Diameter-Controlled Synthesis of Carbon Nanotubes

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Nearly monodisperse iron nanoclusters have been used to define the diameters of carbon nanotubes grown by chemical vapor deposition (CVD). Iron nanoparticles with average diameters of 3, 9, and 13 nm were used to grow carbon nanotubes with average diameters of 3, 7, and 12 nm, respectively. Transmission electron microscopy studies of the nanotubes show that the as-grown nanotubes are single-walled carbon nanotubes (SWNTs) or thin multiwalled carbon nanotubes (MWNTs) with 2 or 3 layers. Investigations of the growth conditions also demonstrate that the supply of carbon reactant is critical for enabling the growth of large diameter nanotubes from large iron nanoclusters, and that the growth temperature is especially important for achieving high-quality large diameter nanotubes. The implications of these results and possible applications of the nanotubes are discussed.

Introduction

Carbon nanotubes are currently the focus of intense research due to their unique properties and potential to impact broad areas of science and technology.[1] The distinctive characteristics of carbon nanotubes arise from the atomic structure and size of these materials. For example, nanotubes can be either metals or semiconductors depending on helicity and diameter.[2] The diameter of a nanotube also affects significantly its mechanical properties, and thus can impact applications ranging from probe microscopy tips,[3] to electromechanical devices,[4] and structural composites.[5] Consequently, the development of methods that control precisely the structural properties of nanotubes offers the possibility of impacting many important areas.

Control of nanotube diameter represents one of the most basic issues in developing nanotube growth methods. Previously, it has been suggested that the size of the growth catalyst used in metal catalyzed chemical vapor deposition (CVD) can define the diameter of as-grown carbon nanotubes.[6] This hypothesis has been supported by the observation that catalytic particles at the ends of CVD-grown nanotubes have sizes commensurate with the nanotubes diameters.[3c,6,7,8] However, direct growth of different diameter carbon nanotubes from monodisperse catalyst such as FeO_x,[3c] Fe/Mo,[9] and Co nanoclusters,[10] which could provide much stronger support for this idea, have not yet been reported.

Here, we demonstrate clearly the concept that different size nanocluster catalysts can be used to control the diameters and structures of CVD-grown nanotubes (Figure 1). We have prepared nearly monodisperse iron nanoclusters having three distinct average diameters, and have used these nanoclusters to grow carbon nanotubes with similar average diameters. In addition, investigations of the CVD growth demonstrate that the supply of carbon reactant is critical for the preparation of large diameter nanotubes from large iron nanoclusters, and that growth temperature is also important for achieving high-quality large diameter nanotubes. The implications and possible applications of these nanotubes are discussed.

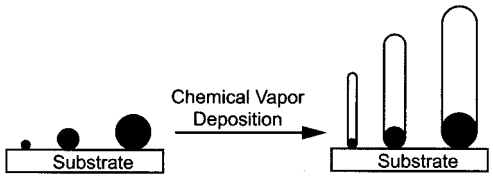

Figure 1. Schematic depicting the use of different diameter iron nanocluster catalysts for the controlled diameter synthesis of carbon nanotubes.

Experimental Section

Iron nanoclusters were synthesized by thermal decomposition of iron pentacarbonyl ($Fe(CO)_5$) (Aldrich, 99.999%) using a procedure based on a previous report.[9] Briefly, 2 mmol of $Fe(CO)_5$ was mixed with either 1−5 mmol of oleic acid (Aldrich, 99+%), lauric acid (Aldrich, 99.5+%) or octanoic acid (Aldrich, 99.5+%) in 10 mL of dioctyl ether (Aldrich, 99%). The solutions were refluxed at 286 °C under nitrogen for 1−3 h to yield iron nanocluster solutions with distinct and nearly monodisperse diameters.

CVD growth of carbon nanotubes catalyzed by the different size iron nanoclusters was carried out using ethylene or methane as the carbon reactant. The catalyst was deposited on oxidized silicon surfaces from toluene solution and then rinsed with hexane. The substrate-supported catalyst was annealed at 800 °C for 5 min in a flow of 600 standard cubic centimeters per minute (sccm) of argon and 400 sccm of hydrogen, and then CVD growth was carried out by the addition of 2−200 sccm of ethylene or 1000 sccm of methane at 800−1000 °C for 10 min.

The diameters of the iron nanoclusters and carbon nanotubes prepared using these catalysts were determined by transmission electron microscopy (TEM) (Philips EM 420, 100 kV, FEI, Hillsboro, OR), and atomic force microscopy (AFM) (Nanoscope IIIa, Digital Instruments, Santa Barbara, CA). The reported uncertainties correspond to ±1 standard deviation.

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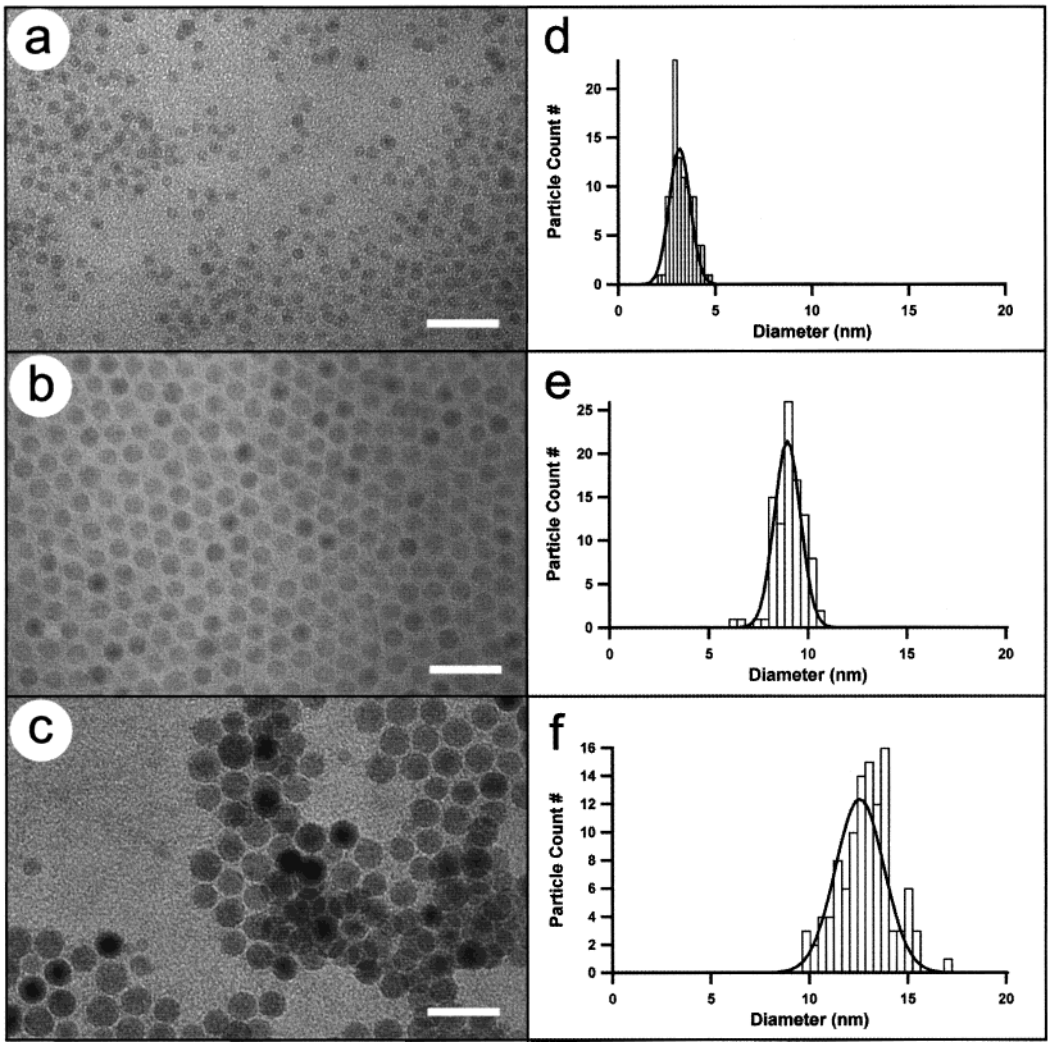

Figure 2. TEM images of iron nanoclusters produced by solution-phase synthesis using (a) oleic acid, (b) lauric acid, and (c) octanoic acid. The scale bars are 30 nm. Corresponding histograms of the nanocluster diameters are plotted in (d), (e), and (f), respectively. The solid lines correspond to Gaussian fits.

Results and Discussion

Critical to our studies of controlled diameter growth of carbon nanotubes is the preparation of iron nanoclusters with narrow average diameter distributions. To achieve this goal we decomposed $Fe(CO)_5$ in the presence of an excess of oleic acid (C18), lauric acid (C12) or octanoic acid (C8) acid, which function as capping ligands for the nanoclusters as they form. Typical TEM images of the iron nanoclusters produced using oleic, lauric, and octanoic acids, parts a, b, and c of Figure 2, respectively, qualitatively show our ability to control the magnitude and uniformity of the nanocluster diameters. In general, we find that the growth of smaller (larger) diameter nanoclusters is favored in the presence of longer (shorter) chain-length capping ligands. To quantify these trends and the dispersity in nanocluster diameters we determined diameter distributions from the TEM data. Histograms of the nanocluster diameters obtained using oleic acid (Figure 2, part d), lauric acid (Figure 2, part e), and octanoic acid (Figure 2, part f) capping ligands demonstrate relatively narrow distributions with average diameters ± 1 standard deviation of 3.2 ± 0.8, 9.0 ± 0.9, and 12.6 ± 1.7 nm, respectively. Significantly, these solutions of well-defined and distinct diameter iron nanoclusters provide us with the catalyst material needed to test clearly the possibility of diameter controlled nanotube growth.

Carbon nanotubes were grown by CVD at 800 °C with ethylene reactant using the 3, 9 and 13 nm average diameter iron nanoclusters as catalysts. Representative TEM images demonstrate clearly that larger nanocluster catalyst diameters can lead to the reproducible growth of larger diameter carbon nanotubes (Figure 3, parts a, b, and c). The key role of the catalyst in defining the nanotube diameters produced by CVD is evident from the analysis of the diameter distributions. Specifically, histograms of the carbon nanotube diameters obtained from TEM and AFM analysis of samples prepared using iron nanoclusters demonstrate a close correlation between diameters of the nanocluster catalysts and nanotubes (Figure 3, parts d, e, and f). The carbon nanotubes obtained from the 3, 9, and 13 nm average diameter iron nanoclusters had diameters of 2.6 ± 0.8, 7.3 ± 2.2, and 11.7 ± 3.2 nm, respectively. The high degree of diameter control and uniformity can also be seen clearly in AFM images of the as grown nanotubes as shown in Figure 4. In addition to the close correlation between average diameters of the catalysts and nanotubes, we find that diameter distribution widths are also similar. For the largest diameter nanotubes, there is some broadening relative to the nanocluster catalyst distribution, and we attribute this to the greater difficulty in achieving uniform nucleation at the largest diameters (see below). Nevertheless, these results show quite clearly that well-

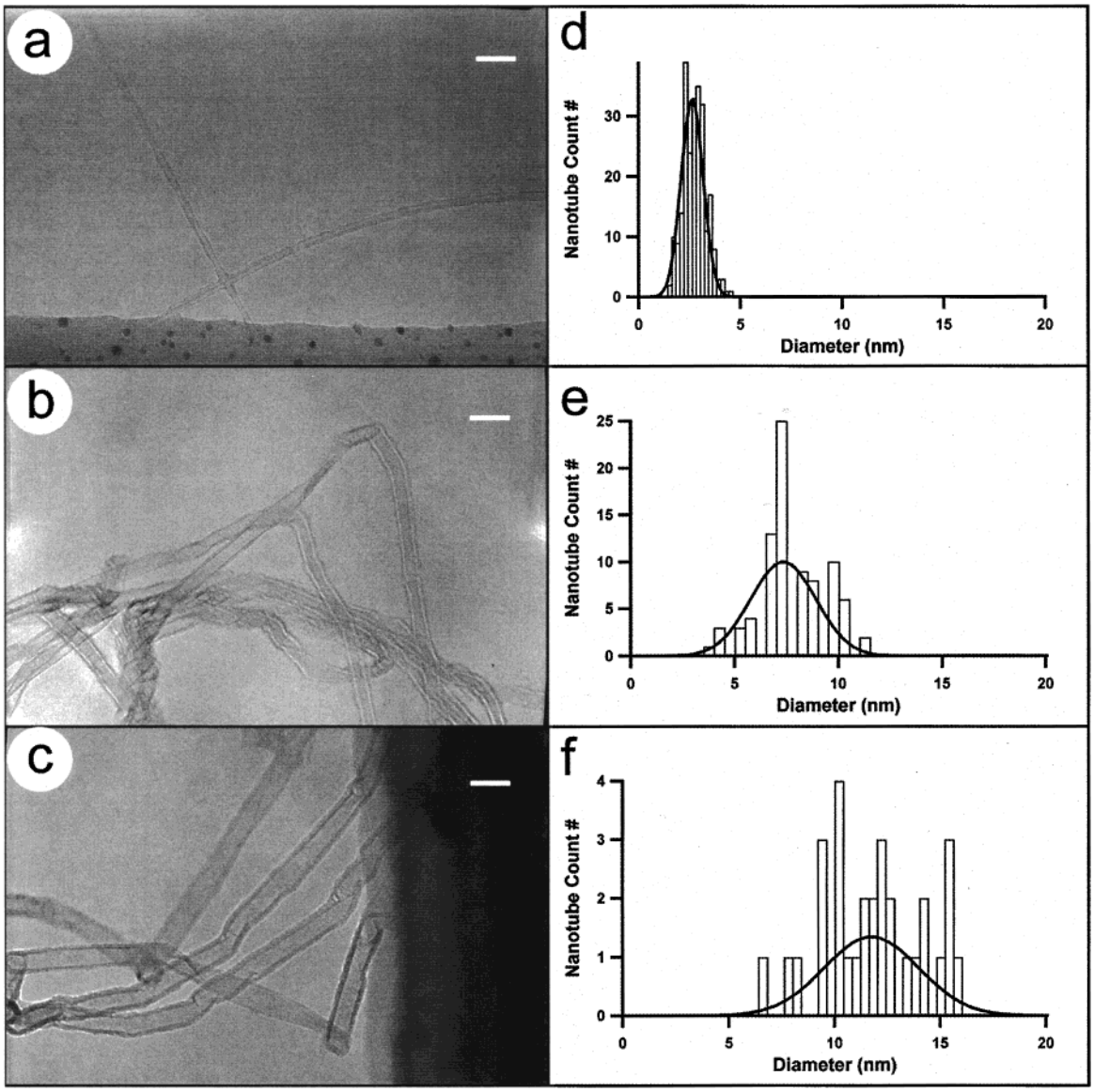

Figure 3. TEM images of carbon nanotubes grown using (a) 3, (b) 9, and (c) 13 nm average diameters iron nanoclusters. Scale bars are 20 nm for (a), (b), and (c). Corresponding histograms of the nanotube diameters are plotted in (d), (e), and (f), respectively. The solid lines correspond to Gaussian fits.

defined nanocluster catalysts can be used for diameter-controlled CVD synthesis of nanotubes.

The structural characteristics of these different diameter carbon nanotubes have also been determined from TEM images. First, nanotubes produced from small (3 nm average diameter) iron nanoclusters consist primarily of SWNTs with ca. 30% double-walled carbon nanotubes (DWNTs) (Figure 3, part a). AFM images also showed that these as-grown SWNTs are straight over lengths of hundreds of nanometers, suggesting a relatively low density of defects. Second, the 9 nm average diameter catalyst nanoclusters produce a mixture of SWNTs and MWNTs (Figure 3, part b). This medium-size-range catalyst produces SWNTs and thin-walled MWNTs with typical wall thicknesses of 2−4 graphene layers. The well-defined lattice fringes in TEM images of the MWNTs indicate that the as-grown nanotubes have a high degree of local crystalline order. Larger scale images also show that the straight, ordered segments are often mixed with kinked and bent segments, which arise from structural defects. Third, the large (13 nm average diameter) diameter nanoclusters catalyze the growth of thin-walled MWNTs with typical wall thicknesses of 2−4 graphene sheets (Figure 3, part c). The structural morphology of these tubes is similar to the MWNTs grown from the medium-size-range catalyst. Although a large fraction of SWNTs have not been produced from the largest catalyst nanoclusters, we note that the observed MWNTs have very thin walls and large open internal volumes.

In addition, the partial pressure of the reactant gas was found to be important to controlled diameter carbon nanotube growth. As the size of nanoclusters increases from 3 to 13 nm, increased ethylene percentages were required to produce carbon nanotubes with diameter distributions similar to those of the corresponding catalysts: for the 3, 9, and 13 nm diameter catalysts, 0.5, 9, and 18, respectively, percent ethylene was used. In contrast, 0.5% ethylene reactant produces small diameter SWNTs irrespective of the diameters of iron nanoclusters used as the catalysts. We believe that these results indicate that the initial nucleation is critical to determining diameters of larger (>5 nm) nanotubes, and that to achieve large size nucleation event requires a larger flux of carbon reactant to the nanocluster catalyst. This interpretation is consistent with results observed

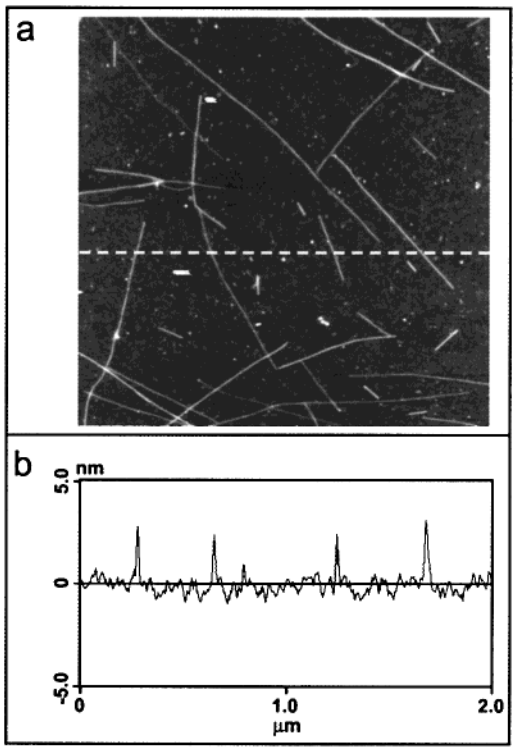

Figure 4. (a) AFM image of SWNTs grown from 3 nm average diameter catalyst on an oxidized silicon surface. The image is 2 μm × 2 μm. (b) Height cross-section taken along the white dashed line in (a). The diameters of nanotubes in the cross-section are (from the left) 2.86, 2.55, 2.56, and 3.11 nm, respectively.

previously using alumina-supported Fe/Mo catalyst,[11] although the catalyst diameters were not known in this earlier work.

Last, we have also carried out experiments exploring how the growth temperature and carbon reactant species affect the nanotubes produced from the different diameter nanocluster catalysts. First, growth at 900 °C using the 9-nm diameter iron nanoclusters produces large diameter, thin-walled MWNTs with typically only 2 or 3 walls (Figure 5, part a). In addition, these large diameter carbon nanotubes exhibit substantially fewer defects (e.g., sharp kinks and bends) compared to similar diameter nanotubes grown at 800 °C. However, high-temperature growth from ethylene can produce substantial amorphous carbon on nanotubes due to homogeneous decomposition of ethylene in the gas phase. To explore the possibility of obtaining high-quality large diameter nanotubes that are also free from amorphous carbon coatings, we have investigated growth using methane, which has higher homogeneous decomposition temperature.[12] Significantly, methane-based growth from 9 nm average diameter nanoclusters yields relatively clean SWNTs and DWNTs with 7 nm average diameters (Figure 5, part b). These results thus suggest that it should be possible through further optimization of growth conditions to produce clean and crystalline large-diameter SWNTs.

Conclusions

We have shown that nearly monodisperse iron nanoclusters can be used to define the diameters of carbon nanotubes grown by metal-catalyzed CVD. Investigations of growth conditions demonstrate that the supply of carbon reactant is important to growth of large diameter nanotubes from large iron nanoclusters, and that growth temperature is especially important for achieving high-quality large diameter nanotubes. We believe that the ability to exert a high degree of control over the diameters of nanotubes will facilitate the study of fundamental properties and the exploration of new applications. For example, large-diameter SWNTs are ideal systems for examining theoretical predictions of reversible changes in the electronic properties of radially deformed nanotubes,[13] and moreover, it might be possible to exploit such large nanotubes as electromechanical devices[14] and nanoreactors. Carbon nanotube samples with narrow diameter distributions also could be used as templates for the elaboration of other nanomaterials such as metal carbide nanowires.[15] In addition, the availability of carbon nanotubes with well-defined and predictable diameters should have a substantial impact on probe microscopy imaging.[3] Last, we believe that the approach demonstrated in this paper can be extended to other types of pyrolytically grown nanotubes, such as $B_xC_yN_z$,[16] and thus could open up exciting opportunities for fundamental studies and technological applications of a wide-range of nanoscale materials in the future.

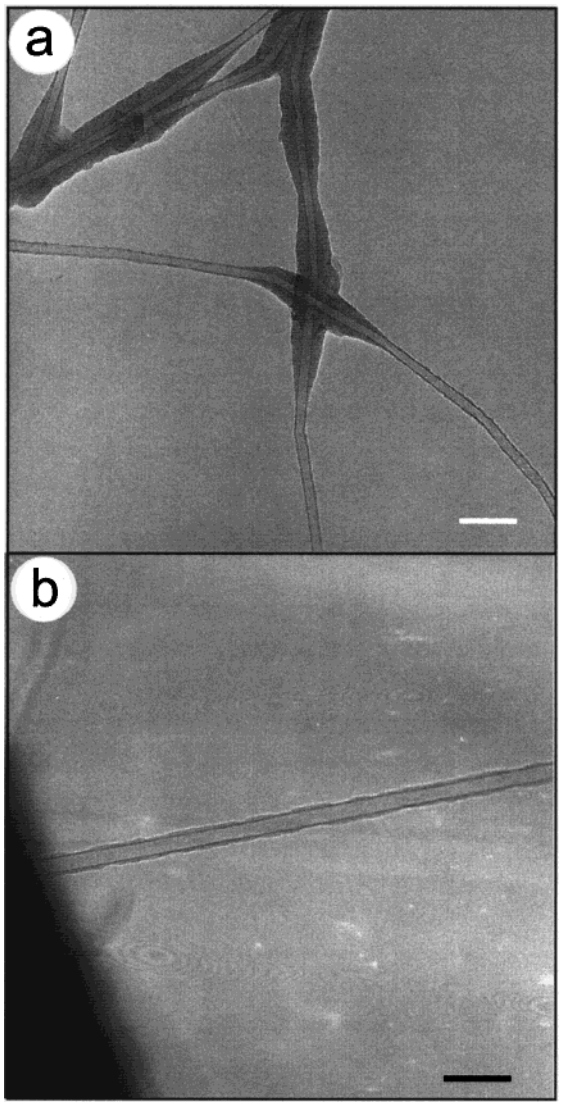

Figure 5. (a) TEM image of ca. 7 nm diameter carbon nanotubes grown at 900 °C using ethylene. (b) TEM image of an ca. 7 nm diameter SWNT synthesized with methane at 850 °C. Scale bars are 40 nm.

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References and Notes

(1) (a) Odom, T. W.; Huang, J. L.; Kim, P.; Lieber, C. M. *J. Phys. Chem. B* **2000**, *104*, 2794. (b) Dai, H. J.; Kong, J.; Zhou, C. W.; Franklin, N.; Tombler, T.; Cassell, A.; Fan, S. S.; M., C. *J. Phys. Chem. B* **1999**, *103*, 11246. (c) Dekker: C. *Phys. Today* **1999**, *52*, 22. (d) McEuen, P. L. *Phys. World* **2000**, *13*, 31. (e) Collins, P. G.; Avouris, P. *Sci. Am.* **2000**, *283*, 62.

(2) (a) Odom, T. W.; Huang, J.-L.; Kim, P.; Lieber, C. M. *Nature* **1998**, *391*, 62. (b) Wildoer, J. W. G.; Venema, L. C.; Rinzler, A. G.; Smalley, R. E.; Dekker: C. *Nature* **1998**, *391*, 59.

(3) (a) Dai, H.; Hafner, J. H.; Rinzler, A. G.; Colbert, D. T.; Smalley, R. E. *Nature* **1996**, *384*, 147. (b) Wong, S. S.; Harper, J. D.; Lansbury, P. T.; Lieber, C. M. *J. Am. Chem. Soc.* **1998**, *120*, 603. (c) Cheung, C. L.; Hafner, J. H.; Lieber, C. M. *Proc. Nat. Acad. Sci. U.S.A.* **2000**, *97*, 3809. (d) Hafner, J. H.; Cheung, C. L.; Oosterkamp, T. H.; Lieber, C. M. *J. Phys. Chem. B* **2001**, *105*, 743.

(4) Rueckes, T.; Kim, K.; Joselevich, E.; Tseng, G. Y.; Cheung, C. L.; Lieber, C. M. *Science* **2000**, *289*, 94.

(5) (a) Andrews, R.; Jacques, D.; Rao, A. M.; Rantell, T.; Derbyshire, F.; Chen, Y.; Chen, J.; Haddon, R. C. *Appl. Phys. Lett.* **1999**, *75*, 1329. (b) Haggenmueller, R.; Gommans, H. H.; Rinzler, A. G.; Fischer, J. E.; Winey, K. I. *Chem. Phys. Lett.* **2000**, *330*, 219.

(6) Dai, H. J.; Rinzler, A. G.; Nikolaev, P.; Thess, A.; Colbert, D. T.; Smalley, R. E. *Chem. Phys. Lett.* **1996**, *260*, 471.

(7) Anderson, P. E.; Rodriguez, N. M. *Chem. Mater.* **2000**, *12*, 823.

(8) Sinnott, S. B.; Andrews, R.; Qian, D.; Rao, A. M.; Mao, Z.; Dickey, E. C.; Derbyshire, F. *Chem. Phys. Lett.* **1999**, *315*, 25.

(9) (a) Bentzon, M. D.; van Wonterghem, J.;, Morup, S.; Tholen A. *Philos. Mag. B* **1989**, *60*, 169. (b) Li, Y.; Liu, J.; Wang, Y. Q.; Wang, Z. L. *Chem. Mater.* **2001**, *13*, 1008.

(10) Ago, H.; Komatsu, T.; Ohshima, S.; Kuriki, Y.; Yumura, M. *Appl. Phys. Lett.* **2000**, *77*, 79.

(11) Hafner, J. H.; Bronikowski, M. J.; Azamian, B. R.; Nikolaev, P.; Rinzler, A. G.; Colbert, D. T.; Smith, K.; Smalley, R. E. *Chem. Phys. Lett.* **1998**, *296*, 195.

(12) Tibbetts, G. G. Academic: Amsterdam, 1990.

(13) Lammert, P. E.; Zhang, P.; Crespi, V. H. *Phys. Rev. Lett.* **2000**, *84*, 2453.

(14) Liang, W.; Cheung, C.-L.; Lieber, C. M.; Park, H. Unpublished results.

(15) Dai, H.; Wong, E. W.; Lu, Y. Z.; Fan, S. S.; Lieber, C. M. *Nature* **1995**, *375*, 769.

(16) Terrones, M.; Benito, A. M.; Manteca-Diego, C.; Hsu, W. K.; Osman, O. I.; Hare, J. P.; Reid, D. G.; Terrones, H.; Cheetham, A. K.; Prassides, K.; Kroto, H. W.; Walton, D. R. M. *Chem. Phys. Lett.* **1996**, *257*, 576.