Patterned Growth and Contact Transfer of Well-Aligned Carbon Nanotube Films

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The preparation of aligned and/or micropatterned carbon nanotubes is important to applications ranging from nanocomposites to field-emitting displays. By pyrolysis of iron (II) phthalocyanine under Ar/H_2 at 800–1100 °C, we have synthesized large arrays of vertically aligned carbon nanotubes on various substrates, including quartz glass plates, from which substrate-free films were obtained simply by immersing the nanotube-deposited quartz plates into an aqueous hydrofluoric acid solution. Micropatterns of the aligned nanotubes suitable for device fabrication were generated either by patterned growth of the nanotubes on a partially masked/prepatterned surface or through a contact printing process involving region-specific transfer of the substrate-free nanotube films to other substrates (e.g., polymer films), which otherwise may not be suitable for nanotube growth at high temperatures.

Carbon nanotubes are promising as new optoelectronic materials,^{1–4} for example, as new electron field emitters in panel displays⁵ and single-molecular transistors in microelectronics.⁶ For most of these applications, it is highly desirable to prepare aligned and/or micropatterned carbon nanotubes so that the properties of individual nanotubes can be easily assessed and they can be incorporated effectively into devices.^{3,7} Although carbon nanotubes synthesised by most of the common techniques, such as arc discharge^{1,2} and catalytic pyrolysis,⁸ often exist in a randomly entangled state,^{2,8} aligned carbon nanotubes have been prepared either by postsynthesis manipulation^{9,10} or by synthesis-induced alignment.^{11–17} However, the preparation of micropatterned and/or free-standing films of aligned nanotubes remains both scientifically and technically challenging. Here, we report a novel method for synthesis of perpendicularly aligned carbon nanotubes over large areas. More importantly, we also describe the first preparation of micropatterns and substrate-free films of the aligned nanotubes, which can be readily transferred onto various substrates including those that otherwise may not be suitable for nanotube growth at high temperatures (e.g., polymer films).

We prepared aligned carbon nanotubes by pyrolysis of iron (II) phthalocyanine, FeC₃₂N₈H₁₆ (Aldrich, designated as FePc hereafter), which, like Ni phthalocyanine,¹⁸ contains both the metal catalyst and carbon source required for the nanotube growth. The pyrolysis of FePc was performed under Ar/H₂ at 800-1100 °C using an appropriate substrate in a flow reactor consisting of a quartz glass tube and a dual furnace fitted with independent temperature controllers (Figure 1). The resulting carbon nanotubes appeared on the substrate (e.g., a quartz glass plate) as a black layer, which could be scraped off from the substrate as powder. More importantly, the black deposit could be easily separated from the quartz glass as a substrate-free, floating film simply by immersing the nanotube-deposited quartz plate into an aqueous hydrofluoric acid solution (10-40% w/w).19 As we discuss later, this technique allows a patternwise/ nonpatternwise transfer of the nanotube films onto various other substrates of particular interest (e.g., electrodes for electrochemistry, polymer films for organic optoelectronic devices) with the integrity of the aligned nanotubes being largely maintained in the transferred films. Alternatively, micropatterns of the aligned nanotubes have also been prepared by patterned growth of the nanotubes on a prepatterned surface or using a mask in the same manner as for patterned plasma polymerization.²⁰

Figure 2a represents a typical scanning electron microscopic (SEM, XL-30 FEG SEM, Philips, at 5 KV) image of the carbon nanotubes, showing that the as-synthesized nanotubes align almost normal to the substrate surface. The aligned nanotubes grow homogeneously over the whole quartz glass plate so that the nanotube growing area is essentially only limited by the size of the substrate. Figure 2b shows a photograph of a film (ca. $4 \times 1 \text{ cm}^2$) of the aligned nanotubes, floating on the HF/ H₂O solution (vide supra). As can be seen in Figure 2a, the aligned nanotubes produced under normal experimental conditions used in this study (see caption of Figure 1) are almost free from pyrolytic impurities (e.g., carbon particles and other carbonaceous materials). Prolonged pyrolysis, however, may generate some amorphous carbon on the top of the aligned nanotube layer. Inspection of the film edge in Figure 2a at a higher magnification (Figure 2c) shows that the aligned nanotubes are densely packed with a fairly uniform tubular length of ca. 9 μ m. However, the length of the aligned nanotubes can be varied over a wide range (up to several tens of micrometers) in a controllable fashion by changing the experimental conditions (e.g., the pyrolysis time, flow rate). A well-graphitized structure with ca. 40 concentric carbon shells and an outer diameter of ca. 40 nm is illustrated in the high-resolution transmission electron microscopic (HR-TEM, CM30, Philips, at 300 KV) image of an individual nanotube (Figure 2d).

Electron energy loss spectroscopy (EELS attached on the HR-TEM, CM 30 Philips) reveals carbon K-edges at 284 and 291 eV, attributable to the π^* and δ^* features of the sp² hybridized carbons, along with a signal at 400 eV due to nitrogen,¹³ indicating that the nanotubes contain nitrogen.^{13,18} This is further confirmed by X-ray photoelectron spectroscopic (XPS, Kratos

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Figure 1. Apparatus for the generation of aligned carbon nanotubes by pyrolysis of FePc. In typical experiments, a predetermined amount of FePc (0.1-0.3 g) and a clean quartz glass plate $(4 \times 1 \times 0.125 \text{ cm}, \text{ultrasonicated in acetone})$ were placed in the quartz glass tube (as shown). A flow of Ar/H₂ (1:1 to 1:2 v/v, 20-40 cm³/min) mixture was then introduced into the quartz tube during heating. After the second furnace reached 800-1100 °C, the first furnace was heated to 500-600 °C for 2-15 min. Thereafter, both furnaces were kept at the pyrolysis temperature (800-1100 °C) for an additional 20-30 min for the deposition of nanotubes to be completed.

Analytical, monochromatised Al K α at 200 W) measurements. While the XPS N1s spectrum is similar to that observed for N-substituted graphite, showing doublets at the binding energies (BE) of 398.4 and 400.7 eV,^{21,18} the corresponding BE value for the C1s peak is almost the same as that of graphite (284.7 eV).

The growth mechanism for aligned nanotubes deposited either in porous matrixes^{11,12} or metal-coated surfaces^{13,14} has been proposed previously. Our SEM images taken at different stages during the pyrolysis (Figure 3) are consistent with the following process. Upon the thermal decomposition of FePc, Fe particles, surrounded by carbon, form on the substrate surface (Figure 3a). Segregation of Fe then occurs, leading to an increase in the size of the catalytic center. Once the Fe particle reaches an optimal size for carbon nanotube nucleation,²² the surrounding carbon transforms into a graphite tube. Further decomposition of FePc provides carbon to the contact region between the Fe particle and the already formed tubule segment, allowing continuous growth of the carbon nanotube in the direction normal to the substrate surface (Figure 3b). Iron atoms may be preferentially left at the first part of the reactor, where the temperature was above the FePc decomposition point during this stage of pyrolysis. This "base-growth" process²³ is supported by the presence of metal particles at the bottom of the nanotubes, as shown in Figure 3c. The high surface density of the growing nanotubes serves as an additional advantage for the constituent nanotubes to be "uncoiled" and allows the as-grown aligned nanotubes to be removed as a substrate-free film.

The perpendicular alignment of the nanotubes should facilitate device construction. In this regard, we have tried to grow aligned carbon nanotubes on various conducting surfaces including Au, Pt, Cu, and ITO (indium tin oxide). Such constructs have many potential applications, especially in electrochemistry. We have also developed techniques for patterning the aligned nanotubes either through patterned growths or by postsynthesis microfabrications. For example, the patterned growth can be achieved by placing a mask (e.g., a TEM grid consisting of hexagonal windows) on the quartz glass substrate. The partially masked quartz glass plate was then coated with aligned nanotubes by the pyrolysis of FePc, as described above. The resulting nanotube films were studied by SEM after careful removal of the TEM grid. An example of the nanotube patterns thus prepared is given in Figure 4a, which shows a close replication of the mask structure. As can be seen in Figure 4a, micropatterns consisting of the densely packed, perpendicularly aligned nanotubes are clearly evident. In this case, the spatial resolution of the patterns is mainly limited by the resolution of the mask used. Furthermore, our preliminary results indicate that the aligned nanotube patterns can also be produced by first depositing a thin, patterned ITO or Au layer onto an appropriate substrate (e.g., a quartz glass plate) using a mask (e.g., a TEM grid) followed by deposition of the pyrolyzed FePc and removal of the ITO- or Au-covered regions by selective dissolution in an aqueous hydrochloride or cyanide solution. This method allowed us to generate a positive image of the mask.

Further investigation on the nanotube microfabrication showed that both a positive and a negative image of the aligned nanotubes can be produced simultaneously simply by lifting up a substrate-free nanotube film floating on the HF/H₂O solution (vide supra) onto a TEM grid, followed by region-specific transfer of it to another substrate (e.g., polystyrene film) through physical contact between the TEM grid and the substrate surface. This contact transfer process is much like the widely used microcontact printing (μ CP) technology for generating selfassembled monolayer patterns.24 In the present study, the nanotubes suspended over the windows were selectively transferred onto the substrate surface as a negative image (Figure 4b) while those on the grid bars remained there as a positive pattern (Figure 4c). The most important feature to note in parts b and c of Figure 4 is that the constituent nanotubes in the μ CPgenerated patterns are still aligned normal to the substrate surfaces.

In summary, we have demonstrated that vertically aligned nanotubes can be prepared over large areas by pyrolysis of iron phthalocyanine under appropriate conditions. We have also developed simple methods for obtaining large-area, substratefree nanotube films and for micropatterning vertically aligned nanotubes. While the substrate-free nanotube films can be transferred onto various substrates of particular interest, the techniques for micropattern formation described in this paper should also be applicable to many other systems. With these methods, we can deposit the aligned nanotubes, in either a patterned or nonpatterned fashion, onto various substrates including those that otherwise cannot be used for nanotube



Figure 2. (a) Typical SEM image of the aligned nanotubes. Part of the carbon nanotube film was peeled off from the quartz substrate with tweezers for examining the orientation and alignment of the nanotubes. (b) Typical photographic image of the large-area, substrate-free, aligned nanotube films floating on a HF/H_2O solution (30% w/w) contained in a polystyrene petri dish. (c) Enlarged view of (a) along the peeled edge. The misalignment seen for some of the carbon nanotubes was caused by the peeling action. (d) Typical HR-TEM image of the individual constituent nanotubes showing ca. 40 concentric graphitic layers.

growth (e.g., polymer films). Therefore, the combination of the simple methods for production of large-area aligned nanotubes

and the simple techniques for micropatterning of them should not only facilitate the characterization of physical properties of







(b)





Figure 3. SEM micrographs showing the growth of the aligned nanotubes during the pyrolysis. (a) Carbon-surrounded iron nanoparticles formed at the initial stage of the pyrolysis. (b) The initial growth of the nanotubes. (c) The resultant aligned nanotubes normal to the substrate surface.

nanotubes but also allow their effective incorporation into devices for practical applications.









(c)

Figure 4. Typical SEM micrographs of patterned films of aligned nanotubes. (a) Film produced by patterned growth using a TEM grid consisting of hexagonal windows as the mask. (b) The microcontact-printed negative image on a Au surface. (Although the negative pattern could also be deposited onto various other substrates including polymers (e.g., polystyrene), Au was chosen for better SEM imaging). (c) The microcontact-printed positive image on a TEM grid used as the stamp. Note that the TEM grides used for (a) and (b, c) have grid bars of ca. 8 and 30 μ m wide and hexagonal windows with a width of 50 and 80 μ m, respectively.

Note Added in Proof. After the submission of our manuscript, we noted that Fan et al. recently reported the synthesis of regular arrays of oriented nanotubes on Fe-patterned porous silicon by pyrolysis of ethylene (Fan, S.; Chapline, M. G.; Franklin, N. R.; Tomber, T. W.; Cassell, A. M.; Dai, H. *Science* **1999**, *283*, 512).

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