An Alternative Route to NbS₂ Nanotubes

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Received: March 27, 2002; In Final Form: May 28, 2002

Novel composite nanotubes, consisting of NbS_2-sheathed carbon nanotubes (CNTs), have been generated successfully employing carbon nanotube template-promoted growth. Detailed experimental procedures, and the associated intermediate oxide phases during NbS_2 conversion, have been evaluated using high-resolution transmission electron microscopy, coupled with EDX analysis. Our results show that CNTs act as templates and that the uniform well-crystallized NbS_2 nanotubes are produced from unevenly wrapped NbO_2. A multi-point nuclei site growth mechanism has been proposed to account for nanotube formation.

The discovery of metal dichalcogenide cage-like layered nanostructures, the inorganic nanotubes, by Tenne et al.[1] has engendered intense scientific interest because they exhibit promising electronic and mechanical properties. Over the past decade, diverse routes to these materials, including chemical transport,[2] gas−solid reactions,[3] and in-situ heating,[4] have resulted in pure MS_2 nanoparticles, short and long tubes, bundles, and even microtubes. As a consequence, the family of inorganic nanostructures has been broadened in various ways, e.g., by creating so-called inorganic−organic dual-phase nanostructures (mixing MS_2 layers with C layers);[5,6] intercalating noble metals (Au and Ag) within the tube walls;[7,8] and Ti- or Nb-doped MS_2 composite nanotubes.[9,10] Recently, significant developments in generating single-layered inorganic nanotubes have been reported,[11,12] several years after single-walled carbon nanotubes were first described.[13] Single-layered MoS_2 nanotubes have been formed successfully using chemical transport[11] and WS_2 nanotubes have been generated using template techniques.[12] However, these experiments have concentrated mainly on W- and/or Mo-based dichalcogenides, other layered transition metal sulfide nanotubes being rarely reported. A theoretical study has shown that NbS_2 nanotubes may superconduct, as do NbS_2 bulk crystals,[14] a fundamental difference from the WS_2 or MoS_2 tubes and crystals which semiconduct.[15] A recent report described a simple route to transition-metal disulfide nanotubes involving hydrogenation of transition-metal trisulfide powders.[16] However, the detailed layered structures of these tubes were not described. Furthermore, the NbS_2 tubes did not superconduct above 4.2 K. Previously, we described briefly the generation of NbS_2 nanotubes via an alternative carbon nanotube template process.[17] We now present the detailed preparative procedures together with a study of their structural features, including the intermediate phases. A multi-point nuclei site growth mechanism is discussed.

The carbon nanotube (CNT) template, produced by a standard graphite arc-discharge process, was treated with aqueous HNO_3 in order to activate the surface. After removing the acid with water, the filtered product was dried at ca. 200 °C, and the CNTs were mixed with CCl_4 (30 cm³). $NbCl_4$ (20 mg, Aldrich Co.) powder was added to the CNT suspension, which was subjected to ultrasound treatment for 30 min, to achieve uniform $NbCl_4$ and CNT distribution. The mixture was set aside for 72 h at
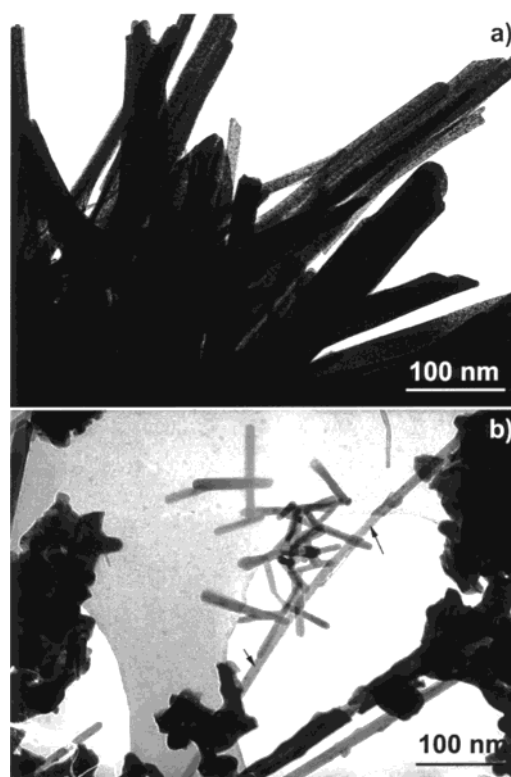
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Figure 1. TEM images of (a) CNTs coated by $NbCl_4$, and (b) CNTs coated by NbO_2.

room temperature, then heated at 80 °C to remove the CCl_4, leaving a dark gray powder of CNTs coated with $NbCl_4$. A small portion of the coated CNTs was subjected to TEM examination. The remainder was transferred to a quartz boat placed in a quartz tube inside a furnace. The sample was heated at ca. 450 °C for 30 min in air, then at ca. 1050 °C in an Ar/H_2S atmosphere for an additional 30 min. After cooling to room temperature under Ar, the nanotubes were examined using a CM-200 high-resolution transmission microscope, with energy-dispersive X-ray analysis equipment attached (EDX, element ≥ B).

After drying at 80 °C, most of the CNTs were found to be fully wrapped in $NbCl_4$ (Figure 1a). Under TEM, the coated nanotubes appeared to be darker than the original nanotubes and the hollow core feature was invisible due to lack of contrast.
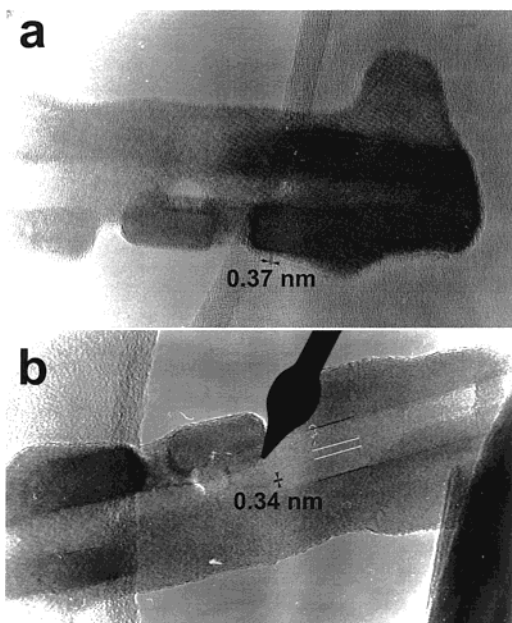
Figure 2. HRTEM images of a NbO$_2$-coated CNT: (a) the irregular NbO$_2$ coating exhibits well-crystallized lattice fringes (0.37 nm separation); (b) the inner hollow core of the CNT is visible, and the layer separation is 0.34 nm.

At this stage, the coating seemed to be uniform, with blister-like particles on the tube surface. However, a majority of the CNT wrappings was entirely or partly removed as a result of the oxidation (at 450 °C); only ca. 20% of these coatings remained (Figure 1b). During TEM examination, we observed irregular coated CNTs, and in particular areas the hollow core was visible (Figure 1b, arrowed). When we reduced the temperature to 400 °C, a similar percentage of coated CNTs was obtained, presumably because the evaporation rate of NbCl$_4$ (mp 204 °C) and its oxidation rate have reached equilibrium well below 400 °C. A further decrease in temperature may result in no oxidation.

HRTEM monitoring of the preheated samples revealed the presence of well-crystallized NbO$_x$ coatings on the CNTs (Figure 2a,b), consisting of Nb, O, and C as verified by EDX analysis. The lattice fringes are highly ordered and appear to be defect-free. However, the morphology of these oxide shells is irregular. They exhibit varying diameters and thicknesses, some CNTs being only partly coated. It is difficult to determine the exact O concentration within the coatings, even though the Nb:O ratio is ca. 1:2. Actually, Nb is oxidized at 250 °C to NbO and thence to NbO$_2$ at 750 °C in the presence of water vapor.[18] Thus, on the basis of their defect-free structure, lattice fringes (ca. 0.36−0.37 nm), and EDX evaluation, we suggest that the coatings can be written as NbO$_2$. In the center of the sample, the original features of the CNTs, i.e., straight and highly graphitized, are generally well-preserved. The cone-like inner layers and tips are still visible, if the focus is adjusted (Figures 2a and 2b). This result shows that the CNTs do act as templates for coating.

Passage of H$_2$S leads to NbS$_2$ tubes (Figure 3a), nanorods and micro- or nano-polygonal particles. The nanotubes vary between 50 and 200 nm in diameter, and are up to few microns in length. The nanorods exhibit similar dimensional features. The particles are large, sometimes approximately a few microns in diameter. The diameter of each tube is uniform, displaying even numbers of NbS$_2$ layer coatings during TEM examination. The NbS$_2$ tube surfaces are generally smooth by comparison with WS$_2$ nanotubes. The interfaces between the outer darker shell and the central brighter CNT are commensurate with
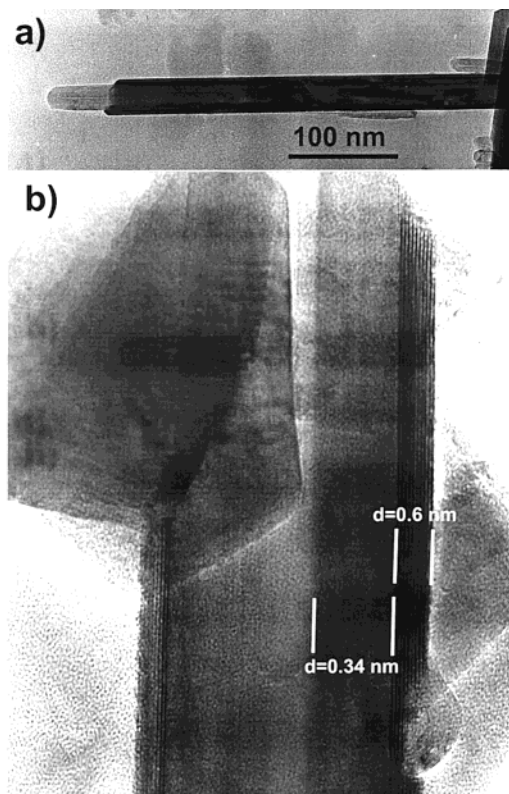

Figure 3. (a) TEM image of a CNT-NbS$_2$ composite nanotube; and (b) enlargement of (a) revealing the layer separations of the NbS$_2$ (0.6 nm) and CNT (0.34 nm).

curving. The CNT template layers (ca. 0.34 nm separation, identical with separation in the starting materials; Figure 3b) are clearly visible, and differ from those of the outer darker and larger NbS$_2$ layers [ca. 0.6 nm separation, corresponding to the hexagonal NbS$_2$ structure ($a = 3.31$ Å, $c = 11.89$ Å)].[19] It is apparent that the carbon template has been sheathed incompletely with NbS$_2$ layers, and that open-ended growth of the NbS$_2$ nanotube is presumably involved. Hollow CNT cores are also present (Figure 3b). It is noteworthy that, even though these tubes were derived from NbO$_2$, the NbS$_2$ tubes display little similarity to NbO$_2$ coating in terms of their morphology. Irregular features associated with the NbO$_2$ were rarely found.

The interlayer separation of NbS$_2$ rods is ca. 0.60 nm, the same as that found for the tubes (Figure 4a). It is not always easy to determine whether a nanorod has a circular cross-section in this context. We often found that many nanorods possess polygonal cross-sections, mostly square-like. Such shapes resemble the structural features of WS$_2$ nanotubes generated by in-situ heating.[4] In some cases, traces of the NbO$_x$ lattice (indicated by the ca. 0.37 nm layer separation) are still attached to the larger NbS$_2$ layers at the edges or tips (Figure 4b insert). These oxide residues are indicative of incomplete oxide-to-sulfide conversion, as found for WS$_2$ and MoS$_2$.[20] Polygonal particles, ca. 5 μm diameter, are often observed and appear to possess an edge construction akin to tube layers.

EDX analysis revealed that most of the tubes/rods contain Nb, S, and C only (Figure 5, C arises from the template and the holey film); the Nb:S ratio is ca. 1:2. The nanoparticles, in which less carbon was detected, exhibit identical Nb:S ratios, indicating that they may form without involvement of any CNT template. These experiments show that NbS$_2$ nanotubes and nanorods have been generated successfully. The carbon nanotubes, located in the middle of the NbO$_2$ and NbS$_2$ shells (Figure
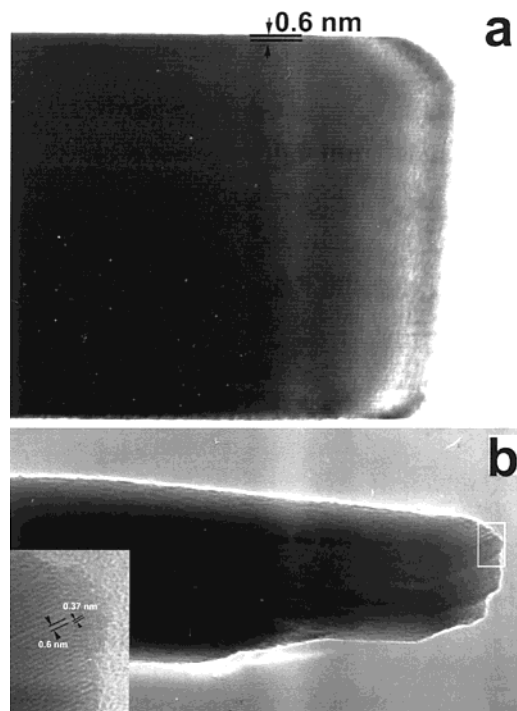
Figure 4. HRTEM images of NbS_2 nanorods. A trace of NbO_2 is apparent at the tip of the NbS_2 nanorods (0.6 nm layer separation).
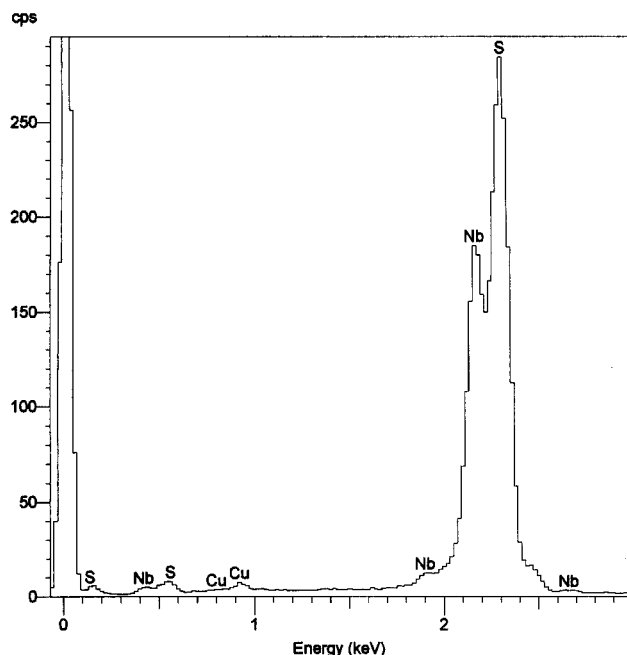

Figure 5. EDX profile of an NbS_2 nanotube.

2 and Figure 3), provide direct evidence for the template effect during NbS_2 formation.

Various phases have been reported for the bulk Nb−S system and the common polytypes for layered NbS_2 are the *2Ha*-type hexagonal and *3R*-type trigonal structures.[18] Meanwhile, other varieties, e.g. $Nb_{1+x}S_2$ (rhombohedral, $x = 0-0.5$ at 800 °C and $x = 0.012-0.025$ at 1100 °C), exist.[18] These forms possess different crystal structures. In our case, we can eliminate the possibilities of their presence either by the absence of their c values, which would be significantly different from NbS_2 (e.g., $c = 1.78$ nm for the rhombohedral $Nb_{1+x}S_2$), or by reference to our experimental conditions, 1050 °C, at which temperature some forms are unstable.[21] To form a tube, the NbS_2 layers

need to roll up, as do WS_2 and MoS_2 nanotubes. Thus, akin to other MS_2 tubes, NbS_2 is expected to adopt a hexagonal structure ($a = 0.331$ nm, $c = 1.189$ nm). In fact, the ca. 0.60 nm interlayer separation (Figure 3b), which is ca. half of the c distance in the bulk-layered form, but with a 1% expansion, confirms its *2Ha*-type structure. Such an expansion, also observed by Nath et al. in their NbS_2 tubes,[16] is comparable with the 2% layer distance enlargement exhibited in MS_2 nanotubes.[10,20] Prior to the report of Nath et al.,[16] we found that the existing approaches to MS_2 nanotubes, e.g., chemical transport,[2] gas−solid reactions,[3] and in-situ heating[4] proved to be inapplicable to NbS_2 tubes. These procedures usually lead to the formation of large crystals and rods of NbS_2, rather than to tubes. It appears that NbS_2 tubes are more difficult to produce than other MS_2 tubes. We conclude that the different atomic layouts between NbS_2 (*2Ha*) and MS_2 (*2Hb*) could be important, and that the temperature-dependent stability of NbS_2 within the Nb−S system is significant.[22]

Carbon nanotubes have often been used as templates for fabricating novel nanostructures. According to the role CNTs play in different processes, i.e., whether CNTs are in some way involved in chemical reactions or simply act as a physical template, we classify their promotion effects into two types. The first was used in the formation of ceramic nanorods (SiC, Si_3N_4, GaN);[23,24] the second was applied to the production of single-layered inorganic nanotubes (WS_2).[12] Taking advantage of such a template, we have endeavored to produce new nanotubes by an alternative method, in which it is apparent that the second type effect took place in this account, similar to that in WS_2.[12] A significant aspect of this process may be that we are able to generate NbS_2 nanotubes with CNT templates remaining in the center. This product is a type of composite and may be used as a nanocable (e.g., metal−metal or semiconducting-metal cable, depending upon the band gaps which are determined by the shape, diameter, and chirality, etc., of the nanotubes[14,15]). The carbon template should be readily removable to obtain pure NbS_2 nanotubes for other purposes, as CNTs will be oxidized at ca. 550 °C in air, whereas NbS_2 remains stable above 800 °C, and we are about to study this procedure.

We have observed uneven and discontinuously formed oxide shells on the template (Figure 2). However after passage of H_2S, this blistered characterization appears not to be transferred as the resulting NbS_2 tubes were generally uniform, exhibiting an equivalent number of layers on either side (Figure 3). This phenomenon was not in accord with normal features inherently observed for MS_2 nanotubes, thus has attracted our attention. In most MoS_2 or WS_2 conversions, transformation proceeds from the outer oxide shell inward, as established by Tenne et al.,[20] and the main topological feature of the initial oxide has been passed to the forming sulfides. Therefore we deduce that the route involved here may differ from those conversions. It is apparent that this must have arisen during the nanotube growth while structural rearrangements occurred during lattice replacement of oxide by sulfide, i.e. from monoclinic NbO_2 (or other oxides) to hexagonal NbS_2. In this context, some incompletely converted oxide residues at the tip (Figure 4, particularly the insert in 4b) were observed, providing direct evidence for an alternative mechanism. We suggest that during the oxide-to-sulfide conversion,[20] i.e. during lattice rearrangement, a multi-point growth may take place. This allows the oxide-to-sulfide conversion to occur simultaneously at several appropriate sites,[17] and the growing sulfide layers to join along the template. A model for such a multi-point growth is shown in Figure 6. The advantage of this mechanism over the single site lies in the fact
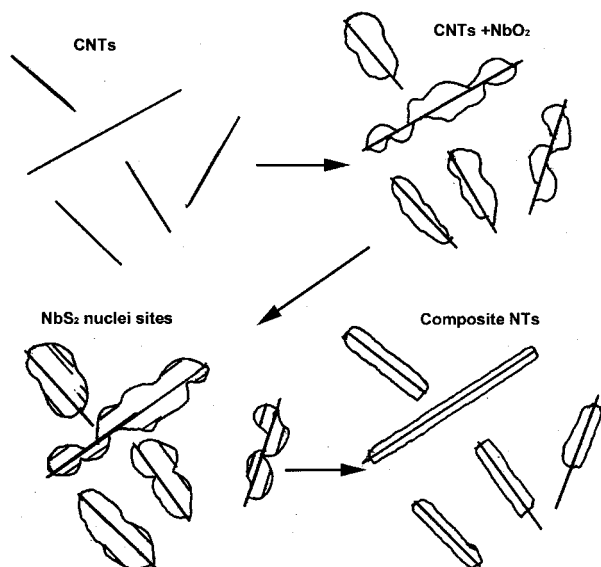
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Figure 6. A schematic illustration of multipoint growth of NbS_2 nanotubes on CNT templates. The straight lines stand for CNTs and the arrows indicate the growth progresses.

that smooth uniform tubes can be created, with the assistance of the template, without involving significantly long distance atomic migration. Meanwhile, the high temperature (1050 °C) could also favor this process, via an annealing effect to eliminate defects arising from the site−site joining. As a result, relatively straight uniform NbS_2 nanotubes/nanorods are produced. This growth, similar to that associated with the continuous growth of WS_2 and MoS_2 nanotubes by in-situ heating (not in terms of single site growth), sometimes results in an open growing end (Figure 3).[4] In fact, the open-tipped NbS_2 tubes have been observed much more often than the close-tipped tubes. There may be two reasons for this. One arises from the oxide coating. Owing to the higher surface tension at CNT tips than at the bodies, the tips are difficult to be fully coated. The other is due to the multi-point growth. Multi-point conversion and structure rearrangement will easily occur on the part-coated body, thus leading to an open-tipped tube by reducing surface energy.

In summary, we report that straight and well-crystallized NbS_2 nanotubes/rods have been successfully generated using CNT-promoted template growth. The structural features and composition of the NbS_2 tubes, as well as the intermediate oxide phase involved, have been investigated by HRTEM and EDX. Our results show that these nanotubes were converted from NbO_2 into NbS_2, through a multi-point nuclei site growth mechanism.

References and Notes

(1) Tenne, R.; Margulis, L.; Genut, M.; Hodes, G. *Nature* **1992**, *360*, 444.

(2) Remskar, M.; Skraba, Z.; Regula, M.; Ballif, C.; Sanjines R.; Levy, F. *Adv. Mater.* **1998**, *10*, 246.

(3) Rothschild, A.; Frey, G. L.; Homyonfer, M.; Tenne, R.; Rappaport, M. *Mater. Res. Innov.* **1998**, *3*, 145.

(4) Zhu, Y. Q.; Hsu, W. K.; Grobert, N.; Chang, B. H.; Terrones, M.; Terrones, H.; Kroto, H. W.; Walton, D. R. M.; Wei, B. Q. *Chem. Mater.* **2000**, *12*, 1190.

(5) Hsu, W. K.; Zhu, Y. Q.; Boothroyd, C. B.; Kinloch, I.; Trasobares, S.; Terrones, H.; Grobert, N.; Terrones, M.; Escudero, R.; Chen, G. Z.; Colliex, C.; Windle, A. H.; Fray, D. J.; Kroto, H. W.; Walton, D. R. M. *Chem. Mater.* **2000**, *12*, 3541.

(6) Hsu, W. K.; Zhu, Y. Q.; Kroto, H. W.; Walton, D. R. M.; Kamalakaran, R.; Terrones, M. *Appl. Phys. Lett.* **2000**, *77*, 4130.

(7) Remskar, M.; Skraba, Z.; Ballif, C.; Sanjines, R.; Levy, F. *Surf. Rev. Lett.* **1999**, *6*, 1283.

(8) Remskar, M.; Skraba, Z.; Stadelmann, P.; Levy, F. *Adv. Mater.* **2000**, *12*, 814.

(9) Hsu, W. K.; Zhu, Y. Q.; Yao, N.; Firth, S.; Clark, R. J. H.; Kroto, H. W.; Walton, D. R. M. *Adv. Funct. Mater.* **2001**, *1*, 69.

(10) Zhu, Y. Q.; Hsu, W. K.; Terrones, M.; Firth, S.; Grobert, N.; Clark, R. J. H.; Kroto, H. W.; Walton, D. R. M. *Chem. Commun.* **2001**, *1*, 121.

(11) Remskar, M.; Mrzel, A.; Skraba, Z.; Jesih, A.; Ceh, M.; Demsar, J.; Stadelmann, P.; Levy, F.; Mihailovic, D. *Science* **2001**, *292*, 479.

(12) Whitby, R. L. D.; Hsu, W. K.; Boothroyd, C. B.; Fearon, P. K.; Kroto, H. W.; Walton, D. R. M. *Chem. Phys. Chem.* **2001**, *10*, 620.

(13) Iijima, S.; Ichihashi, T. *Nature* **1993**, *363*, 603.

(14) Seifert, G.; Terrones, H.; Terrones, M.; Frauenheim, T. *Solid State Commun.* **2000**, *115*, 635.

(15) Seifert, G.; Terrones, H.; Terrones, M.; Jungnickel, G.; Frauenheim, T. *Phys. Rev. Lett.* **2000**, *85*, 146.

(16) Nath, M.; Rao, C. N. R. *J. Am. Chem. Soc.* **2001**, *123*, 4841.

(17) Zhu, Y. Q.; Hsu, W. K.; Kroto, H. W.; Walton, D. R. M. *Chem. Commun.* **2001**, *21*, 2184.

(18) Kilpatrick, M.; Lott, S. K. *J. Less-Common Metals* **1965**, *8*, 299.

(19) Jellinek, F.; Brauer, G.; Muller, H. *Nature* **1960**, *185*, 376.

(20) Feldman, Y.; Frey, G. L.; Homyonfer, M.; Lyakhovitskaya, V.; Margulis, L.; Cohen, H.; Hodes, G.; Hutchison, J. L.; Tenne, R. *J. Am. Chem. Soc.* **1996**, *118*, 5362.

(21) Fairbrother, F. *The Chemistry of Niobium and Tantalum*; Elsevier Publishing Company: Amsterdam, The Netherlands, 1967; p 207.

(22) Levy, F. *Structural Chemistry of Layered-type Phases*; D. Reidel Publishing Company: Dordecht, Holland, 1976; p 235.

(23) Dai, D. J.; Wong, E. W.; Lu, Y. Z.; Fan, S. S.; Lieber, C. M. *Nature* **1995**, *375*, 769.

(24) Han, W. Q.; Fan, S. S.; Li, Q. Q.; Hu, D. Y. *Science* **1997**, *277*, 1287.