

Large-Scale Synthesis of Perpendicularly Aligned Helical Carbon Nanotubes

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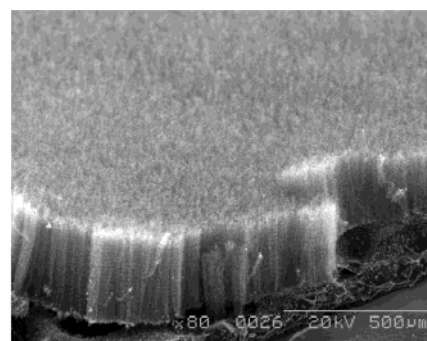
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The finding that carbon nanotubes possess diameter- and helicity-dependent properties has made this new form of solid carbon one of the most studied nanomaterials for a wide range of potential applications.¹ In many cases, it is highly desirable to produce aligned carbon nanotubes so that they can be effectively incorporated into devices and the properties of individual nanotubes may be readily assessed.² Therefore, research on the synthesis of aligned carbon nanotubes has attracted ever-increasing attention since the discovery of carbon nanotubes by Iijima in 1991.^{2,3} Recent developments in the field have revealed a good understanding of the aligned-growth mechanism for straight carbon nanotubes via either a “base-growth” or a “top-growth” process.^{1,2}

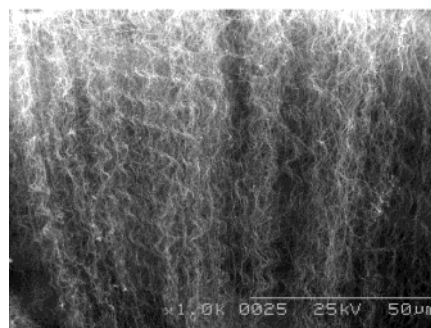
On the other hand, helical carbon nanotubes have been demonstrated to have unique electrical, magnetic, and mechanical properties.^{4,5} For instance, the pass of an electrical current through helical carbon nanotubes could generate an inductive magnetic field, indicating that helical carbon nanotubes, unlike straight nanotubes, are of use as electromagnetic nano-transformers or nano-switches. Although nonaligned helical carbon nanotubes^{5,6} have been reported to form through the occurrence of a concurrent positive and negative curvature caused by periodically incorporating pentagon and heptagon pairs into the hexagonal carbon network,⁷ the synthesis of aligned helical carbon nanotubes is challenging and has not been successful until now. We report here the first synthesis of large-scale, perpendicularly aligned helical carbon nanotubes by co-pyrolysis of Fe(CO)₅ and pyridine.

Our strategy for the successful synthesis of the aligned helical carbon nanotubes lies in a synergetic combination of the systems for producing nonaligned helical⁶ and aligned straight⁸ carbon nanotubes. Along with others,² we have prepared large-scale aligned/micropatterned straight carbon nanotube arrays perpendicular to the substrate surface by pyrolysis of iron(II) phthalocyanine onto the pristine quartz glass plates in a tube furnace at 900–1100 °C under a mixture flow of Ar and H₂.^{8–12} We have also developed techniques for the patterned/nonpatterned transfer of such nanotube arrays to various other substrates of particular interest (e.g., polymer films for organic optoelectronic devices or metal substrates for electrochemistry) and for controlled surface modification.¹³ These modified carbon nanotubes with a tailor-made surface facilitate the use of carbon nanotubes in various applications ranging from polymer nanocomposites to biomedical devices.¹⁴

Just as the successful preparation of large-scale, perpendicularly aligned straight carbon nanotubes has facilitated their efficient device incorporation and controlled structural modification for many applications,^{2,8} there is an urgent need for the synthesis of perpendicularly aligned helical carbon nanotubes. In this context, we carried out the co-pyrolysis of Fe(CO)₅ and pyridine under conditions similar to those used for producing the aligned straight



(a)



(b)

Figure 1. (a) A typical SEM micrograph of the aligned helical carbon nanotube array, which has been turned over from the quartz substrate onto a sticky tape.¹² (b) An enlarged cross-section view of (a), showing densely packed aligned helical nanotubes.

carbon nanotubes.⁸ As a result, we found that perpendicularly aligned helical carbon nanotubes were prepared in the form of a homogeneous black film covering the whole substrate surface (ca. 4 × 1 cm², being essentially limited by the size of the furnace only).

Figure 1a reproduces a typical scanning electron microscopic (HITACHI S-2150 SEM) image of the as-synthesized aligned helical carbon nanotube arrays. To examine the nanotube orientation and length, part of the carbon nanotube film shown in Figure 1a has been peeled off. The spotless removal of the aligned helical carbon nanotubes from the substrate seen in Figure 1a indicates that the black deposit could be easily transferred onto other substrates for particular applications and for micropatterning, as is the case with the aligned straight carbon nanotubes.^{8,12} An enlarged cross-section view of Figure 1a is given in Figure 1b, which shows densely packed aligned helical carbon nanotubes with a few interspersed straight nanotubes. Statistical analysis of the transmission electron microscopic (TEM) images of the nanotubes, including Figure 2, indicates that about 70% of the nanotubes are helical. Figure 2a,b shows TEM (Phillips TECNAI-12, 120 kV) images of individual helical carbon nanotubes taken from the sample

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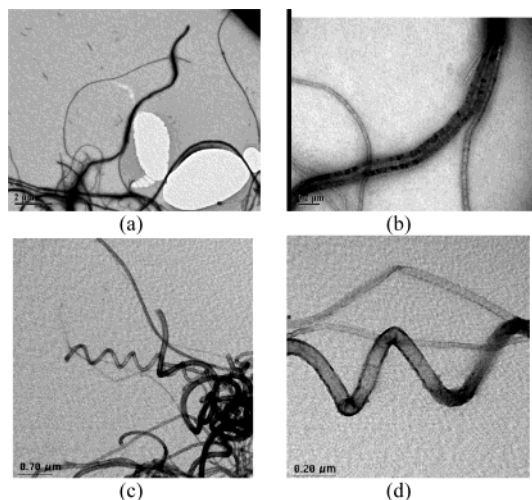


Figure 2. (a) A TEM micrograph of individual helical carbon nanotubes taken from the sample shown in Figure 1 (scale bar: $2\ \mu\text{m}$). (b) An enlarged view of the individual helical nanotube shown in (a) (scale bar: $0.2\ \mu\text{m}$). (c) A TEM micrograph of individual helical carbon nanotubes taken from an aligned helical carbon nanotube array different from that represented by Figure 1, showing a different pitch and diameters for the constituent helical nanotube (scale bar: $0.7\ \mu\text{m}$). (d) An enlarged view of the individual helical nanotube shown in (c) (scale bar: $0.2\ \mu\text{m}$).

shown in Figure 1 and after having been dispersed on a TEM grid, from which a helical nanotube with a pitch of ca. $5\ \mu\text{m}$ and a hollow structure is clearly evident. Aligned helical carbon nanotube arrays with different helical structures have also been produced by changing the pyrolysis conditions (e.g., temperature, flow rate, gas composition), as exemplified by Figure 2c,d that shows the constituent helical nanotube with a pitch of ca. $0.5\ \mu\text{m}$. The graphitized structure of the helical carbon nanotubes is evidenced by an intense Raman peak at $1584\ \text{cm}^{-1}$, along with a relatively weak shoulder centered at $1322\ \text{cm}^{-1}$.¹⁵

The large variety of aligned helical carbon nanotubes with different helical pitches and inner and outer diameters thus produced implies that there is considerable room for tailoring the nanotube structures by controlling the growth conditions. Although the detailed mechanism with which the aligned helical carbon nanotubes can form is not fully understood at the present, it is likely that $\text{Fe}(\text{CO})_5$ first decomposed into atomic iron, CO_2 , and C under the H_2/Ar atmosphere while pyridine molecules decomposed into N_2 , CN, pure carbon, and hydrocarbon species of different carbon numbers. The newly produced iron atoms then segregated on the substrate surface to form carbon-surrounded Fe nanoparticles.^{8,16} Once an Fe particle reaches an optimal size for carbon nucleation, the surrounding carbon transforms into a graphite tube. A high surface packing density of Fe particles facilitates the growing nanotubes to align along the normal direction, as previously demonstrated for the growth of perpendicularly aligned straight carbon nanotubes.^{8,16} A further supply of carbon source to the contact region between the Fe particle and the growing nanotube segment allows a continuous growth of the carbon nanotube in the direction normal to the substrate surface. This growth process is accompanied by a concomitant insertion/formation of pentagon and heptagon pairs into the hexagonal sheet of the growing nanotube,

leading to a helical structure. As already demonstrated for the growth of nonaligned helical carbon nanotubes,⁶ the insertion of a carbon dimer C_2 into a C_6 hexagonal ring could lead to the formation of two pentagon and heptagon pairs. Thereafter, sequential insertions of C_2 into C_7 rings shift the C_5 pentagon and C_7 heptagon rings to the appropriate positions required for the helical formation.

In summary, we have demonstrated, for the first time, that large-scale aligned helical carbon nanotube arrays perpendicular to the substrate surface can be prepared by co-pyrolysis of $\text{Fe}(\text{CO})_5$ and pyridine onto the pristine quartz glass plates in a tube furnace at $900\text{--}1100\ \text{C}$ under a mixture flow of Ar and H_2 . The resultant aligned helical carbon nanotubes should not only facilitate their structure–property characterization but also allow them to be effectively incorporated into devices for practical applications, although the growth process still needs to be further optimized for producing aligned nanotubes with a predetermined helical pitch and/or other structural parameters.

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References

- (1) Harris, P. J. F. *Carbon Nanotubes and Related Structures: New Materials for Twenty-first Century*; Cambridge University Press: Cambridge, 1999. (b) Dai, L. *Intelligent Macromolecules for Smart Devices*; Springer-Verlag: Berlin, 2004.
- (2) For recent reviews, see, for example: (a) Dai, L.; Patil, A.; Gong, X.; Guo, Z.; Liu, L.; Liu, Y.; Zhu, D. B. *ChemPhysChem* **2003**, *4*, 1151 and references therein. (b) Dai, H. *Surf. Sci.* **2002**, *500*, 218. (c) Hu, J. T.; Odom, T. W.; Lieber, C. M. *Acc. Chem. Res.* **1999**, *32*, 435. (d) Baughman, R. H.; Zakhidov, A. A.; de Heer, W. A. *Science* **2002**, *297*, 787. (e) Rao, C. N. R.; Satishkumar, B. C.; Govindaraj, A.; Nath, M. *ChemPhysChem* **2001**, *2*, 78. (f) Ajayan, P. M. *Chem. Rev.* **1999**, *99*, 1787. (g) Special issue of *Acc. Chem. Res.* **2002**, *35*, on nanotubes.
- (3) Iijima, S. *Nature* **1991**, *354*, 56.
- (4) See, for example: (a) Ihara, S.; Itoh, S. *Carbon* **1995**, *33*, 931. (b) Akagi, K.; Tamura, R.; Tsukada, M.; Itoh, S.; Ihara, S. *Phys. Rev. Lett.* **1995**, *74*, 2307.
- (5) See, for example: (a) Iijima, S.; Toshiyari, I.; Ando, Y. *Nature* **1992**, *356*, 776. (b) Amelinckx, S.; Zhang, X. B.; Bernaerts, D.; Zhang, X. F.; Ivanov, V.; Nagy, J. B. *Science* **1994**, *265*, 635. (c) Hsu, W. K.; Terrones, M.; Hare, J. P.; Terrones, H.; Kroto, H. W.; Walton, D. R. M. *Chem. Phys. Lett.* **1996**, *262*, 161. (d) Ajayan, P. M.; Nugent, J. M.; Siegel, R. W.; Wei, B.; Kohler-Redlich, P. *Nature* **2000**, *404*, 243. (e) Kong, X. Y.; Wang, Z. L. *Nano Lett.* **2003**, *3*, 1625.
- (6) Hou, H.; Jun, Z.; Weller, F.; Greiner, A. *Chem. Mater.* **2003**, *15*, 3170.
- (7) Amelinckx, S.; Zhang, X. B.; Bernaerts, D.; Zhang, X. F.; Ivanov, V.; Nagy, J. B. *Science* **1994**, *265*, 635.
- (8) (a) Huang, S.; Dai, L.; Mau, A. *J. Phys. Chem. B* **1999**, *103*, 4223. (b) Dai, L.; Mau, A. *Adv. Mater.* **2001**, *13*, 899.
- (9) Yang, Y.; Huang, S.; He, H.; Mau, A. W. H.; Dai, L. *J. Am. Chem. Soc.* **1999**, *121*, 10832.
- (10) Huang, S.; Mau, A. W. H.; Turney, T. W.; White, P. A.; Dai, L. *J. Phys. Chem. B* **2000**, *104*, 2193.
- (11) Chen, Q.; Dai, L. *J. Nanosci. Nanotechnol.* **2001**, *1*, 43.
- (12) Yang, J.; Dai, L.; Vaia, R. A. *J. Phys. Chem. B* **2003**, *107*, 12387.
- (13) (a) Gao, M.; Huang, S.; Dai, L.; Wallace, G.; Gao, R.; Wang, Z. *Angew. Chem., Int. Ed.* **2000**, *39*, 3664. (b) Chen, Q.; Dai, L.; Gao, M.; Huang, S.; Mau, A. W. H. *J. Phys. Chem. B* **2001**, *105*, 618. (c) He, P.; Dai, L. *Chem. Commun.* **2004**, 348.
- (14) Dai, L.; He, P.; Li, S. *Nanotechnology* **2003**, *14*, 1081.
- (15) The Raman spectrum of the aligned helical carbon nanotubes shows an intense peak at $1584\ \text{cm}^{-1}$, attributable to the E_{2g} mode of the multiwall nanotubes, with a shoulder centered at $1322\ \text{cm}^{-1}$ arising from the amorphous carbon.¹
- (16) Li, D.-C.; Dai, L.; Huang, S.; Mau, A. W. H.; Wang, Z. L. *Chem. Phys. Lett.* **2000**, *316*, 349.

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