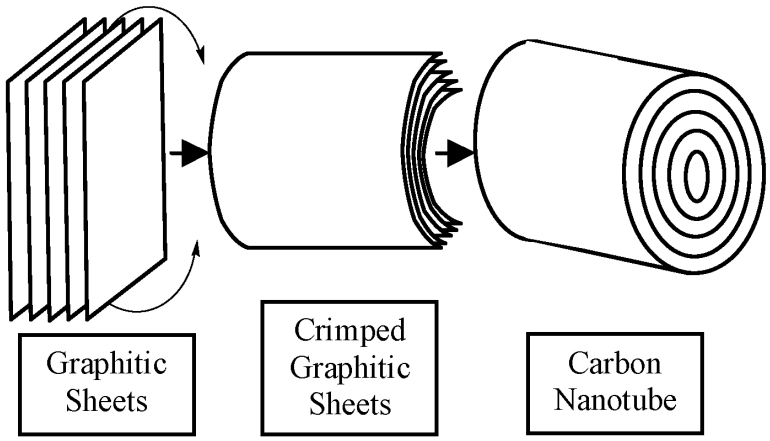
Communication

# One-Step Water-Assisted Synthesis of High-Quality Carbon Nanotubes Directly from Graphite

Zhenhui Kang, Enbo Wang, Lei Gao, Suoyuan Lian, Min Jiang, Changwen Hu, and Lin Xu

*J. Am. Chem. Soc.*, **2003**, 125 (45), 13652-13653• DOI: 10.1021/ja037399m • Publication Date (Web): 18 October 2003






## 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

J|A|C|S
COMMUNICATIONS

Published on Web 10/18/2003

# One-Step Water-Assisted Synthesis of High-Quality Carbon Nanotubes Directly from Graphite

Zhenhui Kang, Enbo Wang,* Lei Gao, Suoyuan Lian, Min Jiang, Changwen Hu, and Lin Xu

*Institute of Polyoxometalate Chemistry, Department of Chemistry, Northeast Normal University, Changchun, Jilin, 130024, P.R. China*

Received July 19, 2003; E-mail: wangenbo@public.cc.jl.cn

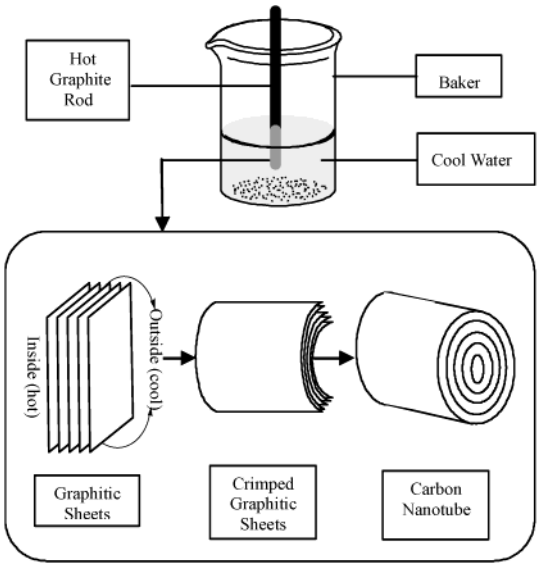
Considerable efforts have been made to synthesize high-quality carbon nanotubes (CNTs) since their discovery in 1991.[1] Numerous methods have been developed for the preparation of CNTs such as laser vaporization, arc discharge, pyrolysis, and plasma-enchanced or thermal chemical vapor deposition (CVD). For most of those strategies, however, complex process control, high reaction temperature, and long synthesis time are always needed. The popular method, catalytic decomposition of hydrocarbons, also requires a complex purification process to get rid of the metal catalyst particles.[2−8] The Yoshimura group once applied hydrothermal processing for the purification of CNTs and transformation from amorphous carbon to CNTs with this method at the pressure of 100 MPa without catalyst.[9−14] In this communication a convenient one-step water-assisted synthesis method is introduced for the fabrication of well-crystalline multiwall carbon nanotubes (MCNTs) at the ambient pressure and in the absence of catalyst.

Every carbon atom in the graphite is $sp^2$ hybridized, forming a sheetlike crystal structure. There are only weak London dispersion forces between layers, and those honeycomb layers are stacked one above another. It is natural to come up with such imagination: wrapping the honeycomb pattern back on top of itself and joining the edges, you will obtain a tube of graphite, a carbon nanotube. It will be a direct and perfect strategy to prepare high-quality CNTs. To realize the transformation from graphite to CNTs, two problems must be solved. The first one is how to obtain the suitable power which can make the graphite sheets crimp; the second one is how to wrap the honeycomb pattern back on top of itself and let the edges join by the C−C $\sigma$ bonds. The water-assisted method applied here brings the realization of the above process.

The typical method employed is as follows. Graphite rods, which were purchased from China National Medicines Shenyang Co. Ltd, were rapidly heated to red-hot (above 800 °C) in air and then were dipped into the cool water (0 °C) immediately. After a slight explosion, the water turned a little turbid. The above steps were repeated many times, and the products containing multiwall carbon nanotubes were finally collected. Counting the tubes on randomly selected grids in the transmission electron microscope (TEM), the yield caculated was about 40%.

Recently, Kaner et al. reported a chemical route to carbon nanoscrolls.[15] The contribution of sonication to the scroll of the graphite sheet indicated that there really exists suitable power which can make the graphite sheets scroll. Here, when the heated graphite rods were dipped into the cool water, the temperature of the surface came down immediately, while the internal temperature was still very high. The power necessary for the graphite sheets to crimp was then produced. Synthesis of carbon "onions" by arc discharge in water[16] and hydrothermal processing for the purification and fabrication of CNTs[14] showed that water is essential in some sense to the formation of closed carbon nanosrtuctures. It is also well-known that many complex chemical reactions exist between red-hot carbon and water. Although the detailed formation mechanism of the CNTs in such condition has not been well understood, it is inevitable that water plays a vital role in the connection of the edges. Scheme 1 shows the formation of MCNTs from graphite rods.

***Scheme 1.*** Scheme for the Formation of MCNTs from Graphite Rods




Electron microscopy studies were carried out with a JEM-2010 at the operating voltage of 200 kV. The observations revealed the formation of the CNTs after water-assisted hot−cool treatment. The typical TEM images of the MCNTs are shown in Figures 1 and 2. The individual fiber exhibits a middle-hollow structure. The nanotubes have the diameters in the range of tens and the lengths in the range of hundreds of nanometers. The inner diameters are between 5 and 10 nm, and the outer diameters are between 30 and 50 nm. The electron diffraction (ED) patterns exhibit that the MCNTs obtained are well-crystalline. The wall of the nanotube is composed of high-quality graphite layers, which show few defects in the crystal lattice. It can also be proved further by the Raman spectrum (Figure 3). Figure 2c shows the high-resolution TEM images for the wall structure of a carbon nanotube. The walls are composed of graphite sheets aligned to the tube axis. The interlayer spacing in the walls, about 0.34 nm, corresponds to the 002 distance of graphitic carbon.[14]

Figure 3 gives the Raman spectrum of the products. The peak at 1580 $cm^{-1}$ (G-band) corresponds to the $E_{2g}$ mode of the graphite and is related to the vibration of $sp^2$-bonded carbon atoms in a two-dimensional (2D) hexagonal lattice.[17] Nanotubes with concentric multiwall layers of hexagonal carbon lattice display the same vibration.[18] The D-band at around 1360 $cm^{-1}$ is associated with the vibrations of carbon atoms with dangling bonds in the plane terminations of disordered graphite or glassy carbons. The inverse


10.1021/ja037399m CCC: $25.00 

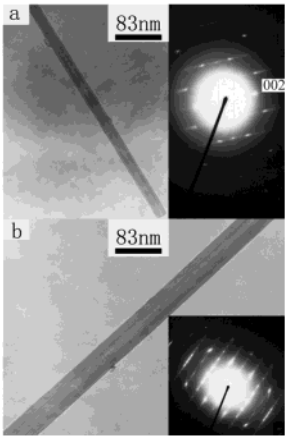



***Figure 1.*** TEM images and ED patterns of individual MCNTs.

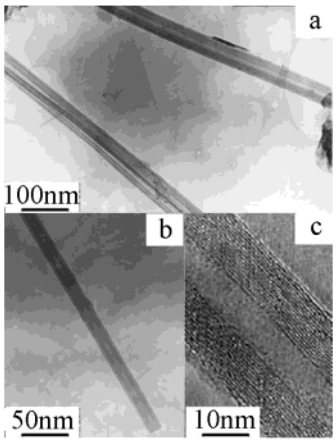



***Figure 2.*** TEM images and high-resolution TEM image of the MCNTs.

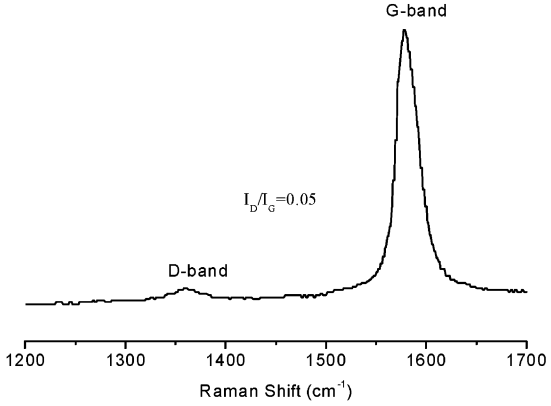



***Figure 3.*** Raman spectrum of the products containing the CNTs.

of the $I_D/I_G$ intensity ratio between G and D bands is a usual measurement of the graphitic ordering and may also indicate the approximate layer size in the hexagonal plane, La,[14,17,19] which in this case is related to the length of pristine (defect-free) graphitic mutiwalls. Raman spectra of MCNTs obtained by other methods reported by Qian and Hou groups exhibit a high intensity of the D band ($I_D/I_G$ ratios are up to about 0.6),[20,21] while in our Raman spectrum, the $I_D/I_G$ ratio is ~0.05. The calculation via the formula $La = 44(I_D/I_G)^{-1}$ yields the value of about 1 $\mu$m which agrees with the length of multiwall carbon nanotubes observed in TEM images. The spectrum also indicates a nearly defect-free lattice ordering and reveals that the multiwalls forming the nanotubes have a perfect lattice without defects, edges, or plane termination, [14] as seen in Figures 1 and 2.

Here an important question emerged: are the tubelike carbon structures prepared with this method genuine multiwall nanotubes or just a simple"scroll" (with two free edges, one inside and the other outside, of the tube)? In our experiment, four pieces of evidence are found which may support the result that the products are really MCNTs. First, the high-resolution TEM image in Figure 2c shows that the wall-to-wall distance is uniform, 0.34 nm, which corresponds properly to the 002 distance of graphitic carbon, while it is nearly impossible for the simple scroll to obtain such perfect structure. Second, the ED patterns of the tubelike carbon structures reveal that the products are single crystalline, which cannot form through a simple scroll. Third, the Raman spectrum in Figure 3 exhibiting no defects, edges, or plane termination in the products combined with the straight figure shown in Figures 1 and 2, a and b, further substantiate the products are well-crystalline MCNTs. Fourth, the simple scroll model cannot explain the seal of the tube tip.

In summary, graphite can be transformed into pristine CNTs with one-step treatment, under the assistance of water, only at atmospheric pressure and without any catalyst. The pure and high-quality CNTs obtained by this process will give birth to a promising method for the production of MCNTs.

**Acknowledgment.** This work was financially supported by the National Natural Science Foundation of China (20171010). We are greatly thankful to Professor Peter Eklund of Departments of Physics and Materials Science & Engineering of the Pennsylvania State University for their profound discussions.

**References**

(1) Iijima, S. *Nature* **1991**, *354*, 56−58.
(2) Iijima, S.; Ichihashi, T. *Nature* **1993**, *363*, 603−605.
(3) Bethune, D. S.; Kiang, C. H.; Devries, M. S.; Gorman, G.; Savoy, R.; Beyers, R. *Nature* **1993**, *363*, 605−607.
(4) Thess, A.; Lee, R.; Nikolaev, P.; Dai, H. J.; Petit, P.; Robert, J.; Xu, C. H.; Lee, Y. H.; Kim, S. G.; Colbert, D. T.; Scuseria, G.; Tománek, D.; Fischer, J. E.; Smalley, R. E. *Science* **1996**, *273*, 483−487.
(5) Ren, Z. F.; Huang, Z. P.; Xu, J. W.; Wang, J. H.; Bush, P.; Siegal, M. P.; Provencio, P. N. *Science* **1998**, *282*, 1105−1107.
(6) Smith, B. W.; Monthioux, M.; Luzzi, D. E. *Nature* **1998**,*396*, 323−324.
(7) Vigolo, B.; Pénicaud, A.; Coulon, C.; Sauder, C.; Pailler, R.; Journet, C.; Bernier, P.; Poulin, P. *Science* **2000**, *290*, 1331−1334.
(8) Zhu, H. W.; Xu, C. L.; Wu, D. H.; Wei, B. Q.; Vajtai, R.; Ajayan, P. M. *Science* **2002**, *296*, 884−886.
(9) Tohji, K.; Takahashi, H.; Shinoda, Y.; Shimizu, N.; Jeyadevan, B.; Matsuoka, I.; Saito, Y.; Kasuya, A.; Ito, S.; Nishina, Y. *J. Phys. Chem. B* **1997**, *101*, 1974−1978.
(10) Tohji, K.; Goto, T.; Takahashi, H.; Shinoda, Y.; Shimizu, N.; Jeyadevan, B.; Matsuoka, I.; Saito, Y.; Kasuya, A.; Ohsuna, T.; Hiraga, K.; Nishina, Y. *Nature* **1996**,*383*, 679−671.
(11) Liu, J.; Rinzler, A. G.; Dai, H. J.; Hafner, J. H.; Bradley, R. K.; Boul, P. J.; Lu, A.; Iverson, T.; Shelimov, K.; Huffman, C. B.; Rodriguez-Macias, F.; Shon, Y. S.; Lee, T. R.; Colbert, D. T.; Smalley, R. E. *Science* **1998**, *280*, 1253−1256.
(12) Gogotsi, Y.; Libera, J. A.; Yoshimura, M. *J. Mater. Res.* **2000**, *15*, 2591−2594.
(13) Calderon-Moreno, J. M.; Swamy, S.; Fujino, T.; Yoshimura, M. *Chem. Phys. Lett.* **2000**, *329*, 317−322.
(14) Calderon-Moreno, J. M.; Yoshimura, M. *J. Am. Chem. Soc.* **2001**, *123*, 741−742.
(15) Lisa, M. V.; Julia, M.; Richard, B. K. *Science* **2003**, *299*, 1361.
(16) Sano, N.; Wang, H.; Chhowalla, M.; Alexandrou, L.; Amaraunga, G. A. J. *Nature* **2001**, *414*, 506−507.
(17) Dresselhaus, M. S.; Dresselhaus, G.; Pimenta, M. A.; Eklund, P. C. In *Analytical Applications of Raman Spectroscopy*; Pelletier, M. J., Ed.; Blackwell Science: Oxford, 1999; Chapter 9.
(18) Kasuya, A.; Sasaki, Y. *Phys. Rev. Lett.* **1997**, *78*, 4434−4437.
(19) Tuinstra, F.; Koening, J. L. *J. Chem. Phys.* **1970**, *53*, 1126−1130.
(20) Liu, J.; Shao, M.; Chen, X.; Yu, W.; Liu, X.; Qian, Y. T. *J. Am. Chem. Soc.* **2003**, *125*, 8088−8089.
(21) Hou, H. Q.; Schaper, A. K.; Jun, Z.; Weller, F.; Greiner, A. *Chem. Mater.* **2003**, *15*, 580−585.

JA037399M