Molecular Nanowires of 1 nm Diameter from Capillary Filling of Single-Walled Carbon Nanotubes

Ching-Hwa Kiang,* Jong-Suk Choi, Todd T. Tran, and Alfred Dirk Bacher

Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90095

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Molecular nanowires inside single-walled carbon nanotubes are produced by capillary filling. Bismuth was drawn into single-walled carbon nanotubes, where it formed single-crystal nanowires of nanometer dimensions. Metal was introduced in its gas, solution, and solid phases, with the solution phase process the most efficient and versatile method of filling. The majority of fillings are one-dimensional nanowires with high length to diameter ratios. The strong capillary effect in single-walled carbon nanotubes should allow these materials to host a wide variety of nanoscale materials.

Introduction

Since the discovery of single-walled carbon nanotubes in 1993,[1−3] this new class of materials has demonstrated a potential to make a major contribution to a variety of nanotechnology applications, including molecular electronics,[4] hydrogen storage media,[5] and scanning probe microscope tips.[6] Carbon nanotubes can be expected to provide a basis for a future generation of nanoscale devices,[6−9] and it has been predicted that modification[10−12] of single-walled carbon nanotubes will lead to an even more diverse range of applications. For example, the electrical property of empty single-walled carbon nanotubes is extremely sensitive to their structure and the existence of defects, which imposes great difficulty for using unfilled nanotubes in electronic device applications. The property of filled single-walled carbon nanotubes, on the other hand, will be dominated by the filling materials, and therefore, filled nanotubes will be more robust in applications such as nanoelectronics. In this work, we present the synthesis of Bi nanowires of 1 nm diameter by filling single-walled carbon nanotubes, since the electronic transport properties of one-dimensional Bi wires have been studied extensively, and the magnetoresistance is expected to be influenced by the dimensionality.[13] The technique may be used to synthesize other materials such as magnetic nanowires, which should allow studies of magnetism in one dimension.

There have been reports on filling of multiwalled[14−16] and single-walled[17] carbon nanotubes. The percentage of filled tubes was either very low[14,17] or with very low length to diameter ratios.[15−17] In addition, it is practically impossible to synthesize uniform multiwalled carbon nanotubes, and hence the filled tubes differ both in diameters and the number of carbon layers, which may affect the properties of these materials. An efficient and reproducible method to filling single-walled carbon nanotubes will be the key to future advances of this field.

Experimental Methods and Results

We synthesized single-walled carbon nanotubes with the arc method.[18] In brief, we used an electric arc running a dc current at 95 A under 400 Torr helium to vaporize the carbon and the catalyst.[2,19,20] The electrodes were 6 mm diameter graphite rods, with the anode containing mixtures of, in atomic percentage, graphite powder (90%), cobalt catalyst (5%), and bismuth cocatalyst (5%).[18,21,22] Bismuth was used to improve the catalytic properties of the primary catalyst for producing high-yield, large-diameter single-walled carbon nanotubes and as a source material for the nanowires. This method produces 20 g/h of raw soot with high content of single-walled carbon nanotubes (∼70%).

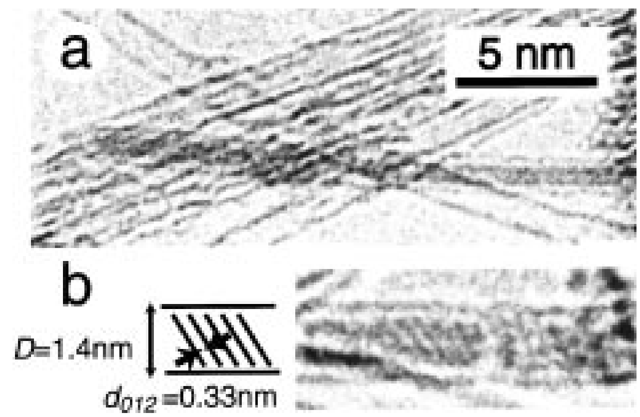

Figure 1. (a) High-resolution transmission electron micrograph of a 1.4 nm diameter single-walled carbon nanotube filled with a single-crystal bismuth nanowire. The filling extend throughout the entire stretch of the nanotube. (b) The middle section of the tube shown in (a), with lattice fringes clearly seen. The lattice spacing $d = 0.33$ nm corresponds to the (012) spacing of a bulk bismuth crystal.

High-resolution transmission electron microscopy (HRTEM) studies were done on Phillips CM200 and CM300 microscopes equipped with Gatan slow-scan cameras and image filters. The nanotube diameter (D) distribution was measured from HRTEM images, which shows 70% of the nanotubes have 0.7 nm $< D < 2$ nm, 15% have 2 nm $< D <$ 3 nm, and 15% have 3 nm $< D <$ 7 nm.

Filling of the nanotubes with bismuth metal occurred during the high-temperature gas phase reaction when the bismuth metal incorporated into the composite anode was vaporized with carbon and cobalt in a helium atmosphere. Figure 1 is a single-walled carbon nanotube entirely filled with a single crystal of bismuth of 1 nm inner diameter and 30 nm in length. While

* To whom correspondence should be addressed. E-mail: chk@chem.ucla.edu.

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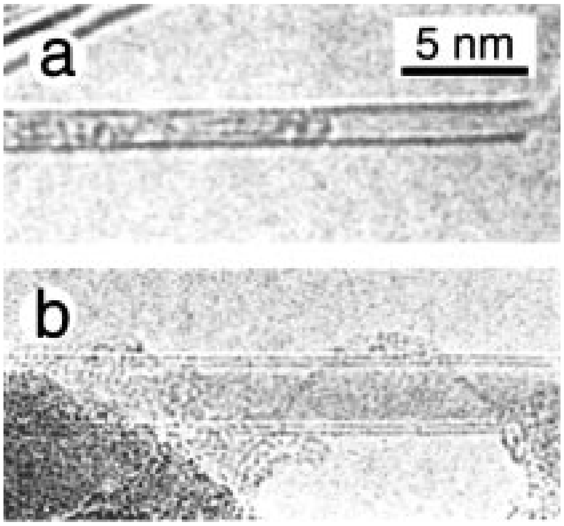

Figure 2. High-resolution transmission electron micrograph of carbon nanotubes after heat treatment. (a) A 1.6 nm diameter single-walled carbon nanotube was opened by heating, providing opportunity for filling and functionalization. The material inside the nanotube is amorphous carbon. (b) Bismuth was drawn into a single-walled carbon nanotube by heating in air at 400 °C. This process often results in the addition of a second protective layer of carbon around the filled single-walled carbon nanotube, giving improved stability and isolation.

less than 1% of the nanotubes were filled with this method, perhaps due to transport limitations, the extent of filling in a given nanotube suggests a strong capillary attraction for bismuth in small diameter carbon nanotubes.

Solid state bismuth metal was also used as starting material and was introduced into single-walled carbon nanotubes by heating. Since single-walled carbon nanotubes can be opened by heating (see Figure 2a),[23] we prepared nanotube soot with excess bismuth metal nanoparticle deposits and heated the soot in air at 400 ° C for 30 min. About 10% of the nanotubes were filled with this technique, compared to 1% achieved for multiwalled nanotubes.[14] Most of the metal nanowires are longer than tens of nanometers. Some of the nanowires do not appear to be crystalline, perhaps due to the short annealing time. About 20% of these filled nanotubes have a protective carbon layer deposited on it, as displayed in Figure 2b. The second layer was formed during the heating process, since the starting materials are exclusively single-layered.[18,19,21] A protective layer wrapped around a filled nanotube should improve the stability and provide a better isolation of an individual nanowire.

We have also achieved filling using solution phase chemistry, a more efficient route that may allow functionalizing carbon nanotubes with a variety of molecules. Single-walled carbon nanotube soot was stirred in concentrated HCl to remove excess metal particles. The solution was centrifuged for 10 min, and the precipitate was then dried, washed, with deionized water, and dried again.[17] To fill in the metal nanowires, the soot sample was stirred in 1 M of $Bi(NO_3)_3$ in HNO_3 solution. After centrifugation, the precipitate was washed, dried, and heated in a H_2 flow at 350 ° C for 3 h.

Figure 3a−d are typical transmission electron micrographs of single-walled carbon nanotubes filled with crystalline bismuth nanowires using solution phase chemistry. More than 30% of the single-walled carbon nanotubes were filled by this technique, and the length of filling ranges from a few nanometers to a few hundred nanometers. Most of the fillings are single bismuth crystals, as determined by energy-dispersive X-ray (EDX) analysis. The most commonly observed lattice spacing, 0.33 nm, corresponds to the (012) spacing (the most intense X-ray diffraction peak) of bulk bismuth crystal. We have also observed other lattice spacings that match the bulk bismuth crystal lattice

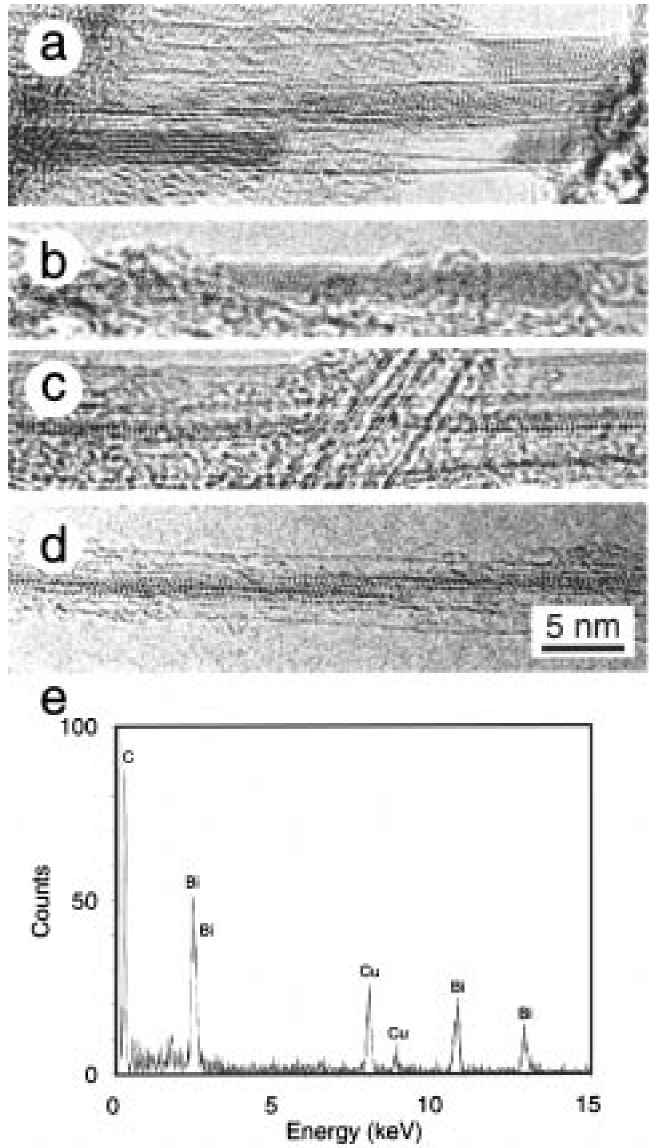

Figure 3. High-resolution transmission electron micrograph of single-walled carbon nanotubes filled by means of an efficient solution chemistry technique. The diameter of the crystal is the same as the inner diameter of the single-walled carbon nanotubes. The lengths of filling range from several tens of nanotubes to hundreds of nanometers, with many of the tubes completely filled, which suggests a strong interaction between the inner surface of the nanotube and the metal atoms. The lattice spacings can been seen clearly throughout the tube filling, with smaller diameter nanotubes showing individual atoms arranged in columns of bismuth nanowires. (a) Single bismuth crystal inside the nanotube. The $d_{012} = 0.33$ nm is the most commonly observed spacing. The bottom nanotube has the (012) lattice fringes perpendicular to the tube axis and the spacing can be determined to high accuracy. The spacing is 0.328 nm, the same as in the bulk bismuth metal. (b) A nanotube with 3 nm inner diameter has crystalline bismuth filling with structure similar to that of bulk bismuth crystals. (c) For small diameter nanotubes ($D \sim 1$ nm), the *d* spacing of the bismuth crystals differs from that of the bulk crystal. (d) Atoms of bismuth arranged in columns inside single-walled carbon nanotubes. There are two to three columns of bismuth nanowires inside each nanotube, indicating that the nanowire is composed of approximately five atoms in the plane perpendicular to the tube axis. (e) Energy-dispersive X-ray (EDX) spectrum of filled tubes shows strong peaks arising from the K_α, K_β, L_α, and L_β transitions of Bi. The peak from C is from the single-walled carbon nanotubes and the weaker peaks from Cu is from the TEM specimen support grid.

spacings, such as 0.37 nm (101) and 0.40 nm (003). Some of the bismuth nanowires with diameters smaller than 1 nm have lattice spacings that deviate from the lattice spacings of bulk bismuth crystal by about 5%, Analogous size effects have been observed in the crystalline structure of small diameter multi-walled carbon nanotubes.[24]

Discussion

Most of the filling is crystalline with a very high aspect ratio, unlike the particle-like filling observed inside multiwalled carbon nanotubes[15,16] and single-walled carbon nanotubes.[17] This suggests that a strong capillary force, stronger than in multiwalled carbon nanotubes,[14] is responsible for efficient filling of single-walled carbon nanotubes. Contrary to the method described by Sloan et al.,[17] we used HNO_3, an environment essential for opening nanotubes during the solution phase filling process, to fill single-walled carbon nanotubes with high yields, while causing little damage to the tubes. The low yield (<1%) filling with Ru observed by Sloan et al. was perhaps limited by the percentage of tubes opened. We solved this problem by using an improved process to produce single-walled carbon nanotubes,[18] which were capable of sustaining the harsh environment necessary for efficient filling in solution.

Our results indicate the tendency for molecules to be drawn into nanotubes in either crystalline or amorphous phases by a strong force; therefore, filling of single-walled carbon nanotubes with gas phase molecules may be considered as a likely event.[5,25] The bonding between the encapsulated materials and the highly curved, nearly one-dimensional single-walled carbon nanotube inner surface is likely to differ from bonding to graphite basal surfaces. Therefore, there should be a range of absorption energies of atomic and molecular species to the inner surface of single-walled carbon nanotubes, depending on the nanotube diameter.[26−28]

Concluding Remarks

We have shown that atoms and molecules in gas, solution, or solid phases can be introduced into single-walled carbon nanotubes to form stable nanostructures. In particular, solution phase chemistry offers an efficient method for producing molecular nanowires by filling single-walled carbon nanotubes, since many molecules can be introduced into solution for subsequent adsorption into nanotubes.

Single-walled carbon nanotubes can be made with a narrow size distribution and are thermally and chemically stable, and hence they are ideal nanowire templates. Filled nanotubes are more stable than empty nanotubes and may be separated based on their distinct chemical or physical properties. Adsorption of molecules in nanotubes may be influenced by an applied potential; therefore, nanotubes may be used as nanocontainers. The carbon layer may be removed, leaving nanowires composed of solely filling materials. Nanowires with novel electrical, superconducting, optical, and magnetic properties may be synthesized. Indeed, chemical and physical functionalization will be a key step in developing nontrivial applications of carbon nanotubes.

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