

Patterned Growth of Well-Aligned Carbon Nanotubes: A Photolithographic Approach

Yongyuan Yang,[†] Shaoming Huang, Huizhu He,[†]
Albert W. H. Mau, and Liming Dai^{*}

CSIRO Molecular Science, Bag 10
Clayton South, Victoria 3169, Australia

Received August 16, 1999

Carbon nanotubes are attractive for many potential applications,^{1,2} including new electron field emitters in panel displays,³ single-molecular transistors in microelectronics,⁴ molecular-filtration membranes,⁵ and artificial muscles.⁶ The preparation of aligned and/or patterned carbon nanotubes is of paramount importance to the above and many other applications. Aligned carbon nanotubes have been prepared either by postsynthesis fabrication⁷ or by synthesis-induced alignment,⁸ while several rational approaches have been reported for fabricating micropatterns of *randomly oriented* carbon nanotubes.^{9,10} Very recently, two research groups have independently reported the preparation of carbon nanotube patterns with constituent nanotubes *aligned normal* to the substrate surface.^{11,12} In particular, we have produced patterns of perpendicularly aligned carbon nanotubes through growth of the nanotubes on a partially masked surface by pyrolysis of molecules containing both the metal catalyst and carbon source required for the nanotube growth (e.g., iron(II) phthalocyanine, FePc).¹² We have also developed a contact printing process for region-specific transfer of a substrate-free aligned nanotube film onto various substrates, including those which otherwise may not be suitable for nanotube growth at high temperatures (e.g., polymer films).¹² As can be seen in both refs 11 and 12, however, the use of physical masks, rather than photomasks, with features on the order of 10–100 μm leads to a rather limited resolution for the resulting nanotube patterns.^{11,12} We report here a novel approach to fabrication of patterns of perpendicularly aligned carbon nanotubes with resolutions down to μm scale by pyrolyzing FePc onto a quartz substrate pre-patterned with a photoresist film.

The use of FePc for producing large-area, aligned carbon nanotubes has been discussed in detail elsewhere.^{8,12} Figure 1

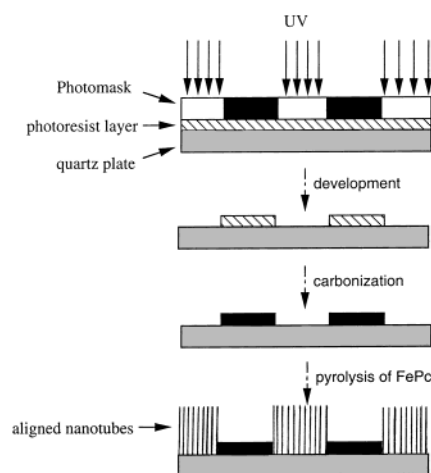
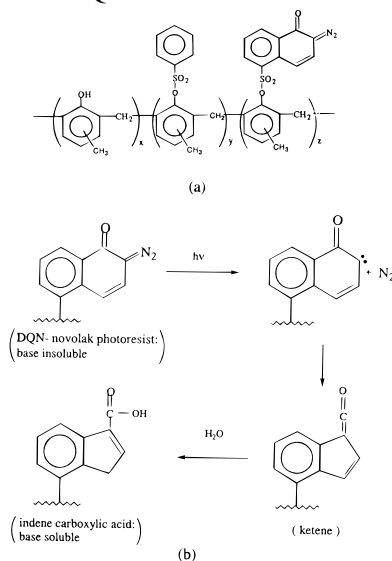


Figure 1. Schematic representation of the micropattern formation of aligned carbon nanotubes by the photolithographic process.

Scheme 1. (a) Molecular Structure of the DNQ-Novolak Photoresist Used in This Study^a and (b) Photochemical Reactions of the DNQ-Novolak Photoresist



^a The weight ratio for the x, y, and z units is 0.840:0.035:0.125.

shows the steps of the photolithographic process.¹³ Prior to the pyrolysis, a thin layer of a diazonaphthoquinone (DNQ)-modified cresol novolak photoresist¹⁴ (Scheme 1a) coating ($\sim 0.2 \mu\text{m}$) was prepared by spin-casting the photoresist solution (30 g resin in 100 mL of ethoxyethyl acetate) onto a quartz glass plate, followed by drying in an oven at 80 $^{\circ}\text{C}$ for 10 min. Upon UV irradiation ($\sim 120 \text{ mJ}/\text{cm}^2$, consisting of major emission components at 365 and 436 nm) through a photomask by a mercury arc lamp (EIMAC, VARIAN R150-8), the DNQ-novolak photoresist film in the regions was rendered soluble in an aqueous solution of sodium hydroxide (1wt % for 8 s) due to photogeneration of the hydrophilic indenecarboxylic acid groups from the hydrophobic DNQ via a photochemical Wolff rearrangement¹⁵ (Scheme 1b).

After having been rinsed with distilled water and baked at 80 $^{\circ}\text{C}$ for 10 min, the photoresist prepatterned quartz plate was first heated at high temperature under Ar atmosphere to carbonize the photoresist polymer into a carbon layer¹⁶ and then used as

(13) Dai, L. *J. Macromol. Sci. Rev. Macromol. Chem. Phys.* **1999**, 39(2), 237 and references therein.

(14) Wallraff, G. M.; Hinsberg, W. D. *Chem. Rev.* **1999**, 99, 1801.

(15) March, J. *Advanced Organic Chemistry*, 4th ed.; John Wiley: New York, 1992.

^{*} Corresponding author. E-mail: liming.dai@molsci.csiro.au.

[†] On leave of absence from Institute of Photographic Chemistry, The Chinese Academy of Sciences, Beijing 100101, China.

(1) Iijima, S. *Nature* **1991**, 354, 56.

(2) See, for example: (a) Yakobson, B. I.; Smalley, R. E. *Am. Sci.* **1997**, 85, 324. (b) Saito, R.; Deesselhaus, G.; Dresselhaus, M. S. *Physical Properties of Carbon Nanotubes*; Imperial College Press: London, 1998. (c) Ajayan, P. M. *Chem. Rev.* **1999**, 99, 1787.

(3) De Heer, W. A.; Bonard, J.-M.; Fauth, K.; Châtelain, A.; Forró, L.; Ugarte, D. *Adv. Mater.* **1997**, 9, 87 and references therein.

(4) See, for example: (a) Bockrath, M. D. H.; Cobden, P. L.; McEuen, N.; Chopra, A.; Zettl, A.; Thess, A. R.; Smalley, R. E. *Science* **1997**, 275, 1922. (b) Frank, S.; Poncharal, P.; Wang, Z. L.; de Heer, W. A. *Science* **1998**, 280, 1744.

(5) Che, G.; Lakshmi, B. B.; Fisher, E. R.; Martin, C. R. *Nature* **1998**, 393, 346.

(6) Baughman, R. H.; Changxing, C.; Zakhidov, A. A.; Iqbal, Z.; Barisci, J. N.; Spinks, G. M.; Wallace, G. G.; Mazzoldi, A.; de Rossi, D.; Rinzler, A. G.; Jaschinski, O.; Roth, S.; Kertesz, M. *Science* **1999**, 284, 1340.

(7) See, for example: (a) Ajayan, P. M.; Stephan, O.; Collix, C.; Trauth, D. *Science* **1994**, 265, 1212. (b) De Heer, W. A.; Bacsá, W. S.; Châtelain, A.; Gerfin, T.; Humphreybaker, R.; Forró, L.; Ugarte, D. *Science* **1995**, 268, 845.

(8) Huang, S.; Dai, L.; Mau, A. W. H. *J. Mater. Chem.* **1999**, 9, 1221 and references therein.

(9) (a) Kong, J.; Soh, H. T.; Cassell, A. M.; Quate, C. F.; Dai, H. *Nature* **1998**, 395, 878. (b) Xu, X.; Brandes, G. R. *Appl. Phys. Lett.* **1999**, 74, 2549.

(10) (a) Burghard, M.; Duesberg, G.; Philipp, G.; Muster, J.; Roth, S. *Adv. Mater.* **1998**, 10, 584. (b) Liu, J.; Casavant, M. J.; Cox, M.; Walters, D. A.; Boul, P.; Lu, W.; Rimberg, A. J.; Smith, K. A.; Colbert, D. T.; Smalley, R. E. *Chem. Phys. Lett.* **1999**, 303, 125.

(11) Fan, S.; Chapline, M. G.; Franklin, N. R.; Tomber, T. W.; Cassell, A. M.; Dai, H. *Science* **1999**, 283, 512.

(12) Huang, S.; Dai, L.; Mau, A. W. H. *J. Phys. Chem. B* **1999**, 103, 4223.

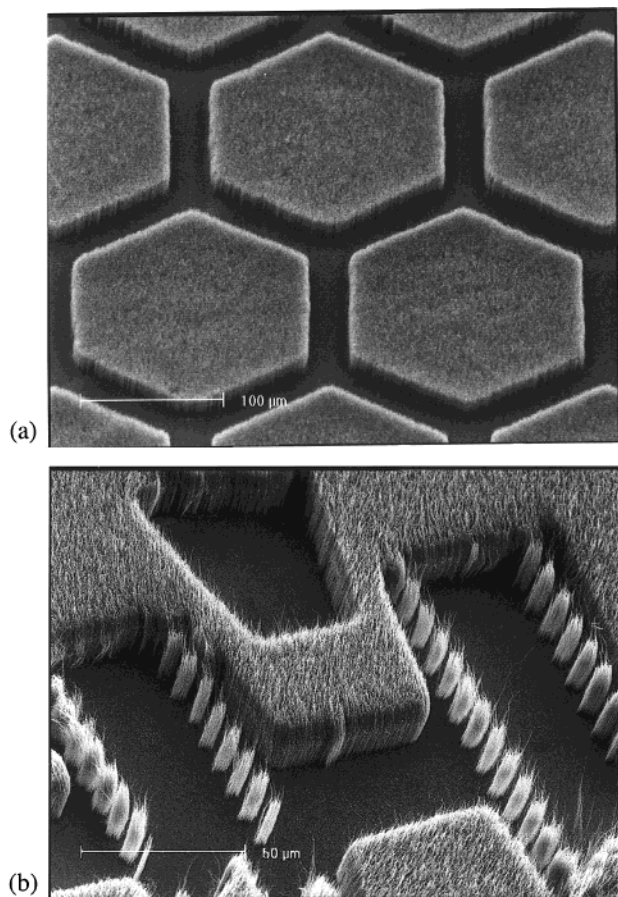


Figure 2. Typical SEM micrographs of the aligned carbon nanotube micropatterns produced by contact photolithography with a TEM grid consisting of hexagonal windows as the mask (a) and a photomask of μm resolution (b). To demonstrate the possibility of transferring the nanotube pattern with full integrity, the nanotube pattern shown in Figure 2b has been turned over from the quartz surface¹² which caused the slight pull-out seen for some of the carbon nanotubes.

the substrate for selectively growing aligned nanotubes in the photoresist-free regions by pyrolysis of FePc under Ar/H₂ at 800–1100 °C.¹² For comparison, we carried out initial experiments using a TEM grid as a “photomask”, which has similar hexagonal windows to the *physical mask* used in our previous study.¹² Although the nanotube patterns prepared on the quartz plate masked with the photolithographically patterned DNQ-novolac photoresist shown in Figure 2a is very similar to that in Figure 4a of ref 12, it is much more uniform than those produced by physical masking with TEM grids. Using a photomask with features on μm scale, *micropatterns* of the perpendicularly aligned carbon nanotubes, suitable for device fabrication, are produced as Figure 2b shows aligned nanotube bundles with a diameter of a few μm . As demonstrated earlier,¹² the constituent straight nanotubes have a well-graphitized structure with an outer diameter in the range of 35–55 nm. Both the geometry and the spatial resolution of the resulting nanotube micropatterns are limited mainly by the structure and resolution of the photomask used. Owing to the generic nature of the photolithographic technique,¹³ the micropatterning methodology developed in this study could be readily transferred to many other nanotube systems.

While the growth mechanism for the aligned nanotubes produced by the pyrolysis of FePc has been described previously,¹² the governing principle for the photolithographic formation of

(16) Carbonization of certain polymers has been previously reported (Parthasarathy, R. V.; Phani, K. L. N.; Martin, C. R. *Adv. Mater.* **1995**, *7*, 896 and references therein). Here, we carried out the carbonization through sequential heating of the DNQ-novolac photoresist coating at 150, 300, 500, 750, and 900 °C for 30 min. Our XPS and EDX analyses on the carbonized layer indicated the presence of carbon with a trace amount of sulfate, which may act as the cross-linking sides by decomposition of the DNQ groups.

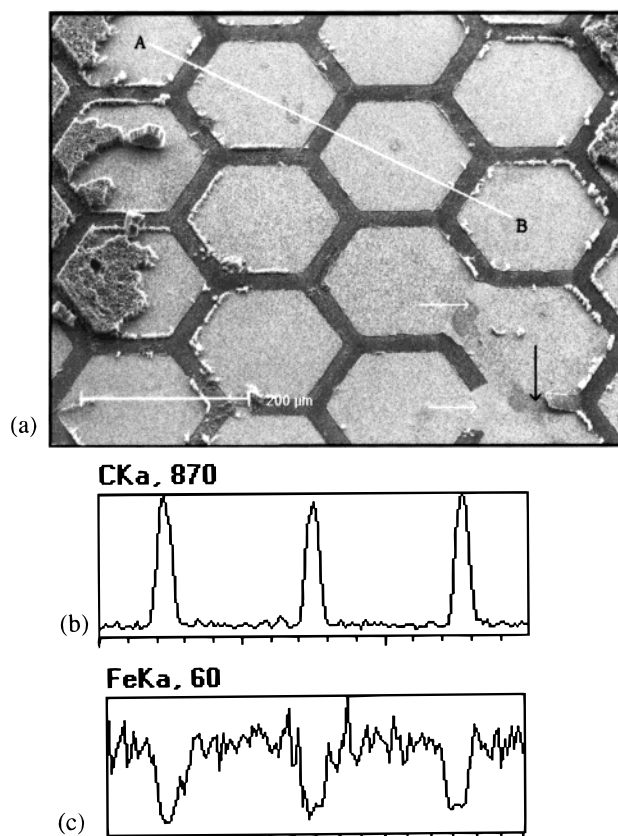


Figure 3. (a) The same SEM micrograph for the aligned carbon nanotube micropatterns as shown in Figure 2a, but most of the carbon nanotubes were removed for examining the carbonized photoresist layer. (Although the as-synthesized aligned nanotubes form a cohesive and adhering film on the quartz surface, they can be peeled off from the substrate by a Scotch tape pre-pressed on the nanotube layer). The arrows indicate the areas where the carbonized photoresist layer were deliberately removed (the black arrow points to the part of the carbonized photoresist layer which was partially peeled off from the quartz substrate). EDX profiles of C K α (b) and Fe K α (c) recorded after and before the removal of nanotubes, respectively. The scanning path for the EDX line analyses is indicated by the line between points A and B in Figure 3a.

the aligned nanotube micropatterns needs to be clarified. Figure 3a, together with the associated energy-dispersive X-ray (EDX) line analysis of C K α (Figure 3b), clearly shows the presence of a thin layer of pinhole-free, carbon-rich coating in the nanotube-free regions. This indicates the formation of a patterned carbon-black layer on the quartz plate prepatterned with the DNQ-novolac photoresist coating upon carbonization.¹⁶ In addition, the EDX line analysis of Fe K α in the same region before the removal of carbon nanotubes (Figure 3c) shows a preferential deposition of Fe in the nanotube-covered areas on the photoresist-patterned quartz surface due, most probably, to the localized surface energy effect on the nucleation of Fe particles.^{8,17} As a result, the photoresist-covered regions cannot support nanotube growth, whereas the photoresist-free areas can effectively stimulate the growth of the aligned carbon nanotubes. The presence of metal catalysts is known to be mandatory for the nucleation and growth of carbon nanotubes by pyrolysis of FePc.¹²

In summary, we have, for the first time, photolithographically fabricated micropatterns of perpendicularly aligned carbon nanotube arrays. The nanotube micropatterns thus prepared have an unprecedentedly high resolution down to μm scale. This, together with the generic character of the photolithographic process, represents a significant advance in the micropatterning of aligned carbon nanotubes for device applications, especially as new electron field emitters in panel displays.

JA992945Q

(17) Ohara, P. C.; Gelbart, W. M. *Langmuir* **1998**, *14*, 3418.