

LETTERS

Oriented Long Single Walled Carbon Nanotubes on Substrates from Floating Catalysts

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A new and feasible method to prepare long and well-oriented SWNTs on substrates in large scale is developed by applying a floating catalyst chemical vapor deposition (CVD) process. The catalysts for SWNT growth come from the decomposition of iron pentacarbonyl ($\text{Fe}(\text{CO})_5$) formed in situ from the reaction of iron powder and carbon monoxide gas. The growth of SWNTs is found to happen both on the substrate and in the gas flow. Both long and short nanotubes are formed on the substrates but only the long SWNTs are aligned by gas flow. The growth direction and the density of the long SWNTs can be easily controlled. In addition, long SWNTs can be cut and patterned using photolithography and water plasma etching techniques, offering a way to prepare patterned SWNTs with controllable orientation, density and lengths for various applications.

SWNTs can be produced mainly by three methods: arc discharge,^{1,2} laser ablation,^{3,4} and chemical vapor deposition (CVD).^{5–17} Among these methods, CVD holds certain advantages over other methods in the ease of large-scale production, low reaction temperature, and controllable fabrication. Various CVD methods have been developed for bulk production of SWNTs.¹⁸ Recently, surface CVD growth of SWNTs has attracted much attention.^{9–15,17,19,20} Direct CVD growth on flat substrates is a relatively inexpensive method to create isolated, low-defect density SWNTs, whereas nanotubes fabricated by laser ablation or arc discharge are initially synthesized as bundles and have to be purified and suspended in solution before deposition onto a surface for device fabrication. These postsynthetic treatments may introduce defects and alter the electronic properties of SWNTs due to the highly oxidative chemicals and ultrasonication processes used for purification and dispersion. For CVD growth of SWNTs on substrates, catalysts were normally predeposited on the substrates before growth.^{9–15,17,19,20} In the meantime, floating-catalyst CVD using ferrocene and iron pentacarbonyl²¹ were reported for bulk synthesis of SWNTs. For example, Rice University developed a commercial SWNTs synthesis method named HiPCo using $\text{Fe}(\text{CO})_5$ as the catalyst

source and high-pressure CO (10 atm) as the carbon feedstock for SWNTs growth.^{7,22} Entangled SWNTs bundles were produced from CO and $\text{Fe}(\text{CO})_5$ at a rate of 450 mg/h under high pressure (30–100 atm) and high temperature (1050 °C). Ultralong SWNTs strands on a vertical furnace using a hexane solution of ferrocene and thiophene was also reported.²³ However, controlled growth of oriented SWNTs on substrates by floating catalyst CVD methods has not been reported. For SWNT-based nanoelectronics application, controlling the location, orientation and electronic properties of the prepared SWNTs are of both scientifically and technically importance. Some effort has been paid to orient the growth direction by applying electric fields.^{13,16,19} Recently we have developed a new “fast-heating” process to grow ultralong (millimeter to centimeter length) well-aligned SWNTs on surface.¹² In this paper, we report another new method to grow ultralong oriented SWNTs on substrates by using iron catalyst formed in situ. The orientation, density, and length of the nanotubes can be controlled. In addition, a simple method is developed to cut and pattern such long and well-oriented SWNTs by water plasma etching.

In a typical experiment, 0.1–0.5 g iron powder (350 mesh) was loaded on a silicon wafer located at the center of the quartz tube reactor. Blank substrates, including silicon wafers, Au-

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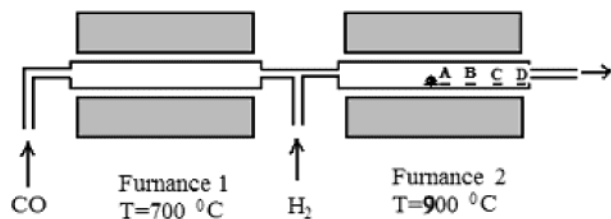


Figure 1. Experimental setup for the growth of long SWNTs on substrate by the in situ floating catalyst process.

coated silicon wafer, Si_3N_4 , and quartz glass, were placed at different positions within the furnace, as shown in Figure 1. The reactor was heated at 700 °C under H_2 atmosphere for 10 min. Then the temperature was raised to 900 °C under H_2 before CO was introduced into the reactor. The flow rates of CO and H_2 were kept at 800 and 200 sccm, respectively. The reaction lasted for 1–60 min.

For cutting and patterning nanotubes, the samples were first patterned by standard photolithography using photoresist. The samples were treated with water plasma at 0.65 Torr for 5–10 min to cut the nanotubes. The remaining photoresist was removed by solvent. The samples were characterized by scanning electronic microscopy (SEM, XL-30 FEG, Philips, at 1 kV), transmission electron microscopy (TEM, Philips), and atomic force microscopy (AFM, Nanoscope IIIA system with a multi-mode controller). The TEM image was taken on a Si_3N_4 window, which was used as substrate for in situ growth of SWNTs.

Figure 2a gives a typical SEM image of the nanotubes formed on the substrate at 900 °C after 30 min reaction (position A). It shows that many nanotubes are long and well-oriented. High-magnification SEM image (Figure 2b) shows that more than 50% of the nanotubes are longer than several hundred micrometers

(even to several millimeters). The orientation of long nanotubes was found to be along the gas flow. In addition, although most of the long nanotubes are well-oriented, the short nanotubes are normally randomly oriented. At position B (Figure 2c), which is 5 cm away from the center of the furnace, the temperature was measured to be about 880 °C and the density of the nanotubes is much less than that of the sample at position A. The density of nanotubes is also related to the growth time. When the reaction time lasted for 1 h, much denser long oriented nanotubes on the substrate (position A) can be prepared, as shown in Figure 2d.

AFM height measurement of the nanotubes on the substrate indicates that the diameters of the nanotubes are between 0.8 and 6.5 nm. Figure 3a gives a typical AFM image of nanotubes after long time growth (30 min), clearly indicating the formation of small bundles. The height measurement shows that the nanotubes have 0.81, 2.2, 3.4, and 3.3 nm, respectively (from left to right). TEM observations of the nanotubes directly grown on the Si_3N_4 substrate (Figure 3b) give direct evidence that the produced nanotubes are SWNTs. The diameters of individual SWNTs are between 0.8 and 2.5 nm. However, most of the long nanotubes are found to be in small bundles containing 2 and 10 SWNTs after long time growth (30 min).

For these nanotubes to grow on the previously blank substrates, there must be a mechanism for the catalysts to transfer from the wafer containing Fe powders to the substrates where nanotubes grow. Thermal evaporation of Fe at the growth temperature (900 °C) cannot be the answer because no nanotubes were observed on blank wafers when methane was used as the feeding gas. We believe that CO plays a very important role as both the carbon source and transporting media of the catalysts. At the reaction temperature, there exists an equilibrium

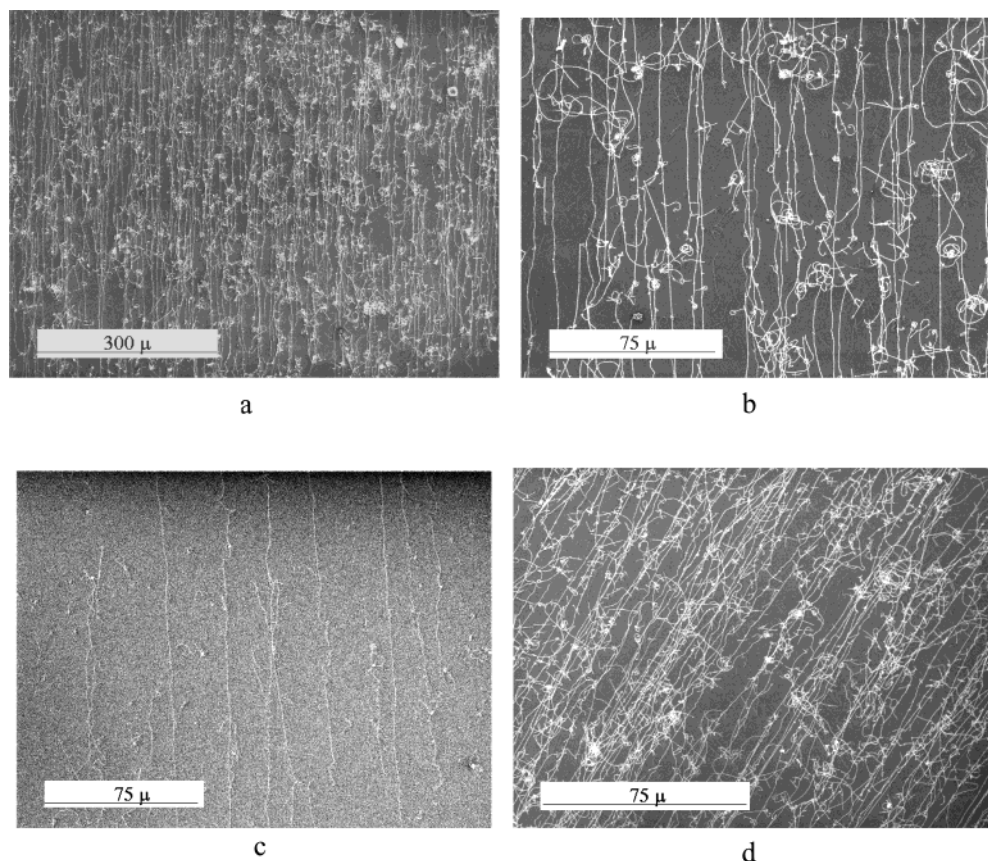


Figure 2. SEM images of as-grown nanotubes on substrates: (a) samples at position A for 30 min; (b) higher magnification image of (a); (c) samples at position B for 30 min; (d) samples at position A for 60 min.

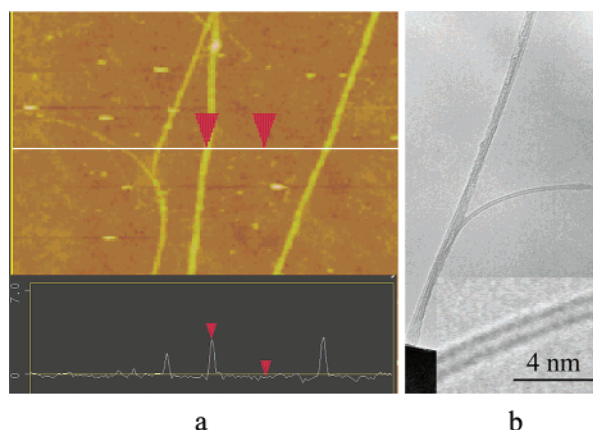


Figure 3. (a) AFM image and (b) TEM image of as grown nanotubes, showing a small bundle of SWNTs.

between CO, Fe, and iron carbonyl. Iron powder reacts with CO to form low concentration iron carbonyl on the wafer containing Fe powders. In the meantime, iron carbonyl decomposes on blank wafers to form small Fe particles, which subsequently function as catalysts for nanotube growth. It is also possible that iron carbonyl decomposes in the gas phase to form floating Fe nanoparticles and nanotubes can grow on the floating catalysts and land on the blank substrates downstream. We also noted that hydrogen plays an important role in the growth of such long oriented nanotubes. Only a very small amount of short nanotubes without any ultralong nanotubes were found on the surface if pure CO was used as feeding gas.¹⁷ The existence of hydrogen not only opens a reaction pathway to produce atomic carbon for nanotube growth ($\text{CO} + \text{H}_2 = \text{C} + \text{H}_2\text{O}$) but also helps the process because of the high activity of hydrogen on the catalyst surface.

To verify the formation mechanism of nanotubes in our experiments, we placed silicon wafers partially coated with 1 μm thick Au near the iron powder (position A) where the temperature is 900 $^\circ\text{C}$ and at the edge of the furnace (position D) where the temperature is between 200 and 300 $^\circ\text{C}$. On the Si wafer placed at position A, we have found many nanotubes on the uncoated portion of the silicon wafer but no nanotubes on the Au-coated areas (Figure 4a). However, some nanotubes were found in the Au-coated region on the wafer at position D (Figure 4b). These observations suggest that the growth of nanotubes occurs both on the substrates and in the gas phase. At position A, the nanotubes on the substrate mainly grow from the catalysts formed on the substrate from the decomposition of iron carbonyl. Because Au is known not to be a good substrate for nanotube growth, no nanotubes were grown within the Au-coated region on the wafer. The nanotubes observed on wafers placed at position D must be nanotubes grown in the gas phase because the local temperature at position D (200–300 $^\circ\text{C}$) is not high enough for nanotube growth. Further evidence of the formation of nanotubes in the gas phase come from the observation of U-shaped nanotubes (Figure 4c) on the substrate at position C, 12 cm from the center of the furnace and where the temperature is 600–650 $^\circ\text{C}$. These U-shaped nanotubes are believed to be nanotubes formed in the gas phase with the middle part landed on the substrate first and the two ends still moved forward in the gas flow, creating the U-shaped structure (the gas flow direction is indicated by an arrow in the figure). It was interesting to note that the substrate at position C had less short nanotubes. This could be explained that the temperature in this region was not high enough for SWNT nanotube growth so all the nanotubes came from those grown in the gas flow rather than from surface growth.

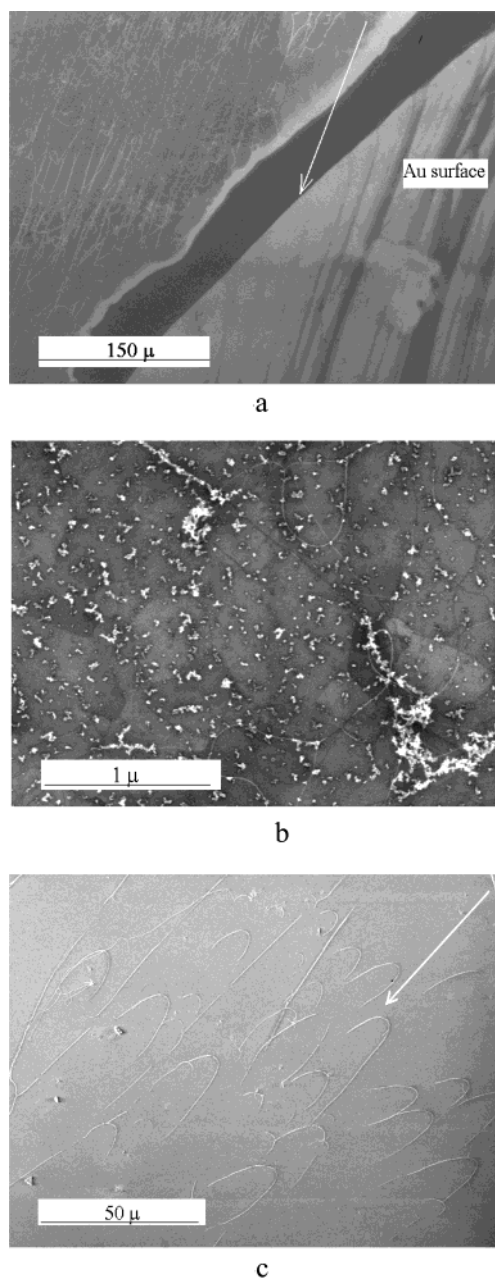


Figure 4. SEM images of nanotubes on (a) partially Au-coated Si wafer at position A for 30 min, (b) Au-coated Si wafer at position D for 30 min, and (c) Si wafer at position C for 30 min.

The long and oriented nanotubes on substrate provide advantages for manipulation and applications. For instance, we are able to cut and pattern the oriented long nanotubes into the same length by use of photolithography and plasma etching. Figure 5 shows a large area SEM images of cutting these long oriented nanotubes by patterning photolithographically followed by H_2O plasma etching for 8 min and removal of polymer. From the high-magnification SEM image (inset in Figure 5), it is clear that the nanotubes were cut into about 10 μm in length and the polymer uncovered nanotubes are completely removed. Basically, the length of the nanotubes can be easily controlled by the pattern line space and high resolution down to micron scale can be achieved by standard photolithography. H_2O plasma has been applied to control etching amorphous carbon on the aligned multiwalled carbon nanotube film.²⁴ Unlike O_2 plasma, H_2O was a mild etching source. Interestingly, the time dependence of H_2O plasma etching shows that short nanotubes were more

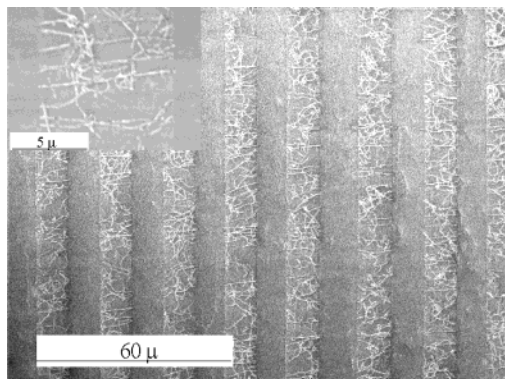


Figure 5. SEM images of nanotubes patterned by photolithography after etching with water plasma for 8 min. The inset is the enlarged image, showing the long nanotubes were cut.

easily removed, which may be due to the high activity at the ends of the nanotubes. This may provide an effective way to selectively remove random short nanotubes from oriented long nanotubes.

In conclusion, we present here a feasible method to grow ultralong well-oriented SWNT arrays on substrate using Fe powder as the source of catalysts. The formation of SWNTs could be either on the surface or in the gas flow. The majority of the ultralong SWNT is small bundles when a long reaction time (>30 min) is applied. The advantages of this method are (1) simplicity. No preformed nanoparticle catalyst or toxic catalyst precursor, such as $\text{Fe}(\text{CO})_5$, is needed. The catalysts for SWNTs growth come from in situ formation and decomposition of $\text{Fe}(\text{CO})_5$ from Fe powder during reaction. (2) The as-produced SWNTs are ultralong and well-oriented. The growth direction of long nanotubes on the substrate is controlled by gas flow and only long nanotubes are aligned. (3) The density and length of SWNTs can be easily controlled by reaction time and location. (4) Aligned ultralong SWNTs on the substrate can be cut and patterned by standard photolithography and water plasma etching technique. This feasible method to generate ultralong and well-oriented SWNTs on the substrate, together with the controlled cutting and patterning, could be useful for many potential applications of SWNTs, e.g., nanoelectronics, field emission, and functional polymer–SWNT composite.

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References and Notes

- (1) Journet, C.; Maser, W. K.; Bernier, P.; Loiseau, A.; Delachapelle, M. L.; Lefrant, S.; Deniard, P.; Lee, R.; Fischer, J. E. *Nature* **1997**, 388, 756.
- (2) Wang, M.; Zhao, X. L.; Ohkohchi, M.; Ando, Y. *Fullerene Sci. Technol.* **1996**, 4, 1027.
- (3) Guo, T.; Nikolaev, P.; Thess, A.; Colbert, D. T.; Smalley, R. E. *Chem. Phys. Lett.* **1995**, 243, 49.
- (4) Thess, A.; Lee, R.; Nikolaev, P.; Dai, H. J.; Petit, P.; Robert, J.; Xu, C. H.; Lee, Y. H.; Kim, S. G.; Rinzler, A. G.; Colbert, D. T.; Scuseria, G. E.; Tomanek, D.; Fischer, J. E.; Smalley, R. E. *Science* **1996**, 273, 483.
- (5) Dai, H. J.; Rinzler, A. G.; Nikolaev, P.; Thess, A.; Colbert, D. T.; Smalley, R. E. *Chem. Phys. Lett.* **1996**, 260, 471.
- (6) Hafner, J. H.; Bronikowski, M. J.; Azamian, B. R.; Nikolaev, P.; Rinzler, A. G.; Colbert, D. T.; Smith, K. A.; Smalley, R. E. *Chem. Phys. Lett.* **1998**, 296, 195.
- (7) Nikolaev, P.; Bronikowski, M. J.; Bradley, R. K.; Rohmund, F.; Colbert, D. T.; Smith, K. A.; Smalley, R. E. *Chem. Phys. Lett.* **1999**, 313, 91.
- (8) An, L.; Owens, J. M.; McNeil, L. E.; Liu, J. *J. Am. Chem. Soc.* **2002**, 124, 13688.
- (9) Cassell, A. M.; Franklin, N. R.; Tomblar, T. W.; Chan, E. M.; Han, J.; Dai, H. J. *Am. Chem. Soc.* **1999**, 121, 7975.
- (10) Derycke, V.; Martel, R.; Radosavljevic, M.; Ross, F. M. R.; Avouris, P. *Nano Lett.* **2002**, 2, 1043.
- (11) Franklin, N. R.; Li, Y. M.; Chen, R. J.; Javey, A.; Dai, H. J. *Appl. Phys. Lett.* **2001**, 79, 4571.
- (12) (a) Huang, S. M.; Cai, X. Y.; Liu, J. *J. Am. Chem. Soc.* **2003**, 125, 5636. (b) Huang, S. M.; Maynor, B.; Cai, X. Y.; Liu, J. *Adv. Mater.* **2003**, 15, 1651.
- (13) Joselevich, E.; Lieber, C. M. *Nano Lett.* **2002**, 2, 1137.
- (14) Kim, W.; Choi, H. C.; Shim, M.; Li, Y.; Wang, D.; Dai, H. *Nano Lett.* **2002**, 2, 703.
- (15) Kong, J.; Soh, H. T.; Cassell, A. M.; Quate, C. F.; Dai, H. J. *Nature* **1998**, 395, 878–881.
- (16) 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.
- (17) Zheng, B.; Lu, C.; Gu, G.; Makarovski, A.; Finkelstein, G.; Liu, J. *Nano Lett.* **2002**, 2, 895.
- (18) Dresselhaus, M. S.; Dresselhaus, G.; Avouris, P. *Carbon Nanotubes Synthesis, Structure, Properties, and Applications*; Springer, 2001; Vol. 80.
- (19) Ural, A.; Li, Y. M.; Dai, H. J. *Appl. Phys. Lett.* **2002**, 81, 3464.
- (20) Gu, G.; Philipp, G.; Wu, X. C.; Burghard, M.; Bittner, A. M.; Roth, S. *Adv. Funct. Mater.* **2001**, 11, 295.
- (21) Ago, H.; Ohshima, S.; Uchida, K.; Yumura, M. *J. Phys. Chem. B* **2001**, 105, 10453.
- (22) Bronikowski, M. J.; Willis, P. A.; Colbert, D. T.; Smith, K. A.; Smalley, R. E. *J. Vac. Sci. Technol. A* **2001**, 19, 1800.
- (23) Zhu, H. W.; Xu, C. L.; Wu, D. H.; Wei, B. Q.; Vajtai, R.; Ajayan, P. M. *Science* **2002**, 296, 884.
- (24) Huang, S.; Dai, L. *J. Phys. Chem. B* **2002**, 106, 3543.