Dissolution of Full-Length Single-Walled Carbon Nanotubes

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Full-length single-walled carbon nanotubes (SWNTs) were rendered soluble in common organic solvents by noncovalent (ionic) functionalization of the carboxylic acid groups present in the purified SWNTs. Atomic force microscopy (AFM) showed that the majority of the SWNTs ropes were exfoliated into small ropes (2−5 nm in diameter) and individual nanotubes with lengths of several micrometers during the dissolution process. The combination of multiwavelength laser excitation Raman scattering spectroscopy and solution-phase visible and near-infrared spectroscopies was used to characterize the library of SWNTs that is produced in current preparations. The average diameter of metallic nanotubes was found by Raman spectroscopy to be smaller than that of semiconducting nanotubes in the various types of full-length SWNT preparations. This observation sheds new light on the mechanism of SWNT formation.

Introduction

Full-length single-walled carbon nanotubes (SWNTs), due to their high aspect ratio, small diameter, light weight, and high strength, are recognized as the ultimate carbon fibers for nanostructured materials.[1−4] The SWNT ropes in purified SWNTs (*p*-SWNTs) samples[5] are usually 10−25 nm in diameter and many micrometers in length, but they are entangled together in the solid state to form a dense, robust, network structure, which is difficult to disperse in organic media and to chemically functionalize.

It has been shown previously that shortened SWNTs (100−300 nm in length)[5] can be rendered soluble in common organic solvents by covalent functionalization of carbon nanotubes.[6,7] Although soluble shortened SWNTs (s-s-SWNTs) are good targets for certain aspects of nanotube science and technology (for example, wall-chemistry[6a] and chromatographic purifications[8]), for applications in nanostructured materials, such as nanotube-based composites and copolymers, full-length carbon nanotubes are preferred because of their high aspect ratio (length/diameter). Here we report a method to prepare soluble, full-length SWNTs (s-l-SWNTs, average length >1 μm) by one-step exfoliation and noncovalent functionalization of the purified SWNT ropes. The resulting s-l-SWNTs are soluble in many common organic solvents. In contrast to the sidewall alkylation of fluorinated SWNTs,[9] which led to soluble SWNTs by

completely disrupting the band structure of SWNTs, our solubilization technology still retains the electronic band structure of the prisitne SWNTs.

Experimental Section

The SWNTs used in this study were obtained from two different sources: Tubes@Rice and Carbon Solutions, Inc. The as-prepared SWNTs (AP-SWNTs) from Tubes@Rice were produced by the pulsed laser vaporization (PLV) technique,[10] whereas the AP-SWNTs from Carbon Solutions were produced by a modified electric-arc (EA) technique.[11] The AP-SWNTs from Tubes@Rice were purified by standard methods[12] at Rice University, whereas the AP-SWNTs from Carbon Solutions were purified by a modified procedure in our laboratory. The purified SWNTs (>90%) from Tubes@Rice are denoted as p-SWNTs-(R) whereas purified SWNTs (>90%) from Carbon Solutions are denoted as p-SWNTs-(C). In the final step of purification, we added HNO_3 to the aqueous suspension of SWNTs before collecting the sample. Hence, the p-SWNTs-(R) and -(C) are obtained in the acidic form with the carboxylic acid groups (−COOH) present in the purified SWNTs: $\nu_{c=o} = 1709$ cm^{-1} (Figure 1).

SWNTs can be wet by low surface tension liquids such as nitric acid.[13] We found that short-term heating (∼1 h) of p-SWNTs(C) solid in 5 M nitric acid at 110 °C can partially disintegrate the originally robust network of p-SWNTs(C) ropes, possibly due to the intercalation of nanotube ropes by nitric acid and further expansion of internanotube spacing within the rope[14] upon heating. The resulting SWNT solid was collected by membrane filtration (0.8 μm pore size), washed with distilled water, and dried at room temperature under vacuum. We prefer to use the nitric acid-treated SWNTs as starting material, since they are easier to exfoliate in our dissolution process.

The typical procedure for the preparation of soluble full-length SWNTs (s-l-SWNTs(C)) is as follows: a mixture of 500 mg

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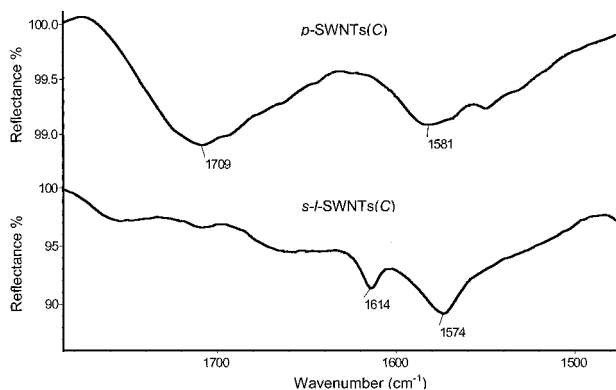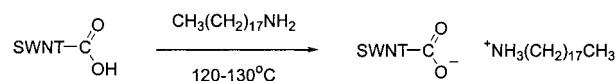
Figure 1. FTIR spectra (Nicolet Magna-IR 560 spectrometer, SpectraTech Thunderdome attenuated total reflectance (ATR) sample stage) of p-SWNTs(C) in acidic form and s-l-SWNTs(C) with baseline correction.

nitric acid-treated p-SWNTs(C) and 5 g of ODA melt was heated at 120−130 °C for 4−8 days. After being cooling to room temperature, the resulting mixture was sonicated in 800 mL of ethanol for 30 min. The solid was collected by membrane filtration (0.8 μm pore size), washed with ethanol, and dried at room temperature under vacuum. The solid was sonicated in 1000 mL of tetrahydrofuran for about 1 h, and the resulting solution was left to stand at room temperature for at least 1 h. After paper filtration (particle retention: 8 μm), a black-colored solution was obtained, and this was concentrated to give a ∼5 mL suspension. The solid was collected by PTFE membrane filtration (0.45 μm pore size), washed with ethanol, and dried at room temperature under vacuum. The yield of s-l-SWNTs-(C) is about 70% (based on p-SWNTs(C)).

Results and Discussion

To produce soluble full-length SWNTs, we formed an octadecylammonium, SWNT-carboxylate zwitterion by the following acid−base reaction. The 4−8 day heating of nitric

$$SWNT-C\overset{O}{\underset{OH}{\big<}} \xrightarrow[120-130^{o}C]{CH_3(CH_2)_{17}NH_2} SWNT-C\overset{O}{\underset{O^-}{\big<}} \quad {}^+NH_3(CH_2)_{17}CH_3$$

acid-treated p-SWNTs(C) in neat octadecylamine (ODA) melt at 120−130 °C also leads to the exfoliation of the majority of the large SWNTs ropes (10−25 nm) into small ropes (2−5 nm in diameter) and individual nanotubes by AFM height measurement. Most of s-l-SWNTs are longer than 1 μm (Figure 2). The IR spectrum of s-l-SWNTs(C) indicated the formation of the carboxylate group: $\nu_{c=0} = 1614$ cm^{-1} (Figure 1). The s-l-SWNTs(C) are soluble (>0.5 mg/mL) in tetrahydrofuran and 1,2-dichlorobenzene and.partially soluble in dichloromethane, chlorobenzene, and similar organic solvents. The filtered (8 μm particle retention), black-colored (unsaturated) s-l-SWNTs(C) solutions are visually nonscattering, and no precipitation occurred upon prolonged standing, which is the operational definition of a solution that is adopted in the present paper (an 0.1 mg/mL solution is usually stable for over 10 days).

The preparation of full-length soluble SWNTs from the Tubes@Rice SWNTs is more difficult, because the ropes in p-SWNTs(R) (length > 5 μm) are generally much longer than those in p-SWNTs(C) (length > 2 μm). We believe that this difference originates from the production techniques used by the two companies (PLV vs EA). Consequently the network structure in solid p-SWNTs(R) is more dense and robust than that in solid p-SWNTs(C). As a result, the s-l-SWNTs(R) is
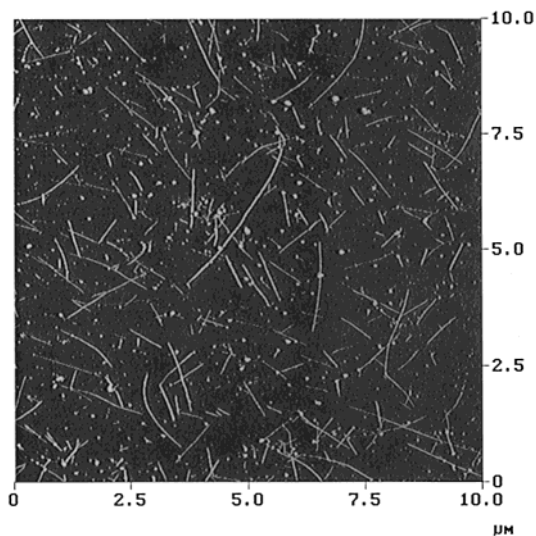

Figure 2. Typical tapping mode AFM image (Nanoscope III, Digital Instruments) of s-l-SWNTs(C) which have been dissolved in chlorobenzene and dispersed on a freshly cleaved meca surface.

obtained in lower yield (usually < 40%) and is only soluble in tetrahydrofuran and 1,2-dichlorobenzene.

We chose ionic functionalization[6c] instead of covalent functionalization[6a] because of the following: (1) We found that the ionic functionalization approach generally gave a much higher yield of s-l-SWNTs than the covalent functionalization approach. For example, the yield of s-l-SWNTs(C) and s-l-SWNTs(R) is usually <30% and <5%, respectively, by the covalent functionalization approach. It seems that the presence of zwitterions can significantly improve the solubility of p-SWNTs. (2) The acid−base reaction represents the simplest possible route to soluble SWNTs and can be readily scaled-up at low cost. (3) Unlike the covalent amide bond, the cation ($^+NH_3(CH_2)_{17}CH_3$) in the ionic bond of SWNT-COO$^-$$^+NH_3$-(CH$_2$)$_{17}CH_3$ of s-l-SWNTs can be readily exchanged for other organic and inorganic cations. Thus it will be possible to adjust the solubility properties of the SWNTs and to use soluble SWNTs (s-SWNTs) as versatile building blocks for advanced SWNTs-based materials via supramolecular chemistry. Furthermore, such ionic feature may allow electrostatic interactions between SWNTs and biological molecules and can serve as the basis for developing biocompatible SWNTs.

Calibrated energy-dispersive X-ray spectroscopy showed the presence of ∼4 at. % O in the s-l-SWNTs samples which provides an estimate of the amount of chemically bonded ODA in s-l-SWNTs (∼3 ODA/100 C$_{SWNTs}$). Since one of the major impurities in p-SWNTs is small-size carboxylated carbons with a high O/C ratio[12] which are also dissolved with the s-l-SWNTs, the actual amount of ODA which is chemically associated with the nanotubes may be lower than 3 ODA/100 C$_{SWNTs}$. If the p-SWNTs contain sidewall defects,[15] these sites will become functionalized during the dissolution process. Although we have been unable to detect the density of sidewall defects by Raman or near-IR spectroscopy, both techniques provide strong evidence for the presence of nanotube band-gap structures in s-l-SWNTs (Figures 3 and 4). Therefore the degree of sidewall functionalization in s-l-SWNTs is much lower than that in soluble sidewall-alkylated SWNTs which showed the complete disappearance of characteristic band-gap signals of SWNTS.[9] Calculations found that a high degree of wall-functionalization only degrades the mechanical strength of SWNTs by an average value of 15%;[16] thus, the functionalization of sidewall defects in s-l-SWNTs will not have major effects on the mechanical

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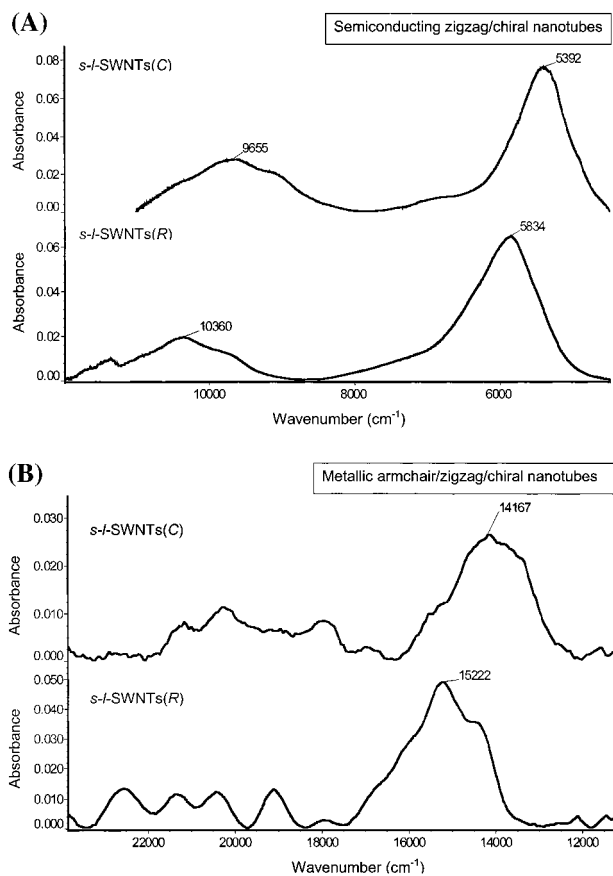
Figure 3. (A) Near-FTIR spectra (quartz cell, light path 1/16 in., Nicolet Magna-IR 560 ESP spectrometer) of s-l-SWNTs(C) in THF solution (0.1 mg/mL) (top) and s-l-SWNTs(R) in THF solution (0.05 mg/mL) (bottom). The solvent background and baseline were corrected. (B) Visible spectra (quartz cell, light path 10 mm, Shimadzu UV-2501PC spectrometer) of s-l-SWNTs(C) in THF solution (0.1 mg/mL) (top) and s-l-SWNTs(R) in THF solution (0.05 mg/mL) (bottom). The solvent background and baseline were corrected.

strength of SWNTs. In fact, functionalization of sidewall defects should be favorable for nanotube composites, because it can provide a bonding site to the polymer matrix, so that the load can be transferred to the nanotubes and thus inhibit separation between the surfaces of polymer and nanotube.[1b]

The dissolution of s-l-SWNTs in organic solvents is not well understood at the present time but may be associated not only with the long-chain ODA which is added to the nanotube ends and to defects in the nanotube wall but also with the remarkable structural flexibility of SWNTs[17] as well as the presence of zwitterions in s-l-SWNTs. We found that the same dissolution process applied to arc-produced multiwalled carbon nanotubes (MWNTs, average length < 1 μm), which are structurally more rigid than SWNTs, only gave rise to very unstable suspensions in organic solvents which were visually scattering. The observation that the ionic functionalization approach generally gave a higher yield of s-l-SWNTs than the covalent functionalization approach indicates that the presence of zwitterions in s-l-SWNTs can enhance the stability of SWNTs solution by effectively preventing the nanotubes from aggregating in solution.

The solution-phase visible and near-IR spectroscopy of s-l-SWNTs(C) show three broad peaks (Figure 3) (cm^{-1} (eV)): 14 167 (1.76); 5392 (0.67); 9655 (1.20). the first two peaks (1.76 and 0.67 eV) can be assigned to band-gap transitions in metallic and semiconducting SWNTs,[18] respectively. The term "band gap" in metallic nanotubes is applied to the energy separation of the first pair of singularities in the electronic
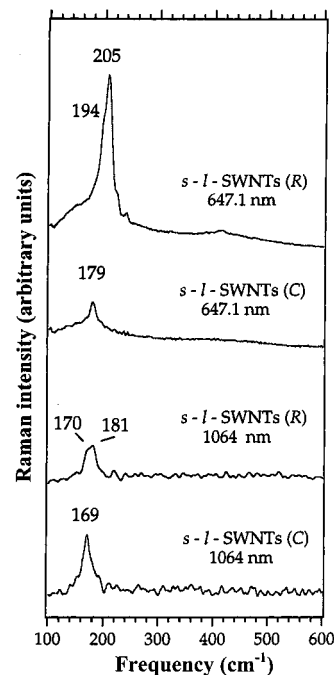

Figure 4. Raman spectra (ω_r region) of solid s-l-SWNTs(C) and s-l-SWNTs(R) excited at 1064 and 647 nm laser frequencies. The tangential mode ω_t intensity is set to a constant value, so that the radial mode intensity can be roughly compared for each spectrum.

density of states (DOS) of metallic tubes.[19] The 9655 cm^{-1} (1.20 eV) feature arises from the second pair of singularities in the DOS of the semiconducting nanotubes. Compared to those of s-l-SWNTs(C), the band gaps of the s-l-SWNTs(R) are shifted to higher energy (Figure 3) (cm^{-1} (eV)): 15 222 (1.89); 10 360 (1.29); 5834 (0.72). Since s-l-SWNTs(R) have smaller nanotube diameters than s-l-SWNTs(C) (from Raman measurements; see below), our band-gap measurement support the expected 1/diameter (d) dependence of the band gap (E_g) of SWNTs.[18,19]

At the same laser wavelength excitation, the Raman tangential mode frequency (ω_t)[20] of s-l-SWNTs(C)/s-l-SWNTs(R) is very similar to that of the AP-SWNTs(C)/AP-SWNTs(R), but the radial mode frequency (ω_r) is upshifted 4–10 cm^{-1} (Figures 4 and 5). The upshift of ω_r is a direct consequence of the decreased energy spacing between van Hove singularities in the density of states for solubilized tubes relative to that of as-prepared bundled tubes.[21] The Raman radial mode of the SWNTs (ω_r) is sensitive to the diameter (d) but not to the symmetry of the nanotube and can be described approximately by $\omega_r = 223.75$ (cm^{-1} nm)/d (nm).[22,23] So Raman spectroscopy can be used to estimate the diameter distribution of nanotubes. It is clear to see from Figures 4 and 5 that SWNTs(C) have larger average diameter than SWNTs(R).

Raman scattering from the vibrational modes in SWNTs is a resonant process that is associated with optical transitions between pairs of singularities in electronic density of states (DOS) of SWNTs.[20,23,24] For example, laser excitation at 647 nm (1.92 eV) gave resonant Raman scattering signals mainly from metallic nanotubes, whose optical transition energy is close to the energy of the incident photon (1.92 eV). Similarly, laser excitation at 1064 nm (1.17 eV) gave resonant Raman scattering signals mainly from semiconducting nanotubes, whose optical transition energy (from the second pair of singularities in the DOS) is around 1.20 eV. The detailed Raman scattering study of coalesced SWNTs[25] provides some evidence that laser excitation at 488 nm (2.54 eV) may give diameter information from chiral nanotubes. It is noteworthy that the radial mode
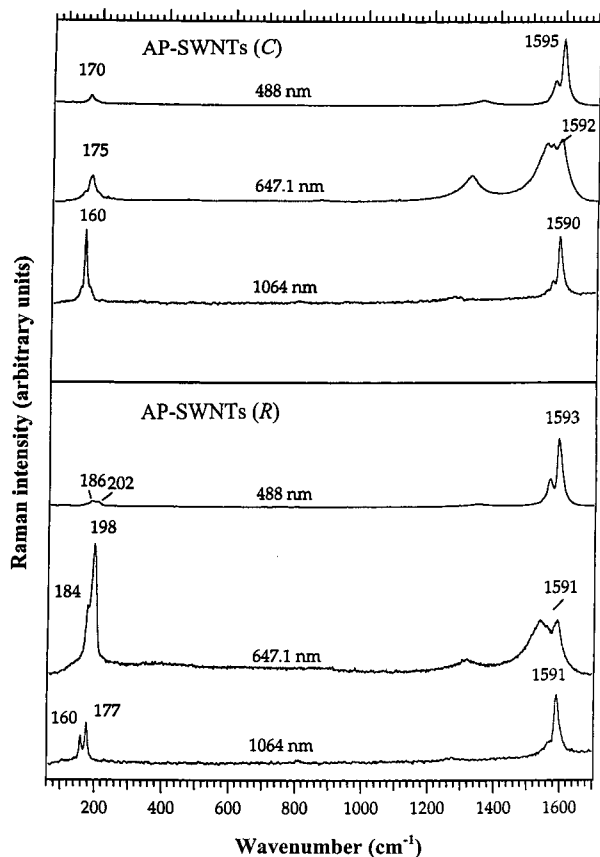
Figure 5. Raman spectra of AP-SWNTs(C) produced by EA and AP-SWNTs(R) produced by PLV excited at 1064, 647, and 488 nm laser frequencies.

frequency (ω_r) with 647 nm excitation is always larger than that with 1064 nm excitation in full-length SWNTs materials (Figures 4 and 5), indicating that the average diameter of metallic nanotubes is smaller than that of semiconducting nanotubes in the various types of full-length SWNT preparations. This observation sheds new light on the mechanism of SWNT formation.

Conclusion

We have demonstrated that full-length single-walled carbon nanotubes (SWNTs) can be solubilized in common organic solvents by noncovalent (ionic) functionalization of the carboxylic acid groups present in the purified SWNTs. Atomic force microscopy (AFM) showed that the majority of the SWNTs ropes were exfoliated into small ropes (2−5 nm in diameter) and individual nanotubes with lengths of several micrometers during the dissolution process. The combination of multiwavelength laser excitation Raman scattering spectroscopy and solution-phase visible and near-infrared spectroscopies was used to characterize the library of SWNTs that is produced in current preparations. The average diameter of metallic nanotubes was found by Raman spectroscopy to be smaller than that of semiconducting nanotubes. The dissolution process can be easily scaled up at low cost, and this will allow the investigation of homogeneous nanotube-based copolymers and polymer composites in the form of monoliths, fibers, films, and coatings.

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