Growth of Metal Carbide Nanotubes and Nanorods

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Transition-metal carbide nanorods have been prepared by reacting carbon nanotubes with volatile Ti and Nb iodides. Systematic temperature-dependent growth studies of TiC nanorods produced from spatially separated Ti metal and carbon nanotubes in the presence of iodine have shown that reaction proceeds initially via the formation of a thin, uniform carbide coating and that further reaction proceeds via inward growth of this coating with a concomitant consumption of the carbon nanotube until a solid nanorod is formed. Transmission electron microscopy, selected area diffraction, and X-ray powder diffraction have been used to show that the coatings and nanorods are polycrystalline, cubic TiC. Similar results were also obtained in growth studies of of NbC nanorods from Nb metal and carbon nanotubes. These data show that the growth of TiC and NbC nanorods involves a template mechanism in which the carbon nanotubes define the overall morphology and, furthermore, demonstrate that new TiC and NbC nanotubes can be prepared by controlling the growth conditions.

Introduction

There has been significant interest and speculation about the properties and potential applications of carbon nanotubes filled with other materials.[1−7] For example, nanotubes filled with metallic elements or compounds might be used to test ideas about dimensionality and localization in quantum wires.[1,7−9] Nanotubes and filled nanotubes may also represent unique materials with which to prepare composites possessing superior mechanical properties.[1,10,11] Several approaches have been explored to prepare carbon nanotubes filled with other materials.[2−6,12] Arc vaporization of metal/carbon composites has led to the production of nanotubes filled to varying extents with metal carbides and metallic elements.[2,6,12] Nanotubes have also been filled with low melting point metals[4] and with metal oxides produced by the pyrolysis of acidic, aqueous solutions of the metals.[3] Although these studies offer great promise, they have not yet led to the preparation of significant quantities of pure, filled nanotubes. Hence, it has not been possible to test directly the possibly unique properties of highly anisotropic, nanometer-scale materials using filled carbon nanotubes.

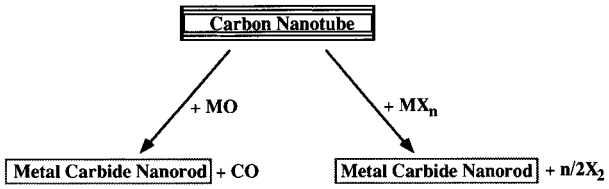

Figure 1. Schematic diagram of the reactions used to prepare carbide nanorods. MO corresponds to a volatile metal or main-group oxide and MX_n corresponds to a volatile metal or main-group halide complex.

Recently, we reported an alternative approach to the preparation of anisotropic nanoscale materials with the growth of carbide nanorods of the transition-metal and main-group elements.[7] In these studies, we found that chemically and physically distinct carbide nanoscale rods could be obtained via the reaction of carbon nanotubes with volatile transition-metal and main-group halide or oxide species. By using pure carbon nanotube reactants, we were able to prepare solid carbide nanorods of TiC, NbC, Fe_3C, SiC, and BC_x in high yield with typical diameters between 2 and 30 nm and lengths up to 20 μm. The mechanism underlying the synthesis of these carbide nanorods was proposed to involve reaction of the volatile halide or oxide reactants with carbon nanotube templates as shown schematically in Figure 1. Herein we address the key issue of mechanism through systematic studies of the growth of TiC and NbC nanorods. Volatile Ti−iodide complexes, generated in situ from titanium metal and iodine, were reacted with carbon nanotubes to form nanotubes uniformly coated with TiC. As the reaction temperature was increased, the TiC coating thickness increased with a concomitant decrease in the diameter of the carbon nanotube until a solid TiC nanorod was formed. Similar results were also obtained in reactions of niobium−iodide complexes with nanotubes. These

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(1) Ruoff, R. S. *Nature* **1994**, *372*, 731.
(2) Guerret-Piecourt, C.; Le Bouar, Y.; Loiseau, A.; Pascard, H. *Nature* **1994**, *372*, 761.
(3) Tsang, S. C.; Chen, Y. K.; Harris, P. J.; Green, M. L. H. *Nature* **1994**, *372*, 159.
(4) Ajayan P. M.; Iijima, S. *Nature* **1993**, *361*, 333.
(5) Ajayan, P. M.; Stephan, O.; Redlich, Ph.; Colliex, C. *Nature* **1995**, *375*, 564.
(6) Seraphin, S.; Zhou, D.; Jial, J.; Withers, J. C.; Loutfy, R. *Nature* **1993**, *362*, 503.
(7) Dai, H.; Wong, E. W.; Lu, Y. Z.; Fan, S.; Lieber, C. M. *Nature* **1995**, *375*, 769.
(8) (a) Mirin, R.; Krishnamurthy, M.; Tan, I.-H.; Bowers, J. E.; Gossard, A. C.; Hu, E. L. *J. Cryst. Growth* **1993**, *127*, 881. (b) Shitara, T.; Tornow, M.; Kurtenbach, A.; Weiss, D.; Eberl, K.; v. Klitzing, K. *Appl. Phys. Lett.* **1995**, *66*, 2385.
(9) (a) Williams, W. D.; Giordano, N. *Phys. Rev. B* **1986**, *33*, 8146. (b) Krans, J. M.; van Ruitenbeek, J. M., Fisun, V. V.; Yanson, I. K.; de Jongh, L. J. *Nature* **1995**, *375*, 767.
(10) Clyne, T. M.; Bader, M. G.; Caplleman, G. R.; Hubert, P. A. *J. Mater. Sci.* **1985**, *20*, 85.
(11) Cooke, T. F. *J. Am. Ceram. Soc.* **1991**, *74*, 2959.
(12) Ata. M.; Yamaura, K.; Hudson, A. J. *Adv. Mater.* **1995**, *7*, 286.

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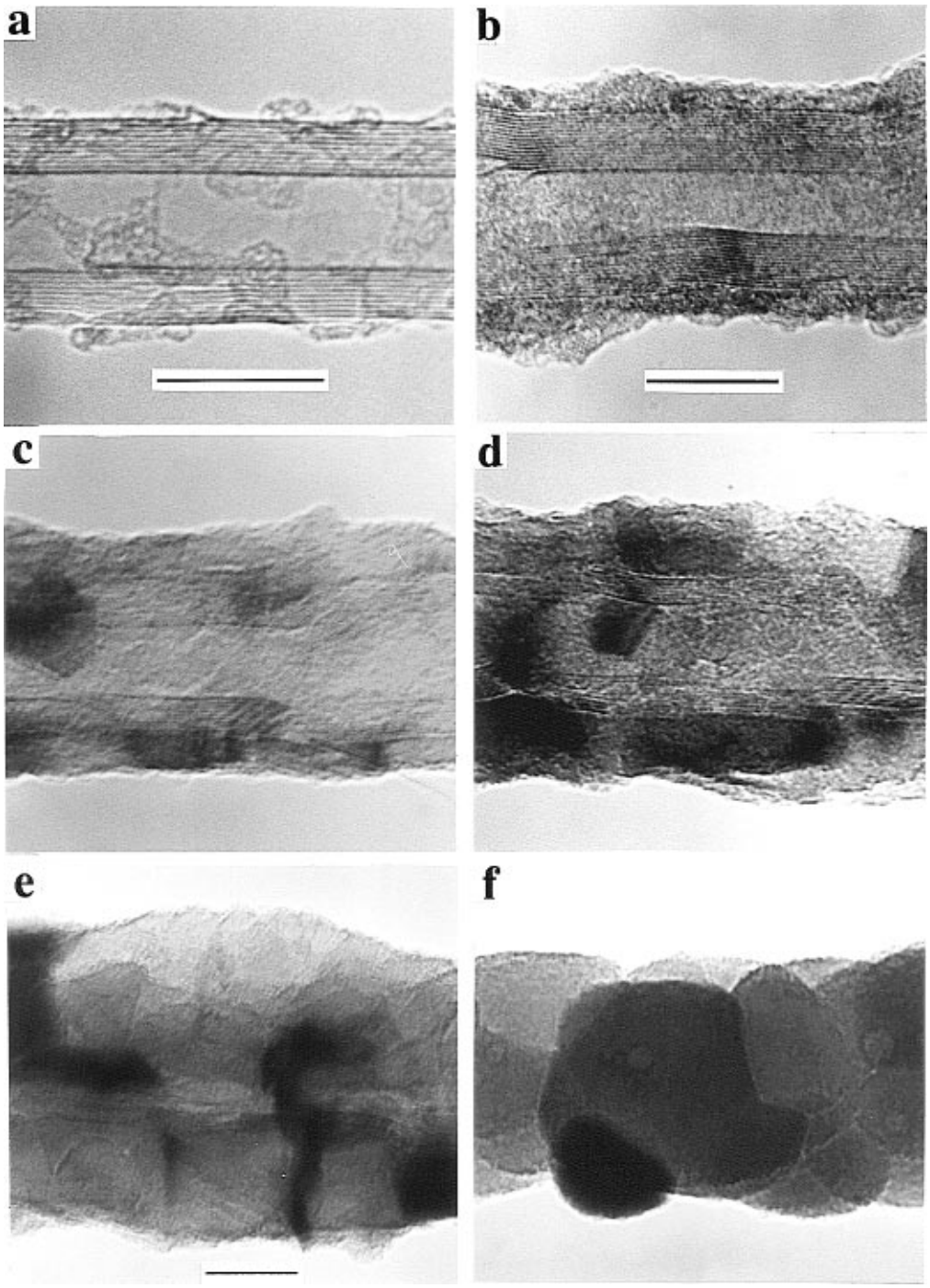

Figure 2. TEM images of (a) an unreacted carbon nanotube, (b) sample A1, (c) sample A3, (d) sample A5, (e) sample A8, and (f) sample A9. The scale bars in all of the images correspond to 100 Å. The magnification of images (c) and (d) is the same as image (b); image (f) has the same magnification as (e).

studies provide unambiguous evidence for a template growth mechanism and, furthermore, show that at intermediate temperatures its is possible to produce new metal carbide nanotubes in addition to solid nanorods. The implications of these results are discussed.

Experimental Methods

Carbon Nanotube Synthesis. The carbon nanotubes used in these studies were prepared by metal-catalyzed decomposition of ethylene in the presence of hydrogen as discussed previously.[7,13] The metal catalyst was obtained by first mixing 4.32 g (0.0107 mol) of ferric nitrate and 0.22 g (6.7×10^{-4} mol) of molybdenum acetylacetonate in 35 mL of methanol and then adding the resulting solution to a paste of 4.40 g of fumed alumina (Degussa) in 35 mL of methanol. The mixture was stirred for 45 min and then dried at 115 °C in vacuum (5×10^{-3} Torr) for 2 h. This resulting solid is the catalyst.

An alumina boat (Aesar) was loaded with approximately 0.06 g of catalyst and placed in a 25 mm quartz tube at the center of a furnace. Argon gas (99.995%) was passed through the tube for 10 min, and then the system was heated to 760 °C at 30 °C/min. When the temperature had stabilized, the argon flow was terminated while simultaneously initiating a 90 sccm flow of hydrogen (99.999+%) and 270 sccm flow of ethylene (99.99+%). After 45 min the argon flow was resumed, the hydrogen and ethylene flows were terminated, and the

(13) Synder, C. E.; Mandeville, W. H.; Tennent, H. G.; Truesdale, L. K.; Barber, J. J. Int. Patent WO 89/07163, 1989.

furnace was turned off and allowed to cool naturally to room temperature. The yield of carbon nanotubes recovered from the alumina boat was ~0.80 g. Transmission electron microscopy (TEM) showed that these samples consisted entirely of carbon nanotubes as reported previously.[7,13]

Synthesis and Characterization of Metal Carbides. In general, the titanium and niobium carbide materials were prepared in sealed quartz tubes containing separated metal and carbon nanotube reactants in the presence of iodine. A typical procedure for the conversion of carbon nanotubes to TiC follows. Carbon nanotubes (6 mg) and iodine (15 mg) were placed in one end of a quartz tube (8 mm o.d. × 6 mm i.d.), while titanium metal (80 mg) was positioned 7 cm away. The quartz tube was then evacuated (5×10^{-3} Torr) and flame sealed at the titanium metal end. The quartz tube was placed into a temperature calibrated tube furnace (1 in. × 12 in.) with the carbon nanotube end in the furnace center. Samples were then reacted under the following conditions: A1, 560 °C (20 h); A2, 560 °C (80 h); A3 560 °C (20 h) and 700 °C (5 h); A4, 560 °C (20 h), 645 °C (24 h), and 750 °C (9 h); A5, 560 °C (5 h), 700 °C (5 h), and 770 °C (5 h); A6, 560 °C (5 h), 700 °C (5 h), and 780 °C (5 h); A7, 560 °C (20 h) and 645 °C (24 h); A8, 560 °C (5 h), 700 °C (5 h), and 790 °C (5 h); and A9, 560 °C (10 h), 645 °C (10 h), 750 °C (10 h) and 790 °C (10 h). Niobium carbide materials were prepared using similar procedures with the following specific conditions: B1, 820 °C (6 h); B2, 820 °C (12 h).

The resulting black products were recovered from the nanotube end of the quartz tube. TEM and selected area diffraction (SAD) were used to assess the structures of individual TiC and NbC structures, while EDAX was used to assess the presence of titanium and niobium. The structure of the bulk products was determined by powder X-ray diffraction. The SAD patterns of all of the products exhibited sharp ring structure that could be indexed to reflections expected for cubic TiC and NbC. In addition, reactions carried out at lower temperatures exhibited a lower angle peak consistent with the (001) reflection from graphitic nanotubes.

The TEM images were obtained on a Philips EM 420 transmission electron microscope operated at 120 keV. Samples were deposited onto holey carbon grids from methanol suspensions prepared by sonication. The average carbide coating thicknesses were obtained by averaging measurements obtained from 770 000 magnification TEM images of at least five distinct nanotubes for each set of conditions; the stated uncertainties in thicknesses correspond to 1 standard deviation. Elemental analysis was carried out in the EM 420 using a Tracor Northern TM 5500 EDAX system. Powder XRD patterns were obtained with a Rigaku DMax-B X-ray diffractometer using Cu Kα radiation.

Results and Discussion

To investigate clearly the formation of metal carbide products from reactions between carbon nanotubes and metal−iodide complexes, we have used carbon nanotubes produced by metal-catalyzed decomposition of ethylene.[7,13] The catalytic growth procedure yields relatively pure, homogeneous nanotube samples that have the multishell structure shown in Figure 2a. The multishell structure and 3.35 Å interlayer spacing is very similar to that reported previously for carbon nanotubes produced by the arc discharge.[14,15] The samples produced by arc-discharge methods contain, however, significant quantities of other carbon products and are thus less suitable for mechanistic studies.

TEM images of the products obtained from sealed tube reactions containing spatially separated titanium metal and carbon nanotubes in the presence of iodine are shown in Figure 2b−f as a function of reaction temperature and reaction time. In general, these images show that (1) a coating is formed on the carbon nanotube exterior surfaces and (2) this coating increases in thickness as the reaction temperature is increased. At the lowest reaction temperature studied, 560 °C, the coating has a relatively uniform thickness of 21 Å (Figure 2b). Longer reaction (80 h) at this same temperature (e.g., sample A2) does not lead to an increase in coating thickness relative to sample A1. This observation suggests that the coating formed initially by the reaction of the Ti−iodide complex at the surface of the nanotube serves as a diffusion barrier that prevents further inward reaction with the nanotube at 560 °C.

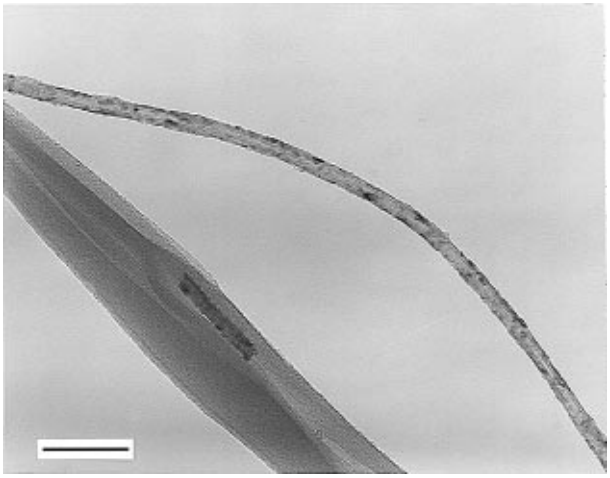

Figure 3. Large area TEM image of sample A3 showing that the TiC coating is uniform over the entire nanotube surface. The TiC coated nanotube has a total length of 4 μm. The large structure in the lower left of the image corresponds to the support grid. The scale bar corresponds to 1000 Å.

However, when samples prepared in a similar way are further reacted at 700 °C for 5 h this coating was found to increase in thickness to 35 Å (Figure 2c). The increase in coating thickness at higher temperature is consistent with an enhanced diffusion of the Ti reactant at higher temperature. It is also important to note that this 35 Å coating, which is typical of those obtained in our reactions, is very uniform over most of the carbon nanotube surface as shown in Figure 3. Reactions carried out at higher temperatures show that as the reaction temperature is increased, the thickness of the coating increases systematically with a concomitant decrease in the thickness of the carbon nanotube wall. Finally, after reaction at 790 °C for 10 h, a solid rodlike structure was obtained with no evidence remaining for the carbon nanotube reactant (Figure 2f). A summary of our experimental results is shown in Table 1.

This latter rodlike structure is similar to the titanium carbide nanorods we have reported previously,[7] and thus it is plausible to suggest that the coatings observed in Figure 2b−e are also TiC. We have confirmed this idea through structural studies of the nanotubes and solid nanorods. SAD patterns recorded on sample A3, which has a 35 Å coating, and sample A9, which has solid rods, are shown in Figure 4. The observed diffraction ring structures, which are consistent with the polycrystalline nature of the samples,[16] can be indexed to the (111), (200), (311), (222), (420), and (422) reflec-

(14) Ebbesen, T. W.; Ajayan, P. M. *Nature* **1992**, *358*, 220.
(15) Colbert, D. T.; Zhang, J.; McClure, S. M.; Nikolaev, P.; Chen, Z.; Hafner, J. H.; Owens, D. W.; Kotula, P. G.; Carter, C. B.; Weaver, J. H.; Rinzler, A. G.; Smalley, R. E. *Science* **1994**, *266*, 1218.

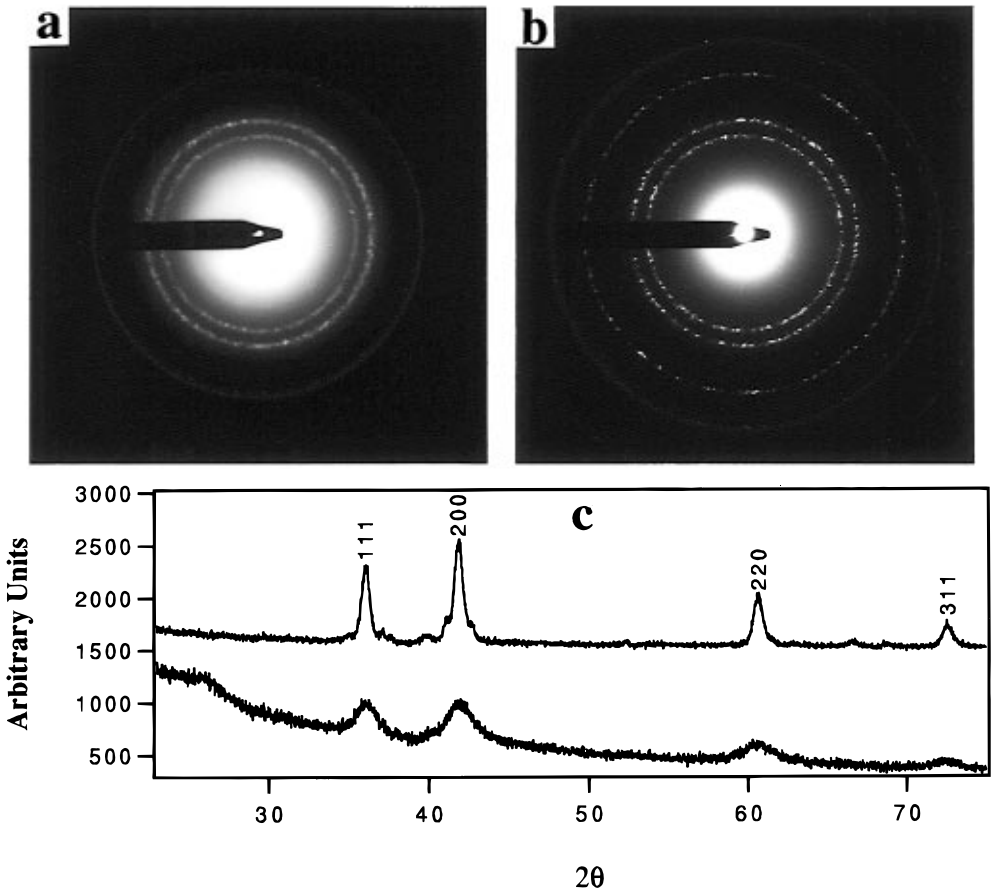

Figure 4. SAD patterns recorded on (a) sample A3 and (b) sample A9. Powder X-ray diffraction patterns (c) recorded on bulk samples of A3 (lower curve) and A9 (upper curve). The four peaks observed in both diffraction patterns match the positions expected for the (111), (200), (220), and (311) reflections of cubic TiC.

Table 1. Summary of the TEM Data Obtained from Samples Prepared in This Study

sample	material	final temp (°C)	time (h)	TEM analysis
A1	TiC	560	20	21 ± 5 Å coating
A2		560	80	23 ± 6 Å coating
A3		700	5	35 ± 9 Å coating
A4		750	9	44 ± 12 Å coating
A5		770	5	50 ± 12 Å coating
A6		780	5	53 ± 15 Å coating
A7		645	24	63 ± 21 Å coating
A8		790	5	120−140 Å coating
A9		790	10	conversion to solid rods
B1	NbC	820	6	partial coatings
B2		820	12	conversion to solid rods

Table 2. Summary of SAD Data Recorded on Samples A3 and A9

hkl	TiC *d* values (Å)	A3 *d* values (Å)	A9 *d* values (Å)
111	2.50	2.59 ± 0.18	2.54 ± 0.12
200	2.16	2.20 ± 0.10	2.21 ± 0.10
220	1.53	1.53 ± 0.07	1.55 ± 0.07
311	1.30	1.34 ± 0.06	1.32 ± 0.06
222	1.25	1.27 ± 0.06	1.25 ± 0.06
420	0.97	0.98 ± 0.05	0.97 ± 0.04
422	0.88	0.89 ± 0.04	0.89 ± 0.04

tions of cubic TiC (Table 2). The lattice parameters determined from these experimental data, a(A3) = 4.40 Å and a(A9) = 4.42 Å are in good agreement with the reported value a = 4.33 Å.[17,18] The SAD of sample A3 also shows a weak reflection with a d value of ~3.34 Å. We believe that this low-angle reflection likely corresponds to the interlayer spacing of the carbon nanotube graphitic shells[14,19] remaining in A3. EDAX measurements recorded at the same time as the diffraction data show that the coatings and rods contain Ti and no other elements of mass ≥aluminum. In addition, X-ray diffraction measurements recorded on bulk samples of A3 and A9 show that the bulk crystalline material in these samples is also TiC. Hence, we conclude that the coatings and solid rods produced from the reaction of volatile Ti−iodide complexes and carbon nanotubes is relatively pure TiC.[20,21]

The generality of these results has been confirmed through studies of the growth of NbC nanorods. TEM images of the products obtained from the sealed tube reactions of spatially separated Nb metal and carbon nanotubes in the presence of iodine are shown in Figure 5. The images show that a coating forms on the carbon

(16) The TEM images of the coatings and solid rods (e.g., Figure 2) show that these samples have a small, randomly oriented grain structure.

(17) Storms, E. K. *The Refractory Carbides*; Academic Press: New York, 1967.

(18) The deviation of the experimental lattice parameters from the literature value for 1:1 TiC may indicate nonstoichiometry in carbon.[17]

(19) Iijima, S. *MRS Bull.* **1994**, *19*, 43.

(20) The final diameter of the solid TiC nanorod is consistent with an estimate based on complete conversion of the carbon nanotube and the bulk density of TiC. This suggests that carbon sources external to the nanotube template do not contribute significantly to the growth of TiC.

(21) It is interesting to note that Ti metal coats the entire quartz tube except in the vicinity of the nanotubes. This observation is true until the last stages of the conversion reaction, after which Ti metal is observed on the quartz tube in the vicinity of the product.

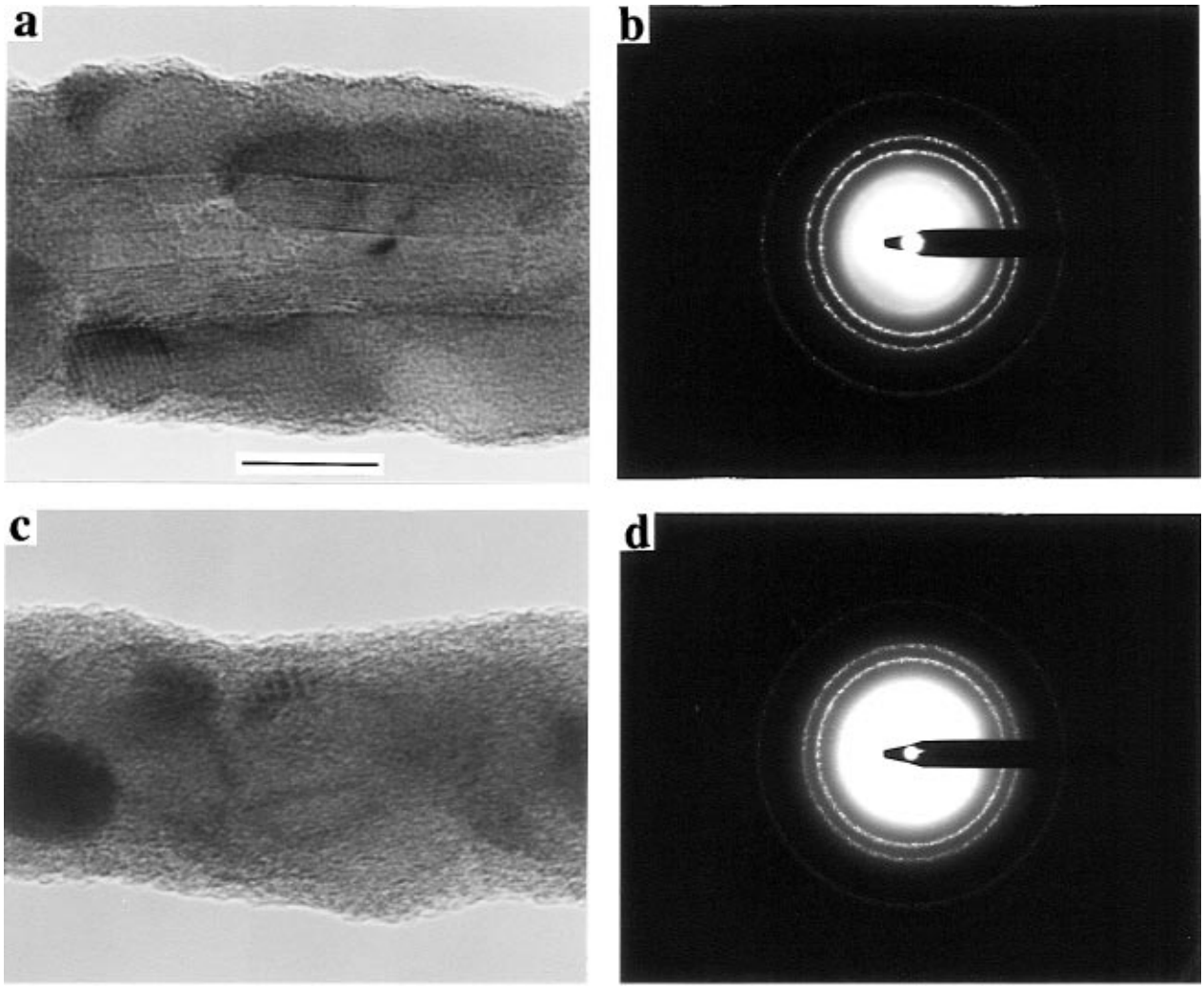

Figure 5. TEM images of the products obtained from the reaction of carbon nanotubes with Nb and I_2 for (a) 6 h at 820 °C and (c) 12 h at 820 °C. SAD patterns recorded on (b) NbC coated sample and (d) a solid NbC nanorod. The scale bar in (a) corresponds to 100 Å; the image in (b) is the same magnification.

nanotubes at the early stages of reaction and that the thickness of this coating increases and ultimately yields a solid rod as the inward reaction proceeds. These results are essentially the same as those discussed above for the case of TiC. SAD patterns recorded from the coated nanotubes and solid nanorods can be indexed to the (111), (200), (220), (311), and (222) reflections of cubic NbC. The cubic lattice constant determined from the data in Figures 5B and D are $a = 4.40$ and 4.48 Å, respectively. These values are in good agreement with that expected for cubic NbC, $a = 4.48$ Å.[17,22] These data show clearly that the coatings and rods are NbC. Significantly, these polycrystalline nanorods are found to be superconducting like bulk NbC and thus may be a unique building block for nanostructured materials.[23]

Taken together, these results provide strong support for the template growth mechanism of carbide nanorods that we proposed in earlier studies.[7] Our results suggest that volatile Ti− or Nb−iodide complexes initially react homogeneously at the surface of carbon nanotube templates to form a uniform TiC or NbC coating. Subsequent reaction may be limited by diffusion through this coating, although at sufficiently high temperatures the metal carbide coating continues to grow toward the tube center until a solid TiC or NbC nanorod is produced.[20] The elucidation of this growth mechanism has several important implications. First, these studies of the growth mechanism demonstrate that it is possible to make not only carbide nanorods but also carbide nanotubes of controllable wall thickness. Although the carbide nanotubes are in fact composite structures comprising an inner carbon nanotube bonded to an outer carbide nanotube, it should be possible to obtain pure carbide nanotubes since carbon is more easily oxidized than TiC (and other carbides).[17] In addition, because many transition metals can be readily transported by halide and related species[24] and form stable metal carbides,[17] it should be possible using our approach to prepare a wide range of metal carbide nanotubes and nanorods.

Summary and Conclusions

Transition-metal carbide nanorods have been prepared by reacting carbon nanotubes with volatile Ti− and Nb−iodides. Systematic temperature-dependent

(22) SAD of a NbC coated sample also shows a weak reflection with a *d* value of ~3.34 Å that likely corresponds to the interlayer spacing of the carbon nanotube graphitic shells remaining in this sample.

(23) Field-cooled magnetization measurements carried out on bulk NbC nanorod samples show diamagnetism below ~9 K. The diamagnetic signal corresponds to a superconducting fraction of 70%.

(24) Schafer, H. *Angew. Chem., Intl. Ed., Engl.* **1971**, *10*, 43.

growth studies of TiC nanorods produced from spatially separated Ti metal and carbon nanotubes in the presence of iodine have shown that reaction initially yields a uniform TiC coating and that further reaction proceeds via inward growth of the TiC until a solid TiC nanorod is formed. Similar results were also obtained in our studies of NbC nanorod growth. We believe that these data provide definitive proof for a template-mediated growth mechanism, and furthermore, these mechanistic studies have led to the synthesis of new TiC and NbC nanotube materials.

We believe that these materials offer exciting opportunities for both fundamental research and technological applications. The controllable size and chemical composition of the nanorods should make them an ideal system in which to probe the effects of confinement and dimensionality in metallic, semiconducting, and superconducting materials. The small diameters and range of chemical compositions available for these carbide nanorods could also make them useful as chemically specific reinforcements in metal and ceramic matrix composites, as well as unique building blocks for new nanomaterials with interesting physical properties.

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