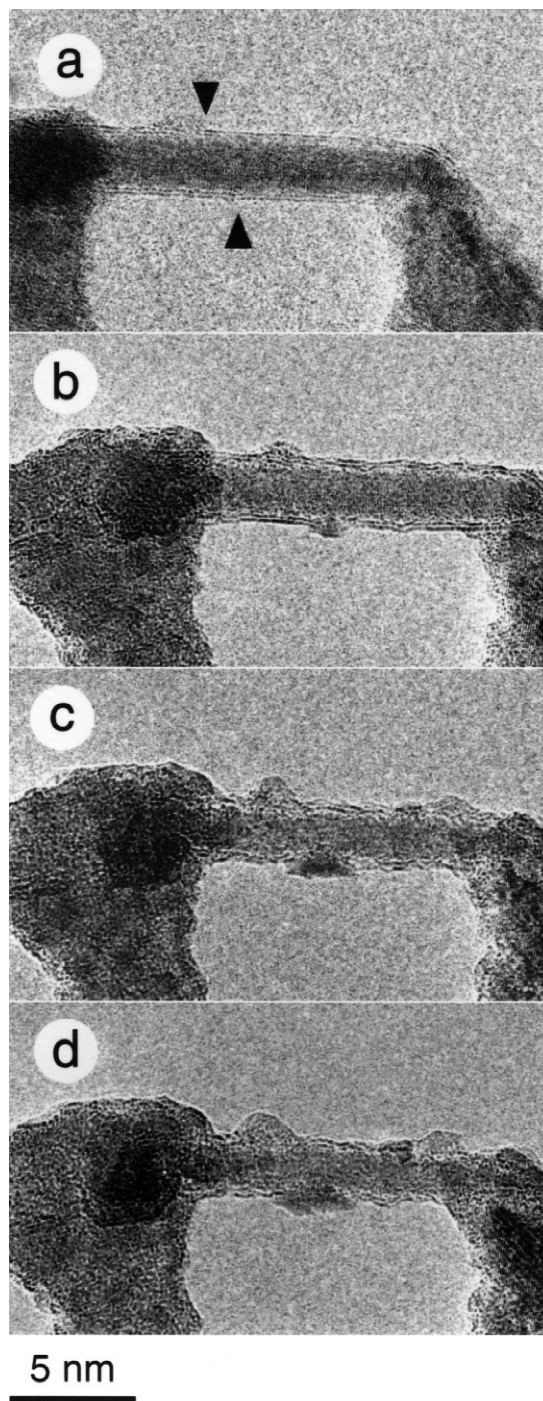


Fig. 4. Electron irradiation of a filled carbon nanotube segment bridged between soot. (a) The original diameter of the Bi-filled nanotube is 2.4 nm. The arrows point to the defects. (b) Filling materials start to diffuse out the nanotube through defect points. (c) More material is lost as the tube continues to deform. (d) The nanotube diameter as shrunk to 2.1 nm as the filling and the wall materials continue to escape. Notice that graphitization occurred around the metal particle near the left end of the nanotube.

nanotubes. To this end we imaged a filled carbon nanotube under electron beam irradiation. Fig. 4 illustrate the irradiation sequence of a filled carbon nanotube. Carbon evaporated from the defect locations in the nanotube, and metal atoms were released through the defect holes. The tube diameter decreases as the atoms evaporates. Similar surface reconstruction and dimensional change in single-walled carbon nanotubes has been reported [23].

## 5. Conclusions

We have successfully filled carbon nanotubes with bismuth by heating solid bismuth with single-walled carbon nanotubes. Irradiation induced dimensional change of filled carbon nanotubes has also been observed. The tube surface reconstructed upon evaporation of carbon atoms during electron irradiation in vacuum, and the filled materials was allowed to escape through defects created by heating. Optimization the filling process should allow one to fill single-walled carbon nanotubes with different materials, whose novel properties will be important to future nanotechnology.

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