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Soluble Ultra-Short Single-Walled Carbon Nanotubes

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Abstract: Soluble, ultra-short (length < 60 nm), carboxylated, single-walled carbon nanotubes (SWNTs) have been prepared by a scalable process. This process, predicated on oleum's (100% H_2SO_4 with excess SO_3) ability to intercalate between individual SWNTs inside SWNT ropes, is a procedure that simultaneously cuts and functionalizes SWNTs using a mixture of sulfuric and nitric acids. The solubility of these ultra-short SWNTs (US-SWNTs) in organic solvents, superacid and water is about 2 wt %. The availability of soluble US-SWNTs could open opportunities for forming high performance composites, blends, and copolymers without inhibiting their processibility.

Introduction

With a Young's modulus of 1000 Gpa,[1] tensile strength of 30 Gpa,[2] ballistic electrical conductance higher than copper,[3] and thermal conductivity equivalent to diamond,[4] single-walled carbon nanotubes (SWNTs) are ranked among the strongest, most electrically conductive, and thermally robust material known. To fully exploit these SWNTs characteristics in macroscopic functional articles such as fibers, films, or composites, one must overcome the critical issue of limited solubility that can affect the processibility of SWNT-infused materials. Due to their high aspect ratio and the strong van der Waals attraction between them, full-length purified SWNTs tend to aggregate into a dense, robust network of ropes,[5] usually 10−50 nm in diameter and several μm in length, that have limited solubility in either organic, acidic, or aqueous media. Recently, there has been much interest[6−9] in improving the dispersivity of SWNTs in common solvents such as water, *N*-methyl-2-pyrrolidone (NMP), and *N*,*N*-dimethylformamide (DMF) for incorporating them into high performance composites. The objective was to obtain microscopic nonsettling, long-term stable dispersions of SWNTs. The primary techniques to achieving this objective include polymer wrapping,[10−13] preparing water-soluble surfactant-wrapped individualized SWNTs by using sodium dodecyl sulfate or Triton X-100, accompanied by sonication and high-speed centrifugation,[14−17] reduction with alkali metals,[9] and covalent end and/or sidewall functionalization.[18] In addition to the solubility problem, the presence of rigid full-length SWNTs increases the bulk viscosity of composites and blends even when they can be homogeneously dispersed into a host matrix.[7,19,20] This increase in bulk viscosity tends to reduce the processibility of these composites, leading to a limit on the amount of SWNTs that can be used in the composites and therefore constraining performance enhancements that might otherwise be observed. In this study, we have developed a new method where purified HiPco SWNTs, or any SWNTs with pristine side-walls, can be cut and functionalized simultaneously. This process produces carboxylated, ultra-short SWNTs (US-SWNTs) with lengths < 60 nm that are readily soluble in polar

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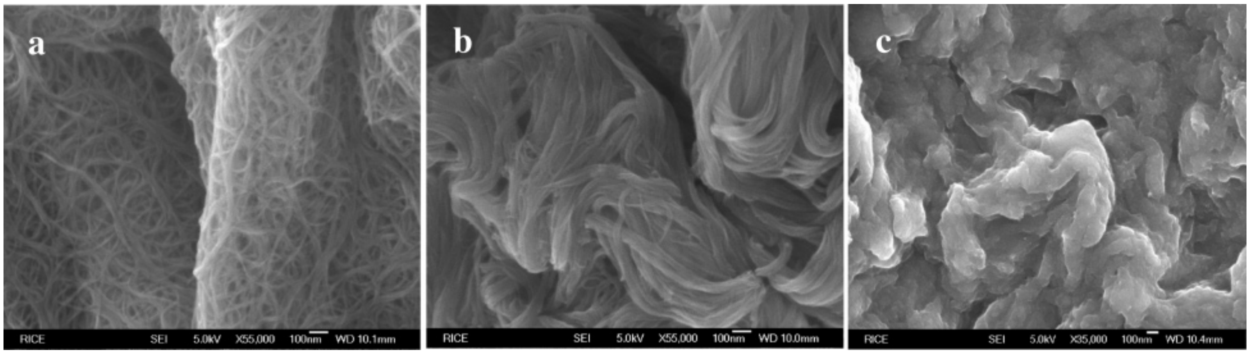

Figure 1. SEM images showing the evolution of purified SWNTs into ultra-short SWNT (US-SWNTs). (a) Tightly entangled network of purified HiPco SWNTs. (b) Aligned super ropes of 50 nm or more in diameter after the disentanglement process. (c) Nonroped structure of US-SWNTs. The scale bar at the bottom of each image is 100 nm.

organic solvents, acids, and water without the aid of sonication, surfactants, or any other means. This high solubility (up to 2 wt % in NMP), coupled with their short length, should enable these US-SWNTs to be dispersed and incorporated as single tubes into other materials to form composites, blends, or block copolymers without significantly diminishing the host's processibility.

The underlying basis for this new method is predicated on oleum's (100% H_2SO_4 with 20% SO_3) ability to effectively intercalate between individual SWNTs inside SWNT ropes.[21] This SWNT−acid intercalation phenomenon is thought to be the result of SWNTs forming charge transfer complexes with the sulfuric acid molecules, a thermodynamically favorable process. Therefore, the current study uses oleum instead of 98% or 96% sulfuric acid, used in the previous method, which forms only bundles of longer SWNTs.[5] This two-step process consists of (1) dispersing purified or raw SWNTs, as long as these SWNTs have pristine side-walls, in oleum; (2) the introduction of the cutting agent, nitric acid, into the acid-intercalated SWNT dispersion. This protocol affords an efficient and more uniform cutting and functionalization of SWNTs than ever seen in the past.[5] Prior work showed that the temperature- and time-dependent oxidation reaction often generated various functional groups (e.g., −COOH, −OH, −C═O, and a small content of sulfur and nitrogen-containing groups) at the open ends and defect sites of the SWNTs structure. However, the prior method was not efficient in that the cutting/functionalization occurred mostly on the surface of the SWNT ropes because 96% H_2SO_4 cannot effectively intercalate into the SWNTs ropes. This resulted in SWNTs that were not functionalized or short enough for dissolution in solvents.

Experimental Section

The purified[22] HiPco[23] SWNTs used in this study were first disentangled to ensure the complete superacid intercalation. This is a multistep process consisting of (1) soaking of SWNTs (0.3 wt % concentration) in oleum[24] (20% SO_3) overnight so that the intercalation of acid into the tightly entangled network of SWNTs (Figure 1a) will loosen the ropes; (2) the use of an immersion blender such as a rotor/stator operating at high speed (10 000 rpm) for up to 72 h to disentangle the network; (3) precipitation and washing of the disentangled SWNTs to rid them of residual acid; and finally, (4) vacuum-drying. These disentangled SWNTs can be readily intercalated with fuming sulfuric acid.

Experimentally, 400 mg of disentangled SWNTs (0.1 wt %; raw SWNTs can be used, but the process is less efficient and impurities from the raw SWNTs might be carried forward) were dispersed in 200 mL of oleum (20% SO_3)[24] in an Erlenmeyer flask and stirred overnight under a blanket of dry nitrogen to ensure complete acid-intercalation. Subsequently, a mixture of 100 mL of oleum (20% SO_3)[24] and 100 mL of 70% HNO_3 was slowly added into the SWNT/oleum dispersion with stirring in an ice bath to maintain the dispersion's temperature as close to room temperature as possible.[24] Afterward, the SWNTs dispersion was stirred at 65 °C for 2 h. The dispersion was then carefully poured into 1.2 L of Nanopure water (Barnstead Internationals, Dubuque, IA) while being cooled by an external ice bath to room temperature. The black slurry was vacuum filtered onto a 5 μm Teflon membrane, which retained most of the US-SWNTs. After most of the liquid had been pulled through the filter cake, the vacuum line was removed from the flask and the filter cake was stirred with 50 mL of methanol in the Büchner funnel using a spatula; the particles were then coagulated by adding 200 mL of diethyl ether and stirring. Little if any organic wash solvent drained through the filter. The aqueous acidic filtrate was poured from the filter flask, vacuum was reapplied, and the methanol/diethyl ether wash liquid was pulled through the filter. The filter cake was washed with additional 200 mL portions of diethyl ether until the pH of the filtrate was neutral. The diethyl ether-wet filter cake was transferred to a Petri dish or beaker, and the clumps were broken apart with a spatula to provide fine powdered US-SWNTs as the diethyl ether evaporated. The US-SWNTs were vacuum-dried at room temperature overnight, typically yielding 440 mg of product. The increase in mass is due to the significant increase in oxidation.

Results and Discussion

The striking result of the disentanglement process is illustrated in Figure 1. Before disentanglement, purified HiPco SWNTs exists as tight networks (Figure 1a) of fine (10−20 nm in diameter), entangled, randomly oriented "primordial" ropes. After the process, disentangled, locally aligned super ropes of 50 nm or more in diameter are produced (Figure 1b).

After the above prescribed oleum/nitric acid treatment, the US-SWNTs (Figure 1c) produced from disentangled SWNTs dissolve spontaneously in polar aprotic solvents such as NMP, DMSO, DMF, alcohol, and in water, without the aid of sonication. However, sonication can help shorten the time of dissolution. Figure 2 shows sequential photographs, taken every

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(24) **CAUTION!** Oleum and 70% nitric acid are extremely hazardous materials that should be handled with utmost care. Users should wear an acid-proof apron, heavy gloves, safety glasses, and a face shield, and all operations should be done in a fume hood when handling these reagents.

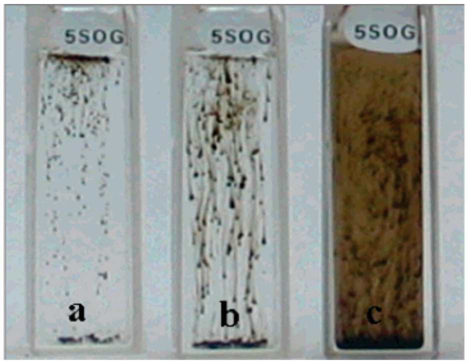

Figure 2. Sequential photographs of the spontaneous dissolution of US-SWNTs in deionized water in quartz cuvettes. (a) 0 min, (b) 1 min, (c) 2 min.

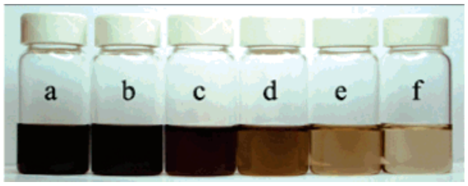

Figure 3. Photograph of US-SWNTs solutions of various concentrations in NMP; a = 500 mg/L, b = 250 mg/L, c = 125 mg/L, d = 62.5 mg/L, e = 31.3 mg/L, and f = 15.6 mg/L.

1 min, of this spontaneous dissolution process after dusting US-SWNT powder onto water without stirring.

Figure 3 shows photographs of US-SWNTs solutions of various concentrations in NMP. These are true solutions because they are optically transparent and homogeneous. On the basis of optical microscope examinations, the solubility limit of these US-SWNTs is approximately 2 wt % in NMP, water, or superacids. The reason for the high solubility is due to the high level of functionalization on the US-SWNTs. Specifically, these SWNTs are highly carboxylated and, to a lesser degree, sulfonated. Raman spectra, obtained on a Renishaw Ramascope with 785 cm^{-1} diode laser, of the US-SWNTs are shown in Figure 4a. The results show that these SWNTs are undoubtedly single-walled carbon nanotubes with the characteristic tangential mode (G-band at 1590 cm^{-1}) and the SWNT-unique radial breathing mode (RBM at 100−300 cm^{-1}). For both the disentangled and raw SWNTs, the intensity ratio (D/G ratio) of the disorder mode (D-band at around 1300 cm^{-1}) and the tangential mode is usually less than 1/20, indicating that their sidewalls are pristine. In comparison, the D/G ratio of the US-SWNTs has increased to close to unity in the case of those produced from disentangled SWNTs. This indicates that there is a high level of sidewall functionalization after the acid treatment. One unexpected result is that the roping peak at 267 cm^{-1} has disappeared for these US-SWNTs (Figure 4b). This surprising result, which infers that these US-SWNTs are no longer roped, is consistent with SEM observation shown in Figure 1c.

The X-ray photon-electron spectrum (XPS) (Figure 5a) indicates a high concentration of covalently bonded carboxylic acid groups (−COOH, binding energy ∼288 eV) and C═O groups (binding energy ∼286 eV) on the surface and ends of these SWNTs. Elemental analysis based on the XPS data shows an approximate stoichiometry of 3:1 C/(COOH), i.e., one of every four SWNT carbons has been functionalized with a 30% carbon yield from the starting SWNTs. This is in agreement

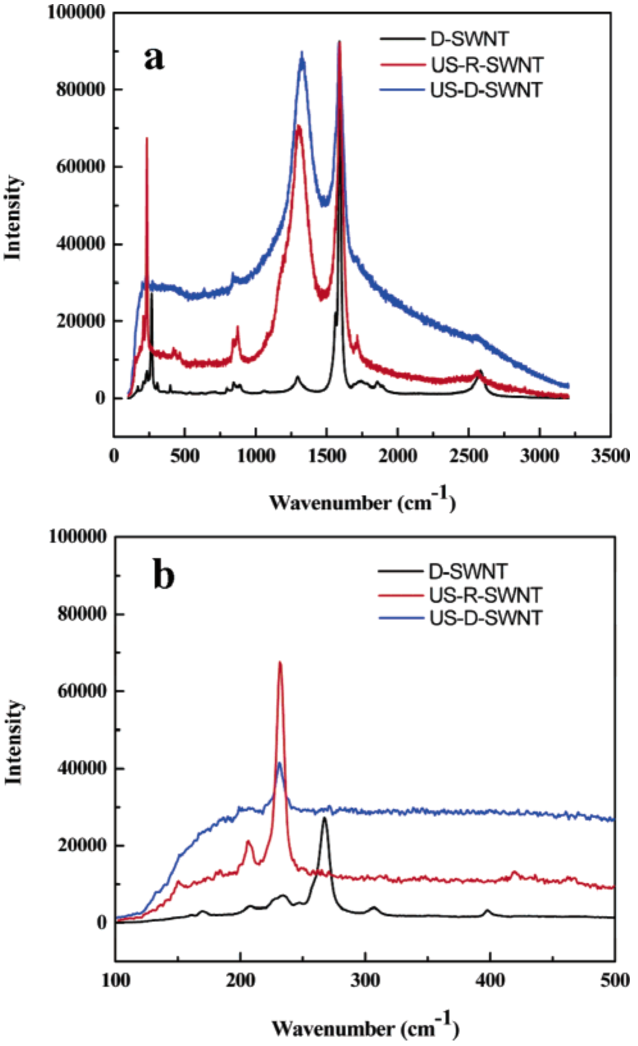

Figure 4. (a) Raman spectra of disentangled SWNT (D-SWNT), ultra-short raw HiPco-derived SWNTs (US−R−SWNT), and ultra-short disentangled SWNT (US-D-SWNT). (b) Detailed radial breath mode indicates the disappearance of the roping mode at 260 cm^{-1} after cutting.

with the thermogravimetric analysis (TGA) results in nitrogen. The functionality is higher than that of a prior study where one of every five SWNT carbons was carboxylated by microwave-assisted treatment in acidic mixture.[25] Using our current method, the level of functionalization on the sidewalls, as determined by the D/G ratio, can be varied as a function of duration and/or temperature of the nitric acid treatment, and/or the oleum/nitric acid ratio. By cutting the nitric acid reaction time from 2 to 1 h at 65 °C, the D/G ratio decreases to 1/3, indicating that the level of functionalization has decreased dramatically. However, by increasing the reaction time to 2.5 h and raising the temperature to 75 °C, the D/G ratio only increases to 1.16, indicating that the level of functionalization may have leveled-off. The sample for the FTIR (Nicolet FTIR Microscope) spectrum was prepared by dissolving US-SWNTs in a small amount of methanol, mixing with KBr, and vacuum-drying at 50 °C. The spectrum, shown in Figure 5b, confirms the existence of −COOH and −C═O groups on the sidewalls of the US-SWNTs. The peak at 1707 cm^{-1} is assigned to the C═O stretching mode of the −COOH groups, whereas the broad peak between 2500 and 3300 cm^{-1} is the −OH stretching mode of

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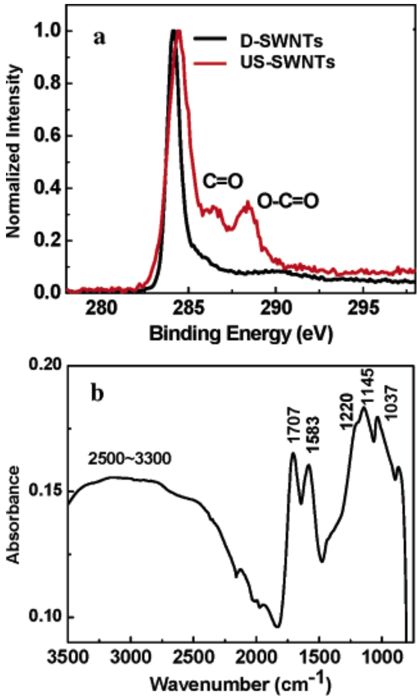

Figure 5. (a) X-ray photoelectron spectroscopy of disentangled SWNTs (D-SWNTs) and US-SWNTs. (b) IR spectra of US-SWNTs (KBr) indicate the existence of carboxylic groups on the sidewalls.

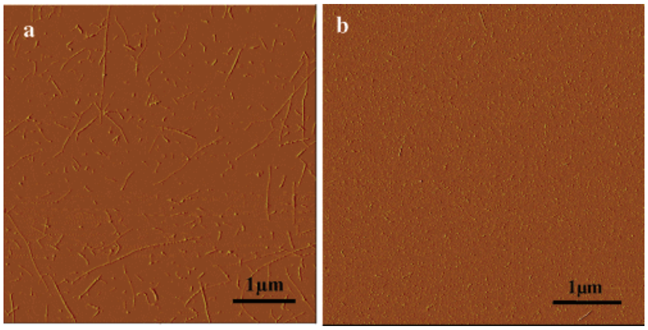

Figure 6. Typical tapping mode AFM images of (a) purified HiPco SWNTs that are alkylated with dodecyl groups to keep them from bundling (b) US-SWNTs.

the −COOH group. The peak at 1583 cm^{-1} is the SWNTs $C{=}C$ graphitic stretching mode. The peaks observed at 1220, 1145, and 1037 cm^{-1} are due to the C−O stretching. These results, consistent with the Raman data, show the levels of functionalization on these US-SWNTs are high and the functional groups are mostly carboxylic groups.

Morphologically, a scanning electron microscopy (SEM) image of the disentangled SWNTs shows the distinct rope structures (Figure 1b), whereas for US-SWNTs, this normal SWNT-characteristic feature (Figure 1c) is absent. One reasonable interpretation is that these US-SWNTs are ultra-short with low aspect ratios and, therefore, do not aggregate into long ropes during the coagulation process. To determine the length of the SWNTs before and after the acid-treatment, atomic force microscopy (AFM) was employed. Purified starting SWNTs used in this study were first alkylated ($C_{12}H_{25}I$) in lithium/liquid ammonia[18a] and then dispersed in chloroform and spin coated onto mica wafers.[16] In this manner, an unbundled sample of SWNTs is observable. A typical tapping mode AFM image of these purified SWNTs, shown in Figure 6a, indicates that they have an average length of 200 nm before the acid treatment. In contrast, AFM images (Figure 6b) of the US-SWNTs deposited on mica from a water solution indicate that they are indeed ultra short with lengths less than 100 nm and that they are mostly beyond the resolution of the microscope, which has the tip scale of ∼30 nm. To accurately determine the lengths of the US-SWNTs, a high-resolution transmission electron microscope (TEM) was employed.

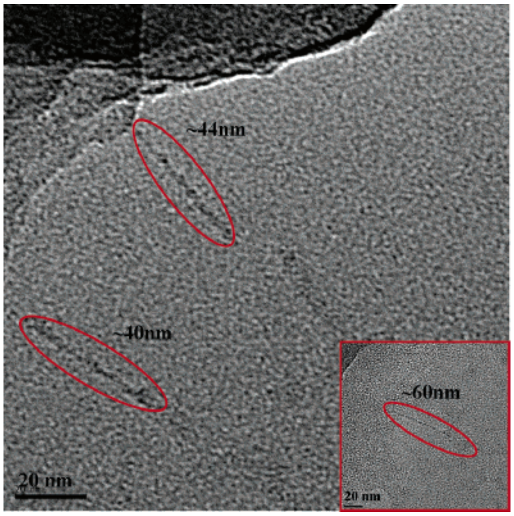

Figure 7. TEM image of US-SWNTs.

The TEM sample was prepared by sonicating US-SWNTs in methanol, and the suspension was deposited onto an ultrathin carbon film on holey carbon grids. Because the contrast between US-SWNTs and carbon film is low, their TEM images have been difficult to obtain. However, some TEM images of US-SWNT with lengths of less than 60 nm are clearly seen in Figure 7. Similar to prior studies, the rough edges of the US-SWNTs in the TEM image are indications of the high level of functionalization on the side-walls of the US-SWNT.[6,8] Also, the inset of Figure 7c shows an isolated, individual US-SWNT on carbon film at 60 nm, which is the longest observed SWNT structure.

Conclusions

In summary, we have developed a new protocol to simultaneously cut and functionalize SWNTs to improve their solubility and processibility. This is an efficient and scalable process. This method produces organic solvent, acid, and water soluble, ultra-short (length $<$ 60 nm), carboxylated SWNTs. The availability of soluble US-SWNTs could open opportunities for forming high- performance composites, blends, and copolymers without inhibiting their processibility.

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Supporting Information Available: The complete list of authors for ref 21 can be downloaded free of charge via the Internet from http://pubs.acs.org.

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