Preparation of Aligned Carbon Nanotubes with Prescribed Dimensions: Template Synthesis and Sonication Cutting Approach

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Aligned multiwalled carbon nanotubes (CNTs) with good crystallinity have been obtained by cutting the CNTs grown on an anodic aluminum oxide (AAO) template by a sonication method. AAO templates were fabricated by two-step anodization of Al. After the cobalt catalyst had been electrochemically deposited at the bottom of the pores in the AAO template, CNTs were grown in a gas mixture of 10% C_2H_2 and 20% H_2 in an Ar carrier gas at 650 °C. After the 40 min growth, CNTs grew out of pores up to 10 μm with a wide length distribution. Sonication of CNTs on the AAO template in an acetone solution cut the overgrown CNTs effectively, resulting in short multiwalled CNTs on the AAO template. We obtained CNTs with a narrow length distribution by etching the AAO template away. The formation mechanism of these cut CNTs is discussed along with their potential applications.

Introduction

Carbon nanotubes (CNTs) have been drawing much attention because of their unique properties and wide variety of applications.[1−4] Depending on the diameter and chirality of the graphene layer, CNTs can exhibit semiconducting or metallic behavior.[5] Potential applications include field emitters in field emission displays,[6,7] hydrogen storage,[8] and molecular sieves.[9]

A reliable preparation method to control the dimension, location, and structure of CNTs is highly desirable for most of these applications as well as for fundamental studies. For example, in the fabrication of field emitters using CNTs, an outstanding problem to be solved is the control of the length of aligned CNTs in the submicron scale without their outgrowth from a gate hole.[10,11] Although there have been a few investigations to control the height of aligned CNTs via CNT growing time,[10−12] precise and reproducible control of the length of CNTs has seldom been achieved.

Anodic aluminum oxide (AAO) has been used for the fabrication of CNTs.[13−18] CNTs synthesized in this method have very uniform diameter and length, which are the same dimensions of the pores in the AAO template. However, these CNTs have very poor crystallinity.[17−19] Recently, Sui et al.[17] showed that CNTs prepared by the pyrolysis of C_2H_2 at 650 °C in an AAO template had tube wall structures consisting of numerous stacked carbon flakes, instead of straight coaxial cylindrical graphite units. This is due to the carbon deposition by the catalytic action of the pore walls in the AAO template itself.[17,20]

In our previous works,[20,21] we showed that highly graphitized CNTs, which have almost the same diam-

(1) De Heer, W. A.; Chatelain, A.; Ugarte, D. *Science* **1995**, *270*, 1179.
(2) Collins, P. G.; Zettle, A.; Bando, H.; Thess, A.; Smally, R. E. *Science* **1997**, *278*, 100.
(3) Ugarte, D.; Stockli, T.; Bonard, J.-M.; Chatelain, A.; De Heer, W. A. *Appl. Phys. A* **1998**, *67*, 101.
(4) Murakami, H.; Hirakawa, M.; Tanaka, C.; Yamakawa, H. *Appl. Phys. Lett.* **2000**, *76*, 1776.
(5) Carroll, D. L.; Redlich, P.; Ajayan, P. M.; Charlier, J. C.; Blase, X.; De Vita, A.; Car, R. *Phys. Rev. Lett.* **1997**, *78*, 2811.
(6) De Heer, W. A.; Basca, W. S.; Chatelain, A.; Gerfin, T.; Humphreybaker, R.; Forro, L.; Ugarte, L. D. *Science* **1995**, *268*, 845.
(7) Fan, S.; Chapline, M. G.; Franklin, N. R.; Tomber, T. W.; Cassell, A. M.; Dai, H. *Science* **1999**, *283*, 512.
(8) Liu, C.; Fan, Y. Y.; Liu, M.; Cong, H. T.; Cheng, H. M.; Dresselhaus, M. S. *Science* **1999**, *286*, 1127.
(9) Che, G.; Lakshmi, B. B.; Fisher, E. R.; Martin, C. R. *Nature* **1998**, *393*, 346.
(10) Xu, X.; Brandes, G. R. *Mater. Res. Soc. Symp. Proc.* **1998**, *509*, 107.
(11) Lee, Y.-H.; Jang, Y.-T.; Kim, D.-H.; Ahn, J.-H.; Ju, B.-K. *Adv. Mater.* **2001**, *13*, 479.
(12) Kim, H. J.; Han, J.-H.; Yang, W.-S.; Yoo, J.-B.; Park, C.-Y.; Han, I.-T.; Park, Y.-J.; Jin, Y.-W.; Jung, J. E.; Lee, N.-S.; Kim, J.-M. *Mater. Sci. Eng. C* **2001**, *16*, 27.
(13) Kyotani, T.; Tsai, L.; Tomita, A. *Chem. Mater.* **1995**, *7*, 1427.
(14) Parthasarathy, R. V.; Phani, K. L. N.; Martin, C. R. *Adv. Mater.* **1995**, *7*, 896.
(15) Li, J.; Papadopoulos, C.; Xu, J. M.; Moskovits, M. *Appl. Phys. Lett.* **1999**, *75*, 367.
(16) Suh, J. S.; Lee, J. S. *Appl. Phys. Lett.* **1999**, *75*, 2047.
(17) Sui, Y. C.; Acosta, D. R.; Gonzalez-Leon, J. A.; Bermudez, A.; Feuchtwanger, J.; Cui, B. Z.; Flores, J. O.; Saniger, J. M. *J. Phys. Chem. B* **2001**, *105*, 1523.
(18) Hornyak, G. L.; Dillon, A. C.; Parilla, P. A.; Schneider, J. J.; Czap, N.; Jones, K. M.; Fasoon, F. S.; Mason, A.; Heben, M. J. *Nanostruct. Mater.* **1999**, *12*, 83.
(19) Bonard, J.-M.; Kind, H.; Stöckli, T.; Nilsson, L.-O. *Solid State Electron.* **2001**, *45*, 893.

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eter as that of pores in an AAO template, overgrow out of pores by catalytic action of a Co catalyst in the pyrolysis of C_2H_2 with added H_2. Although these CNTs possess crystallinity as good as the CNTs grown on a silicon wafer by a conventional chemical vapor deposition process, precise control of the length of aligned CNTs has not been possible in this case.

Recently, much work has been undertaken on the cutting method of CNTs and the understanding of properties of cut CNTs. Liu et al.[22] reported the sonication method with an oxidizing acid to cut single-walled CNTs. Short, multiwalled CNTs have been prepared by boiling CNTs in a concentrated acid solution,[23] grinding in a ball mill,[24,25] or treating abrasively.[26] Short CNTs with open ends are advantageous to overcome the diffusion limitation[24,27] for the applications of hydrogen storage or molecular sieves. However, the conditions for preparing cut CNTs in the conventional methods are very severe, and the length of cut CNTs has a broad distribution. Moreover, they exist in a randomly dispersed state, so that placing these CNTs in the exact locations is not straightforward in the application of electronic devices.

In this paper, we report an efficient and reliable cutting method of CNTs, which are attached on a substrate by template-assisted sonication. Because the aligned CNTs with good crystallinity can be prepared on an AAO substrate by this method, there is a clear advantage in the fabrication of various electronic devices. Almost identical CNTs with good crystallinity can also be obtained by etching the template away.

Experimental Section

First, a high-purity (99.999%) aluminum sheet was degreased in acetone with ultrasound and rinsed in an ethanol solution. Subsequently, the aluminum sheet was electropolished in a mixture of perchloric acid and ethanol to obtain the mirror finish. A two-step anodization was chosen to prepare an ordered AAO template.[28] An Al sheet was anodized at 40 V in a 0.3 M oxalic acid solution at 15 °C for 12 h. After the AAO film was chemically etched in a mixture of phosphoric acid and chromic acid, reanodization was performed under the same conditions for 10 min, which resulted in the formation of a highly ordered AAO template with a pore depth of 1 μm. At the end of the second anodization, the voltage was dropped from 40 to 14 V by 1 V steps in order to decrease the thickness of the alumina layer at the bottom of the pores, which is important to facilitate the uniform electrodeposition of the Co catalyst.

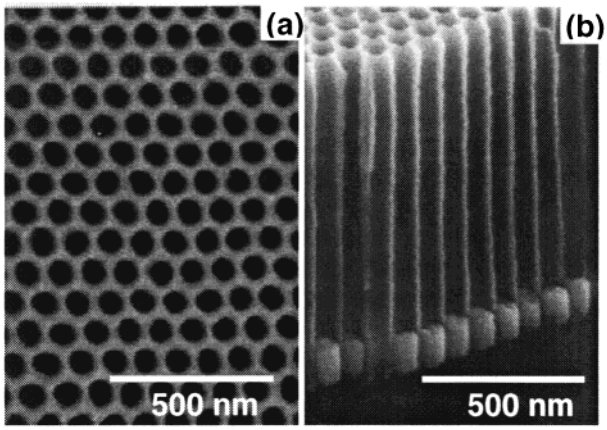

Figure 1. SEM images of (a) the AAO template surface (40 V anodization and 50 min of widening) and (b) Co catalyst particles at the bottom of the pores.

After the voltage drop process, the pore diameter of the AAO template was adjusted to 80 nm in a pore-widening solution of 0.1 M phosphoric acid. The Co catalyst was electrochemically deposited at the pore bottom of the AAO template in a 5% $CoSO_4 \cdot 7H_2O$ solution stabilized with 2% H_3BO_3 by applying 18 V_{rms} ac voltage for 1 min.

Co particles were reduced in a gas mixture of 10% H_2 and 90% Ar at 500 °C for 1 h. CNTs were then grown by catalytic pyrolysis of 10% C_2H_2 and 20% H_2 in an Ar carrier gas for 40 min at 650 °C in a quartz tube reactor. The total flow rate was 200 sccm.

Cutting of CNTs was performed as follows. In a typical experiment, overgrown CNTs with the AAO template were dipped in a 50 mL acetone solution in a 100 mL test tube and sonicated in a water bath (Jeio Tech, 1505) at 40 kHz for several seconds to about 1 h at 30−40 °C.

The morphology and structure of CNTs were observed with a field emission scanning electron microscope (FE-SEM; Hitachi S-4200) and a high-resolution transmission electron microscope (HRTEM; Philips CM20) after etching the AAO template in a chromic acid and phosphoric acid solution. CNTs were collected on a 0.1 μm pore filter membrane (type VCTP; Millipore) and washed with an ethanol solution several times before microscopic observation.

Results and Discussion

Figure 1a shows the SEM image of the AAO template after two-step anodization and pore widening treatment. Nanopores of the AAO template form a periodic hexagonal close-packed array. The domain size of this perfect two-dimensional array is about 3−4 μm. The average diameter and the density of pores in the AAO template are 79.8 ± 3.4 nm and 1.0×10^{10} pores/cm^2, respectively. Figure 1b is the cross-sectional view of the AAO template after Co electrodeposition. We can observe the straight parallel pores of 1 μm depth, perpendicular to the AAO template surface. Co catalysts were uniformly electrodeposited at the bottom of the pores in the AAO template.

Figure 2 is the SEM image of the CNTs grown out of the pores of the AAO template. The inset is the high-magnification SEM image of CNTs near the pore mouth of the AAO template. CNTs are highly uniform in diameter with an average of 90.2 ± 3.2 nm. The diameter of CNTs is somewhat larger than that of the pores in the AAO template, which is thought to be due to water loss[16] of the template during the CNT growth. In our blank experiment without C_2H_2 flow, 4.5 wt % mass loss and a diameter increase of about 10 nm of

(20) Jeong, S.-H.; Hwang, H.-Y.; Lee, K.-H.; Cho, W.-K.; Kim, K.-Y.; Jeong, H.-S. Cold Cathodes. In *Proceedings of the 198th Meeting of the Electrochemical Society*; Cahay, M., et al., Eds.; The Electrochemical Society: Pennington, NJ, 2000; p 65.
(21) Jeong, S.-H.; Hwang, H.-Y.; Lee, K.-H.; Jeong, Y. *Appl. Phys. Lett.* **2001**, *78*, 2052.
(22) 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.; Macias, F. R.; Shon, Y.; Lee, T. R.; Colbert, D. T.; Smalley, R. E. *Science* **1998**, *280*, 1253.
(23) Jia, Z.; Wang, Z.; Liang, J.; Wei, B.; Wu, D. *Carbon* **1999**, *37*, 903.
(24) Pierard, N.; Fonseca, A.; Konya, Z.; Willems, I.; Tendeloo, G. V.; Nagy, J. B. *Chem. Phys. Lett.* **2001**, *335*, 1.
(25) Li, Y. B.; Wei, B. Q.; Liang, J.; Yu, Q.; Wu, D. H. *Carbon* **1999**, *37*, 493.
(26) Maurin, G.; Stepanek, I.; Bernier, P.; Colomer, J.-F.; Nagy, J. B.; Henn, F. *Carbon* **2001**, *39*, 1273.
(27) Stepanek, I.; Maurin, G.; Bernier, P.; Gavillet, J.; Loiseau, A.; Edwards, R.; Jaschinski, O. *Chem. Phys. Lett.* **2000**, *331*, 125.
(28) Masuda, H.; Sotoh, M. *Jpn. J. Appl. Phys.* **1996**, *35*, L126.

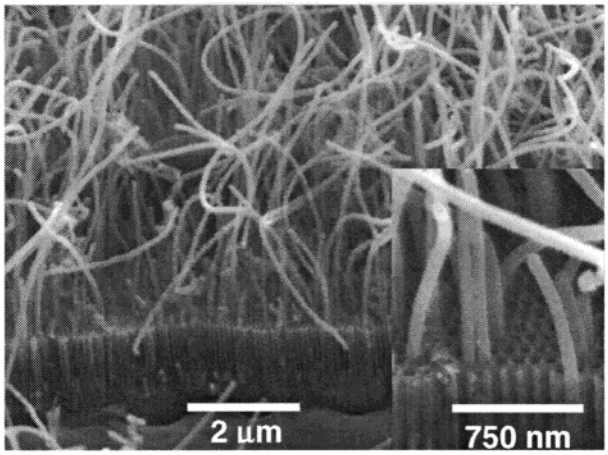

Figure 2. SEM image of the CNTs grown out of the AAO template pores. Inset: SEM image of high magnification near the pore mouth.

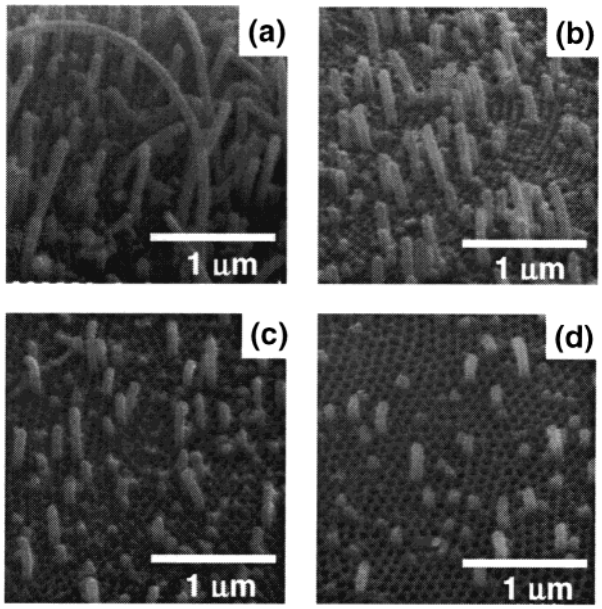

Figure 3. SEM images of the CNTs on the AAO template after the sonication process in an acetone solution. Sonication periods are 10 s (a), 1 min (b), 10 min (c), and 60 min (d).

the AAO template were found. We can also observe that the packing density of overgrown CNTs from the pore of the AAO template lies in the range of $(2-3) \times 10^9$ CNTs/cm^2. CNTs have a tendency to align normal to the surface near the pore mouth. However, as the length of the CNTs increases, they become more curved. This observation is a consequence of the disappearance of the pore confinement effect,[29] which made the CNTs stand normal to the AAO template surface near the pore mouth. However, it should be noted that the diameters of the CNTs observed at the tip and near the pore mouth are the same, within measurement error.

Figure 3 is the SEM images of the cut CNTs on the AAO template after sonication in an acetone solution with different time periods. SEM observation of these samples reveals that the length of overgrown CNTs above the AAO template decreases with sonication time. As is seen in Figure 3a, most of the overgrown CNTs

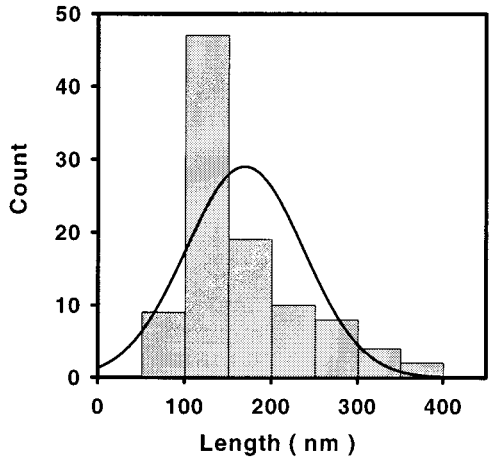

Figure 4. Histogram of measured length of the overgrown CNTs above the AAO template after 60 min of sonication.

are shorter than 2 μm after sonication for 10 s, and only a few long CNTs remain above the AAO template. After a 1 min sonication treatment, no overgrown CNTs longer than 1 μm are found over the observation area (Figure 3b). As the cutting process proceeds, the length of overgrown CNTs above the AAO template continuously decreases (Figure 3c,d).

Our method of cutting CNTs is different from other methods in view of the uniformity in the length of cut CNTs. As shown in Figure 4, most of the CNTs above the template have a length of 100−200 nm after a 60 min sonication treatment. Because the length of pores in the AAO template can be extended in the order of a hundred microns, the total lengths of cut CNTs are almost identical to each other. On the other hand, cut CNTs, prepared either by ball milling or by sonication in an acidic solution,[24−27] have a wide length distribution. For example, Pierard et al.[24] obtained the cut multiwalled CNTs with a length of 100 nm to 2 μm after 120 h of ball milling.

Another advantage of our method is the protection of the surface of CNTs by the AAO template during sonication. It is well-known that cavitation bubbles produced in the sonication bath can instantaneously generate local spots of several thousand degrees Celsius and thousand atmospheres.[30] These local spots attack the surface of the CNTs during sonication as well as the chemical attack by a strong acid in the conventional method, which is not the case with our method.

The cut CNTs on a substrate by our method align normal to the surface of the AAO template. This fact becomes advantageous to many microelectronic device applications.

Figure 5 depicts a plausible mechanism for the cutting of CNTs on an AAO template. A CNT on an AAO template can be considered as a cantilever. The stress caused by the bending and vibration of a CNT in an ultrasound atmosphere is largest at the point of the pore mouth of the AAO template, so that the breakage will most likely occur at this point. Because the stress is larger with a longer cantilever, longer CNTs break first, and then the shorter ones follow. The stress on a shorter CNT is smaller, so that the cutting process slows down with time.

(29) 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.

(30) Mason, T. J. *Sonochemistry*; Oxford University Press: New York, 1999.

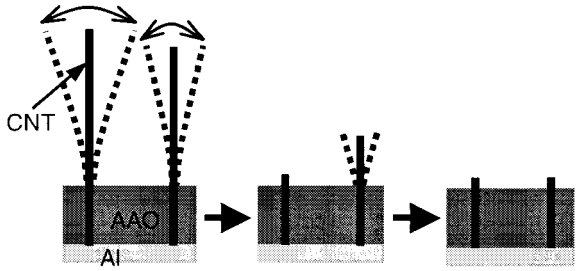

Figure 5. Schematic of the cutting sequence of the CNTs during sonication.

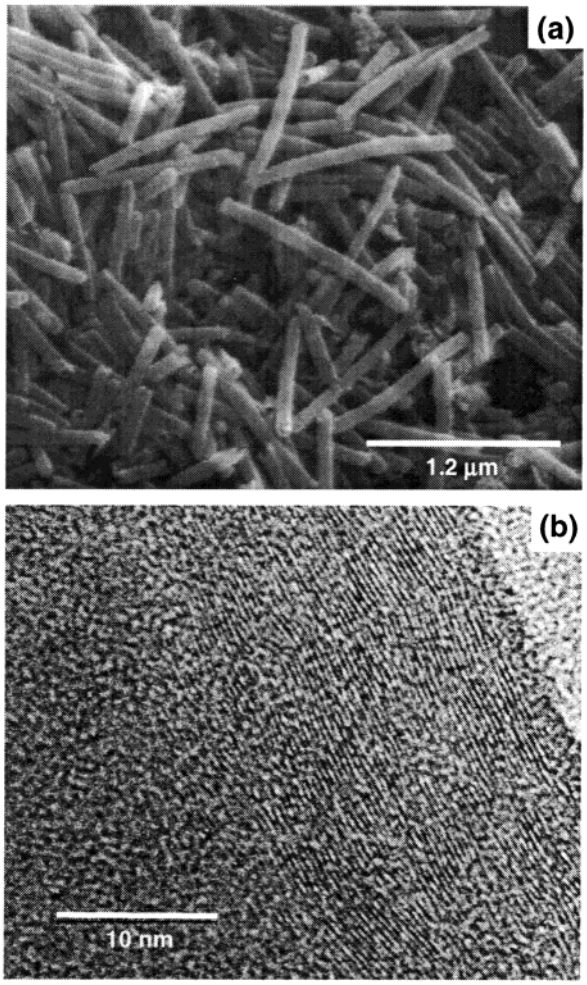

Figure 6. (a) SEM image of the CNTs collected on a filter membrane after 60 min of sonication and dissolution of the AAO template. (b) HRTEM image of the CNT.

CNTs are extremely tolerant to bending stress[31] provided the crystal structure is good and the diameter is sufficiently small. However, CNTs synthesized by catalytic pyrolysis of hydrocarbon have some structural defects. Moreover, cavitation would attack the surface of the CNTs, resulting in additional defects. Under these conditions, a relatively weak point will readily be ruptured. Therefore, breakage of CNTs can also occur at random points where the structures have been weakened (depicted as the CNT on the right-hand side in the middle cartoon of Figure 5). This is the reason every CNT is not broken at the pore mouth. However, the short-cut CNTs again involve in a new cutting sequence, and the aligned CNTs with a narrow length distribution can eventually be obtained.

To investigate the morphology and structure of CNTs, AAO templates were etched away in a chromic and phosphoric acid solution. Then, CNTs were collected on a filter membrane. Figure 6 a shows the SEM image of CNTs collected on a filter membrane after 60 min of sonication cutting. The diameter of CNTs is very uniform. The length of CNTs is about 1.2 μm, which is in good agreement with the sum of the lengths of cut CNTs over the AAO template and the pore depth. Therefore, one could easily control the dimensions of CNTs by template-based synthesis and cutting.

Figure 6b is the HRTEM image of a CNT prepared in this way. Because the CNTs have a relatively large diameter, only the right half of a CNT is shown in this figure. Well-ordered graphitic layers are clearly seen on the right side, while part of the hollow core appears on the left corner. Most of CNTs grown in this method have cobalt catalysts at the tip.[20] The thickness of the tube wall lies in the range of 16−20 nm, and it consists of 40−50 graphitic walls. The interwall distance (d_{002}) was 3.5 Å, slightly larger than the interlayer distance of graphite (d_{002} = 3.35 Å). There is no noticeable difference in structure and diameter over the whole length of the CNTs.

Conclusion

We have developed a method of controlling the dimensions of CNTs. This novel method consists of the preparation of an AAO template, the synthesis of CNTs by chemical vapor deposition with a Co catalyst, and the cutting of overgrown CNTs by sonication. This method enables us to easily obtain vertically aligned, crystalline CNTs in a controlled diameter and length. We expect that this method can be directly applied to the fabrication of an integrated triode structure for the CNT-based field emission device. The length of CNTs in a small gate hole can be controlled to a desired height, so that an unwanted short circuit between CNTs and the gate electrode can be avoided. Etching of the template gives us CNTs with very similar dimensions. Because the template protects CNTs during the cutting process, the surface structure of these CNTs is relatively good. They are thought to be very useful to a model study for many CNT-based applications.

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(31) Tersoff, J.; Ruoff, R. S. *Phys. Rev. Lett.* **1994**, *73*, 676.