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LETTERS

Patterned Growth of Well-Aligned Carbon Nanotubes: A Soft-Lithographic Approach

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Using microcontact printing (μCP) and micromolding techniques, we have prepared micropatterns of carbon nanotubes aligned in a direction normal to the substrate surface. While the μCP process involves the region-specific transfer of self-assembling monolayers (SAMs) of alkylsiloxane onto a quartz substrate and subsequent adsorption of polymer chains in the SAM-free regions, the micromolding method allows the formation of polymer patterns through solvent evaporation from a precoated thin layer of polymer solution confined between a quartz plate and a poly(dimethylsiloxane) (PDMS) elastomer mold. The polymer patterns formed in both cases were then carbonized into carbon black for region-specific growth of the aligned nanotubes in the polymer-free regions by pyrolysis of iron(II) phthalocyanine (FePc) under Ar/H_2 atmosphere at 800−1100 °C. Micropatterns of aligned nanotubes thus prepared have resolutions down to 0.8 μm, suitable for fabrication of various electronic and photonic devices.

Owing to their interesting physicochemical properties and molecular symmetries, carbon nanotubes are attractive materials for a variety of potential applications.[1] It has been a major challenge for researchers to find ways to control the arrangement of carbon nanotubes,[1] although a few approaches have recently been reported for fabricating aligned and/or patterned carbon nanotubes.[2] Soft-lithography has recently become a very promising technique for micro-/nanostructuring a wide range of materials.[3] Various strategies, including microcontact printing (μCP), mechanical scraping, and micromolding, have been developed for nanoscale patterning that otherwise is difficult by photolithography.[4] Using a poly(dimethylsiloxane) (PDMS) elastomer stamp, μCP has been shown to be a convenient method for generating self-assembled monolayer (SAM) patterns of certain "molecular inks" (e.g., alkanethiol, alkylsiloxane) on appropriate substrate surfaces (e.g., gold, silver, copper, aluminum, and silicon dioxide).[5] Alternatively, the solvent-assisted micromolding (SAMIM) technique allows pattern formation through solvent evaporation from a thin layer of polymer solution confined between a PDMS elastomer mold and a substrate surface.[6]

Following our previous investigation on patterning aligned nanotubes,[2a,c,d] we found that micro-/nanopatterns of certain polymers formed on quartz plates by soft-lithographic techniques (e.g., μCP and SAMIM) can be used as the substrate for patterned growth of carbon nanotubes. In this paper, we report the soft-lithographic generation of micro-/nanopatterns of carbon nanotubes well aligned in a direction normal to the substrate surface and their microscopic evaluation.

Figure 1a,b schematically shows the micro-/nanopatterning processes by μCP and SAMIM, respectively. To start with, all of the quartz glass plates were cleaned by heating in a Piranha solution (a mixture of 98% H_2SO_4 and 30% H_2O_2 at 7:3 v/v) at 70 °C for ca. 30 min, followed by thoroughly rinsing with deionized water. In the case of μCP (Figure 1a), a PDMS stamp was used for region specifically transferring a SAM of octadecyltrichlorosilane (OTS) onto a cleaned quartz surface. In a typical experiment, the PDMS stamp precoated with the OTS "molecular ink" (i.e., 0.2% w/w of OTS in hexane) was kept in

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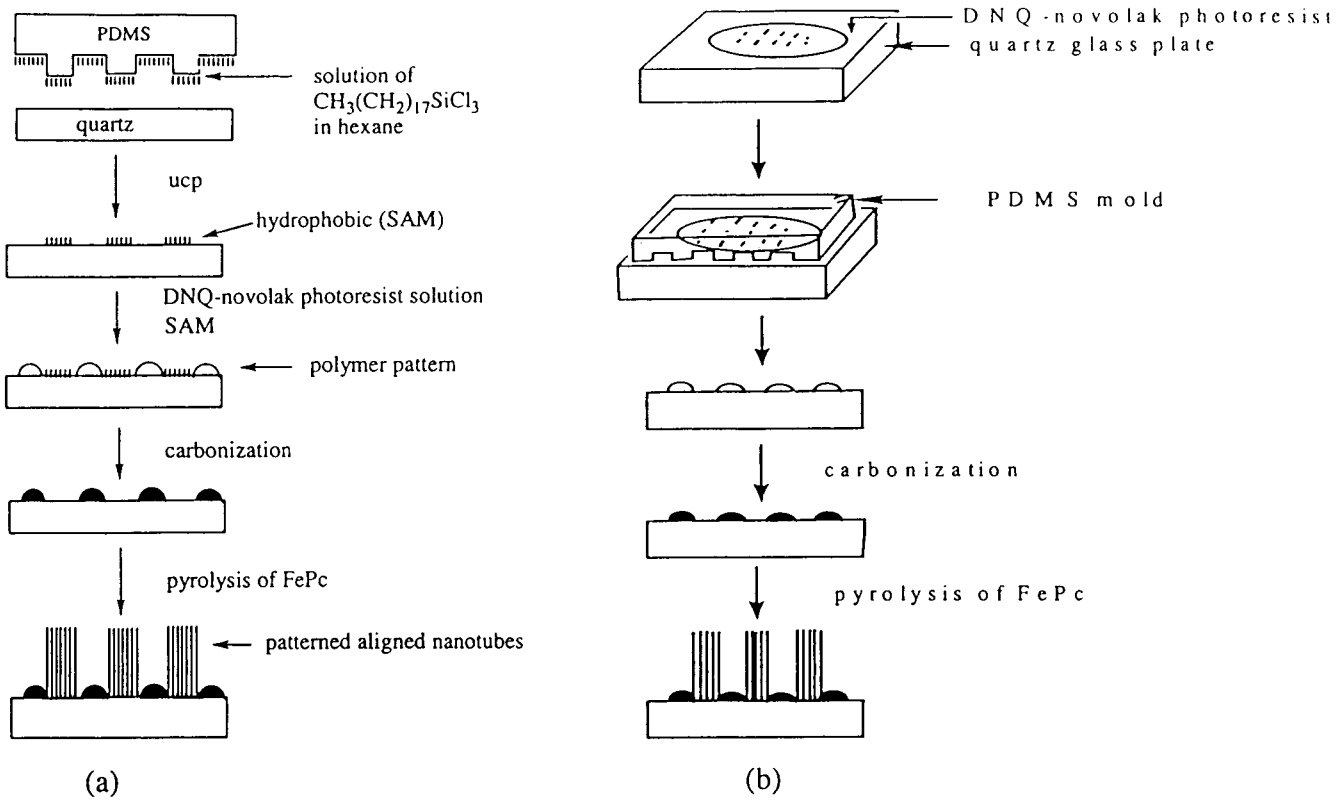


Figure 1. Schematic illustration of the procedure for fabricating patterns of aligned nanotubes by (a) microcontact printing (μCP); (b) solvent-assisted micromolding (SAMIM).

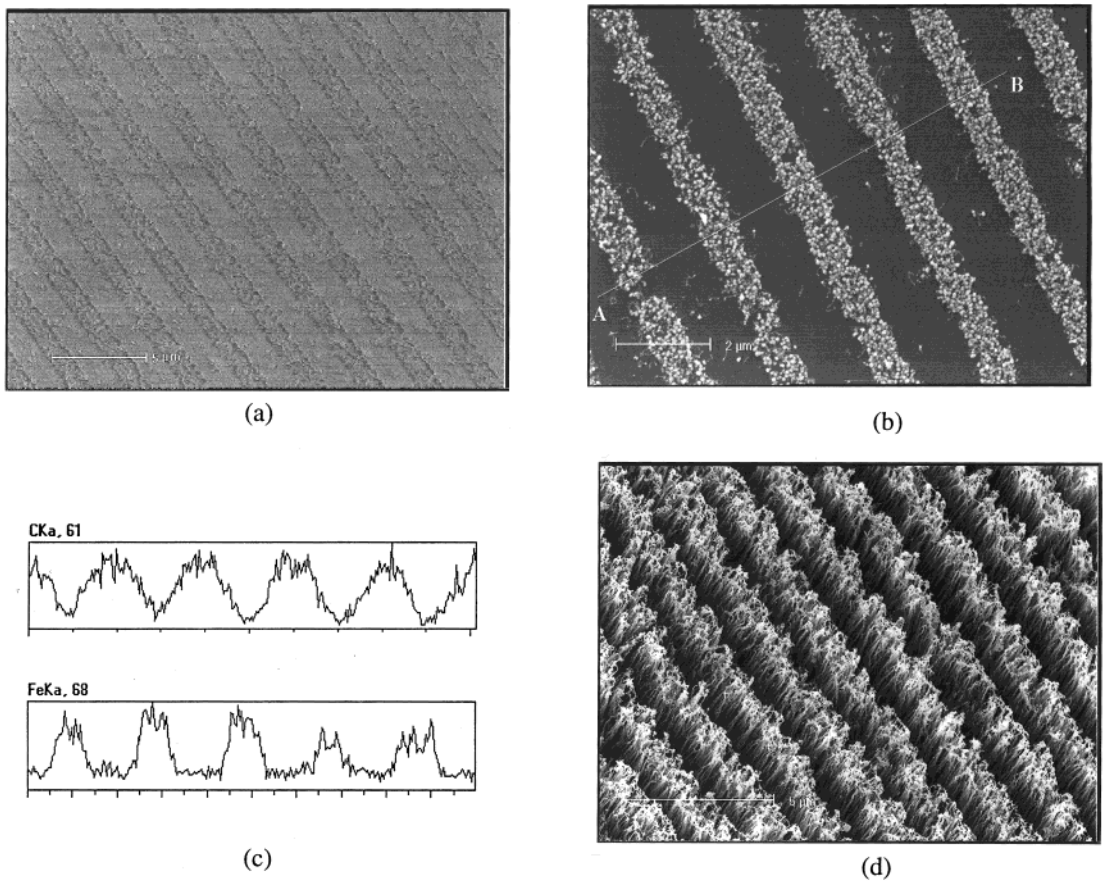


Figure 2. SEM images of (a) DNQ-novolak photoresist pattern formed on an OTS-prepatterned quartz glass plate; (b) carbon-surrounded Fe particles selectively deposited in the photoresist-free regions; (c) EDX profiles of C and Fe (the scanning path for the EDX analyses are indicated by the line between points A and B in Figure 2b; (d) aligned nanotube arrays growing out from the photoresist-free regions.

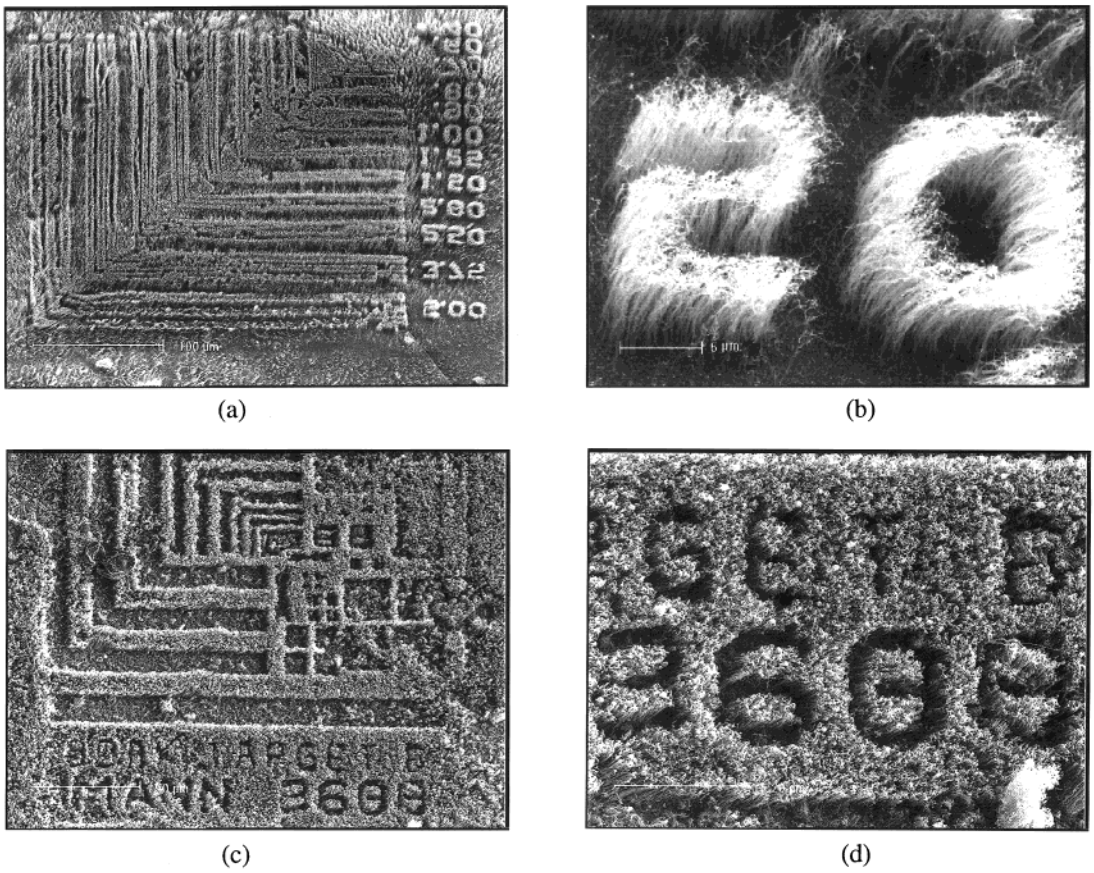
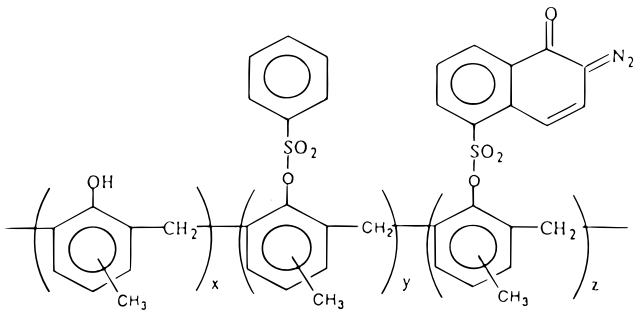


Figure 3. (a) Positive SEM image of aligned nanotube pattern on the photoresist prepatterned quartz substrate made by micromolding technique; (b) enlarged view of two chosen Arabic numerals in (a); (c) negative SEM image of aligned nanotube pattern on the photoresist prepatterned quartz substrate made by micromolding technique using a different mold from (a); (d) as for (c), under a higher magnification.

contact with the substrate for 15−30 s. The OTS patterned substrate was then immersed into a solution of diazonaphthoquinone (DNQ)-modified cresol novolak photoresist (Chart 1, 0.5−1.0 mg/mL) in ethoxyethyl acetate/acetone (1/10−1/5 v/v) for ca. 1−5 s, leading to selective adsorption of the polymer chains in the OTS-free regions. In the case of SAMIM (Figure 1b), a drop of the DNQ-novolak photoresist in the ethoxyethyl acetate/acetone (150−200 mg/mL) was spread out on a clean quartz plate and region specifically confined with a PDMS stamp by pressing. After drying in an oven at 80−100 °C for about 30 min, polymer patterns were observed upon the removal of the PDMS stamp. Prior to the nanotube growth, the polymer prepatterned quartz plates prepared in both cases were heated at high temperature under Ar atmosphere to carbonize the photoresist polymer into carbon black.[7] The carbon black prepatterned quartz plates were then used for patterned growth of well-aligned nanotubes in the photoresist-free regions by pyrolysis of FePc under Ar/H_2 at 800−1100 °C.[2a]

Figure 2a reproduces a scanning electron microscopic (SEM, XL-30 FEG SEM, Philips) image of the DNQ-novolak photoresist pattern formed on an OTS-prepatterned quartz glass plate through selective adsorption of polymer chains in the OTS-free regions. The driving force for the selective adsorption lies in the polar−polar interaction between the DNQ-novolak photoresist chains and the regions of *bare* quartz surface. Upon heating the prepatterned quartz plate shown in Figure 2a at high temperatures under an Ar atmosphere,[7] the DNQ-novolak photoresist pattern was carbonized into carbon black and remained on the quartz substrate whereas the μCP-transferred OTS molecules desorbed from the surface. Carbonization of the photoresist polymer arose, most probably, from the cross-

CHART 1. Chemical Structure of the DNQ-novolak Photoresist Used in this Study (the weight ratio for the *x*, *y*, and *z* units is 0.840:0.035:0.125, and the weight-averaged molecular weight is about 7500).



linking effect of sulfate species originating from decomposition of *o*-diazonaphoquinone groups along the polymer backbone, as our X-ray photoelectron spectroscopic (XPS, Kratos Analytical, monochromatized Al Kα at 200 W) and energy-dispersive X-ray (EDX) analyses on the carbonized layer indicated the presence of carbon with a trace amount of sulfate.

Figure 2b represents a typical SEM image taken at the initial stage of the pyrolysis of FePc using a carbon black prepatterned quartz plate as the substrate. Comparing Figure 2b with the corresponding EDX profiles for C and Fe (Figure 2c), it is evident that the carbon-surrounded Fe particles formed at the initial stage of the nanotube growth[2a] preferentially deposited in the regions uncovered by the carbonized polymer pattern, presumably due to a localized surface energy effect associated with the prepatterned substrate.[2a,8] The presence of metal

catalysts is known to be mandatory for the nucleation and growth of carbon nanotubes by pyrolysis of FePc.[2a,c,d] Patterned deposition of the carbon-surrounded Fe particles, therefore, led to region-specific growth of aligned nanotubes.[2] A typical SEM micrograph of the aligned nanotube micropatterns thus prepared is given in Figure 2d, which shows arrays of the same width (ca. 0.8 μm) as those OTS lines. As can be seen in Figure 2d, the aligned nanotubes are densely packed along the line length, but certain parts of the nanotube lines contain only a few nanotubes across the line width. Clearly, therefore, it should be of interest to fabricate aligned nanotube arrays with a single-nanotube width.

While the present work was in progress, μCP of catalysts for confined nanotube growth was reported.[9] Just as μCP has broadened our capability for micro-/nanostructuring of aligned carbon nanotubes, SAMIM has been shown to be another effective method for the same purpose. In this regard, we prepared the DNQ-novolak photoresist patterns by the SAMIM method described above (Figure 1b). Prior to the region-specific growth of aligned nanotubes by pyrolysis of FePc under Ar/H_2 at 800−1100 °C,[2a] the polymer patterned quartz plate was carbonized at high temperatures under Ar atmosphere, as was the case with the μCP approach.[7] Figure 3a shows a typical positive SEM image for the aligned nanotube pattern thus prepared. Inspection of Figure 3a at a higher magnification (Figure 3b) clearly shows Arabic numerals consisting of aligned nanotube bundles on a μm scale. As demonstrated earlier,[2a] the constituent straight nanotubes have a well-graphitized structure with an outer diameter in the range of 35−55 nm. Negative SEM images for the aligned nanotube patterns prepared with a different mold are given in Figure 3c,d. In all the cases, the spatial resolution is limited by the resolution of the mask used. Unlike μCP patterning, SAMIM method eliminates the SAM pattern formation and selective adsorption of DNQ-novolak photoresist chains, and hence could serve as a more convenient approach for fabricating micro-/nanopatterns of the aligned nanotubes.

In summary, we have demonstrated the use of soft lithographic techniques, including μCP and micromolding, for fabricating patterned carbon nanotube arrays aligned perpendicularly to the substrate. The aligned nanotube patterns thus prepared have resolutions down to submicrometer scale. These facile methods for generating micro-/nanopatterns of aligned nanotubes could open avenues for fabricating various nanodevices for a wide range of potential applications, ranging from novel electron emitters in flat panel displays[1d] to artificial muscles.[10] The ease with which micro-/nanopatterns of organic materials can be made on curved surfaces by the soft lithographic techniques[3] should provide additional benefits to this approach, especially for the construction of flexible devices.

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References and Notes

(1) See, for example: (a) Dresselhaus, M. S.; Dresselhaus, G.; Eklund, P. C. *Science of Fullerenes and Carbon Nanotubes*; Academic Press: New York, 1996. (b) Ebbesen, T. W. *Phys. Today* **1996**, 26 (June). (c) Yakobson, B. I.; Smalley, R. E. *American Scientist* **1997**, *85*, 324 (July-August). (d) de Heer, W. A.; Bonard, J.-M.; Fauth, K.; Châtelain, A.; Forró, L.; Ugarte, D. *Adv. Mater.* **1997**, *9*, 87. (e) Ebbsen, T. *Carbon Nanotubes*; CRC Press: Boca Raton, Florida, 1997. (f) Ajayan, P. M.; Ebbesen, T. W. *Rep. Prog. Phys.* **1997**, *60*, 1025. (g) Edelmann, F. T. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 1381. (h) Birkett, P. R.; Terrones, M. *Chem. Brit.* **1999**, *May*, 45. (i) Poncharal, P.; Wang, Z. L.; Ugarte, D.; de Heer, W. A. *Science* **1999**, *283*, 1513. (j) Dekker, C. *Phys. Today* **1999**, *May*, 22. (k) Ajayan, P. M. *Chem. Rev.* **1999**, *99*, 1787. (l) Xia, Y.; Rogers, J. A.; Paul, K. E.; Whitesides, G. M. *Chem. Rev.* **1999**, *99*, 1823.

(2) See, for example: (a) Huang, S.; Dai, L.; Mau, A. W. H. *J. Phys. Chem. B* **1999**, *103*, 4223, and reference cited therein. (b) Fan, S.; Chapline, M. G.; Franklin, N. R.; Tomber, T. W.; Cassell, A. M.; Dai, H. *Science* **1999**, *283*, 512. (c) Huang, S.; Dai, L.; Mau, A. W. H. *J. Mater. Chem.* **1999**, *9*, 1221. (d) Yang, Y.; Huang, S.; He, H.; Mau, A. W. H.; Dai, L. *J. Am. Chem. Soc.*, in press.

(3) See, for example: (a) Xia, Y.; Whitesides, G. M. *Annu. Rev. Mater. Sci.* **1988**, *28*, 153. (b) Xia, Y.; Whitesides, G. M. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 550. (c) Jackman, R. J.; Whitesides, G. M. *CHEMTECH* **1999**, *May*, 18.

(4) Dai, L. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1999**, *39*, 273, and references therein.

(5) See, for example: (a) Kumar, A.; Whitesides, G. M. *Appl. Phys. Lett.* **1993**, *63*, 2002. (b) Jacoby, M. *C&E News* **1997**, *October 6*, 34. (c) Kumar, A.; Biebuyck, H. A.; Whitesides, G. M. *Langmuir* **1994**, *10*, 1498.

(6) (a) Kim, E.; Xia, Y.; Zhao, X.-M.; Whitesides, G. M. *Adv. Mater.* **1997**, *9*, 651. (b) Rogers, J. A.; Bao, Z.; Dhar, L. *Appl. Phys. Lett.* **1998**, *73*, 294.

(7) Carbonization of certain polymers has been previously reported (see, for example: (a) Kyotani, T.; Nagai, T.; Inoue, S.; Tomita, A. *Chem. Mater.* **1997**, *9*, 609. (b) Parthasarathy, R. V.; Phani, K. L. N.; Martin, C. R. *Adv. Mater.* **1995**, *7*, 896). In the present study, we carried out the carbonization through sequential heating of the DNQ-novolak photoresist coating at 150, 300, 500, 750, and 900 °C for 30 min under Ar atmosphere.

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

(9) (a) Cassell, A. M.; Franklin, N. R.; Tombler, T. W.; Chan, E. M.; Han, J.; Dai, H. *J. Am. Chem. Soc.* **1999**, *121*, 7975. (b) Kind, H.; Bonard, J.-M.; Emmenegger, C.; Nilsson, L.-O.; Hernadi, K.; Maillard-Schaller, E.; Schlapbach, L.; Forró, L.; Kern, K. *Adv. Mater.* **1999**, *11*, 1285.

(10) 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.