

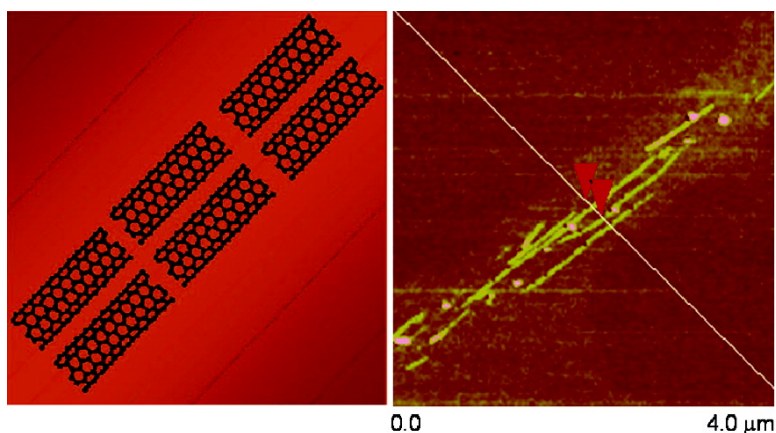
Communication

Large-Scale Fabrication of Aligned Single-Walled Carbon Nanotube Array and Hierarchical Single-Walled Carbon Nanotube Assembly

Junbo Gao, Aiping Yu, Mikhail E. Itkis, Elena Bekyarova, Bin Zhao, Sandip Niyogi, and Robert C. Haddon

J. Am. Chem. Soc., **2004**, 126 (51), 16698-16699 • DOI: 10.1021/ja044499z • Publication Date (Web): 07 December 2004

Downloaded from <http://pubs.acs.org> on April 5, 2009



More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 6 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)



ACS Publications
High quality. High impact.

Large-Scale Fabrication of Aligned Single-Walled Carbon Nanotube Array and Hierarchical Single-Walled Carbon Nanotube Assembly

Junbo Gao,^{†,‡} Aiping Yu,[†] Mikhail E. Itkis,[†] Elena Bekyarova,[†] Bin Zhao,[†] Sandip Niyogi,[†] and Robert C. Haddon^{*,†}

Center for Nanoscale Science and Engineering, Departments of Chemistry and Chemical & Environmental Engineering, University of California, Riverside, California 92521-0403, and Carbon Solutions, Inc., Riverside, California 92506

Received September 10, 2004; E-mail: robert.haddon@ucr.edu

The assembly of single-walled carbon nanotubes (SWNTs) in predetermined patterns is one of the most challenging tasks in the fabrication and mass production of SWNT electronic devices, such as sensors¹ and field effect transistors.² Carbon nanotubes have been aligned by post-treatment techniques utilizing electrical,³ magnetic,⁴ mechanical⁵ forces and self-assembly⁶ and in situ during their growth.⁷ In the post-treatment methods, it is very difficult to obtain a uniform SWNT alignment with a small bundle size. The assembly of individual tubes is even more difficult because of the very poor solubility of SWNTs in organic solvents and their spontaneous aggregation into large bundles. The tube aggregation problem also occurs during in situ alignment because the as-prepared SWNTs are usually produced as bundles. Moreover, the in situ method, which has mainly been carried out by the chemical vapor deposition (CVD) process,⁷ requires high temperatures (>800 °C) and a reactive environment and is therefore not applicable to devices with limited stability.

Electrospinning is an electrostatic method for the fabrication of long organic fibers.⁸ Carbon nanotube–polymer composite fibers have also been fabricated by using this technique.⁹ Although the nanotubes are confined to the fiber, they are not aligned macroscopically because the fibers are randomly distributed.⁹ Recent advances in the electrospinning technique have allowed the alignment of the resulting fibers in predetermined directions.¹⁰ By applying this modified electrospinning technique we have succeeded in fabricating SWNT–polymer composite fibers with all of the SWNTs oriented along the axial direction of the fiber. After removing the polymer component from the fiber, we obtained large-scale aligned SWNT arrays. This method allows us to transfer the local SWNT orientation in the electrospun composite fiber to macroscopically aligned SWNT structures. Moreover, the SWNTs resulting from this procedure exist primarily as individual nanotubes that are apparently exfoliated by the electrostatic charging generated during the electrospinning experiments.

We selected poly(vinylpyrrolidone) (PVP) to blend with SWNTs for electrospinning because of the compatibility of PVP with SWNTs and because the SWNTs are expected to form a homogeneous dispersion in the PVP matrix.¹¹ When the PVP/SWNT solution was electrospun using a single piece of grounded aluminum sheet as negative electrode, the composite fibers were randomly distributed (Supporting Information Figure 1). When two strips of aluminum foil were attached to a polystyrene plate and used as the negative electrode (Supporting Information Figure 2), the electrostatic force drives the positively charged composite fibers so that they align between the two counter electrodes.

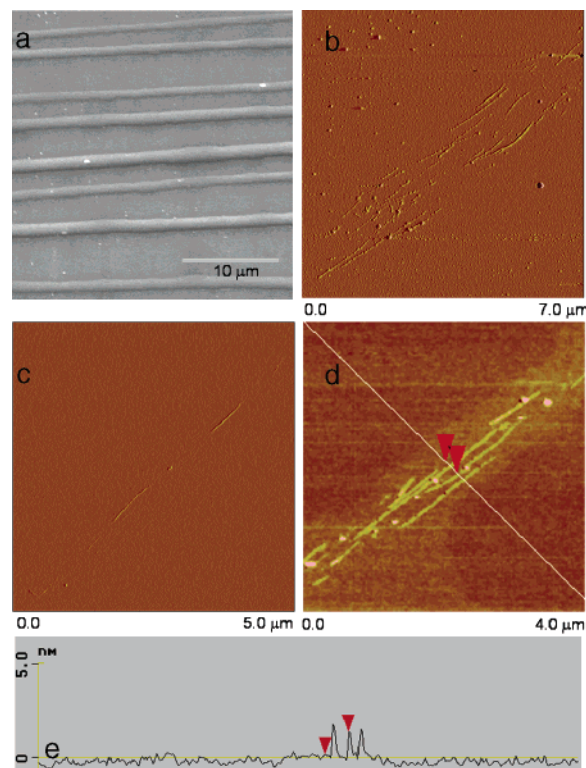


Figure 1. (a) SEM image of aligned electrospun fibers. (b–d) AFM images of aligned SWNTs prepared by heating the electrospun fiber: (b) aligned SWNT array, (c) single line of SWNTs, (d) aligned individual SWNTs, and (e) their height cross-sectional analysis.

The aligned electrospun fibers were collected on a silicon wafer (1 cm × 1 cm) placed between the two counter electrodes. The SEM image (Figure 1a) indicates a high degree of alignment. The existence of SWNTs inside the fiber is demonstrated by Raman spectroscopy (Supporting Information Figure 3); the characteristic SWNT peaks were observed in the SWNTs/PVP composite fiber but not in pure PVP fiber.

The SWNT alignment within the electrospun fiber is clearly evident on removal of the polymer component by heating or chemical vapor etching. By raising the temperature of the fibers to 600 °C in an argon atmosphere, the PVP component in the composite fiber is decomposed, leaving the aligned SWNTs; Figure 1b shows the SWNTs resulting from the thermal treatment of a single fiber. On the basis of the fiber coverage in Figure 1a, a 1 cm × 1 cm silicon wafer contains many thousands of similarly aligned SWNT arrays patterned along the same direction. The number of nanotubes inside a particular electrospun composite fiber

[†] University of California, Riverside.

[‡] Carbon Solutions, Inc.

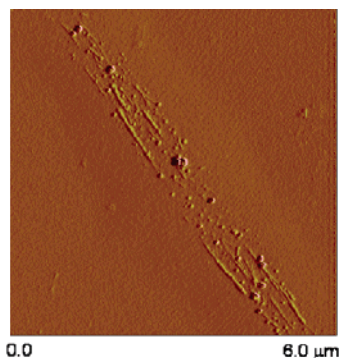


Figure 2. AFM image of aligned SWNTs prepared by ethanol vapor etching method.

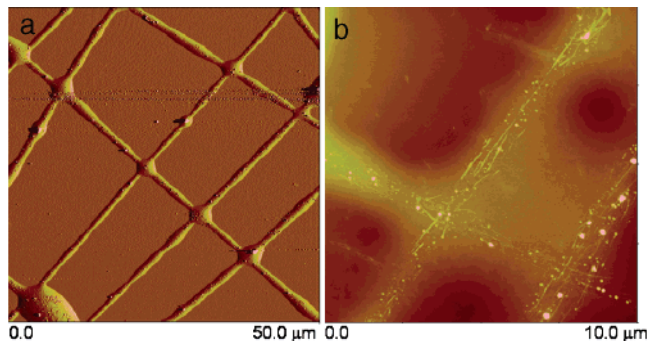


Figure 3. AFM images of (a) cross-aligned SWNTs/PVP composite fibers and (b) cross-aligned SWNT array.

can be controlled by adjusting the diameter of the nanofiber, and decreasing the fiber diameter lowers the nanotube coverage to the point that a single line of SWNTs can be observed in some cases (Figure 1c).

The average diameter of the aligned tubes is ~ 2.2 nm, which is much smaller than that of the tubes before electrospinning (~ 4.0 nm). In most cases, the aligned SWNTs were observed to occur as individual nanotubes (Figure 1d), and the AFM height cross-sectional analysis (Figure 1e) indicates nanotube diameters of approximately 1.4 nm, as expected for electric arc SWNTs. SWNTs are known to aggregate because of the intertube van der Waals attraction, and a high shear force is necessary to exfoliate the nanotube bundles.¹² The exfoliation of SWNT bundles observed in the present study is probably due to the electrostatic repulsion that is generated between the SWNTs during the electrospinning process. As solvent evaporates, the radius of the jet becomes progressively smaller, and this causes an increase in the local charge density.^{8a} At some point the Coulombic repulsion between nanotubes becomes sufficiently large to overcome the van der Waals attraction, and bundles start to split into individual tubes. A rough estimate based on atomic point charges indicates that this should occur at a charge density of about 1 positive charge for every 15 SWNT carbon atoms.

For sensitive devices, low-temperature polymer removal is desired, and we therefore developed a room-temperature ethanol vapor etch to remove the polymer from the composite fiber. Because of the small diameter of the electrospun fiber (several tens to a few hundred nanometers), a 12-h exposure to a saturated ethanol vapor at room temperature was sufficient to dissolve and spread the polymer component on the silicon wafer. This exposed the SWNTs and left them aligned along the axial direction of the fiber after the vapor etch (Figure 2).

To demonstrate the directional control of SWNT alignment, we deposited electrospun fibers along perpendicular directions by simply rotating the substrate between depositions. The cross-aligned nanofibers are shown in Figure 3a; after exposure to ethanol for 12 h, the polymer component was removed and the hierarchical SWNT assembly was revealed (Figure 3b).

In summary, we have developed a flexible approach to SWNT alignment that allows their hierarchical assembly by use of electrospinning, and we show that the SWNT orientation is directionally controllable. In addition, the electrospinning procedure exfoliates the carbon nanotube bundles and leads to a high yield of aligned individual SWNTs. The method offers great promise for the controlled assembly of SWNT devices based on individual nanotubes.

Acknowledgment. This research was supported by DOD/DARPA/DMEA (Award No. DMEA90-02-2-0216). Carbon Solutions acknowledges support from a DARPA SBIR Phase I Award administered by the U.S. Army Aviation and Missile Command (W31P4Q-04-C-R171).

Supporting Information Available: Experimental procedure and Supporting Information Figures 1–3. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) Kong, J.; Franklin, N. R.; Zhou, C. W.; Chapline, M. G.; Peng, S.; Cho, K. J.; Dai, H. J. *Science* **2000**, *287*, 622–625. (b) Chopra, S.; Pham, A.; Gaillard, J.; Parker, A.; Rao, A. M. *Appl. Phys. Lett.* **2002**, *80*, 4632–4634.
- (2) (a) Bachtold, A.; Hadley, P.; Nakanishi, T.; Dekker, C. *Science* **2001**, *294*, 1317–1320. (b) Bockrath, M.; Liang, W.; Bozovic, D.; Hafner, J. H.; Lieber, C. M.; Tinkham, M.; Park, H. *Science* **2001**, *291*, 283–285. (c) Collins, P. G.; Zettl, A.; Bando, H.; Thess, A.; Smalley, R. E. *Science* **1997**, *278*, 100–103.
- (3) (a) Diehl, M. R.; Yaliraki, S. N.; Beckman, R. A.; Barahona, M.; Heath, J. R. *Angew. Chem., Int. Ed.* **2002**, *41*, 353–356. (b) Chung, J. Y.; Lee, K. H.; Lee, J. H.; Ruoff, R. S. *Langmuir* **2004**, *20*, 3011–3017.
- (4) Hone, J.; Llaguno, M. C.; Nemes, N. M.; Johnson, A. T.; Fischer, J. E.; Walters, D. A.; Casavant, M. J.; Schmidt, J.; Smalley, R. E. *Appl. Phys. Lett.* **2000**, *77*, 666–668.
- (5) (a) Hertel, T.; Martel, R.; Avouris, P. *J. Phys. Chem. B* **1998**, *102*, 910–915. (b) Jin, L.; Bower, C.; Zhou, O. *Appl. Phys. Lett.* **1998**, *73*, 1197–1199. (c) Jiang, K. L.; Li, Q. Q.; Fan, S. S. *Nature* **2002**, *419*, 801. (d) Lay, M. D.; Novak, J. P.; Snow, E. S. *Nano Lett.* **2004**, *4*, 603–606. (e) Meitl, M. A.; Zhou, Y.; Gaur, A.; Jeon, S.; Usrey, M. L.; Strano, M. S.; Rogers, J. A. *Nano Lett.* **2004**, *4*, 1643–1647.
- (6) (a) Rao, S. G.; Huang, L.; Setyawan, W.; Hong, S. H. *Nature* **2003**, *425*, 36–37. (b) Xin, H.; Woolley, A. T. *J. Am. Chem. Soc.* **2003**, *125*, 8710–8711. (c) Dierking, I.; Scalia, G.; Morales, P.; LeClere, D. *Adv. Mater.* **2004**, *16*, 865–869.
- (7) (a) Zhang, Y. G.; Chang, A. L.; Cao, J.; Wang, Q.; Kim, W.; Li, Y. M.; Morris, N.; Yenilmez, E.; Kong, J.; Dai, H. J. *Appl. Phys. Lett.* **2001**, *79*, 3155–3157. (b) Huang, S. M.; Woodson, M.; Smalley, R.; Liu, J. *Nano Lett.* **2004**, *4*, 1025–1028. (c) Li, Y. L.; Kinloch, I. A.; Windle, A. H. *Science* **2004**, *304*, 276–278.
- (8) (a) Reneker, D. H.; Chun, I. *Nanotechnology* **1996**, *7*, 216–223. (b) MacDiarmid, A. G.; Jones, W. E.; Norris, I. D.; Gao, J.; Johnson, A. T.; Pinto, N. J.; Hone, J.; Han, B.; Ko, F. K.; Okuzaki, H.; Llaguno, M. *Synth. Met.* **2001**, *119*, 27–30. (c) Dzenis, Y. *Science* **2004**, *304*, 1917–1919. (d) Bognitzki, M.; Czado, W.; Frese, T.; Schaper, A.; Hellwig, M.; Steinhart, M.; Greiner, A.; Wendorff, J. H. *Adv. Mater.* **2001**, *13*, 70–72.
- (9) (a) Sen, R.; Zhao, B.; Perea, D. E.; Itkis, M. E.; Hu, H.; Love, J.; Bekyarova, E.; Haddon, R. C. *Nano Lett.* **2004**, *4*, 459–464. (b) Ko, F.; Gogotsi, Y.; Ali, A.; Naguib, N.; Ye, H.; Yang, G.; Li, C.; Willis, P. *Adv. Mater.* **2003**, *15*, 1161–1165. (c) Dror, Y.; Salalha, W.; Khalfin, R. L.; Cohen, Y.; Yarin, A. L.; Zussman, E. *Langmuir* **2003**, *19*, 7012–7020.
- (10) Li, D.; Wang, Y. L.; Xia, Y. N. *Nano Lett.* **2003**, *3*, 1167–1171.
- (11) O'Connell, M. J.; Boul, P.; Ericson, L. M.; Huffman, C.; Wang, Y. H.; Haroz, E.; Kuper, C.; Tour, J.; Ausman, K. D.; Smalley, R. E. *Chem. Phys. Lett.* **2001**, *342*, 265–271.
- (12) O'Connell, M. J.; Bachilo, S. M.; Huffman, C. B.; Moore, V. C.; Strano, M. S.; Haroz, E. H.; Rialon, K. L.; Boul, P. J.; Noon, W. H.; Kittrell, C.; Ma, J.; Hauge, R. H.; Weisman, R. B.; Smalley, R. E. *Science* **2002**, *297*, 593–596.

JA044499Z