NANO LETTERS

2009
Vol. 9, No. 4
1673-1677

"Cloning" of Single-Walled Carbon Nanotubes via Open-End Growth Mechanism

Yagang Yao, Chaoqun Feng, Jin Zhang,* and Zhongfan Liu*

Beijing National Laboratory for Molecular Sciences (BNLMS), Key Laboratory for the Physics and Chemistry of Nanodevices, State Key Laboratory for Structural Chemistry of Unstable and Stable Species, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, People's Republic of China

Received January 20, 2009

ABSTRACT

Using the concept of "cloning", we report herein a rational approach to grow single-walled carbon nanotubes (SWNTs) with controlled chirality via an open-end growth mechanism. Specifically, by using open-end SWNTs as "seeds/catalysts" (without metal catalysts), "new/duplicate" SWNTs could be grown and cloned from the parent segments via an open-end growth mechanism. Using this strategy, we have measured more than 600 short seed segments and have found that the yield of cloning is relatively low (around 9%). This yield can be greatly improved up to 40% by growing SWNTs on quartz substrate. Atomic force microscopy and micro resonance Raman spectroscopy characterization indicate that the parent nanotube and the duplicate nanotube have the same structure. These findings provide a potential approach for growing SWNTs with controlled chirality, which are important for the application of SWNTs in nanoelectronics.

To realize the application of single-walled carbon nanotubes (SWNTs) in nanoelectronics,[1,2] the chirality-selective synthesis of SWNTs is a critical step.[3] Although various attempts have been made to grow SWNTs with controlled chirality, such as using a solid supported catalyst[4] or bimetallic FeRu catalyst,[5] using different carbon precursors[6] and by controlling the carbon monoxide pressure[7] on Co−Mo Catalysts, and so forth, it has only been possible to get a narrow diameter and chirality distribution. Smalley and co-workers have demonstrated the continued growth of SWNTs from the open-end SWNTs docked with nanometer-sized metal catalysts, but amplifying the original (*n*, *m*) type remained to be proven.[8−11] Furthermore, the presence of metallic particles in the final product would arise obvious disadvantages for complex purification process that can alter the quality of the tubes and result in the SWNTs exhibiting lower degradation temperatures.

Metal-catalyst-free growth of aligned carbon nanotube (CNT) film could be achieved on the C face of hexagonal silicon carbide perpendicular to the surface after heating at 1700 °C for half an hour in a vacuum, and on the contrary, a very thin layer of graphite sheets parallel to the surface was formed on the Si face under the same condition.[12] However, the resulting nanotubes were multiwalled. Derycke et al. also reported that nanotubes were produced without metal catalyst and grew with their axis parallel to the surface on the Si face of SiC annealed in vacuum and the resulting materials had a very narrow size distribution in the 1.2 to 1.6 nm range.[13] But atom resolved scanning tunneling microscopy studies of large numbers of tubes showed no chirality selection. In addition, very recently, Takagi et al. reported that even semiconductor nanoparicles of SiC, Ge, and Si produce single-walled and double-walled CNTs in catalytic chemical vapor deposition (CVD) with ethanol.[14] They thought that that nanosize structures might act as a template for the formation of SWNT.

In this letter, using the concept of "cloning", we presented a rational approach to control the chirality of SWNTs by growing SWNTs via an open-end growth mechanism without using metal catalysts. Briefly, by using open-end SWNTs as "seeds/catalysts", "new/duplicate" SWNTs could be grown and cloned from the parent segments via an open-end growth mechanism. Using this strategy, we have measured more than 600 short seed segments and found the yield of cloning is relatively low (around 9%). This yield can be greatly improved up to 40% by growing SWNTs on quartz substrate. Atomic force microscopy and micro resonance Raman spectroscopy characterization indicated that the parent nanotube and the duplicate nanotube had the same structure.

Figure 1a−c depicts the schematic diagrams of SWNTs cloning from the open-end parent SWNTs. First, as shown in Figure 1a,d,e, ultralong SWNTs[15−18] were grown on

* To whom correspondence should be addressed. Tel/Fax: 86-10-6275-7157. E-mail: jinzhang@pku.edu.cn.

10.1021/nl900207v CCC: $40.75
Published on Web 03/13/2009

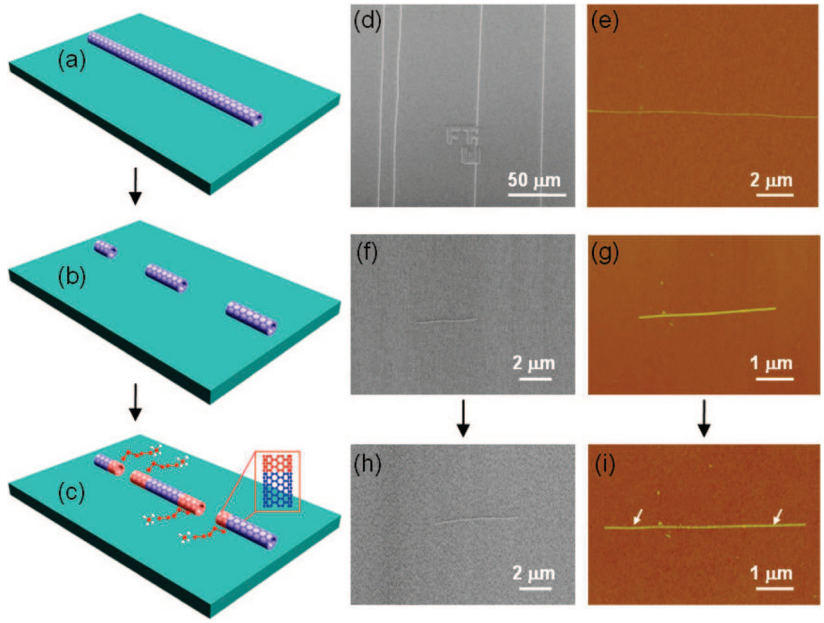

Figure 1. (a−c) Schematic diagrams of as-grown ultralong SWNTs (a) on substrate by low feeding gas flow, which could be cut into short segments, open-end SWNTs seeds (b), and the duplicate SWNTs (red in color) which could be continued to grow from the parent SWNTs segments via directly adding of C_x (C_2 and/or C_3) radicals to the open-end seed (c). (d,e) SEM image and AFM image of ultralong SWNTs used for preparing open-end SWNTs seeds, respectively. (f,g) Representative SEM image and AFM image of short parent SWNTs segments for the second growth. (h,i) SEM image and AFM image of duplicate SWNTs continued grown from the SWNTs in panels f and g, respectively.

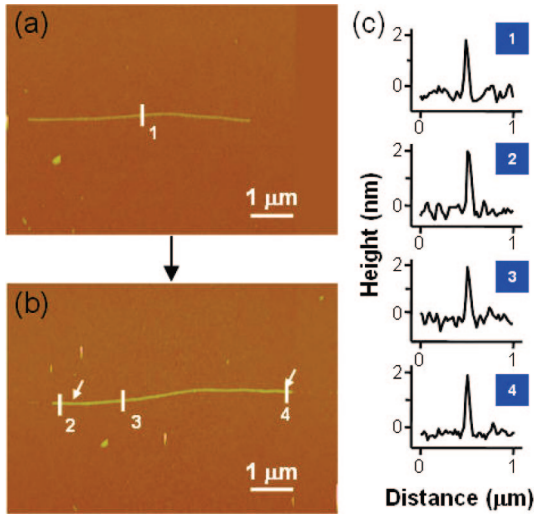

Figure 2. (a) AFM image of a short SWNT seed segment. (b) AFM image of the duplicate SWNT that was continued from the seed SWNT in panel a. The white arrows denote the start of the regrowth. (c) Typical height profile across the SWNT in panel a (position 1) and panel b (positions 2, 3, and 4), showing nearly identical height of 2.0 nm over several points measured along its entire length in panels a and b.

SiO_2/Si substrate for preparing open-end SWNTs seeds. The detailed process of CVD growth of parallel ultralong SWNTs with ultralow gas flow is shown in part I of Supporting Information. Figure S1 of Supporting Information and Figure 1d show typical scanning electron microscopy (SEM) images of well-separated, parallel SWNTs synthesized at 975 °C. The SWNT length is only limited by the substrate size, the hot zone of the furnace, and the growth time. To locate the SWNTs, we made patterned markers by photolithography and wet etching on SiO_2/Si substrate (shown in Figure S1a of Supporting Information and Figure 1d). It is convenient for addressing any SWNT on the substrate and doing SEM (Hitachi S-4800, operated at 1 kV), AFM (Nanoscope III, operated at tapping-mode) and Raman spectroscopy (Renishaw 1000 with the excitation energy of 1.96 eV (632.8 nm)) characterization.

Second, shown in Figure 1b, ultralong SWNTs were then cut into short segments (usually 1∼10 μm in length) by electron beam lithography (EBL), oxygen plasma ion etching, and lift-off, which could be served as seeds/catalysts and the stencil in the second growth. The detailed information are shown in the part II of Supporting Information. Using the markers in the SEM images such as "FFW" in Figure 1d, we could accurately expose the PMMA covered over ultralong SWNTs to get the targeted length on the same ultralong SWNT (shown in Figure S2). Figure 1f and 1g show the representative short SWNTs with two open-ends after EBL. AFM measurement shows that the short SWNTs were free of metal catalysts at each end.

Third, the duplicate SWNTs (red in color) were grown from the open-end parent SWNTs shown in the schematic diagram of Figure 1c. Briefly, the open-end seeds were put into the CVD furnace in flowing Ar/H_2 (500 sccm/300 sccm) gas mixture at 700 °C for 30 min to get rid of −COOH and −OH at the end-functionalized SWNTs, which could help to expose the active open-end, and then 100 sccm CH_4 and 5 sccm C_2H_4 carbon source were introduced into the system at 975 °C for 15 min with other gas turning off. At the end of synthesis duration, the reactor was purged with Ar/H_2 (500 sccm/300 sccm) and cooled to room temperature.

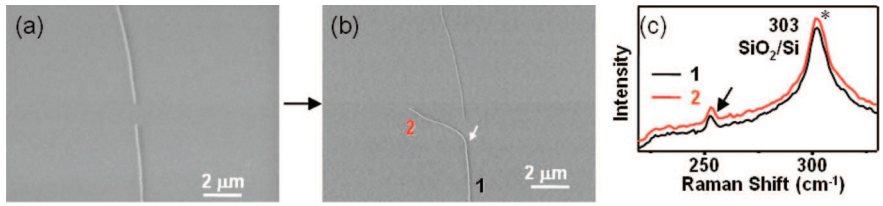

Figure 3. (a) SEM image of open-end SWNT seeds. (b) SEM image of the duplicate SWNT grown from the SWNT seed on the bottom in panel a. The white arrow denotes the start of the regrowth. (c) Typical Raman spectroscopy across the SWNT of the bottom in panel b, which shows the same RBM shift at 252.7 cm^{-1} (G-band was not shown here), and the other peak at ~303 cm^{-1} marked by * is from the SiO_2/Si substrate. Moreover, there is no more RBM peak at low frequency for larger tubes.

The absolute orientation of any SWNTs before and after the second growth was confirmed by SEM and AFM. Three types of phenomena[8] were mainly observed: (a) continued growth, (b) tube closure (shown in Supporting Information, Figure S4a−d), and (c) SWNT etching (in Supporting Information, Figure S4e−h). Panels h and i in Figure 1 are the representative SEM and AFM images of the duplicate SWNTs, continued growth from the seeds in Figure 1f,g, respectively. The white arrows in Figure 1i point out the beginning of the new growth. It is clear to see that the duplicate SWNTs were continued growth from the parents at each end (Figure 1h,i). It usually grew as much as a few micrometers in length and the longest length of amplified growth was 4.6 μm (shown in Figure 3b). We thought that if the second growth is not constrained by the substrate such as the open-end SWNTs are suspending, the new SWNTs will grow longer. More data are shown in Supporting Information.

The key point of SWNT cloning is to verify the duplicate SWNTs have the same chirality of the parent SWNTs (seeds). The diameter evolution along the SWNTs before and after the second growth was measured using AFM, and a typical result is shown in Figure 2. AFM section analysis shows the height from the parent SWNTs (position 1 in Figure 2a and position 3 in Figure 2b) to the duplicate SWNT (position 2 and 4 in Figure 2b) is constant, suggesting the same diameter. To verify that the duplicate SWNT has the same predetermined chirality as the seeds, we collected the resonance Raman data of individual SWNT using a micro-Raman spectroscope coupled with a confocal imaging microscope and a 1 μm excitation spot size, and Figure 3 denotes a typical result. Raman spectroscope characterization of the SWNT in Figure 3b, continued growth from the SWNT in Figure 3a, shows the same radial breathing mode (RBM) shift at 252.7 cm^{-1} (assigned as (10, 3) tube through resonant Raman theory[19−21]). Estimating from the equation $d = 248\ cm^{-1}/\omega_{RBM}$, where ω_{RBM} is the RBM frequency, which was derived for SWNTs on silicon substrates, the diameters indeed stayed uniform. This finding demonstrates that it is possible to duplicate any desired (n, m) tube and thus the chirality-selective synthesis of SWNTs can be carried out by using the open-end SWNTs as seeds/catalysts.

The next question is to find out the growth mechanism of the SWNT cloning. Do they grow via catalyst or not?[22,23] As shown in Figure 1i and Figure 2b, the end of the seeds (in Figure 1g and Figure 2a) and the new grown SWNTs (in Figure 1i and Figure 2b) were free of catalysts, and the white arrows in the figure denote the start of the new growth. To avoid the interference from the nanosize catalysts, we used a new quartz tube for the second growth and collected more data by AFM shown in Supporting Information. This is suggested that the cloning is metal catalyst free and the duplicate SWNTs grew from the open-end seeds.

As shown in Figure 1c, based on these catalysts-free-growth process, we proposed a possible open-end growth mechanism of SWNTs cloning. First of all, predetermined chirality of SWNTs with open-ends is prepared as seeds. When the temperature is higher than the decomposition temperature of the carbon source, C_x (mainly C_2 and C_3) radical can be released, and then directly add to the open-end SWNTs seeds. Thus the duplicate SWNTs can be continued grown from the parent seed SWNTs, called SWNTs cloning. The open-end of SWNTs might be the only seeds/catalysts for SWNTs cloning. The quantum chemical method calculation indicated that an intermediate between C_2 radical and an open-end SWNT was formed first without an energy barrier, then via a transition state the reaction produces the product, that is, C_2 becomes the component of the hexagon of the nanotube. This result suggested that our open-end growth model is reasonable. On the basis of this model,[24] the following items are very important for SWNTs cloning: (1) how to get open-end seeds in an effective way, (2) how to confirm the open-ends without metal catalysts, (3) how to get the proper amount of C_x radicals, and (4) how to improve the collision probability of C_x radicals with the open-end of SWNTs.

Using our strategy, we had 600 short seed segments in total and found only 56 segments can continue to grow at each end. That is to say, the yield of the continued growth is about 9.3% (56/600 = 9.3%), and it is relatively low. Moreover, three kinds of experimental phenomena were observed during SWNTs cloning, including continued growth (the seeds being longer), tube closure (the seeds with no change in length), and SWNT etching (the seeds becoming shorter). Representative results are shown in Supporting Information, Figure S4−6. The main reasons of low yield might be as follows. (a) The open-end automatically closed under appropriate condition that was energetically favored. The initially formed C−C bond between the open-end and C_x radicals would not allow normal growth of the SWNT. Because further addition of C_x radicals would cause defections in SWNT or seal the open end of the SWNT and thereby quenching the growth reaction.[24] (b) SWNTs might be etched by H_2 during the high temperature growth or by

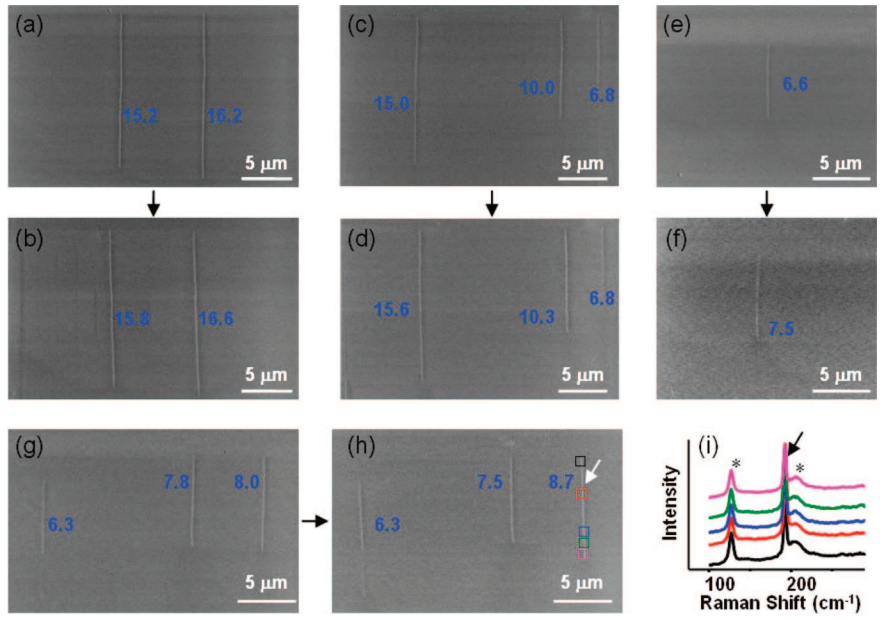

Figure 4. (a,c,e,g) SEM images of short parent SWNTs segments for the second growth. (b,d,f,h) SEM images of SWNTs after the second growth, corresponding to the SWNTs in panels a, c, e, and g, respectively. It is clear to see continued growth, tube closure, and SWNT etching in these images. The numbers in the images show the length of SWNT nearby. (i) Typical Raman spectroscopy across the SWNT denoted by the white arrow in panel h, which shows the same RBM shift at 192.8 cm^{-1} (G-band was not shown here), and the peaks marked by * are from the quartz substrate.

trace amount of O_2 inside the chamber, or by the end-functionalized oxo-radicals.[8] (c) The probability of C_x collision with the open-end was very low because of the stereospecific blockade of the seeds lying down on the substrate surface. (d) The reactive probability of the open-end with C_x radicals was low due to the interaction[25] between the substrate and the open-end SWNT forming at high temperature.

In order to increase the yield, first, we dealt the open-end SWNTs at 700 °C for 30 min to get rid of −COOH and −OH at the end, which can help to expose the active open-end.[26] Second, we put the temperature of the second growth at 975 °C. It is usually enough to use 800∼900 °C to grow SWNTs with several micrometers in length under normal CVD. However, when setting the growth temperature below 945 °C, we did not observe any amplified growth. So it is necessary to set to the higher temperature to promote CH_4 noncatalytic decomposition. Third, 5 sccm C_2H_4 was used in the second growth at 975 °C, which was more adequate to facilitate the decomposition of CH_4;[27] if using more C_2H_4, the sample would suffer from being covered with a large amount of amorphous carbon, so we thought that the C_x radicals were the proper amount in the CVD system. If we did not introduce C_2H_4 into the CVD system, there was no amplified growth at 975 °C.

And finally, we chose stable temperature (ST)-cut quartz as the growth substrate. Recently, Yuan et al. reported that 13 kinds of metals showed horizontally lattice-aligned growth of CNTs on quartz substrates.[28] Additionally, Mg and Al were first reported to grow SWNTs. They proposed that metal particles only provide a platform for the decomposition of carbon. Moreover, by using single crystal surfaces including quartz and sapphire,[28−33] researchers could obtain well-aligned arrays of SWNTs with density as high as 22 SWNTs/μm. However, the result has not been obtained on other substrates. Thus we thought that surface lattice might be a crucial factor for the high efficiency growth of SWNTs. Thereby, we chose the quartz substrate for SWNTs cloning, and the experimental process was the same as the cloning on SiO_2/Si substrate stated above. As shown in Supporting Information, Figure S7, horizontally aligned SWNTs were grown on quartz. Then, SWNTs on quartz were cut into short segments. Figure 4a,c,e,g show typical short SWNTs with open-ends. Lastly, the second time growth was performed. Figure 4a−h shows typical results before and after the second growth. As same as the case in our last experiment, three kinds of experimental phenomena were also observed during SWNTs cloning, including continued growth (the seeds being longer), tube closure (the seeds with no change in length), and SWNT etching (the seeds becoming shorter). To verify the duplicate SWNTs have the same chirality of the parent SWNTs (seeds), Raman spectroscopy was used to characterize the sample. As shown in Figure 4i, the SWNTs denoted by the white arrow in Figure 4h show constant RBM signals along the length so that reinforced the cloning. Furthermore, there is an important experimental phenomenon that must be stated, the growth yield of second growth were greatly improved (24/59 = 40.7%). But the origin of why the quartz substrate could increase the growth efficiency is still not well understood. Further study is under way to investigate why quartz substrate can improve SWNTs cloning and to increase the yield, for example, to suspend the SWNT seeds to reduce the substrate interaction.

In conclusion, we have discovered an effective method, cloning, to synthesize any special (n, m) indices SWNTs via open-end growth mechanism using the open-end SWNTs

seeds. This will be not only helpful to understand the formation mechanism of the SWNT, but also turn the controllable growth of SWNT into reality. Moreover, this open-end growth mechanism might be an effective way for cloning of graphene from small graphene sheets.

Acknowledgment. This work was supported by NSFC (20673004, 20725307, and 50821061) and MOST (2006CB-932701, 2006CB932403, and 2007CB936203). Y.G.Y. acknowledges Professor J. Kong (Massachusetts Institute of Technology) for her useful discussion and Mr. X. F. Song (Peking University) and Mr. Y. Z. Wang (Peking University) for their great help at EBL.

Supporting Information Available: Experimental details for synthesis of ultralong SWNTs by CVD and cloning of SWNTs. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Avouris, P.; Chen, Z. H.; Perebeinos, V. *Nat. Nanotechnol.* **2007**, *2*, 605–615.
(2) McEuen, P. L. *Nature* **1998**, *393*, 15–17.
(3) Zheng, M.; Semke, E. D. *J. Am. Chem. Soc.* **2007**, *129*, 6084–6085.
(4) Bachilo, S. M.; Balzano, L.; Herrera, J. E.; Pompeo, F.; Resasco, D. E.; Weisman, R. B. *J. Am. Chem. Soc.* **2003**, *125*, 11186–11187.
(5) Li, X. L.; Tu, X. M.; Zaric, S.; Welsher, K.; Seo, W. S.; Zhao, W.; Dai, H. J. *J. Am. Chem. Soc.* **2007**, *129*, 15770–15771.
(6) Wang, B.; Poa, C. H. P.; Wei, L.; Li, L. J.; Yang, Y. H.; Chen, Y. *J. Am. Chem. Soc.* **2007**, *129*, 9014–9019.
(7) Wang, B.; Wei, L.; Yao, L.; Li, L. J.; Yang, Y. H.; Chen, Y. *J. Phys. Chem. C* **2007**, *111*, 14612–14616.
(8) Crouse, C. A.; Maruyama, B.; Colorado, R.; Back, T.; Barron, A. R. *J. Am. Chem. Soc.* **2008**, *130*, 7946–7954.
(9) Ren, Z. F. *Nat. Nanotechnol.* **2007**, *2*, 17–18.
(10) Smalley, R. E.; Li, Y. B.; Moore, V. C.; Price, B. K.; Colorado, R.; Schmidt, H. K.; Hauge, R. H.; Barron, A. R.; Tour, J. M. *J. Am. Chem. Soc.* **2006**, *128*, 15824–15829.
(11) Wang, Y. H.; Kim, M. J.; Shan, H. W.; Kittrell, C.; Fan, H.; Ericson, L. M.; Hwang, W. F.; Arepalli, S.; Hauge, R. H.; Smalley, R. E. *Nano Lett.* **2005**, *5*, 997–1002.
(12) Kusunoki, M.; Suzuki, T.; Hirayama, T.; Shibata, N.; Kaneko, K. *Appl. Phys. Lett.* **2000**, *77*, 531–533.
(13) Derycke, V.; Martel, R.; Radosvljevic, M.; Ross, F. M. R.; Avouris, P. *Nano Lett.* **2002**, *2*, 1043–1046.
(14) Takagi, D.; Hibino, H.; Suzuki, S.; Kobayashi, Y.; Homma, Y. *Nano Lett.* **2007**, *7*, 2272–2275.
(15) Yao, Y. G.; Li, Q. W.; Zhang, J.; Liu, R.; Jiao, L. Y.; Zhu, Y. T.; Liu, Z. F. *Nat. Mater.* **2007**, *6*, 283–286.
(16) Huang, S. M.; Cai, X. Y.; Liu, J. *J. Am. Chem. Soc.* **2003**, *125*, 5636–5637.
(17) Jin, Z.; Chu, H. B.; Wang, J. Y.; Hong, J. X.; Tan, W. C.; Li, Y. *Nano Lett.* **2007**, *7*, 2073–2079.
(18) Yao, Y. G.; Liu, R.; Zhang, J.; Jiao, L. Y.; Liu, Z. F. *J. Phys. Chem. C* **2007**, *111*, 8407–8409.
(19) Jorio, A.; Saito, R.; Hafner, J. H.; Lieber, C. M.; Hunter, M.; McClure, T.; Dresselhaus, G.; Dresselhaus, M. S. *Phys. Rev. Lett.* **2001**, *86*, 1118–1121.
(20) Dresselhaus, M. S.; Dresselhaus, G.; Jorio, A. *J. Phys. Chem. C* **2007**, *111*, 17887–17893.
(21) Dresselhaus, M. S.; Dresselhaus, G.; Jorio, A.; Souza, A. G.; Saito, R. *Carbon* **2002**, *40*, 2043–2061.
(22) Jin, C.; Suenaga, K.; Iijima, S. *ACS Nano* **2008**, *2*, 1275–1279.
(23) Jin, C. H.; Suenaga, K.; Iijima, S. *Nat. Nanotechnol.* **2008**, *3*, 17–21.
(24) Li, R. F.; Shang, Z. F.; Xu, X. F.; Wang, G. C. *Acta Phys. Chim. Sin.* **2006**, *22*, 1388–1392.
(25) Miwa, R. H.; Orellana, W.; Fazzio, A. *Appl. Phys. Lett.* **2005**, *86*, 213111.
(26) Kuznetsova, A.; Mawhinney, D. B.; Naumenko, V.; Yates, J. T.; Liu, J.; Smalley, R. E. *Chem. Phys. Lett.* **2000**, *321*, 292–296.
(27) Qian, W. Z.; Tian, T.; Guo, C. Y.; Wen, Q.; Li, K. J.; Zhang, H. B.; Shi, H. B.; Wang, D. Z.; Liu, Y.; Zhang, Q.; Zhang, Y. X.; Wei, F.; Wang, Z. W.; Li, X. D.; Li, Y. D. *J. Phys. Chem. C* **2008**, *112*, 7588–7593.
(28) Yuan, D. N.; Ding, L.; Chu, H. B.; Feng, Y. Y.; McNicholas, T. P.; Liu, J. *Nano Lett.* **2008**, *8*, 2576–2579.
(29) Han, S.; Liu, X. L.; Zhou, C. W. *J. Am. Chem. Soc.* **2005**, *127*, 5294–5295.
(30) Kang, S. J.; Kocabas, C.; Ozel, T.; Shim, M.; Pimparkar, N.; Alam, M. A.; Rotkin, S. V.; Rogers, J. A. *Nat. Nanotechnol.* **2007**, *2*, 230–236.
(31) Ding, L.; Yuan, D. N.; Liu, J. *J. Am. Chem. Soc.* **2008**, *130*, 5428–5429.
(32) Kocabas, C.; Shim, M.; Rogers, J. A. *J. Am. Chem. Soc.* **2006**, *128*, 4540–4541.
(33) Ismach, A.; Segev, L.; Wachtel, E.; Joselevich, E. *Angew. Chem., Int. Ed.* **2004**, *43*, 6140–6143.

NL900207V