Chem. Mater. **2000,** *12,* 599−601

Formation of Single-Wall Carbon Nanotube Superbundles

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Received November 8, 1999

Since their discovery in 1993,[1,2] carbon single-wall nanotubes (SWNTs) have been of great interest because of their expected novel electronic,[3] mechanical,[4] and gas adsorption properties.[5] Difficulties arise in measuring these various properties because the SWNTs currently available for analyses have very small bundle sizes (10−20 nm) and are typically in random orientations. A vital step for the industrial application of SWNTs is to align the individual tubes into bundles of a size that allows facile measurement of the various physical and chemical properties. This paper is the first to illustrate a set of procedures for the preparation and isolation of aligned SWNT "superbundles".

The synthesis of raw SWNT soot is similar to the pulsed laser vaporization technique described by Guo et al.[6] A Nd:YAG laser (1064 nm) was employed to synthesize the carbon nanotubes from 1.2 atom % metal-doped (50:50 Co/Ni) pressed graphite targets.[7] The targets were placed in a quartz tube that was heated to a temperature of 1200 °C in a clam-shell furnace. With the laser operating at a frequency of 10 Hz, the laser power and beam size were adjusted to provide ~20 J/(pulse cm^2) at a ~450-ns pulse width. An argon flow of 100 sccm at 500 Torr was maintained through the reaction vessel for the duration of the synthesis. The raw soot was purified by refluxing in 3 M nitric acid for 16 h, filtering and washing with deionized water on a polytetraflouroethylene (PTFE) filter, and then heating the obtained paper in air for 30 min at 550 °C. This procedure results in tubes of greater than 98 wt % purity when target material is not sputtered and trapped in vaporized soot.[7] A representative TEM image of the resultant pure tubes is shown in Figure 1a. The random orientation and small size of the long bundles are apparent.

The SWNTs exist as a random tangle because of the conditions under which they are synthesized and purified. The tubes are formed within the high-temperature plasma generated by the laser striking the graphite target, and their formation is rapidly quenched as the tubes diffuse out of the plasma plume. The resulting SWNTs exist in small bundles and are accompanied by other graphitic and amorphous carbon fractions as well as metal nanoparticles. The purification process succeeds in removing the non-nanotube carbon fractions and the metal, but the bundles are still randomly oriented with diameters of only ~5−20 nm. We have discovered that through the use of ultrasound and polar solvents. it is possible to unwind the intertwined SWNT bundles. Subsequent removal of the ultrasonic perturbation results in realignment and collapse of the SWNTs into the much larger superbundle configuration.

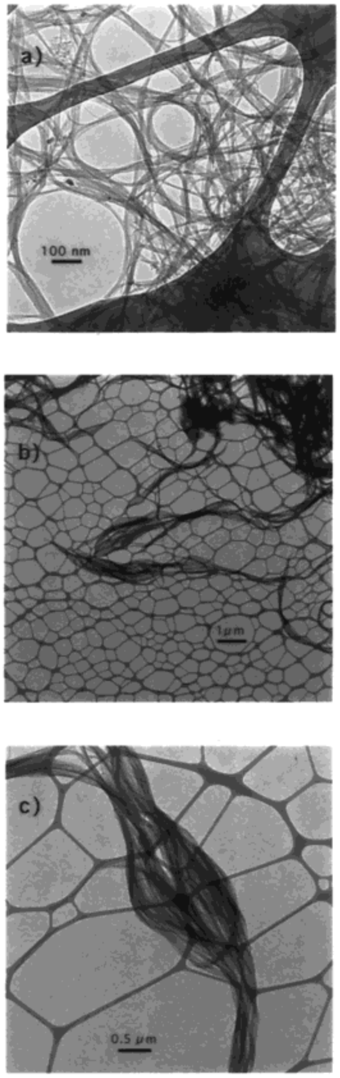

Figure 1. TEM images of (a) purified single-wall nanotubes with small diameter bundles, (b) SWNT superbundles extracted from a 50:50 water/methanol solvent mixture, and (c) a SWNT superbundle at higher magnification.

A 1.0-mg sample of purified SWNTs was placed in a cylinder containing 10 mL of deionized water or other polar solvents or solvent mixtures. A Heat Systems-Ultrasonics Inc. model w-220F Cell Disrupter sonic horn was submersed into the solution and the power was slowly increased to 90 W/cm^2. The ultrasonic agitation was continued for a maximum of 120 min. Normally,

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10.1021/cm9907108 CCC: $19.00

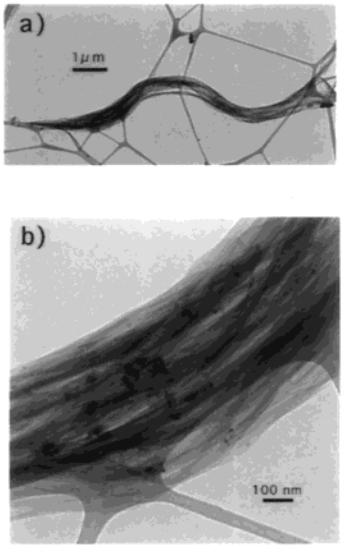

Figure 2. TEM images of a SWNT superbundle extracted from water at (a) low magnification illustrating the length of the fiber and (b) high magnification displaying the width and dense packing of the superbundle.

SWNTs are not dissociated in aqueous solution without the use of surfactants. With the use of the sonic horn, however, the purified SWNT sample was almost immediately dispersed throughout the solvent. The SWNT material agglomerated in the solution when the ultrasonic agitation was turned off. Gentle shaking of the solution redistributed the tube agglomerations into an apparently homogeneous suspension. When the sonicated solution was allowed to settle, a thin layer of SWNT superbundles was observed at the solvent−air interface. These superbundles could be isolated via several different procedures and on a series of substrates. For example, a TEM grid could be used to lift off the SWNT interface layer to extract fibers. The resulting isolated SWNT superbundles were ∼0.4−1 μm in diameter, 5−10 μm in length, and present in many locations on the TEM grid. Other collection strategies included the use of silver, platinum, silicon, or highly ordered pyrolytic graphite substrates, sonication of the tubes in the presence of the substrate, or spin coating the sonicated solution onto a prepared substrate surface. The polarity of the solvent greatly affects the size and density of the bundles after sonication. Solvents such as toluene, hexane, alcohols, and water have been employed thus far, and SEM images showed that sonication in toluene produces the smallest bundle diameters (∼50 nm) while water produces the largest (∼1 μm).

Figure 1b displays a TEM image of SWNTs on a grid dipped into the film formed following sonication in a 50:50 methanol/water mixture. The large superbundles are readily apparent, and it is clear that some of these superbundles are completely isolated. An image of an isolated bundle at higher magnification is displayed in Figure 1c. The superbundle configuration evidently arises from the minimization of the interactions between hydrophobic SWNT surfaces and the polar solvent such that the van der Waals interactions along the axial length of the tubes are maximized. The extent of collapse of the superbundle into a tight bundle depends on solvent polarity. Figure 2a displays a TEM image of a highly collapsed bundle extracted from water. The dense bundle is displayed at higher resolution in Figure 2b. Some of the bundles extracted from water were so dense that a TEM image could not be obtained as the electron beam could not penetrate through the tight nanotube packing. These bundles were shown to contain aligned tubes using scanning electron microscopy.

Shelimov et al.[8] found that 12-nm-wide SWNT bundles purified by ultrasonically assisted filtration could be formed into 30-nm-wide nanoropes by refluxing in dilute nitric acid. Introduction of defects by sonication resulted in cutting during reflux so tangled raw SWNTs could be unraveled and isolated bundles could be formed. In contrast, our starting material was purified with a process that has a nitric acid reflux step and no sonication so the SWNT mat was left tangled.[7] Bundles nearly as large as those obtained by Shelimov et al. were found immediately after purification (∼20 nm). Surprisingly, the purified mat of hydrophobic SWNTs could be easily dispersed by sonication into polar solvents such as water and methanol. We speculate that dissolution occurred because tube−tube interactions were weakened by the disruption of bundle packing brought about by nitric acid intercalation[9] during purification. Removal of the ultrasonic agitation allowed the dispersed, unraveled, and perhaps shortened tubes to precipitate from the polar solvents to form superbundles 5−10 μm long with thicknesses 30 times greater than previously observed.[8]

Through an analysis of the angular spread between the axes of the nanotubes comprising the dense superbundle in Figure 2b, we estimate that virtually all tubes are aligned within ±20°, and a vast majority of tubes are oriented within ±10°. The degree of alignment is expected to improve as the density, and therefore the crystallinity, is increased. Although several methods have been introduced for aligning multiwalled nanotubes,[10−12] we are unaware of any other work which describes the postsynthesis alignment of SWNTs. Cheng et al. recently grew SWNTs directly from hydrocarbons in ribbons as wide as 100 μm,[13] but the tubes within the ribbons were not nearly as well-aligned or condensed as those described here.

The ability to form organized SWNT superbundles is important because of the possibility of performing macroscopic analyses on well-defined samples. Of particular interest would be polarized Raman spectroscopy studies that would allow unambiguous assignment of observed spectral bands to specific types of SWNTs. Superbundle formation may also be a first step toward the production of longer fibers which would enable macroscopic mechanical testing. Control over the superbundle length and diameter at either the formation step or subsequently through the use of other means

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may provide a route to electrical connectors of predetermined resistance, or perhaps superbundle crystals and films that would be useful as hydrogen adsorbents or gas transport membranes.

We are working on improving the tube alignment and rebundling procedures. A variety of solvents including alcohols, acids, and nonpolar solvents are currently under investigation to determine the extent of hydrophobic/hydrophilic interactions on superbundle formation, and how solvent oxidative strength affects tube fracture. The use of electrical fields to align the superbundles is also being pursued.

Through the use of an ultrasonic cell disrupter and experimental control over dissolution and precipitation, the number of tubes in a pure bundle was increased from several hundred to several thousand. The micrometer-sized superbundles contain SWNTs which are fairly well aligned and are therefore better suited for studies and applications than the disorganized nanometer-sized bundles found after synthesis and purification. The possibility of fiber production and mechanical, optical, and electrical testing are greatly simplified. With further manipulation, the superbundles may be useful as electrical connectors, or as building blocks for crystals or films that may be useful as hydrogen adsorbents or gas transport membranes.

Acknowledgment. This work was supported by the Office of Science, Basic Energy Sciences, Division of Materials Science and the Office of Energy Efficiency and Renewable Energy Hydrogen Program of the Department of Energy under Contract No. DE-AC36-99-GO10337.

CM9907108