Inorg. Chem. **2001,** *40,* 2751−2755

The Synthesis of Megatubes: New Dimensions in Carbon Materials

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Received May 23, 2000

Extremely large carbon tubes, some exceeding 5 μm in diameter, were produced with both laser and electric arc techniques using graphite, a transition metal catalyst, and a reactive third-body gas. We have named these structures carbon megatubes. They are the first carbonaceous tubes large enough to observe using optical microscopy. We also report the synthesis of what we believe to be the first self-assembled branched nanotubes. In addition to their extreme diameters and unique morphologies, X-ray photoelectron spectroscopy has shown that these tubes also contain a significant amount of nitrogen atom incorporation into the graphite lattice. Subsequently, these nitrogen functionalities were shown to interact with rhenium pentacarbonyl bromide and serve as anchor points to tether molecules to the surface of the tubules.

Introduction

Exploration of the unique physical and electronic properties of carbon nanotubes has been the focus of many research groups over the past decade. It has been shown that nanotubes can be used in a wide range of applications such as gas storage devices,[1] circuit components,[2] composite fillers,[3] and probe tips.[4] Investigations of these applications have been limited by the availability of only a few sizes and morphologies of carbon nanotubes, which consist of both single-wall and multiwall varieties. Nanotubes usually have atomically smooth graphitic surfaces that are difficult to functionalize except under extreme conditions.[5] The ability to control the size of nanotubes would be very useful in some of their applications. The addition of manipulatable chemical functional groups on the surface of the tubules would also allow for the additional tailoring of the nanotubes' properties.

Our recent study explored the interaction of reactive third-body gases with carbon vapor created by either laser ablation or electric arc evaporation of graphite laden with various transition metal catalysts. The tubes produced with this reactive third-body gas method have shown themselves to have many unique chemical and structural features. These features may prove to be useful in many of the current applications for carbon nanotubes. This paper describes the first synthesis for carbon tubes that can produce an easily collectible deposit that contains tubes of controllable size and structure, which can then be easily functionalized through their inherent nitrogen moieties.

Experimental Section

Compound Preparation. Reagents and solvents were purchased commercially and used as received.

CAUTION! Cyanogen is a highly poisonous and flammable gas. The operator should take all necessary safety precautions and be well versed in what to do in case of accidental ingestion.

Preparation of Megatubes. Tubules were found in a mushroom-cap-like deposit above the graphite target in a laser ablation reactor[6] or surrounding the graphite anode in an electric arc reactor.[7] This cap deposit can weigh 100 mg after 10 min of carbon vaporization. For the laser experiment, the apparatus consisted of a 6.5 mm graphite rod with a 4 mm diameter hole drilled 30 mm into the tip. A mixture of nickel and yttrium powder[8] along with graphite was packed into the cavity. The rod was then placed into a 40 mm diameter water-cooled graphite holder. The reactor was evacuated and flushed with helium before being filled to 500 Torr of total pressure with a mixture of helium and varying amounts of cyanogen usually between 1% and 40% by volume. The graphite target was vaporized using 500 W of power (Spectra Physics, CO_2, 10.2 μm). For the arc reaction, a graphite anode similar to the rod used in the laser experiment was employed. The arc discharge was initiated by contact, and the electrodes were mechanically adjusted to maintain the proper spark gap of a few millimeters. The arc was generated with 70 A of dc current at 26 V. All other conditions were identical.

Preparation of Megatube/Rhenium Carbonyl Adduct. A cap deposit was collected from a cyanogen/nickel/yttrium catalyzed reaction and forced through a #120 sieve to yield a fine black powder. Seven milligrams of powdered nanotubes was added to 8 mg of $Re(CO)_5Br$ in 25 mL of hexane. The apparatus was attached to an oil bubbler, and stirring was continued for 24 h. The resultant mixture was filtered through a 0.2 μm UPE membrane and rinsed five times with hexane. The product was then resuspended in hexane and filtered again to ensure

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10.1021/ic000551q CCC: $20.00 © 2001 American Chemical Society
Published on Web 05/11/2001

complete removal of unreacted carbonyl compound. The nanotube adduct was then dried at 80 °C and weighed to yield 9 mg of a dark gray powder. IR spectrum (ZnSe plate): ν(C═O) 2115 (s), 2018 (s), 1999 (s), 1930 (s) cm^{-1}. XPS (Re): 4f$_{7/2}$ 41.6 eV, 4f$_{5/2}$ 43.9 eV.

Physical Characterization. All X-ray photoelectron spectroscopy experiments were done using a Physical Electronics 5700 with Al Kα monochromatic radiation. The samples were ground into a fine black powder and then dispersed in dichloromethane. This mixture was then deposited on a nickel stage as a thin film. All samples were outgassed overnight at $\sim 10^{-10}$ Torr.

X-ray powder diffraction was carried out on samples ground into a black powder using a Siemens D5000 automated diffractometer, Cu Kα radiation.

Transmission electron microscopy images were obtained using a Phillips 420 operating at 120 keV. Scanning electron microscopy images were taken on a Hitachi S-4500 working at 15 keV.

Transmission infrared spectra were obtained using a Bio-Rad FTS-40. Samples were finely ground, dispersed in dichloromethane, and deposited on ZnSe plates.

Raman spectra were taken at room temperature with 514.5 nm excitation in backscattered mode. The samples were ground into a fine powder and placed in a glass capillary tube for the measurements.

MM2 calculations for nitrogen atoms bonded within a graphite fragment were done using Chem 3D Pro software from Cambridge Software Inc.

Results

Reaction deposits were collected from various regions inside the reactors and examined using transmission electron microscopy and scanning electron microscopy. Tubules and “onions” could be observed intermixed with large amounts of amorphous carbon soot in all of the locations sampled, with the exception of the “cap” deposit that formed above the target rod (laser method) or around the anode (arc method). The cap deposit is a fibrous bundle consisting primarily of tubelike structures with very little soot or amorphous material present. It typically accounts for 75% of the total mass of graphite vaporized in the laser experiment and for 25% in the arc setup. This deposit contained many distinct tube morphologies: branched[9] (figures 1, 3, 4, and 9), bamboo-like (Figure 2), pearl-on-a-string (Figure 2), “chirally wound”(Figure 5), segmented (Figures 2, 4, and 8). In a particular sample, these morphologies could be observed (TEM/SEM/optical microscopy) in a variety of sizes ranging from 5 nm to 5 μm with the majority of the tubes having diameters on the order of hundreds of nanometers. Lengths ranging from a few microns to hundreds of microns (Figure 6) were observed. Some of these tubes are an order of magnitude larger, in diameter, than previously reported[10] multiwall nanotubes.

Their composition was confirmed using X-ray photoelectron spectroscopy (XPS) data. An XPS elemental survey revealed that some samples, produced with cyanogen, contained up to 5% nitrogen atom incorporation as well as about 0.5 atom % residual catalyst particles, based on analysis of the peak areas. The peak that corresponds to the nitrogen 1s electrons was centered at 399 eV, which can be representative of nitrogen bonded in an organic matrix as an amine, pyridine, or a nitrile.[11] This peak also exhibited a broad tail that extended out to 402 eV indicating that there are at least two chemically different nitrogen functional groups present in the tubes. The carbon 1s electron peak, located at 284.5 eV, was sharp, but had a small

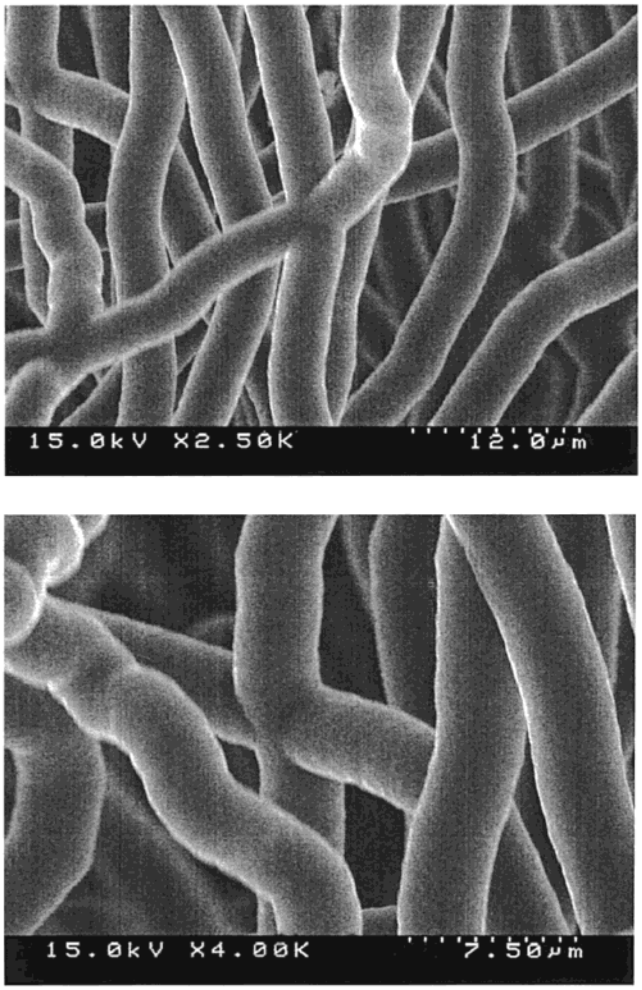

Figure 1. SEM images of branched carbon megatubes. Upper: The center of this micrograph features an X-branched tube with two more truly branched tubes visible at the left of this image. Lower: In a close-up of the upper image, tubes are clearly seen going over and under a tube that features a true four-way branch. The diameter of these tubes is approximately 4 μm.

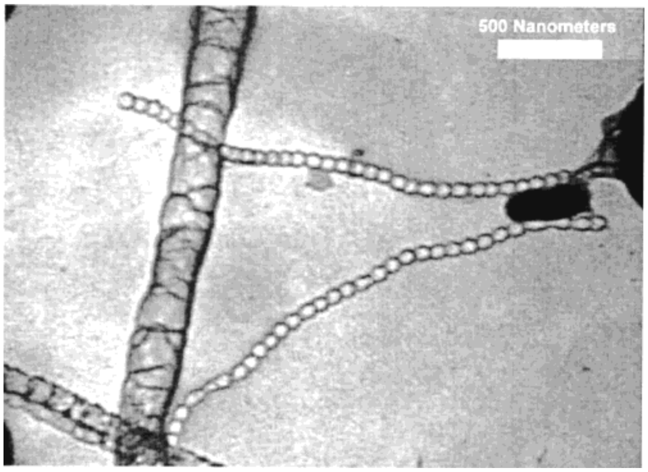

Figure 2. TEM view of two pearl-on-a-string tubes overlapping a larger bamboolike tube. The dark particle ajoining the two pearl tubes is a residual catalyst particle. These tubes have extremely thin walls relative to their contained volumes when compared to multiwall nanotubes synthesized from previously reported techniques. Scale bar: 500 nm.

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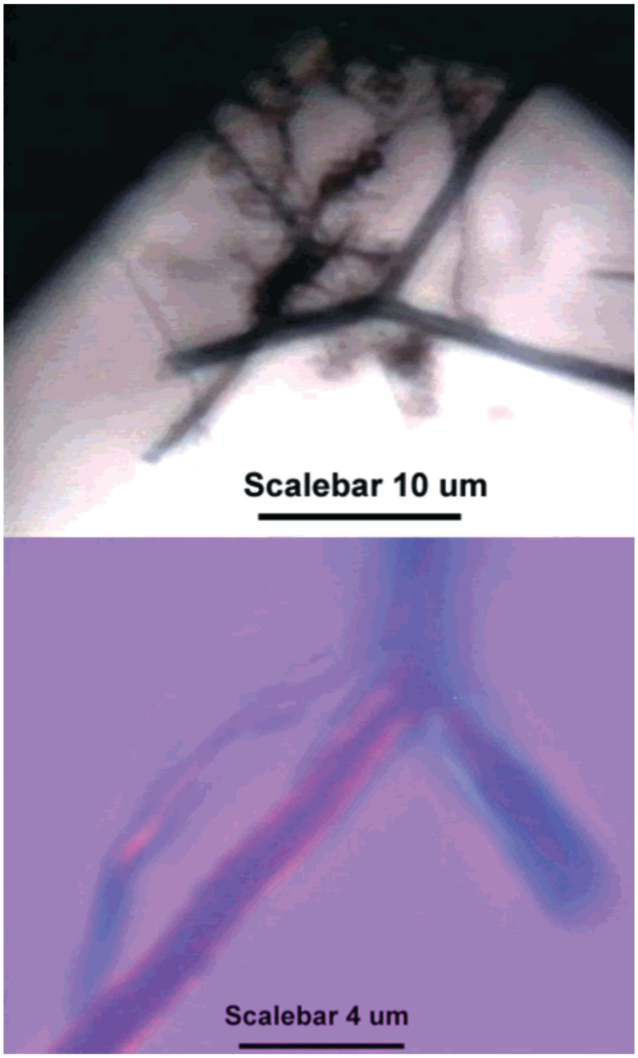

Figure 3. Images of carbon megatubes obtained with an optical microscope. Upper: Brightfield image of megatubes, including a branched one, mounted on a formvar substrate that spans over an electron microscope grid. Lower: Image of several tubules using polarization microscopy. First-order red compensator inserted. Note blue "addition" and orange "subtraction" colors which indicate the major axis of the highly oriented, birefringent components of the megatubes. The "slow" axis of retardation is parallel to the branched megatube with the blue color.

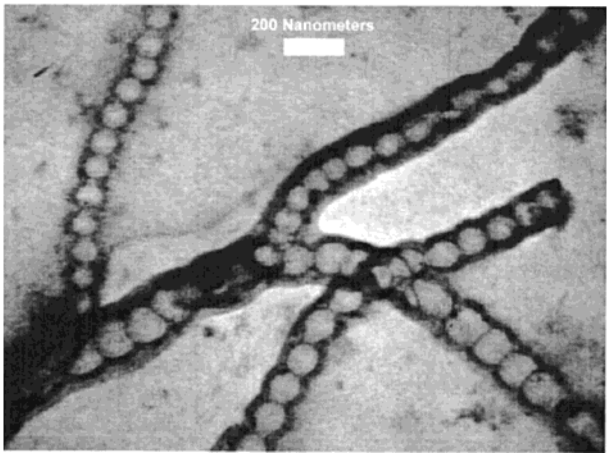

Figure 4. TEM showing several segmented tubules. The feature in the center of the micrograph is an example of a true Y-branch. This tube has a tube overlapping the lower branch as well. Scale bar: 200 nm.

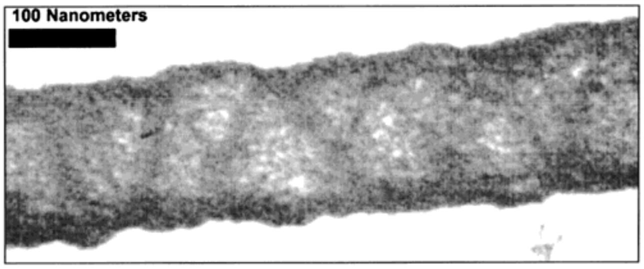

Figure 5. TEM image of a "chirally wound" tube displaying a spiral motif. Scale bar: 100 nm.

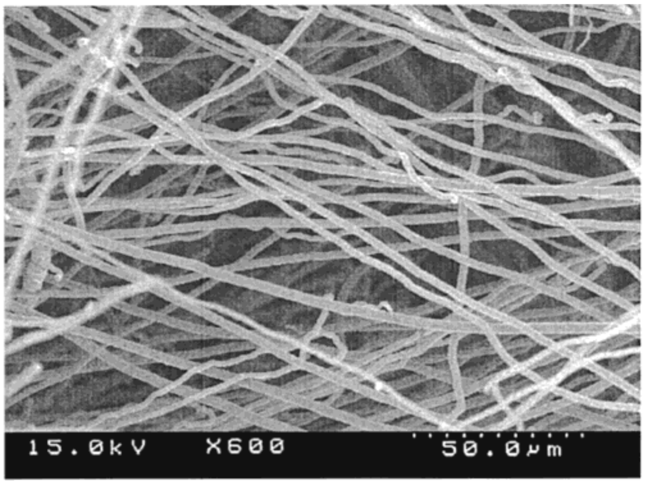

Figure 6. SEM image of megatubes from a native, "as prepared", cap deposit. The tubules shown are microns in diameter, and most are in excess of 200 μm (approximately $^4/_3$ the width of the image) in length. Note the lack of soot and other nontubular material present in this micrograph.

amount of tailing most likely arising from the carbon atoms adjacent to the nitrogens.

The tubes were analyzed by X-ray powder diffraction. Diffraction peaks were observed for the residual metal catalyst particles and for the graphite layers. The 200 graphite reflection, which corresponds to the spacing between adjacent layers, is centered at a *d* spacing of 3.42 Å. This peak is broad in most of the samples and is expanded from the usual graphite interplane spacing of 3.35 Å. In some samples a distinct less intense peak at 3.35 Å would emerge from the shoulder of the broad peak, but in most samples this was not the case.

An infrared study was undertaken with the tubes in their native state and after complexation with rhenium pentacarbonyl bromide. Absorbances at 1574 and 808 cm^{-1} were observed in the transmission IR spectrum for the uncomplexed tubules. These have been assigned[12] to the E_{1u} and A_{2u} vibrational modes, respectively, of the graphite layers. No additional absorbances corresponding to the nitrogen moieties were present, probably due to their concentrations relative to the graphite present and its broad absorbance across the IR spectrum. After the addition of the rhenium compound to the surface of the tubes, additional vibrations were observed for the carbonyl ligands at 2115, 2018, 1999, and 1930 cm^{-1}. These are shifted from that of the starting compound and are appropriate for rhenium tetracarbonyl bromide complexed to a neutral two-electron donor.[13] Currently,

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(11) (a)Dibyendu, S. B.; Sukumar, M. *J. Polym. Sci., Part B* **1997**, *35*, 2049. (b)Pels, J. R.; Kapteijn, F.; Moulijn, J. A.; Zhu, Q.; Thomas, K. M. *Carbon* **1995**, *33*, 1641.

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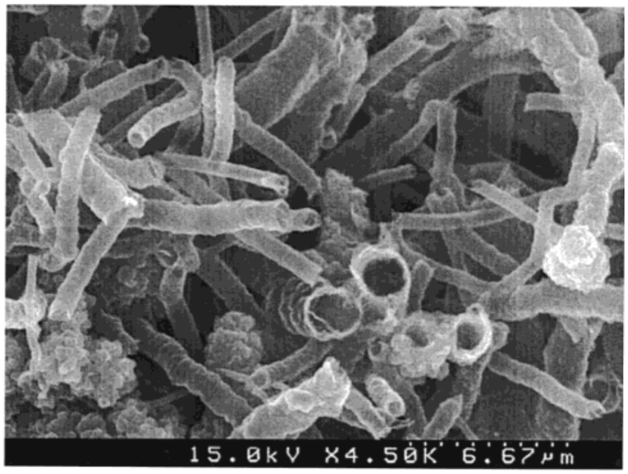


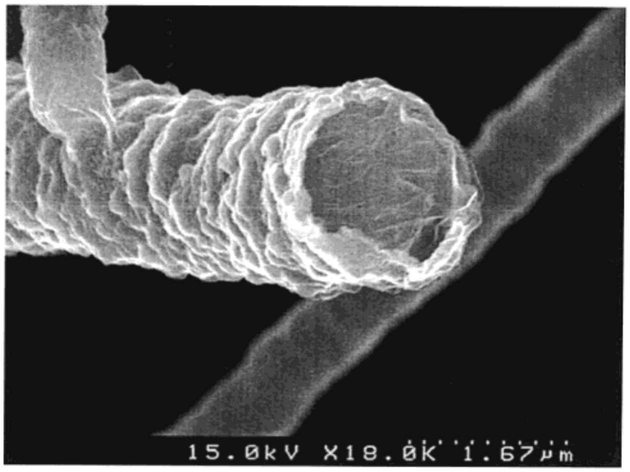
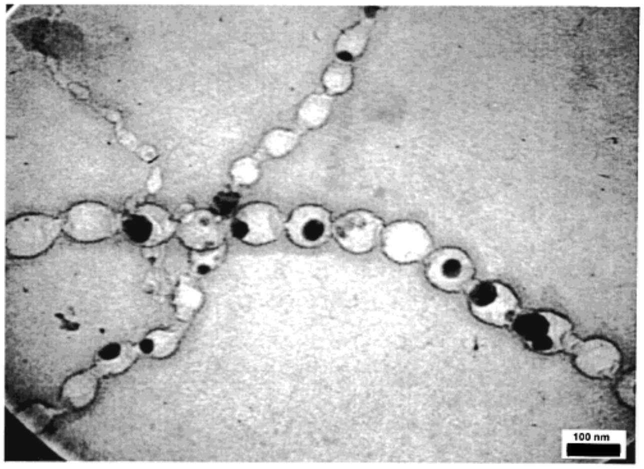


Figure 7. SEM image of “cut” megatubes. Upper: A tuft of tubes was cut with a scalpel to illustrate their hollowness. Lower: Close-up of a “cut” megatube. This image reveals that these tubes have very thin walls relative to their contained volume. This property may lend itself to a variety of “host” applications.



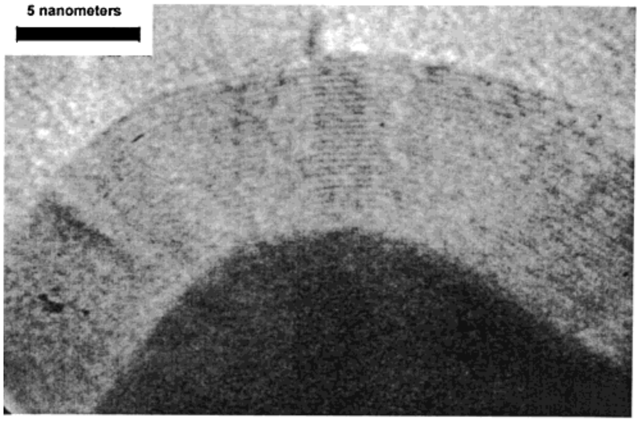


Figure 8. TEM images of carbon nanotubes. Upper: In this image three segmented tubules containing residual catalyst particles are shown. Lower: Under higher magnification the graphite layers, that form the walls of the tube, are seen encapsulating one of the catalyst particles. There appear to be defects present in the layers, especially in the middle of this micrograph.

more rigorous IR spectroscopic methods are being undertaken to elucidate the nature of the nitrogen bonding relative to carbon.

Raman spectroscopy was also used to characterize the tubes. A broad peak was seen at 1350 cm^{-1}, as well as its overtone at 2702 cm^{-1}, which is assigned to the D band.[12] A strong sharp peak at 1582 cm^{-1} represents the E_{2g} mode of the concentric graphite shells. Peaks were also recorded at 794, 921, 1075, 1152, and 2329 cm^{-1} and were unassigned at the time of publication.

Discussion

No unique morphology nanotubes were observed if any one the three components—inert gas, reactive third-body gas, or metal catalyst—was absent. To some extent the morphology and the diameter could be affected by adjusting the concentration and the nature of the reactive third-body gas. By far cyanogen gave the best results; ammonia, hexafluoroethane, hydrogen, and chlorine also generated unique morphology nanotubes, but with far less efficiency than cyanogen. Increased concentrations of cyanogen typically led to larger tube diameters, with thicker side walls. cyanogen concentrations around a few percent yielded structures typical of those presented in the figures.

The “cap” deposit, which contained most of the tubules, formed in the same location above the heated graphite rod whether the laser or the electric arc was employed as the heat source. The bulk appearance of this deposit was also the same for the two sources, but some differences could be observed upon inspection with TEM. The same morphologies could be found in the two products, but the laser method seemed to produce tubes that, in general, had thinner side walls (fewer layers of graphite) relative to their diameters than tubes made with the arc method. The amount of nitrogen atom incorporation was similar for a given concentration of cyanogen (XPS) for the two methods. The arc method is less efficient relative to the laser method due to the large dense mass, of mostly amorphous carbon, that collects on the cathode.

The tubes have also been shown to contain a significant amount of nitrogen incorporation into the graphite lattice that may lend itself to increased functionalization of the tube’s surface. The nitrogen atoms contained in the tubules are most likely to be bonded in a three-coordinate fashion within and on the surface of the graphite layers. Models of graphite fragments containing one nitrogen atom were used to calculate energetically favorable bonding arrangements. On the basis of MM2 calculations, it is energetically possible for nitrogen to be bonded within the plane as an ene−amine or pyridine and on the surface as an amine or nitrile. These groups are also in agreement with the XPS data.[11] All of the functionalities contain at least some nitrogen lone pair character which would be able to coordinate to electron deficient metal centers, perhaps serving as a support for catalytically active metals. We employed rhenium penta-

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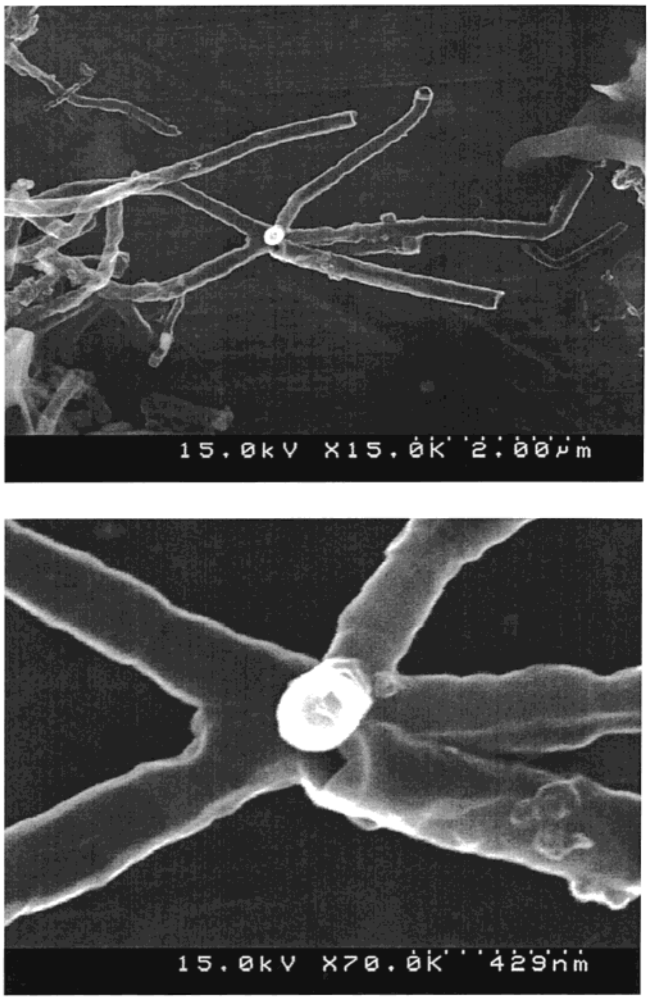

Figure 9. SEM images of a "star" nanotube. The bright spot in the center of the array is a branch rising vertically out of the image plane.

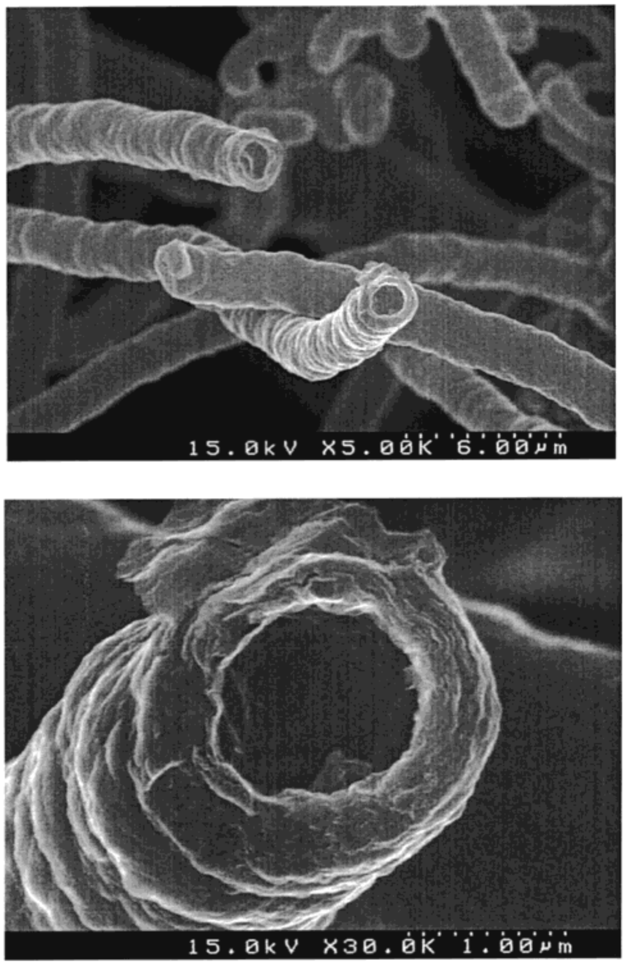

Figure 10. SEM image of megatubes that have been cut with scissors. Upper: The hollowness of megatubes is apparent after being sliced. This sample was made with a higher cyanogen concentration than those pictured in Figure 7. This results in the thicker sidewalls observed in these images relative to those in Figure 7. Lower: A close-up reveals a cavity over one micron in diameter.

carbonyl bromide to test the electron-donating ability of the nitrogen moieties. The tubes displaced a carbonyl to form an adduct between the tubes' surface and the rhenium molecule. The progress of this reaction was monitored by weight gain and carbon monoxide evolution and confirmed by studying the shift of the remaining carbonyl groups using infrared spectroscopy. In addition, these nitrogens should be manipulatable through conventional organic chemistry techniques and could serve as an anchor point for a variety of organic molecules. We are currently investigating the possibility of using these rhenium-coated tubules as heterogeneous catalysts for olefin polymerization as well as trying to attach other catalytically active metals.

The mechanism that creates carbon nanostructures is still not well understood, but it does not seem to be dependent on the heating source used. The combination of metal catalysts and reactive third-body gases seems to stabilize the intermediate carbon vapor species and allows for these unique nanostructures to form rather than aggregate into amorphous sootlike particles. If the reactive gas is absent from the reaction mixture, but the nickel−yttrium catalyst is present, a similar "cap" deposit is formed that consists exclusively of single-wall nanotubes. If the metal catalyst is absent, but the reactive gas is present, then the primary product now becomes amorphous soot containing a small amount of carbon capture products. In the case of cyanogen these capture products are nitrile terminated polyynes;[7] for chlorine, polychlorinated aromatics[14] are produced. If both the metal catalyst and the reactive gas are omitted, fullerenes along with soot will be produced.[8] In any case, our results indicate that the addition of a reactive third-body gas is another parameter that expands the amount of useful products that may be created from the condensation of carbon vapor.

Our reactive third-body gas method for generating unique morphology nanotubes, from either laser ablation or electric arc evaporation of graphite, produces macroscopic quantities of product in a relatively pure and easily collectible deposit. This feature along with the tubules' unique topographies, large sizes, and nitrogen moieties has the potential to expand the applications of nanotubes beyond their present boundaries.

Acknowledgment. Supported by the Welch Foundation (F-0700 and F-1217) and the Advanced Technology Program of Texas (003658-0901-1999). The authors thank Dr. Jose Lozano for his XPS measurements and Dr. Steve Swinnea for his help with X-ray powder diffraction.

Supporting Information Available: X-ray powder patterns, XPS, IR and Raman spectra for native and rhenium carbonyl bromide complexed tubules. This material is available free of charge via the Internet at http://pubs.acs.org.

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