Low-Temperature, Controlled Synthesis of Carbon Nanotubes**

*Liming Dai**

Keywords:
- carbon nanotubes
- dendrimers
- halides
- low-temperature synthesis
- supercritical carbon dioxide

A carbon nanotube may be viewed as a graphite sheet that is rolled up into a nanometer-scale tubular form (that is, a single-walled carbon nanotube, SWNT) or with additional graphene tubes that form around the core of a SWNT (that is, a multi-walled carbon nanotube, MWNT).[1] Because the graphene sheet can be rolled up with varying degrees of twist along its length, carbon nanotubes can have a variety of chiral structures. Depending on their diameter and the helicity of the arrangement of graphitic rings in the walls, carbon nanotubes have been demonstrated to possess unusual electronic, photonic, magnetic, thermal, and mechanical properties.[1,2] For instance, these tiny elongated carbon nanotubes with a hollow core can be stronger than steel (yet flexible), lighter than aluminum, and more conductive than copper.[1–3] These peculiar properties have made carbon nanotubes particularly attractive as new materials for a variety of applications, from reinforcement fillers in advanced nanocomposites to wires for nanoelectronics.[3,4] However, if the price of carbon nanotubes remains as high as it is today (e.g., US$ 500 per gram for SWNT materials—more than 30 times as expensive as gold), any large-scale application of carbon nanotubes will be unrealistic. Consequently, a low-temperature, and hence low-cost, synthesis of carbon nanotubes with a controllable structure and high purity has become absolutely crucial to the development of the whole field of carbon nanoscience and nanotechnology.

Since the discovery of carbon nanotubes in 1991,[5] it has been a perpetual endeavor to cost-effectively synthesize carbon nanotubes in both a random and an ordered form (e.g., aligned and patterned) at low temperature so that they can be directly incorporated into composite materials and flexible functional devices, using substrates such as plastics. The past thirteen years of strenuous research around the world has led to the development of several effective synthetic methods, including arc-discharge,[5,6] laser evaporation,[7] and chemical vapor (pyrolytic) deposition,[8] for the production of carbon nanotubes with an aligned[9] and/or nonaligned[10] structure. However, it is the recent efforts to exploit leading-edge synthetic methods for the low-temperature production of carbon nanotubes,[11,12] along with the aligned growth of SWNTs,[13,14] that could open up an avenue for the cost-effective synthesis of carbon nanotubes with controllable structures for practical applications.

In this article, a recent and significant advance in the low-temperature, controlled synthesis of carbon nanotubes, which was reported by Vohs, Fahlman, and co-workers, is highlighted.[15] Instead of using the more-conventional hydrocarbon-based precursors, the authors used carbon tetrachloride (CCl_4) with weaker carbon–halide (C–X) bonds for the pyrolytic growth of MWNTs in a supercritical carbon dioxide medium, in the presence of iron catalysts encapsulated in polypropyleneimine (PPI) dendrimers (designated as Fe@PPI dendrimer) (Figure 1).

As demonstrated by Vohs et al.,[15] the use of supercritical carbon dioxide as a medium for the decomposition of CCl_4 can completely eliminate the co-reactants, such as alkali metals and lithium acetylide, which were required for enhancing the decomposition of chlorinated hydrocarbon precursors.[16,17] The high pressure exerted by the CO_2 (8.3–27.6 MPa) further assists in the decomposition of CCl_4 and facilitates the delivery of the intermediate species to the encapsulated iron surface for the nucleation and growth of carbon nanotubes at a record low temperature (that is, 175 °C).[18] The resultant nanotubes have an average diameter of 20–25 nm with branched and bent nanotube morphologies, which indicates different catalytic rates for nanotube growth from the encapsulated and peripheral iron atoms within the Fe@PPI dendrimer catalysts. Therefore, by controlling the distribution of the catalyst iron nanoparticles within various dendritic structures,[19] it is possible to pro-

---

[*] L. Dai
Department of Chemical and Materials Engineering
School of Engineering
University of Dayton
300 College Park, Dayton, OH 45469-0240 (USA)
Fax: (+1) 937-229-3433
E-mail: ldai@udayton.edu

[**] I am grateful to Prof. Richard Smalley for useful discussions, particularly on Ref. [14], and to AFRL/ML, Wright Brothers Institute, Dayton Development Colations, and the University of Dayton for a WBI Endowed Chair Professorship in Nanomaterials.

DOI: 10.1002/smll.200400153

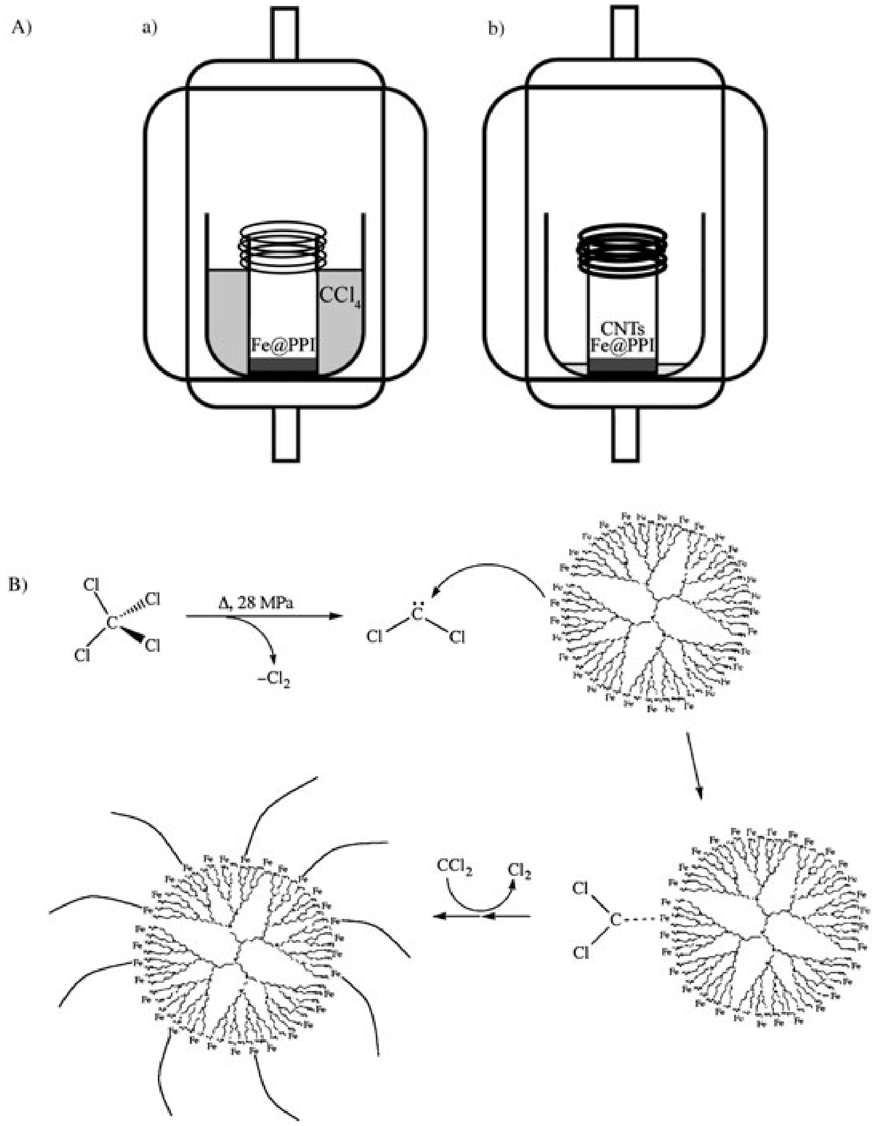

Figure 1. A) A diagram of the supercritical fluid reactor before (a) and after (b) the growth of multi-walled carbon nanotubes (MWNTs). Spirals of copper wire were used to sacrificially remove the Cl_2 gas produced during the synthetic process; B) the MWNT growth mechanism, which shows how nanotubes are formed on individual Fe–dendrimer catalyst particles (after Ref. [15]).

duce carbon nanotubes of different diameters and structures. The temperature and pressure involved in the growth of carbon nanotubes by the Fe@PPI-dendrimer-based catalytic decomposition of carbon tetrachloride are not high enough to decompose the PPI dendrimer. Hence, it is likely that there are intact nanotube–dendritic linkages in the resultant materials, which suggests that a rational approach toward heterojunctions between carbon nanotubes and organic materials for flexible, functional devices (e.g., nanotube–dendrimer electronic circuits) might be achieved.

The study that is highlighted above has not only revealed the significance of the use of weakly bonded carbon–halide precursors for the low-temperature synthesis of carbon nanotubes in supercritical fluid media, but has also offered potential for the control of nanotube structures and nanotube herterojunctions by using metal catalysts encapsulated in well-defined dendritic carriers. The work indicates that the long-desired low-temperature synthesis of carbon nanotubes with controllable structures is becoming a reality. Continued research efforts in this important area could significantly advance the ongoing race towards the institution of large-scale applications of carbon nanotubes in the marketplace.

---

[1] P. J. F. Harris, *Carbon Nanotubes and Related Structures—New Materials for the Twenty-First Century*, Cambridge University Press, Cambridge, **2001**.

[2] R. Saito, G. Dresselhaus, M. S. Dresselhaus, *Physical Properties of Carbon Nanotubes*, Imperial College Press, London, **1998**.

[3] L. Dai, *Intelligent Macromolecules for Smart Devices: From Materials Synthesis to Device Applications*, Springer, London, **2004**.

[4] R. H. Baughman, A. A. Zakhidov, W. A. de Heer, *Science* **2002**, *297*, 787.

[5] S. Iijima, *Nature* **1991**, *354*, 56.

[6] See, for example: a) T. W. Ebbesen, P. M. Ajayan, *Nature* **1992**, *358*, 220; b) D. S. Bethune, C. H. Kiang, M. S. de Vries, G. Gorman, R. Savoy, J. Vazquez, R. Beyers, *Nature* **1993**, *363*, 605; c) Y. Saito, T. Yoshikawa, M. Okuda, N. Fujimoto, K. Sumiyama, K. Suzuki, A. Kasuya, Y. Nishina, *J. Phys. Chem. Solids* **1993**, *54*, 1849.

[7] See, for example: A. Thess, R. Lee, P. Nikolaev, H. J. Dai, P. Petit, J. Robert, C. H. Xu, Y. H. Lee, S. G. Kim, A. G. Rinzler, D. T. Colbert, G. E. Scuseria, D. Tomanek, J. E. Fischer, R. E. Smalley, *Science* **1996**, *273*, 483.

[8] See, for example: a) M. Endo, K. Takeuchi, S. Igarashi, K. Kobori, M. Shiraishi, H. W. Kroto, *J. Phys. Chem. Solids* **1993**, *54*, 1841; b) J. Kong, A. M. Cassell, H. J. Dai, *Chem. Phys. Lett.* **1998**, *292*, 567; C. N. R. Rao, A. Govindaraj, *Acc. Chem. Res.* **2002**, *35*, 998.

[9] L. Dai, A. Patil, X. Gong, Z. Guo, L. Liu, Y. Liu, D. Zhu, *ChemPhysChem* **2003**, *4*, 1151, and references therein.

[10] a) P. M. Ajayan, T. W. Ebbesen, *Rep. Prog. Phys.* **1997**, *60*, 1025, and references therein; b) C. N. R. Rao, B. C. Satishkumar,

A. Govindaraj, M. Nath, *ChemPhysChem* **2001**, *2*, 78, and references therein.
[11] J. K. Vohs, J. J. Brege, J. E. Raymond, A. E. Brown, G. L. Williams, B. D. Fahlman, *J. Am. Chem. Soc.* **2004**, *126*, 9936.
[12] S.-H. Jeong, J.-H. Ko, J.-B. Park, W. Park, *J. Am. Chem. Soc.* **2004**, *126*, 15982.
[13] Y. Murakami, S. Chiashi, Y. Miyauchi, M. Hu, M. Ogura, T. Okubo, S. Maruyama, *Chem. Phys. Lett.* **2004**, *385*, 298.
[14] K. Hata, D. N. Futaba, K. Mizuno, T. Namai, M. Yumura, S. Iijima, *Science* **2004**, *306*, 1362.
[15] J. K. Vohs, J. J. Brege, J. E. Raymond, A. E. Brown, G. L. Williams, B. D. Fahlman, *J. Am. Chem. Soc.* **2004**, *126*, 9936.
[16] J. L. O'Loughlin, C.-H. Kiang, C. H. Wallace, T. K. Reynolds, L. Rao, R. B. Kaner, *J. Phys. Chem. B* **2001**, *105*, 1921.
[17] Y. Jiang, Y. Wu, S. Zhang, C. Xu, W. Yu, Y. Xie, Y. Qian, *J. Am. Chem. Soc.* **2000**, *122*, 12383.
[18] A sonochemical route has recently been reported to synthesize SWNTs via the ultrasonication of a mixed solution of ferrocene and *p*-xylene in the presence of silica powder at atmospheric pressure and room temperature (S.-H. Jeong, J.-H. Ko, J.-B. Park, W. Park, *J. Am. Chem. Soc.* **2004**, *126*, 15982). As cavitation bubbles produced in a liquid solution during sonication can instantaneously generate local temperature hot-spots of several-thousand degrees Celsius and several-thousand atmospheres of pressure (K. S. Suslick, *MRS Bull.* **1995**, *20*, 29), it is most likely that it is the sonication-induced high temperature and pressure that provides the required energy to decompose ferrocene and *p*-xylene, thus providing the Fe catalyst and carbon source for carbon nanotube growth. Therefore, the SWNTs actually grew under the high temperature and pressure in this particular case, although the sonochemical process can be carried out with the solution mixture being held at ambient temperature. Similarly, carbon nanotubes could have also grown at high temperature in a recently reported microwave plasma-enhanced nanotube growth process (S. Hofmann, B. Kleinsorge, C. Ducati, A. C. Ferrai, J. Robertson, *Diamond Relat. Mater.* **2004**, *13*, 1171), although the microwave plasma can be generated with the gas molecules being maintained at a relatively low temperature, due to the thermodynamic non-equilibrium between the gas molecules and the plasma species (H. Yasuda, *Plasma Polymerization*, Academic Press, Orlando, **1978**).
[19] H. C. Choi, W. Kim, D. Wang, H. J. Dai, *J. Phys. Chem. B* **2002**, *106*, 12361.

Received: December 14, 2004