J|A|C|S
COMMUNICATIONS

Direct Growth of Semiconducting Single-Walled Carbon Nanotube Array

Guo Hong,[†] Bo Zhang,[†] Banghua Peng,[†] Jin Zhang,*[,†] Won Mook Choi,[‡] Jae-Young Choi,*[,‡]
Jong Min Kim,[‡] and Zhongfan Liu*[,†]

Beijing National Laboratory for Molecular Sciences, 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, P. R. China, and Samsung Advanced Institute of Technology, San 14-1, Nongseo-Dong, Giheung-Gu, Yongin, Gyeonggi-Do 446-712, Korea

Received August 12, 2009; E-mail: jinzhang@pku.edu.cn; jaeyoung88.choi@samsung.com

Single-walled carbon nanotubes (SWNTs) have been regarded as one of the best candidates for future applications in nanoelectronic devices due to its high mobility, high current-carrying capacities, and superb subthreshold characteristics.[1−3] The bottleneck of SWNT application in nanoelectronics is that almost all of the current available technologies can only produce a mixture of metallic and semiconducting SWNTs, which largely decreases the device performances. Many groups are devoted to developing separation methods for this material, such as electrophoresis,[4] density gradient induced centrifugation,[5] gas-phase plasma etching,[6] and others.[7−10] All these approaches can effectively separate semiconducting tubes with a very high percentage. However, for the solution-based separation methods, SWNTs are easily chemically decorated and usually in random formation; for other post-treatment methods, SWNTs are damaged or contaminated inevitably during the process of removing metallic SWNTs.

Herein, we present a simple way to directly grow a semiconducting SWNT array with the assistance of ultraviolet (UV) irradiation. As shown in Figure 1A, the UV beam was introduced into our homemade chemical vapor deposition (CVD) system from a hole on the top of the furnace, and the effective wavelength was from 200 to 400 nm (see Figure S1 in Supporting Information (SI)). By using the homemade CVD system, an SWNT array can be grown on a quartz substrate with a diameter distribution from 1.2 to 2.3 nm. Raman spectra and electrical measurement data indicated that the percentage of semiconducting SWNTs can be higher than 95%.

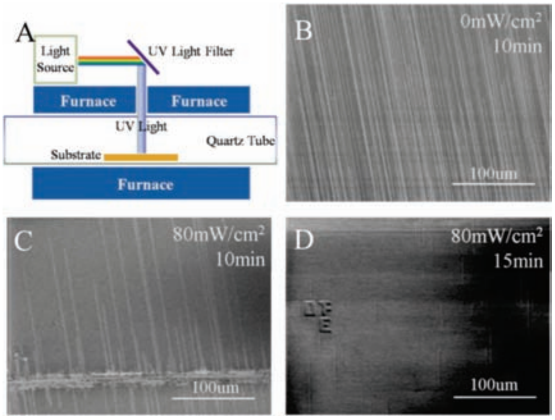

Figure 1. (A) Sketch map of the homemade chemical vapor deposition system. (B−D) SEM images of growth result with different parameters.

Single-polished ST-cut quartz substrates (miscut angle <0.5°, surface roughness <5 Å) were used for growing SWNTs, which were bought from Hefei Kejing Materials Technology Co., China. After the cleanning process, the substrates were annealed at 900 °C for 8 h. After this process, an aligned SWNT array can be obtained along the surface lattice of the substrate.[11]

The growth experiments were performed in a furnace with a 1 in. quartz tube at temperatures from 880 to 920 °C. 50 mM $CuCl_2$/ethanol solution was used as the catalyst. The substrate was heated in air to the desired temperature and kept for 20 min in a gas flow of 30 sccm of argon and 80 sccm of hydrogen for catalyst deoxidization, followed by 14 sccm of hydrogen and 7 sccm of methane for SWNT growth, and UV irradiation was applied to the system during the growth. We tried different growth times from 10 to 30 min with the corresponding irradiation time the same as the growth time. Figure 1B−D were SEM images of the growth result under different growth conditions. As shown in Figure 1B, a high density SWNT array can be obtained without UV irradiation. When a UV beam acted on the substrate, the density of the SWNT array decreased significantly. From Figure 1C and D, the shorter the irradiation time, the longer and denser the SWNTs were. If we continued increasing the irradiation time or the irradiation intensity, the SWNTs would become shorter and shorter and eventually disappear (see Figure S2 in SI). These phenomena confirmed that the UV irradiation played a very important role in the SWNT growth. To make sure that the difference was exclusively determined by the UV irradiation, we designed an experiment of comparison to further confirm this result.

As shown in Figure 2A, a long and narrow substrate was placed into our CVD system, leaving only part A of the substrate under the hole of the setup, and then a shield was inserted above part B. Because the UV beam irradiated from a parallel light source, and the depth of the hole was quite larger than its diameter, the UV beam can only act on part A. Under the same growth conditions, a high density SWNT array was obtained on part B (Figure 2B) while a lower density of SWNT array was obtained on part A (Figure 2C). This experiment directly confirmed the effect of UV irradiation on SWNT growth. Because the quartz substrate was not friendly to Raman characterization and electrical measurement, the SWNT array was transferred onto a SiO_2/Si substrate by applying the peel-off method.[12]

After transfer onto the SiO_2/Si substrate, the sample was examined by Raman spectroscopy with 632.8 and 514.5 nm excitation for both of the two parts. On part B, both metallic and semiconducting SWNT signals were found in the yellow and blue rectangles separately (Figure 2D), under 514.5 nm excitation. The Raman signals showed a wide distribution of RBM frequencies between 110 and 190 cm^{-1}. While on Part A, only semiconducting SWNT signals were found under both 514.5 nm (Figure 2E) and 632.8 nm excitation (Figure 2F) in the blue rectangle, according to the Kataura plot.[13] The Raman spectra demonstrated an amazing result that almost 100% SWNTs were semiconducting ones.

[†] Peking University.
[‡] Samsung Advanced Institute of Technology.

10.1021/ja9068529 CCC: $40.75

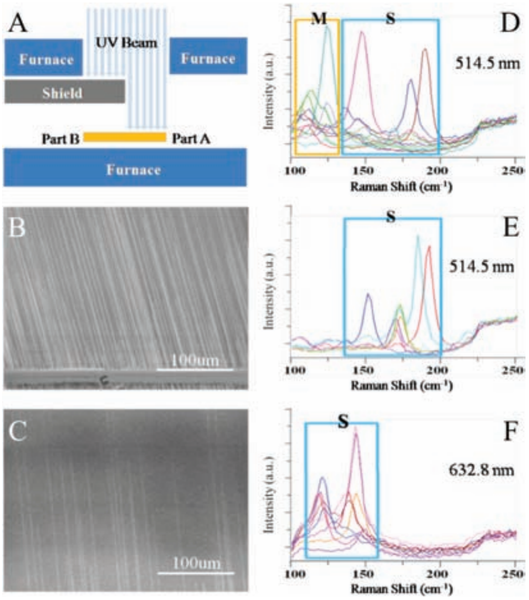

Figure 2. (A) Sketch map of the comparison experiment for SWNT growth with and without UV irradiation. (B, C) SEM images of the growth result without/with UV irradiation. (D) Raman spectrum for part B with 514.5 nm excitation. (E, F) Raman spectra for part A with 514.5/632.8 nm excitation. The metallic SWNT signals were collected in the yellow rectangle while the semiconducting SWNT signals were collected in the blue rectangle separately for all the three spectra.

To further confirm the percentage of the semiconducting SWNTs in this sample, we performed electrical measurement in the single-tube field effect transistors (FET) form. Figure 3A and 3B were the low and high magnified SEM images of the single-tube FET structure. Figure 3C was the plot of I_{ON} vs $R = \log(I_{ON}/I_{OFF})$ for each device (a few devices contained more than one SWNT and behaved as semiconducting). The bias voltage was 100 mV, the channel length was 5.6 um, and the SiO_2 thickness was 800 nm. The electrical measurement data showed that more than 95% SWNTs were semiconducting ones.

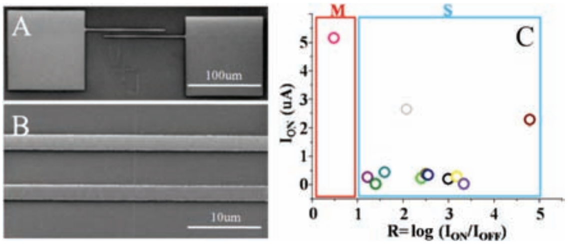

Figure 3. Electrical measurement of the sample transferred on the SiO_2/Si substrate. (A, B) Low/high amplified SEM images of the FET structure. (C) Plot of I_{ON} vs $R = \log(I_{ON}/I_{OFF})$ for each device (a few devices contained more than one SWNT and behaved as semiconducting).

Although it had been reported that UV irradiation can selectively destroy metallic SWNTs,[14] the mechanism is not clear yet. For our direct growth method, we believe that the separation process occurred at the very beginning of SWNT formation, because we did not see any SWNTs remain on the substrate after irradiation (see Figure S3 in SI).[14] Since SWNTs were more easily destroyed during growth than after growth, the metallic SWNT cap might be destroyed at the very beginning while the semiconducting SWNT cap survived from the UV irradiation. After that, the semiconducting cap could continue growing into a semiconducting tube under an appropriate growth condition, which would lead to an acceptable growth result with neglectable damage (see Figure S4A in SI). On the other hand, if a metallic SWNT cap was not destroyed at the selection process, it could also grow into a metallic tube. Moreover, this approach only led to the semiconducting/metallic selection effect rather than diameter selection, because very small diameter metallic SWNTs can be observed in a Raman spectrum (see Figure S4B in SI).

For the reason why UV irradiation can destroy SWNTs, many possibilities should be taken into consideration, such as oxidation, temperature fluctuation, free radical reaction, and so on. For the matter of oxidation, it had been confirmed that the separation process can happen not only in air but also in some other atmosphere without oxygen, such as nitrogen or hydrogen.[14] Considering the factor of temperature fluctuation, we had confirmed that UV irradiation would only lead to a negligible temperature fluctuation during the growth process (see Figure S5 in SI). It had been demonstrated that methane[6] and hydrogen[9] plasma can selectively destroy metallic SWNTs or convert metallic SWNTs into semiconducting ones. Furthermore, we also found that, under UV irradiation, the amorphous carbon formed at the end of the furnace after growth was less than that formed under ordinary conditions (see Figure S6 in SI). Therefore, a free radical reaction might be the most reasonable explanation for the effect of UV irradiation.

In summary, by introducing the UV beam into our homemade CVD system, we had obtained a well aligned SWNT array on an ST-cut quartz substrate. After transfer onto a SiO_2/Si substrate, the SWNT array was detected by Raman spectroscopy and electrical measurement, which showed that over 95% of the SWNTs were semiconducting ones. We believe that the selection process took place at the very beginning of the SWNT formation rather than destroying the metallic SWNTs after growth. Besides this, we suppose that the function of the UV irradiation might due to the process of free radical reaction. This result can be a very important contribution to the future applications in nanoelectronics.

Acknowledgment. This work was supported by NSFC (20673004, 20725307 and 50821061) and MOST (2006CB932701, 2006CB932403, and 2007CB936203).

Supporting Information Available: Experimental details for the UV light source, SEM images of the growth result with different growth conditions, and evidence supporting the hypothesis of the separation mechanism and the function of the UV irradiation. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Javey, A.; Kim, H.; Brink, M.; Wang, Q.; Ural, A.; Guo, J.; McIntyre, P.; McEuen, P.; Lundstrom, M.; Dai, H. J. *Nat. Mater.* **2002**, *1*, 241.
(2) Zhou, X. J.; Park, J. Y.; Huang, S. M.; Liu, J.; McEuen, P. L. *Phys. Rev. Lett.* **2005**, *95*, 146805.
(3) Yao, Z.; Kane, C. L.; Dekker, C. *Phys. Rev. Lett.* **2000**, *84*, 2941.
(4) Krupke, R.; Hennrich, F.; von Lohneysen, H.; Kappes, M. M. *Science* **2003**, *301*, 344.
(5) Arnold, M. S.; Green, A. A.; Hulvat, J. F.; Stupp, S. I.; Hersam, M. C. *Nat. Nanotechnol.* **2006**, *1*, 60.
(6) Zhang, G. Y.; Qi, P. F.; Wang, X. R.; Lu, Y. R.; Li, X. L.; Tu, R.; Bangsaruntip, S.; Mann, D.; Zhang, L.; Dai, H. J. *Science* **2006**, *314*, 974.
(7) An, K. H.; Park, J. S.; Yang, C. M.; Jeong, S. Y.; Lim, S. C.; Kang, C.; Son, J. H.; Jeong, M. S.; Lee, Y. H. *J. Am. Chem. Soc.* **2005**, *127*, 5196.
(8) Li, Y. M.; Mann, D.; Rolandi, M.; Kim, W.; Ural, A.; Hung, S.; Javey, A.; Cao, J.; Wang, D. W.; Yenilmez, E.; Wang, Q.; Gibbons, J. F.; Nishi, Y.; Dai, H. J. *Nano Lett.* **2004**, *4*, 317.
(9) Zheng, G.; Li, Q. Q.; Jiang, K. L.; Zhang, X. B.; Chen, J.; Ren, Z.; Fan, S. S. *Nano Lett.* **2007**, *7*, 1622.
(10) Ding, L.; Tselev, A.; Wang, J. Y.; Yuan, D. N.; Chu, H. B.; McNicholas, T. P.; Li, Y.; Liu, J. *Nano Lett.* **2009**, *9*, 800.
(11) 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.
(12) Jiao, L. Y.; Xian, X. J.; Wu, Z. Y.; Zhang, J.; Liu, Z. F. *Nano Lett.* **2009**, *9*, 205.
(13) Dresselhaus, M. S.; Dresselhaus, G.; Saito, R.; Jorio, A. *Phys. Rep.* **2005**, *409*, 47.
(14) Zhang, Y. Y.; Zhang, Y.; Xian, X. J.; Zhang, J.; Liu, Z. F. *J. Phys. Chem. C* **2008**, *112*, 3849.

JA9068529