CHEMISTRY OF MATERIALS

VOLUME 16, NUMBER 14 JULY 13, 2004

Communications

Silica-Coated Single-Walled Nanotubes: Nanostructure Formation

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Received February 25, 2004
Revised Manuscript Received May 5, 2004

Over the past decade, perhaps no material has enjoyed more widespread attention with regard to its application in nanotechnology than the carbon nanotube (CNT).[1] This interest is due to the appealing properties that CNTs offer, which include, but are certainly not limited to, high mechanical strength and large thermal and electrical conductivities.[2] Unfortunately, their use has been limited by certain drawbacks. With regard to incorporating CNTs in material composites, problems still exist with the compatibility of CNTs with the other substances in the composite and with the dispersion of CNTs throughout the composite.[3] This is primarily due to the CNTs' strong affinity for one another.[4] Given that CNTs, especially single-walled carbon nanotubes (SWNTs), represent a bridge between present silicon-based electronic devices and "next-generation" molecular electronics, it is desirable to develop methods to promote their incorporation into present processes while moving toward molecular devices. It is the intention of our research program to overcome the difficulties regarding incorporation of SWNTs in structural and functional composites. The initial step toward this goal involves coating SWNTs with materials that will eliminate the undesirable attractive interactions between the nanotubes and facilitate their incorporation into composites. To promote compatibility with existing silicon-based technology, we have focused our initial studies on silica-based coatings.

Previously, we have demonstrated that treating a dispersion of SWNTs in an aqueous surfactant solution with an *acidic* solution of fumed silica results in silica-coated SWNTs.[5] Herein, we report a complementary method for generating silica-coated SWNTs that uses a *basic* solution of aqueous sodium silicate. Our results indicate that the resulting silica-coated SWNTs can be readily deposited onto flat substrates to form mats composed of overlapping coated tubes or bundles of tubes. Imaging of the mats using scanning electron microscopy (SEM) reveals that the coated tubes assemble into interesting nanoscale structures.

Our method of using a basic sodium silicate solution to coat SWNTs with silica is adapted from methods applied to coating gold nanoparticles.[6] A general description of the synthesis of silica-coated SWNTs under basic conditions is as follows. A 0.54 wt % SiO_2 solution was prepared by mixing 1 g of 27 wt % SiO_2 sodium silicate (Na_2SiO_3) solution with 49 g of Millipore-filtered

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10.1021/cm049710k CCC: $27.50
Published on Web 06/11/2004

deionized H_2O. A 0.20 wt % (5.7 mM) sodium dodecyl benzene sulfonate (SDBS) aqueous solution was prepared by dissolving 0.2 g of SDBS in 99.8 g of pure H_2O. Raw HiPCO SWNTs were purified using a literature method[7] that involves baking at 200 °C in air for 12 h, followed by washes with concentrated HCl (aq) and then deionized H_2O to remove residual iron catalyst from the synthesis process. The purified SWNTs were then annealed at 800 °C in argon for 1 h.[8] An aqueous suspension of purified and annealed SWNTs (PA SWNTs) was prepared according to Islam et al. by agitating a mixture of 1 mg of PA SWNTs and 20 mL of 0.2 wt % SDBS (aq) at 50 °C for 12 h using a tabletop ultrasonic cleaner.[9] The resulting suspension was filtered through filter paper to remove excess unsuspended PA SWNTs and give a clear gray solution (SWNT/SDBS).[10,11] Into a 50-mL polypropylene centrifuge tube were placed 5 mL of SWNT/SDBS solution and 10 mL of 0.54 wt % SiO_2 solution to give a clear light gray solution. The solution was stirred for 5 min at room temperature to ensure that the mixture was homogeneous. No cloudiness or precipitation was observed over this period or longer periods (i.e., several weeks). As the solution was stirred, 25 mL of absolute ethanol was added. Immediately after the addition, the solution became hazy and small gray particles were visibly suspended uniformly throughout the entire volume of the liquid. After 5 additional minutes of stirring, the sample was centrifuged at 4400 rpm, 25 °C for 5 min. The supernatant was discarded and the pellet was redispersed in 40 mL of absolute ethanol using 5 min of ultrasonication at room temperature. The centrifugation/redispersion process was repeated five times. Mats of SiO_2−SWNTs were generated on polished aluminum substrates for subsequent characterization using SEM by drop coating concentrated ethanolic suspensions of coated tubes. Prior to imaging, samples were sputtered with a thin layer of chromium to prevent charging. Images were obtained with a Philips XL-30 ESEM using an acceleration voltage of 30 kV.

Coating of the suspended SWNTs occurs through the ethanol-induced formation of silica acid [i.e., hydrated silica, $Si(OH)_4$] according to eq 1.[12]

$$Na_2SiO_3 + H_2O + 2\ EtOH \rightarrow Si(OH)_4 + 2\ NaOEt \quad (1)$$

The free silica acid quickly begins to condense to form polysilicic acid (i.e., amorphous silica or silica gel) which precipitates from solution and coats the suspended nanotubes. Our previously reported acidic method of coating individual nanotubes worked best with cationic surfactants (e.g., DTAB, CTAB), because anionic surfactants (e.g., SDS, SDBS) become unstable in acidic solution.[5] The present method allows for the use of more common anionic surfactants because the initial reaction mixture is a basic solution. Moreover, the acidic method produces hydrofluoric acid (HF) that converts portions of the silica coatings to fluorosilicates. However, this basic method is completely free of fluorine, yielding coatings that are composed entirely of silicon and oxygen.

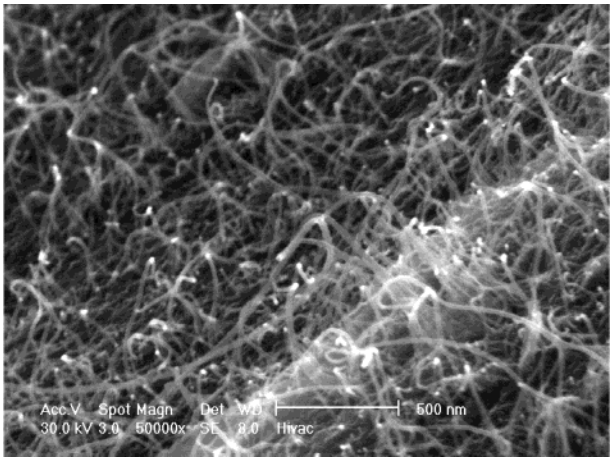

Figure 1. SEM images showing a mat of coated SiO_2−SWNTs.

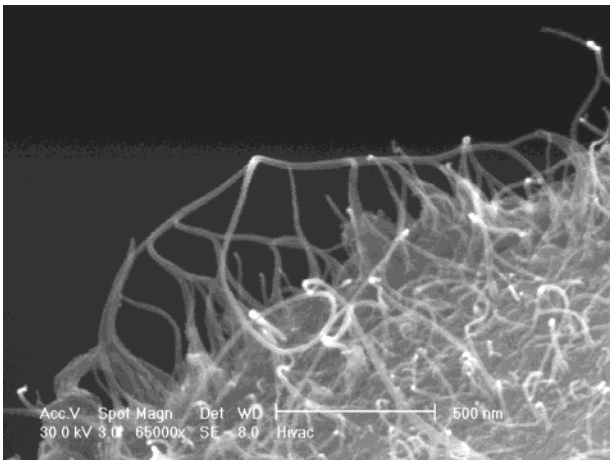

Figure 2. SEM images showing a complex structure consisting of welded SiO_2−SWNTs.

Films of silica-coated SWNTs were deposited onto aluminum substrates by allowing drops of ethanolic suspensions of coated tubes to evaporate completely. Imaging these films using SEM revealed that the coated tubes assemble into mats. The surfaces of the mats are composed primarily of overlapping and interwoven coated tubes and coated bundles of tubes; however, images of the edges of mats or at torn regions within the mats reveal large numbers of distinctly separate (i.e., unwoven) coated tubes or bundles (Figure 1). Most probably during the drying process, regions of the mats split either completely to form the edges of new smaller mats or incompletely to form gashes within an existing mat. This process appears to cause the tubes to unravel from one another into a more separated state. At the mat edges, the coated tubes tend to possess either looped

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(10) When SWNTs are suspended in water by a surfactant, they can be suspended both as individual tubes or bundles, surrounded by a surfactant micelle. Although the method used suspends a large number of SWNTs as individuals, no special effort is made to separate these individuals from any suspended bundles. Consequently, the method described herein produces both silica-coated individual tubes and silica-coated bundles.

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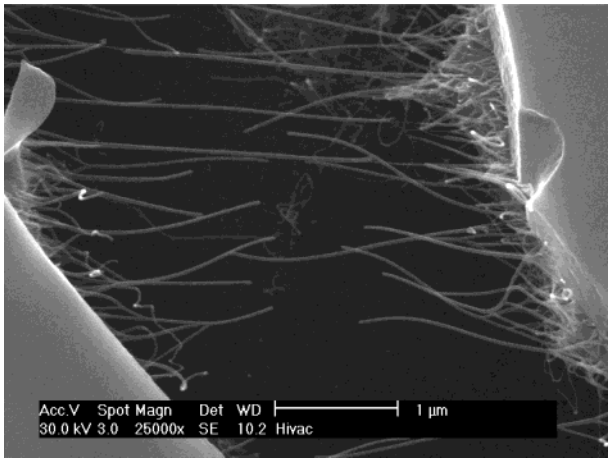

Figure 3. SEM image showing long filaments consisting of shorter tubes glued together by the silica coating.

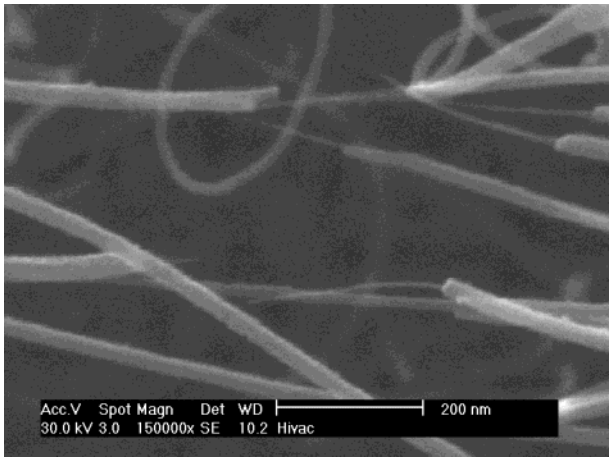

Figure 4. SEM image showing uncoated middle sections of SiO_2−SWNTs, broken by extended exposure to the e-beam.

or curled ends or ends that are interconnected (i.e., welded together) with their nearest neighbors to form complex structures (Figure 2). Within existing gashes, SiO_2−SWNTs are stretched parallel to their neighbors and bridge/span the width of the gash. Interestingly, a number of bridging tubes appear significantly longer (ca. 5 μm) that the average length of HiPCO SWNTs (<1 μm),[13] indicating that the coatings are able to "glue" nanotubes end to end to form longer filament structures (Figure 3). In addition, the coated tubes both at the mat edges and within the gashes possess diameters that are significantly narrower than those of tubes composing the interwoven regions (ca. 25 nm) suggesting that the thicker features (60−100 nm) represent bundles of coated tubes which unravel during the splitting process. Furthermore, we have observed bridging tubes that expose uncoated sections of tubes at their middles. If the e-beam was focused at these regions, the SWNTs snapped in two (Figure 4). Figure 4 shows that the diameter of the silica coating is ca. 25 nm while the thickness of the broken inner uncoated tube is ca. 3−6 nm demonstrating that this method coats individual tubes or small bundles of tubes.

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In summary, we have developed a method for coating SWNTs with silica under basic conditions. Images of the dried films of the coated tubes reveal assembly into a variety of unique nanostructures. The coating process traps SWNTs in irregular conformations such as loops, curls, interconnects, and bridging structures. In addition, the coatings fasten shorter tubes together into longer structures. We are currently examining the potential of our solution-based methods of producing silica-coated SWNTs and mats for manipulating conducting/semiconducting SWNTs and insulating coatings to assemble useful nanoelectronic devices.

Acknowledgment. This work is dedicated to the memory of Prof. John L. Margrave (1924−2003) for his contributions to chemistry and in particular to the field of SWNTs. Financial support for this work was provided by the National Science Foundation. We thank R. E. Smalley for the supply of raw HiPCO SWNTs.

Supporting Information Available: SEM images showing a mat of coated SiO_2−SWNTs and looped coated SiO_2−SWNTs (pdf). This material is available free of charge via the Internet at http://pubs.acs.org.

CM049710K