

DOI: 10.1002/sml.200800231

Composite Carbon Nanotube/Silica Fibers with Improved Mechanical Strengths and Electrical Conductivities**

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Carbon nanotube (CNT)/silica composites have been extensively investigated due to their superior combined properties, which come from both CNTs and silica.^[1] For example, CNTs impart good mechanical, electrical, and chemical performance to the composites,^[2] while silica makes the composites stable in harsh environments (such as high temperatures and strong acids/bases) and easy to fabricate.^[3] A combined set of desired properties for CNT/silica composites cannot be found in their individual constituents, thus making these composite materials very useful in many applications. To synergistically utilize their excellent properties, CNT/silica composites with various morphologies, including films synthesized by solution casting,^[4] powders by hot pressure,^[5] xerogels by sol-gel technique,^[6] and nanocomposite films or powders by covalent connection between CNTs and silica,^[7] have been widely studied. One of the main challenges for the manufacture of these materials is the random dispersion of CNTs in the resulting composites, which leads to much reduced mechanical and electrical properties. For example, CNT/silica composites with up to 30 vol% CNT processed by hot pressing show a maximum mechanical stress of only 85 MPa.^[3b]

Here, we report the first synthesis of composite CNT/silica fibers in which the CNTs are highly aligned. These composite fibers show much improved mechanical properties and electrical conductivities compared with CNT/silica films, powders, or xerogels. The CNT/silica fibers show good tensile strengths due to the formation of robust and strong cross-

linked silica networks. In addition, they lack several of the drawbacks (e.g., aging and degradation) of composite CNT/polymer fibers and can be used in harsh environments such as high temperature and strong acids/bases.^[4]

Pure CNT fibers were spun from high-quality CNT arrays, which were synthesized using the chemical-vapor-deposition process. Figure 1(a and b) shows scanning electron microscopy (SEM) images of a spinnable CNT array on silicon. Individual CNTs are vertical to the substrate and highly aligned with each other. These properties are important for fiber spinning. The inset in Figure 1b (transmission electron microscopy image) indicates that the synthesized CNTs are multi-walled with diameter ≈ 10 nm. Representative Raman spectra (Figure 1c) of the array shows a strong peak at 1307 cm^{-1} for D-band and a weak peak at 1598 cm^{-1} for G-band, similar to other spinnable CNT arrays.^[8] Figure 1d shows a typical SEM image of a pure CNT fiber with a diameter of $\approx 10\text{ }\mu\text{m}$. The diameter of CNT fibers can be controlled from $4\text{ }\mu\text{m}$ to $20\text{ }\mu\text{m}$, depending on the initial ribbon width during the spinning. The ribbon is defined as a bunch of CNTs pulled out of a CNT array at the beginning of the spinning.

Two methods were utilized to synthesize composite CNT/silica fibers from pure CNT fibers and two silica precursors, $(\text{EtO})_3\text{Si}(\text{CH}_2)_3\text{NCO}$ (C1) and $(\text{EtO})_3\text{Si}(\text{CH}_2)_3\text{NH}_2$ (C2): 1) directly casting the precursor (either C1 or C2) on the outer surface of CNTs by spinning pure CNT fibers through precursor solutions, followed by evaporation of solvents (see Figure S1); and 2) hydrogen bonding of C2 to CNTs by chemical modification of the outer surface of the CNTs (see Fig. S2). In the second case, CNT fibers were first treated with 5 M HNO_3 to produce functional carboxylic acid groups on the outer surface of the CNTs. C2 molecules were then connected to the CNTs by hydrogen bonding. For both methods, hydrolysis and condensation reactions of precursors were carried out under acidic conditions. ^{29}Si nuclear magnetic resonance spectroscopy was used to investigate the state of Si atoms in the composites. Three peaks were observed for the composite CNT/silica fiber derived from C1, and they are attributed to T^1 ($\delta = 49$, $\text{CSi}(\text{OH})_2(\text{OSi})$), T^2 ($\delta = 58$, $\text{CSi}(\text{OH})(\text{OSi})_2$), and T^3 signals ($\delta = 67$, $\text{CSi}(\text{OSi})_3$), respectively; while two main peaks at 57 ppm for T^2 and 66 ppm for T^3 were observed for the composite CNT/silica fiber derived from C2.^[9] The element contents of Si, O, and C obtained using energy-dispersive X-ray spectroscopy, using standard samples, are listed in Table 1. The weight content of silica is therefore calculated as 8.15%, 9.27%, and 17.73% for the C1-derived CNT/silica fibers made by direct casting, C2-derived CNT/silica fibers made by direct casting, and C2-derived CNT/silica fibers made by chemical modifications, respectively. The details are discussed in the Supporting Information.

Figure 2(a and b) shows SEM images of the composite fibers derived from C1 and C2 by direct casting. The fibers are uniform along the axial direction with a diameter of $10\text{ }\mu\text{m}$ in both cases. Figure 2c represents a typical SEM image of a C2-derived fiber by chemical modification. This fiber also shows a diameter of $10\text{ }\mu\text{m}$. For both fabrication methods, the composite fibers do not show obvious changes in size compared to the original pure CNT fibers.

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[**] We gratefully acknowledge the support of the U.S. Department of Energy through the LANL/LDRD program for this work.

Supporting Information is available on the WWW under <http://www.small-journal.com> or from the author.

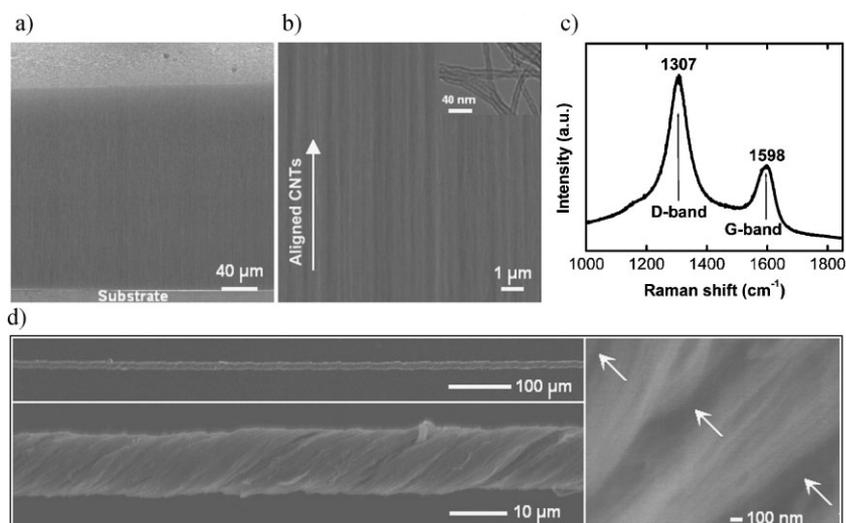


Figure 1. CNT arrays and derived fibers. a) Scanning electron microscopy (SEM) image of a CNT array from a side view; b) SEM image of highly aligned CNTs in the array (inset, transmission electron microscopy image); c) typical Raman spectrum of the CNT arrays; d) SEM images of a CNT fiber with different magnifications. The white arrows in (d) show voids and defects in the CNT fiber.

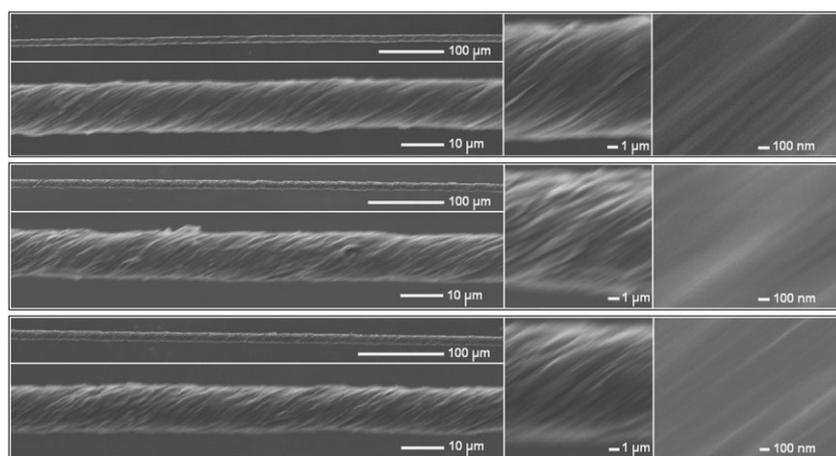


Figure 2. SEM images of composite CNT/silica fibers at different magnifications. a) A composite fiber derived from C1 synthesized by direct casting; b) a composite fiber derived from C2 synthesized by direct casting; c) a composite fiber derived from C2 synthesized by chemical modification.

Table 1. The weight contents of Si, O, C, and SiO₂ in the composite CNT/silica and pure CNT fibers. Samples 1, 2, 3, and 4 correspond to the CNT/silica fibers derived from C1 by direct casting, the CNT/silica fiber derived from C2 by direct casting, the pure CNT fiber treated by HNO₃, and the CNT/silica fiber derived from sample 3 followed by connection of C2 through chemical modification, respectively.

Sample	Si (wt %)	O (wt %)	C (wt %)	SiO ₂ (wt %)
1	3.81	5.77	90.42	8.15
2	4.78	4.94	90.28	9.27
3	0	12.88	87.12	0
4	9.50	19.28	71.22	17.73

Due to defects and ineffective load transfer, pure CNT fibers often show low mechanical strengths.^[10] To improve the strength, other components, such as polymers, have been incorporated into CNT fibers.^[11,12] For the composite CNT/silica fibers, the building silicate molecules can penetrate into much smaller voids or defects in the fiber through a solution process than big polymer molecules. Consequently, these silicates produce robust and strong silica networks after hydrolysis and condensation reactions. Therefore, these composite CNT/silica fibers are expected to exhibit much improved mechanical properties. This hypothesis has been verified in our experiments.

Pure CNT fibers spun from our current CNT arrays exhibit a tensile strength of 0.32 GPa (Figure 3a). The strengths increase to 0.37 GPa (Figure 3b) and 0.42 GPa (Figure 3c) after the incorporation by direct casting of C1 and C2 matrices, respectively. In other words, the silica network derived from C1 and C2 enhance the strength of the CNT fibers by 16% and 31%, respectively. The limited mechanical strength improvement is due to the fact that many precursor molecules are peeled off the fiber and dissolved in water during the hydrolysis and condensation reactions. We observed silica aggregates in the acid solution. To improve the adhesion between the silicate molecule and the CNT, we connected C2 molecules to the outer surface of CNTs by hydrogen bonding (i.e., using chemical modification). These hydrogen bonds are stable in acid solutions.^[13] This allows the resulted silica networks to bond with the neighboring CNTs more effectively, producing much stronger composite fibers. As shown in Figure 3d, the tensile strength of C2-derived CNT/silica fibers with hydrogen bonding is 0.92 GPa, about three times that of the original pure CNT fiber, and more than twice that of the C2-derived fiber synthesized by direct casting.

The CNT/silica fibers also show excellent electrical conductivities. The conductivities of C2-derived composite fibers by direct casting and chemical modification are 121 S cm⁻¹ and 208 S cm⁻¹ at room temperature, respectively, slightly lower than 256 S cm⁻¹, the conductivity of the original pure CNT fibers. Note that besides a higher tensile strength, chemical modification also produces composite CNT/silica fibers with higher conductivity than those synthesized by direct casting. Figure 4 further shows the temperature dependence of the conductivity for both pure CNT fibers and composite CNT/silica fibers between 140 K and 310 K, measured by a four-probe

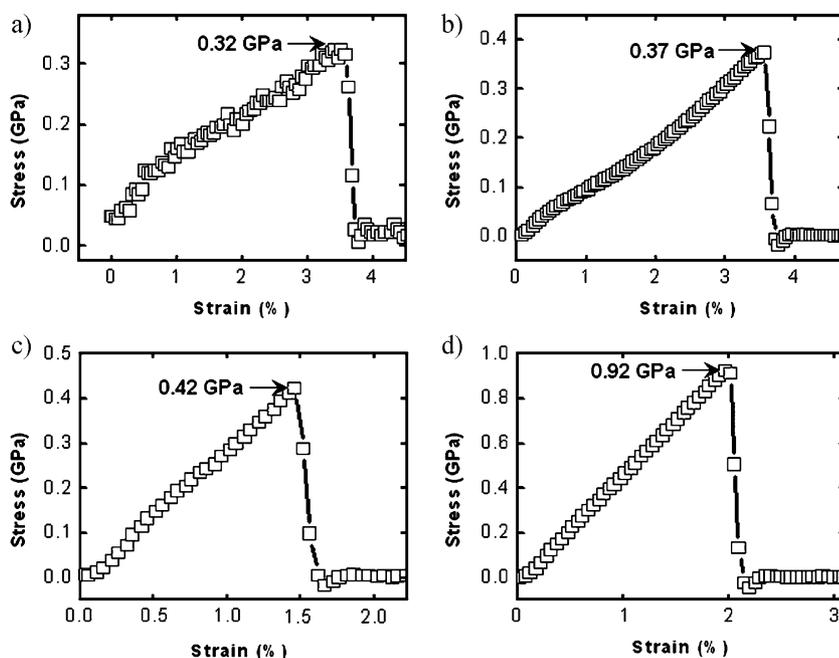


Figure 3. Mechanical properties of a) a pure CNT fibers; b) a composite fibers derived from C1 synthesized by direct casting; c) a composite fibers derived from C2 synthesized by direct casting; and d) a composite fibers derived from C2 synthesized by chemical modification.

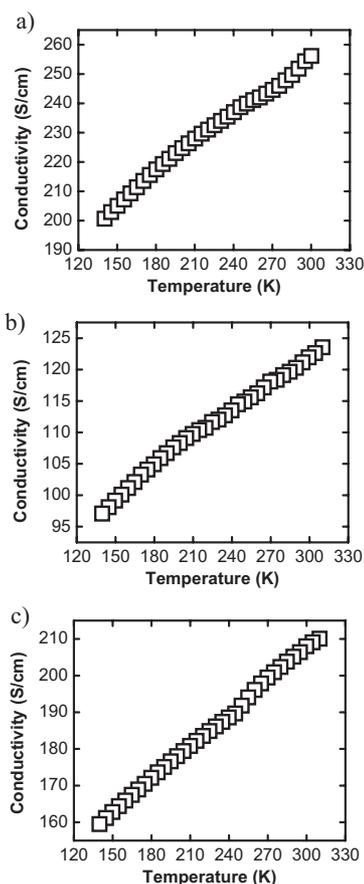


Figure 4. The temperature dependence of the conductivity of a) pure CNT fibers; b) composite fibers derived from C2 synthesized by direct casting; and c) composite fibers derived from C2 synthesized by chemical modification.

method. Conductivities for all of them increase with increasing temperature, suggesting a semiconducting behavior for these fibers.^[14]

In summary, we have demonstrated the first synthesis of composite CNT/silica fibers with much improved mechanical strengths and electrical conductivities by two approaches. Chemical modification produces much stronger composite CNT/silica fibers with higher conductivity than those synthesized by direct casting. The high strength, good conductivity, and superior thermal and chemical stability of the composite CNT/silica fibers are expected to make the use of these fibers advantageous in many advanced applications.

Experimental Section

Synthesis of Spinnable CNT Arrays: CNT arrays were synthesized in a quartz tube furnace with a diameter of 2.54 cm. Ethylene served as the carbon source, and Ar with 6% H₂ was used as the carrying gas. The catalysts used in this study were Fe (0.3–1.0 nm)/Al₂O₃ (10 nm) on SiO₂ (thickness of ≈1 μm)/Si wafers. Fe and Al₂O₃ films were deposited by sputtering and ion-beam-assisted deposition techniques, respectively. More synthesis details have been reported elsewhere.^[8]

Fiber Spinning: CNT fibers were spun from CNT arrays using a spindle with a microprobe at the top. A CNT ribbon was first pulled off from the substrate (or CNT arrays). The microprobe was then steered to touch the ribbon so that CNT fibers could be pulled out from the ribbon. The fiber diameter could be controlled by varying the initial ribbon width during the spinning. For easy spinning, silicon nitride particles were first coated at the microprobe tip to increase the roughness. The microprobe with adjustable speeds was controlled by a motor. In order to control fiber diameters, the spinning was done under an optical microscopy.

Fabrication of composite fibers: Two different precursors were first dissolved in tetrahydrofuran with a concentration of 10 mg mL⁻¹. For the formation of composite fibers by direct casting, pure CNT fibers were dipped into the precursor solution, followed by evaporation of the solvent at room temperature. For the formation of composite fibers by chemical modification, CNT fibers were first treated with 5 M HNO₃ for approximately two days to produce COOH groups on the outer surface of CNTs. The resulting fibers were soaked into C2 solutions for approximately 1 day. The detailed experimental conditions can be found elsewhere.^[15] Hydrolysis and condensation reactions were carried out in 1 M HCl solution for three days. All operations were performed at room temperature.

Characterizations: Scanning electron microscopy images, as well as energy-dispersive X-ray spectroscopy data, were obtained on a JEOL 6300FXV equipped with an Ametek V4.6 EDS system, at an accelerating voltage of 5 kV. The structure of CNTs was further characterized by transmission electron microscopy (TEM, Philips

CM30 operated at 200 kV). Samples for TEM measurements were prepared by dropcasting CNT/ethanol solutions onto copper grids in the open air. The mechanical properties of the CNT fibers were characterized by a Shimadzu Table-Top Universal Testing Instrument. The CNT fibers were mounted on paper tabs with a gauge length of 5 mm. The fiber diameter was measured using a laser-diffraction method and further confirmed by SEM. The conductivities were measured using a four-probe method from 140 K to 310 K. For better electrical contact between the fiber and electrodes, a pre-patterned glass substrate with four Ag electrode stripes was made through a shadow mask. The fibers were then transferred onto the pre-patterned substrates. Finally, a thin layer of silver paste was cast on the fiber to stabilize them on the electrodes.

Keywords:

carbon nanotubes · composite fibers · hydrogen bonding · silica

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Received: February 13, 2008
Revised: April 17, 2008
Published online: October 23, 2008