

# Multicomponent Interposed Carbon Nanotube Micropatterns by Region-Specific Contact Transfer and Self-Assembling

Junbing Yang and Liming Dai\*

Laboratory of Functional Polymers and Carbon Nanomaterials, Department of Polymer Engineering,  
The University of Akron, Akron, Ohio 44325-0301

Richard A. Vaia

Air Force Research Laboratory, Materials and Manufacturing Directorate, AFRL/MLBP, Bldg 654,  
2941 P St. Wright-Patterson AFB, Ohio 45433-7750

Received: July 28, 2003; In Final Form: October 2, 2003

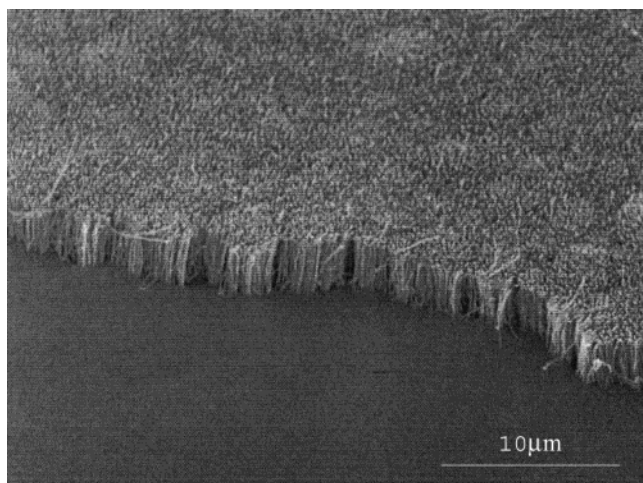
In our further investigation on the microfabrication of carbon nanotubes, we found that micropatterns of *perpendicularly aligned* carbon nanotubes can be prepared by simply pressing an adhesively sticky tape (e.g., Scotch tape) prepatterned with a nonadhesive layer onto a nonpatterned aligned carbon nanotube film, followed by peeling off the sticky tape from the quartz substrate in a dry state. In conjunction with the region-specific surface modification, this dry contact transfer method has enabled us to produce multicomponent carbon nanotube micropatterns in which different components are interposed in an intimate fashion, as exemplified by the newly produced micropatterns with self-assembled nonaligned carbon nanotubes interdispersed into the discrete areas in the patterned structure of aligned carbon nanotubes.

Carbon nanotubes have been widely investigated for their potential applications in many micro- or nanoscale electronic and photonic devices.<sup>1</sup> The abilities to manipulate them on a micro- to nanometer scale and to control their interaction with and orientation on substrates are paramount to both fundamental characterization and potential applications of carbon nanotubes in advanced optoelectronic devices, including nanotube electron emitters, single-molecular transistors, sensors, and sensor chips.<sup>1,2</sup> During the past decade or so, there has been tremendous progress in the development of techniques for producing aligned and micropatterned carbon nanotubes.<sup>3</sup> Ajayan et al.<sup>4</sup> and de Heer et al.<sup>5</sup> were among the first to align preformed carbon nanotubes in polymer matrixes, whereas Xie and co-workers<sup>6</sup> reported in 1996 the first large-scale chemical vapor deposition (CVD) growth of aligned carbon nanotubes from a mesoporous silica template with embedded iron nanoparticles. These earlier research activities provoked an ever-increasing interest in micro-/nanofabrication of carbon nanotubes.<sup>3</sup> Consequently, a large variety of carbon nanotube micropatterns, with the nanotubes randomly oriented on or aligned into different directions from the substrate surface, have since been reported.<sup>7</sup> In particular, we have produced perpendicularly aligned carbon nanotube arrays<sup>8</sup> and their micropatterns by pyrolysis of iron(II) phthalocyanine (FeC<sub>32</sub>N<sub>8</sub>H<sub>16</sub>, designated as FePc) onto a quartz glass plate with or without a prepatterned thin polymer layer.<sup>9</sup> By separating the nanotube arrays from the quartz substrate in an aqueous hydrofluoric acid solution followed by lifting up the substrate-free nanotube film floating on the HF/HO<sub>2</sub> solution, we have also demonstrated a *wet contact transfer* technique for a patternwise/nonpatternwise transfer of the aligned nanotube arrays onto various other substrates.<sup>8</sup> In our further investigation on the microfabrication of aligned carbon nanotubes produced by the pyrolysis of FePc, we have recently found that micro-

patterns of the *perpendicularly aligned* carbon nanotubes can be prepared by simply pressing an adhesively sticky tape (e.g., Scotch tape) prepatterned with a nonadhesive layer onto the FePc-generated carbon nanotube film, followed by peeling off the nanotubes together with the sticky tape from the quartz substrate in a dry state (hence, we designated this newly developed method as a *dry contact transfer*). Like the wet contact transfer, the dry contact transfer also allows the aligned carbon nanotubes to be deposited, in either a patterned or nonpatterned fashion, onto various substrates. Unlike the wet contact transfer, however, the dry contact transfer would not only maximize the retention of the structural integrity of the perpendicularly aligned carbon nanotubes after the contact transfer but also allow the region-specific interposition of other component(s) into the discrete areas interdispersed in the patterned nanotube structure, as we shall see later. Just as the integrated circuits have been dispensable to our modern semiconducting industry, the development of carbon nanotube micropatterns in which multicomponents are interposed in a controllable fashion could be important to advanced nanotechnology. In this Letter, we describe a novel approach to the first multicomponent interposed carbon nanotube micropatterns prepared by the simple, but very effective, dry contact transfer technique involving a region-selective transfer of the FePc-generated perpendicularly-aligned carbon nanotubes onto a Scotch tape pre-patterned with a thin layer of heptylamine-plasma-treated silver, followed by region-specific adsorption of acid-oxidized carbon nanotubes<sup>10</sup> onto the plasma-treated areas interdispersed in the patterned nanotube structure.

In a typical experiment, the pyrolysis of FePc was performed within a Ar/H<sub>2</sub> flow at 800–1100 °C on a dual furnace equipped with a quartz glass tube and independent temperature controllers, according to the method we developed previously.<sup>8</sup> Figure 1 reproduces a typical scanning electron microscopic (HITACHI

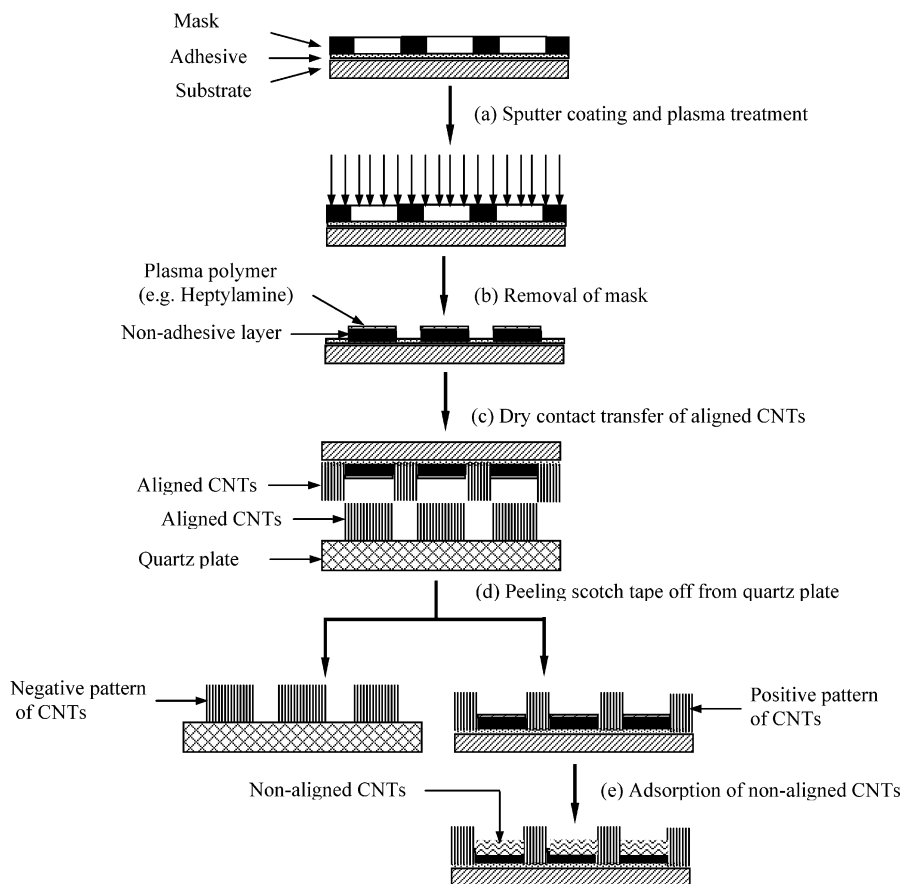
\* Corresponding author. E-mail: ldai@uakron.edu.



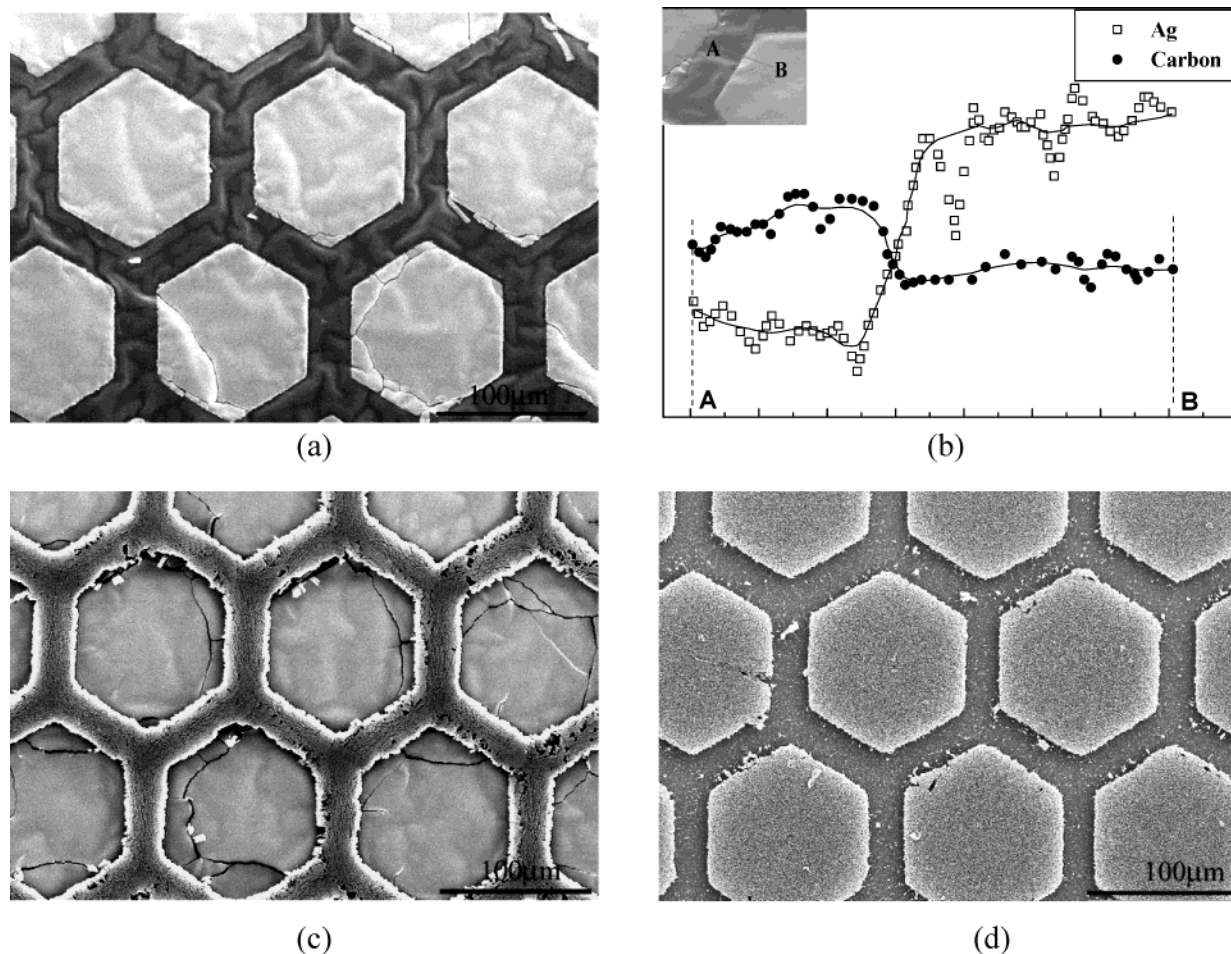
**Figure 1.** Typical SEM micrograph of the aligned carbon nanotube film prepared by pyrolysis of FePc.

S-2150 SEM) image of the resultant carbon nanotube arrays, showing that the *as-synthesized* nanotubes align perpendicularly onto the substrate. To examine the nanotube orientation and length, part of the carbon nanotube film shown in Figure 1 has been peeled off from the quartz substrate with tweezers. Elsewhere, we have demonstrated that the constituent carbon nanotubes are well graphitized with ca. 40 layers of graphite sheets and an outer diameter of ca. 50 nm.<sup>11</sup> As seen in Figure 1, the aligned carbon nanotubes can be spotlessly removed from the substrate by the mechanical force. This finding prompted us to develop the dry contact transfer technique for producing micropatterns of the aligned carbon nanotubes by region-specific transferring them onto a prepatterned Scotch tape.

Figure 2 shows the steps used for micropatterning the Scotch tape with a thin layer of silver, the subsequent plasma treatment of the silver surface, the contact transfer of the aligned carbon nanotubes, and the region-specific adsorption of nonaligned carbon nanotubes. To start with, a TEM grid consisting of hexagonal windows was adhered onto commercially available Scotch tape (3M, polypropylene-film-supported acrylic adhesive) as a mask, followed by sputter coating with silver through the mask (Figure 2a). Thereafter, the silver-patterned Scotch tape was subjected to a heptylamine-plasma treatment at 250 kHz, 30 W, and a monomer pressure of 0.18 Torr for 180 s while the TEM grid mask was kept intact during the plasma polymerization (Figure 2a). After careful removal of the TEM grid (Figure 2b), a SEM image of the plasma-treated silver hexagons was recorded (Figure 3a). The corresponding energy-dispersive X-ray (EDX) line analyses of C K $\alpha$  and Ag K $\alpha$  given in Figure 3b clearly show the presence of a thin layer of silver-rich coating in the hexagonal region. This indicates the formation of hexagonal silver micropatterns on the adhesive layer of the Scotch tape. Aligned carbon nanotubes were then transferred onto the adhesive-covered area by pressing the Scotch tape on the *as-synthesized* aligned carbon nanotube film on a quartz plate (cf. Figure 1), followed by peeling off the Scotch tape from the quartz substrate (Figure 2c,d). As expected, the nanotubes underneath the silver-free regions were selectively transferred onto the Scotch tape as a positive image of the TEM grid (Figure 3c) whereas those covered by the silver-patterned areas remained on the quartz substrate as a negative pattern (Figure 3d). As can be seen in Figure 3c,d, the integrity of those carbon nanotubes (e.g., alignment, packing density) transferred onto the Scotch tape is almost the same as the *as-grown* nanotubes remaining on the quartz plate under the present



**Figure 2.** Schematic illustration of the procedures for fabricating multicomponent interposed carbon nanotube micropatterns by dry contact transfer, followed by region-specific adsorption.



**Figure 3.** SEM micrographs of the aligned carbon nanotube micropatterns produced by dry contact transfer with a TEM grid consisting of hexagonal windows as the mask: (a) micropatterned structure of silver on Scotch tape; (b) EDX profiles of Ag K $\alpha$  ( $\square$ ) and C K $\alpha$  ( $\bullet$ ) (the scanning path for the EDX line analyses is indicated by the line from A to B in the inserted SEM picture); (c) aligned carbon nanotube patterns after being transferred onto the Scotch tape (i.e., positive pattern); (d) aligned carbon nanotube patterns left on the quartz plate after the dry contact transfer (i.e., negative pattern).

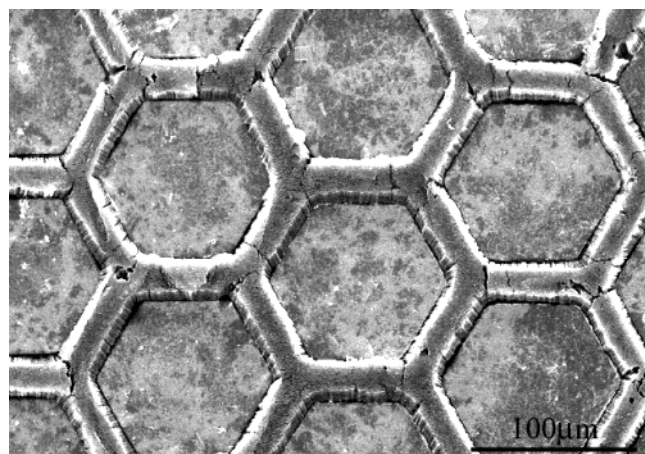
transfer conditions. However, the newly transferred carbon nanotubes with a robust aligned and/or micropatterned structure are supported by a flexible substrate. The crack edges seen within the hexagonal areas in Figure 3c were, most probably, caused by mechanical deformation of the silver layer when the overlaying flexible Scotch tape was pressed downward to the nanotube film during the transfer process. Although some care may be needed to prepare the aligned carbon nanotube micropatterns with interposed crack-free silver patterns on flexible Scotch tape, the soft nature of the Scotch tape used for the dry contact transfer should allow us to develop multicomponent nanotube micropatterns even for flexible device applications.

To demonstrate the potential of this technique for the development of sophisticated nanotube micropatterns, such as the multicomponent interposed carbon nanotube patterns, for certain specific applications, we carried out the region-specific adsorption of acid-oxidized nonaligned carbon nanotubes onto the heptylamine-plasma-treated silver surface within the hexagonal areas in Figure 3c. We have previously demonstrated that the plasma-induced  $-\text{NH}_2$  groups interacted strongly with the  $-\text{COOH}$  groups of the acid-oxidized carbon nanotubes,<sup>10</sup> leading to self-assembling of the acid-oxidized nanotubes onto the heptylamine-plasma surface.<sup>12</sup> The  $\text{COOH}$ -containing carbon nanotubes used in this study were prepared by acid treatment ( $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$ ) of the FePc-generated nanotubes according to a published procedure.<sup>10</sup> The presence of carboxylic groups in

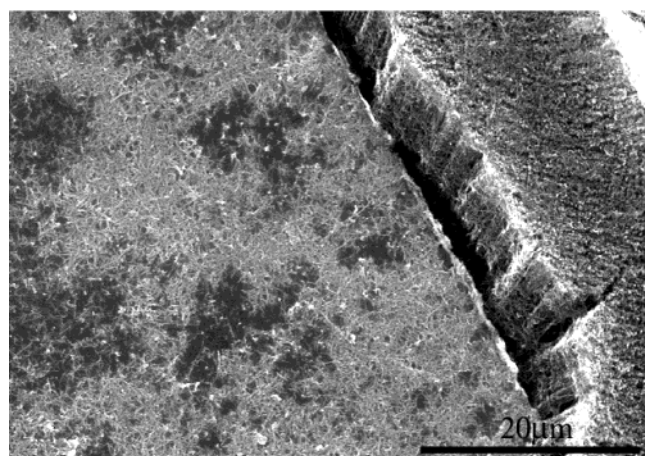
the acid-treated carbon nanotubes was evidenced by a peak at 288.8 eV in the XPS C1 spectrum, as previously demonstrated.<sup>12</sup>

Figure 4a shows a typical SEM image of the aligned carbon nanotube micropatterns, as the one represented by Figure 3c, after having been immersed in an aqueous solution of the  $\text{COOH}$ -containing carbon nanotubes (1.5 mg/5 mL of  $\text{H}_2\text{O}$ , 20 °C) for physical adsorption for 2 h. Though some distortion of the aligned carbon nanotube micropattern is observed (Figure 4a) due to possible deformation of the Scotch tape in water, the adsorbed carbon nanotubes are clearly evident by inspection of the plasma-patterned areas of Figure 4a under a higher magnification (Figure 4b). Figure 4b also shows that both the contact transferred aligned carbon nanotubes and the adsorbed nonaligned carbon nanotubes are well registered in their respective areas. Controlled experiments were performed by adsorption of the acid-oxidized carbon nanotubes onto the *as-synthesized* perpendicularly aligned carbon nanotube films before and after being transferred onto the Scotch tape in a nonpatterned fashion. Although possible adsorption of the acid-oxidized carbon nanotubes onto the pristine aligned nanotube film cannot be ruled out, adsorption of the highly oxidized carbon nanotubes onto the pure aligned nanotube film was found to be insignificant. Under the present experimental conditions, the acid-oxidized carbon nanotubes were shown to preferentially adsorb onto the heptylamine-plasma surface with respect to the





(a)



(b)

**Figure 4.** SEM micrographs of the multicomponent interposed carbon nanotube micropatterns with the nonaligned carbon nanotubes region-specifically adsorbed between aligned carbon nanotube patterns: (a) a low magnification image and (b) a high magnification image, showing the individual adsorbed carbon nanotubes within the hexagonal regions of Figure 4a.

aligned carbon nanotube arrays because of the strong interaction between the  $-\text{COOH}$  and  $-\text{NH}_2$  groups.

In summary, we have developed a simple, but very effective, method for producing multicomponent interposed carbon nanotube micropatterns by region-specific contact transfer of perpendicularly aligned carbon nanotubes generated from FePc onto a Scotch tape prepatterned with a nonadhesive layer (e.g., heptylamine-plasma-treated silver), followed by self-assembling of nonaligned carbon nanotubes within the discrete areas of the heptylamine-plasma surface interdispersed in the patterned aligned nanotube structure through the region-selective adsorption of  $\text{COOH}$ -containing nanotubes. Due to the generic nature characteristic of the plasma technique and the adhesive-based contact transfer, the micropatterning methodology developed

in this study can be used to prepare multidimensional, multi-component carbon nanotube micropatterns interposing with many other materials on various substrates. The conducting nature of the aligned carbon nanotubes should allow electrical contacts to be made to and from the component(s) interposed in the discrete areas surrounded by the aligned nanotube micropatterns. The demonstration of the formation of multi-component interposed carbon nanotube micropatterns by the newly developed micropatterning technique could thus be very attractive to applications of carbon nanotubes in various micro-to nanometer scale optoelectronic devices and many other systems.

**Acknowledgment.** We are grateful for financial support from the U.S. Air Force Office for Scientific Research through the AirForce/UAkron Collaborative Center on Polymer Photonics.

## References and Notes

- (1) See, for example: (a) Dresselhaus, M. S.; Deesselhaus, G.; Eklund, P. *Science of Fullerenes and Carbon Nanotubes*; Academic Press: New York, 1996. (b) Terrones, M.; Hsu, W. K.; Hare, J. P.; Kroto, H. W.; Terrones, H.; Walton, D. R. M. *Philos. Trans. R. Soc. London A* **1996**, 354, 2025. (c) Yakobson, B. I.; Smalley, R. E. *Am. Sci.* **1997**, 85, 325. (d) Ajayan, P. M.; Ebbesen, T. W. *Rep. Prog. Phys.* **1997**, 60, 1026. Rao, C. N. R. *J. Mater. Chem.* **1999**, 9, 1.
- (2) See, for example: (a) Wang, Q. H.; Setlur, A. A.; Lauerhaas, J. M.; Dai, J. Y.; Seelig, E. W.; Chang, R. P. H. *Appl. Phys. Lett.* **1998**, 72, 2912. (b) Kouwenhoven, L. *Science* **1997**, 275, 1896. (c) Tans, S. J.; Verschueren, A. R. M.; Dekker, C. *Nature* **1998**, 393, 49.
- (3) For recent reviews, see: (a) Rao, C. N. R.; Govindaraj, A. *Acc. Chem. Res.* **2002**, 35, 998. (b) Dai, H. *Acc. Chem. Res.* **2002**, 35, 1035. (c) Zhou, O.; Shimoda, H.; Gao, B.; Oh, S.; Fleming, L.; Yue, G. *Acc. Chem. Res.* **2002**, 35, 1045. (d) Andrews, R.; Jacques, D.; Qian, D.; Rantell, T. *Acc. Chem. Res.* **2002**, 35, 1008. (e) Baughman, R. H.; Zakhidov, A. A.; de Heer, W. A. *Science* **2002**, 297, 787. (f) Wang, Z. L.; Gao, R. P.; Pan, Z. W.; Dai, Z. R. *Adv. Eng. Mater.* **2001**, 3, 657. (g) Huang, S.; Dai, L. *J. Nanoparticle Res.* **2002**, 4, 145.
- (4) Ajayan, P. M.; Stephan, O.; Colliex, C.; Trauth, D. *Science* **1994**, 265, 1211.
- (5) de Heer, W. A.; Bacsá, W. S.; Châtelain, A.; Gerfin, T.; Humphreybaker, R.; Forró, L.; Ugarte, D. *Science* **1995**, 268, 845.
- (6) Li, W. Z.; Xie, S. S.; Qian, L. X.; Chang, B. H.; Zou, B. S.; Zhou, W. Y.; Zhao, R. A.; Wang, G. *Science* **1996**, 274, 1701.
- (7) See: for example: (a) Terrones, M.; Grobert, N.; Olivares, J.; Zhang, J. P.; Terrones, H.; Kordatos, K.; Hsu, W. K.; Hare, J. P.; Townsend, P. D.; Prassides, K.; Cheetham, A. K.; Kroto, H. W.; Walton, D. R. M. *Nature* **1997**, 388, 52. (b) Rao, C. N. R.; Sen, R.; Satishkumar, B. C.; Govindaraj, A. *J. Chem. Soc., Chem. Commun.* **1998**, 1525. (c) Ren, Z. F.; Huang, Z. P.; Xu, J. H.; Wang, P. B.; Siegal, M. P.; Provencio, P. N. *Science* **1998**, 282, 1105. (d) Fan, S.; Chapline, M. G.; Franklin, N. R.; Tomber, T. W.; Cassell, A. M.; Dai, H. *Science* **1999**, 283, 512. (e) Dai, L.; Mau, A. W. H. *Adv. Mater.* **2001**, 13, 899, and references therein. Wei, B. Q.; Vajtai, R.; Jung, Y.; Ward, J.; Zhang, R.; Ramanath, G.; Ajayan, P. M. *Nature* **2002**, 416, 495.
- (8) Huang, S.; Dai, L.; Mau, A. W. H. *J. Phys. Chem.* **1999**, 103, 4223.
- (9) (a) Yang, Y.; Huang, S.; He, H.; Mau, A. W. H.; Dai, L. *J. Am. Chem. Soc.* **1999**, 121, 10832. (b) Huang, S.; Mau, A. W. H.; Turney, T. W.; White, P. W.; Dai, L. *J. Phys. Chem. B* **2000**, 104, 2193.
- (10) (a) Tsang, S. C.; Chen, Y. K.; Harris, P. J. F.; Green, M. L. H. *Nature* **1994**, 372, 159. (b) Liu, J.; Rinzler, A. G.; Dai, H.; Hafner, J. H.; Bradley, R. K.; Boul, P. J.; Lu, A.; Iverson, T.; Shelimov, K.; Huffman, C. B.; Rodriguez-Macias, F.; Shon, Y.; Lee, T.; Colbert, D. T.; Smalley, R. E. *Science* **1998**, 280, 22.
- (11) Li, D. C.; Dai, L.; Huang, S.; Mau, A. W. H.; Wang, Z. L. *Chem. Phys. Lett.* **2000**, 316, 349.
- (12) Chen, Q.; Dai, L. *Appl. Phys. Lett.* **2000**, 76, 2719.