J|A|C|S
COMMUNICATIONS

Synthesis of Nearly Uniform Single-Walled Carbon Nanotubes Using Identical Metal-Containing Molecular Nanoclusters as Catalysts

Lei An,† Jessica M. Owens,‡ Laurie E. McNeil,‡ and Jie Liu*,†

Department of Chemistry, Duke University, Durham, North Carolina 27705, and Department of Physics and Astronomy, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599

Received June 27, 2002

It is well-known that the physical and chemical properties of single-walled carbon nanotubes (SWNTs) vary strongly with their diameters and helicities.[1−3] For example, SWNTs could be metallic or semiconducting, depending on their helicity, which has a close correlation with their diameters;[1−3] the energy gaps of the semiconducting SWNTs are inversely proportional to their diameters;[4] and nanotubes with certain diameters are believed to have stronger interaction with hydrogen to achieve the target as hydrogen storage medium in practical fuel cells.[5] As a result, one of the main goals in the synthesis of SWNTs is to control the diameters of SWNTs.[6−9]

Compared with other methods for the preparation of SWNTs, chemical vapor deposition (CVD) has shown a clear advantage in controlling the growth of SWNTs because it has a number of controllable variables, such as temperature, feeding gas, and catalyst.[10] Recently, Dai et al.[8] and Lieber et al.[9] have demonstrated that the diameters of SWNTs are proportionally related to the sizes of the catalytic nanoparticles used in CVD processes. There are also reports that by lowering the growth temperature, the diameter of the produced nanotubes can shift to a smaller diameter.[11] But consistently uniform SWNTs have not been produced because of the fairly broad diameter distributions of the nanoparticles used as catalysts in these studies. In this communication, we describe the use of identical molecular nanoclusters containing Fe and Mo atoms to grow extremely small but uniform SWNTs on silicon dioxide surfaces using the CVD method. With a standard deviation of 17%, the SWNTs grown in our experiments have the narrowest size distribution for CVD-grown nanotubes. In addition, the preparation method for such identical catalyst nanoparticles is much simpler than methods used previously, providing an approach that can be easily scaled up to larger scale.

The nanocluster used in the experiment has a formula: $[H_xPMo_{12}O_{40}\subset H_4Mo^{VI}_{72}Fe^{III}_{30}(CH_3COO)_{15}O_{254}(H_2O)_{98}]\cdot 60H_2O$. It is a member of a large family of molecular nanoclusters based on molybdenum oxide.[12,13] The specific nanocluster used in our experiment is made up of two parts: one is a spherical icosahedral giant cluster cage of the $\{(Mo^{VI})Mo^{VI}_5\}_{12}Fe^{III}_{30}$ type; the other is a tetrahedral reduced Keggin $[H_xPMo_{12}O_{40}]^{3-}$ ion inside the cage as nucleus. The spherical cage consists of 12 pentagonal fragments of the type $\{(Mo)Mo_5O_{21}\}$ (formed by a central bipyramidal MoO_7 group sharing edges to five MoO_6 octahedra), which are linked by 30 $\{Fe^{III}(H_2O)_2\}^{3+}$ connectors. The bidentate acetate ligands, which are inside the cage, link the metal centers, namely the Fe and Mo sites.[12] The total number of Mo atoms in each cluster is 84, and the total number of Fe atoms in each cluster is 30. It was synthesized using a previously described method.[12] Typically, $H_3[P(Mo_3O_{10})_4]$ (1.25 g, 0.69 mmol), H_2O (37.5 mL), $FeCl_2\cdot 4H_2O$ (0.5 g, 2.52 mmol), $Na_2MoO_4\cdot 2H_2O$ (1.0 g, 4.14 mmol), and CH_3COOH (100%, 5 mL) were mixed together. About 0.213 mL of 37.5% HCl acid (pH of the reaction mixture ≈ 2.0) was added to the solution, and then the solution was stirred for 45 min at room temperature before being filtered. The filtrate was kept in an open 250-mL beaker for crystallization for 5 days. The crystals were filtered, washed with ultrapure water, and dried at room temperature. The nanoclusters can be dissolved in polar solvents such as methanol, ethanol, and water. The nanocluster crystals are dark blue and highly soluble in ionizing solvents, such as water, methanol, and ethyl acetate. The solid IR spectrum of the nanoclusters made in our laboratory was consistent with the solid IR data published previously.[13] In particular, the asymmetric vibration of P−O bonding has a wide peak at 1065 cm^{-1}, and the vibration of Mo=O is represented by the peak at 960 cm^{-1}.

To grow SWNTs, Si wafers deposited with the nanoclusters were put into a quartz tube in a furnace with a small amount of powder catalyst used for bulk growth of SWNTs placed in the upper flow position of the wafers as promoter.[14] The effect of promoter is to increase the yield of SWNTs (Supporting Information 1). The wafers were first annealed in the air for 5 min at 700 °C to decompose the organic ligand of the molecular cluster and yield clusters made of Fe and Mo oxides and then reduced in H_2 (200 sccm) for 5 min at the 900 °C to form metal nanoclusters containing only Fe and Mo. Subsequently, CVD growth of SWNTs was performed with methane (800 sccm) as feeding gas for 15 min at the same temperature. Finally, the system was cooled to room temperature under an argon atmosphere. The same procedure in SWNT growth was applied to silicon nitride membranes by substituting these substrates for the silicon wafers to obtain Raman spectra without the stronger background signal from the Si substrates.

The samples were studied with a Nanoscope IIIA atomic force microscope (Digital Instruments, Santa Barbara, CA) operated in taping mode. The nanocluster crystal was characterized with a BOMEM MB-100 infrared spectroscope. The silicon nitride membranes with SWNTs were examined by a Dilor Raman triple spectrograph, which has been fitted with a liquid nitrogen-cooled CCD camera for detection. The excitation wavelength was 514.5-nm light from an argon ion laser. The beam size was 3 μm in diameter, and the power incident on the sample was about 6 mW.

Using the molecular nanoclusters, we have successfully produced SWNTs on the SiO_2 surface. Although the results are exciting since it is the first time nanotubes were grown using identical molecular clusters as catalyst, the diameter distribution of the SWNTs grown was relatively broad. The diameters of nanotubes range from 0.7 to 2.6 nm (Figure 1). From the observation that there are two peaks in the size distribution curve and the fact that we have prepared the samples by simply letting the nanocluster solution evaporate on the substrates, we have speculated that the broad size distribution results from the aggregated nanoclusters during the solvent evapora-

---

* To whom correspondence should be addressed. E-mail: jliu@chem.duke.edu.
† Duke University.
‡ University of North Carolina at Chapel Hill.

10.1021/ja0274958 CCC: $22.00

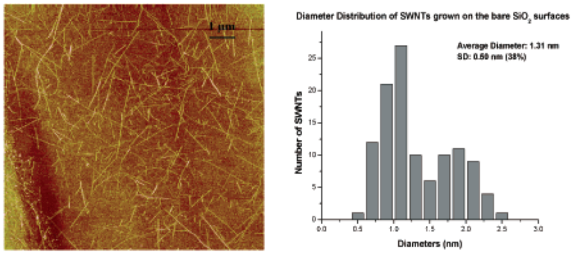

Figure 1. AFM image and the diameter distribution of the SWNTs grown on the Fe/Mo nanoclusters on bare silicon dioxide surfaces. The AFM image is 10 μm × 10 μm. The average diameter is 1.31 nm. The standard deviation is 0.50 nm or 38%.

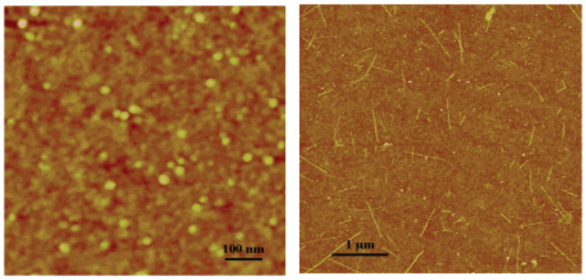

Figure 2. AFM images of the chemically attached Fe/Mo nanoclusters (left) and the SWNTs grown on them (right).

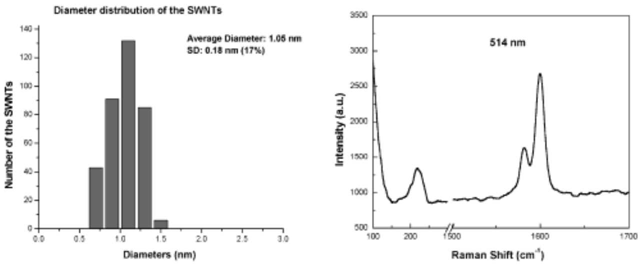

Figure 3. (Left) Diameter distribution of the SWNTs grown on the chemically attached Fe/Mo nanoclusters on the silicon dioxide surfaces. The average diameter is 1.0 nm, and the standard deviation is 0.18 or 17%. (Right) Raman spectrum of the SWNTs grown upon the chemically attached Fe/Mo nanoclusters on the silicon nitride membranes.

tion. Although the nanoclusters themselves have the same structure and consequently the same diameter, these nanoclusters are known to easily aggregate together upon the evaporation of the solvent.[13] This tendency to aggregate is a major problem in obtaining uniform SWNTs since the size of metal nanoparticles that were obtained by reducing the molecular nanoclusters in hydrogen had a wider size distribution. Therefore, it was not the individual nanoclusters that were catalyzing the growth of SWNTs but the aggregates of the nanoclusters. To obtain SWNTs with more uniform diameters, we have to develop a method to limit the aggregation of the nanoclusters during the solvent evaporation.

To limit the aggregation, 3-aminopropyltriethoxysilane was used to modify the silicon dioxide surface. Through the Coulombic attraction, the negatively charged nanoclusters were bonded strongly with the positively charged $-NH_2$ groups on the substrate to obtain well-separated nanoclusters. Figure 2 shows the surface of a substrate with well-separated nanclusters and uniform SWNTs grown from these clusters. Figure 3a illustrates the diameter distribution of more than 350 SWNTs produced in this way. The diameters of the SWNTs range from 0.7 to 1.5 nm with an average size of 1.0 nm. The standard deviation of the diameter distribution is 0.18 nm or 17%. The Raman spectrum of nanotubes obtained in the same way but on Si_3N_4 substrates (Figure 3b) also confirms this result. There is only one peak in the range of the breathing mode of SWNTs, which proves the existence of SWNTs in our sample and indicates that the uniformity of the SWNTs is exceptional. This peak corresponds to SWNTs with the average diameter at 1.0 nm, and the width of the peak indicates that the range of the diameters could be from 0.8 to 1.3 nm in good agreement with the AFM measurement.

The diameter of the SWNTs also agrees well with the hypothesis that they are grown from individual nanoclusters. According to the radii of the Fe atom (126 pm) and the Mo atom (140 pm), if all of the 84 Mo atoms and 30 Fe atoms in one nanocluster were left and packed tightly together after being reduced in hydrogen at 900 °C, the diameter of the residue should be about 1.3 nm. This estimate reasonably explains the observation that the SWNTs with a diameter of 1.2 nm are dominant in this distribution. However, some metal atoms could have been evaporated during the growth process. As a result, the nanoclusters became even smaller than 1.3 nm. That is why there are SWNTs with diameters less than 1.2 nm. As for the SWNTs with diameters more than 1.2 nm, a possible explanation is that, despite the usage of the chemical adsorption method, there were still a small number of nanoclusters that aggregated together to form bigger particles.

In summary, we have successfully produced very uniform SWNTs on the silicon dioxide surfaces using identical molecular nanoclusters. SWNTs produced have a narrow diameter distribution, from 0.7 to 1.5 nm with a standard deviation of 17%. This experiment represents the first time that nanoparticles with a defined formula and a specific structure have been used to catalyze the growth of SWNTs. Although it is still possible that local variations of experimental conditions may yield different nanotubes with similar diameters from identical catalysts, this work represents a real possibility to precisely control the diameter of SWNTs and will facilitate research on the fundamental properties and the future applications of SWNTs. In addition, the preparation of these nanoclusters is simple and can be scaled up to large scale, providing a convenient way to produce the catalysts for SWNTs growth.

Acknowledgment. This work is partially supported by ONR Grant A00014-98-1-0597. We thank Professor Jeff Long from UC Berkeley for helpful discussions and Eric Harley at UNC for help with Raman experiments.

Supporting Information Available: Experimental details and Raman spectra for SWNTs with broad diameter distribution (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Mintmire, J. W.; Bunlap, B. I.; White, C. T. *Phys. Rev. Lett.* **1992**, *68*, 1579.
(2) Hamada, N.; Sawada, S.; Oshiyama, A. *Phys. Rev. Lett.* **1992**, *68*, 1579.
(3) Saito, R.; Fujita, M.; Dresselhaus, G.; Dresselhaus, M. S. *Appl. Phys. Lett.* **1992**, *60*, 2204.
(4) Saito, R.; Dresselhaus, G.; Dresselhaus, M. S. London, 1998.
(5) Dillon, A. C.; Jones, K. M.; Bekkedahl, T. A.; Kiang, C. H.; Bethune, D. S.; Heben, M. J. *Nature* **1997**, *386*, 377.
(6) Rao, A. M.; Richter, E.; Bandow, S.; Chase, B.; Eklund, P. C.; Williams, K. A.; Fang, S.; Subbaswamy, K. R.; Menon, M.; Thess, A.; Smalley, R. E.; Dresselhaus, G.; Dresselhaus, M. S. *Science* **1997**, *275*, 187.
(7) Tang, X. P.; Kleinhammes, A.; Shimoda, H.; Fleming, L.; Bennoune, K. Y.; Sinha, S.; Bower, C.; Zhou, O.; Wu, Y. *Science* **2000**, *288*, 492.
(8) Li, Y.; Kim, W.; Zhang, Y.; Rolandi, M.; Wang, D.; Dai, H. *J. Phys. Chem. B* **2001**, *105*, 11424.
(9) Cheung, C. L.; Kurtz, A.; Park, H.; Lieber, C. M. *J. Phys. Chem. B* **2002**, *106*, 2429.
(10) Dai, H.; Kong, J.; Zhou, C.; Franklin, N.; Tombler, T.; Cassell, A.; Fan, S.; Chapline, M. *J. Phys. Chem. B* **1999**, *103*, 11246.
(11) Harutyunyan, A. R.; Pradhan, B. K.; Kim, U. J.; Chen, G. G.; Eklund, P. C. *Nano Lett.* **2002**, *2*, 525−530.
(12) Muller, A.; Das, S. K.; Kogerler, P.; Bogge, H.; Schmidtmann, M.; Trautwein, A. X.; Schunemann, V.; Krickemeyer, E.; Preetz, W. *Angew. Chem., Int. Ed.* **2000**, *39*, 3413.
(13) Muller, A.; Das, S. K.; Bogge, H.; Schmidtmann, M.; Botar, A.; Patrut, A. *Chem. Commun.* **2001**, 657.
(14) Su, M.; Zheng, B.; Liu, J. *Chem. Phys. Lett.* **2000**, *322*, 321.

JA0274958