Aggressively Oxidized Ultra-Short Single-Walled Carbon Nanotubes
Having Oxidized Sidewalls

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The structural characterization of single-walled carbon nanotubes is evaluated after careful purification, disentanglement, oxidation, and base treatments. The analyses confirm a small weight percent of non-nanotube material is present, that can be effectively removed with base. The resulting nanotubes remain soluble in water due to oxidized sidewalls and are dramatically shorter after oxidation.

Introduction

The modification of single-walled carbon nanotubes (SWCNTs) is often necessary in order to take advantage of their unique mechanical properties.1 In many cases, the SWCNTs are chemically modified to increase solubility and dispersion in aqueous or organic solvents.2,3 When needed, the SWCNTs are oxidized to yield carboxylic acid and hydroxyl groups on the ends and/or sidewalls of the SWCNTs; the number and location of those addends depends on the oxidation conditions.4 We have reported that when SWCNTs are aggressively oxidized in a mixture of fuming sulfuric acid (oleum) and nitric acid that (a) the length of the SWCNTs are shortened or “cut”, (b) the sidewalls are functionalized, and (c) the majority of the addends are carboxylic acids. These proposed oxidized and ultrashort SWCNTs (US-SWCNTs) have formed the basis for many of our subsequent research studies in materials and medicinal applications with nanotubes.2 Therefore, we were naturally concerned regarding the recent suggestion by Salzmann et al.,6 where they concluded that so-called oxidized SWCNTs maintain a carbon sp² framework along their sidewalls, that they are only soluble in water due to the presence of “carboxylated carbonaceous fragments (CCFs)” that are produced during oxidation, and that the CCFs subsequently strongly physisorbed to the parent and unoxidized SWCNT scaffolds.7 There are several reports in the literature8 with methods to oxidize SWCNTs to various degrees; each method using experimentally different conditions. In order to repeat a protocol and obtain the same products, the procedures must be well-described and strictly followed. Our motivation here was not to reproduce the work by Salzmann et al. but merely to use their protocol of subsequent strong base treatment to remove the CCFs, if any, and report upon the more precise identity of the US-SWCNTs. Here we describe, in detail, the method to produce US-SWCNTs by purification, disentanglement using fuming sulfuric acid, aggressive oxidation with fuming sulfuric acid and nitric acid, treatment with strong base (per the work of Salzmann et al.8), and work protocols that remove CCFs (Scheme 1). We conclude that our US-SWCNTs (a) are shortened and that the length of the cut nanotubes can be tuned based on the temperature of oxidative treatment and (b) have heavily compromised sidewalls; however, (c) the majority of addends are converted to the carboxylate salts after the subsequent strong base treatment. There is also a possibility that some deoxygenation occurs during base treatment in a manner analogous to graphite oxide conversion to graphene in the presence of a hot strong base. Therefore, the Salzmann...
et al. protocol of hot base treatment is an effective method to remove trace amounts of CCFs from the US-SWCNTs, but the oxidative cutting as we had originally described does indeed perform the previously suggested oxidation and cutting of the nanotubes.

Experimental Section

All SWCNT starting materials were obtained from the Rice University Carbon Nanotechnology Laboratory HiPco Mach III apparatus, Batch no. 166.12. X-ray photoelectron spectroscopy (XPS) was performed on a PHI Quantera SXM Scanning X-ray Microprobe with a pass energy of 26.00 eV, 45° takeoff angle, and a 100 μm beam size. Raman spectroscopy was performed on a Renishaw Raman scope using a 633 nm He—Ne laser at 100%. Atomic force microscopy (AFM) images were obtained on a Digital Instrument Nanoscope IIIA using the tapping mode. The tips used were from Nanosensors, type PPP-NCH. Samples were spin coated onto freshly cleaved mica dropwise and dried overnight in a vacuum desiccator. A Nicolet FTIR Infrared Microscope with an attenuated total reflectance (ATR) attachment was used for Fourier transform infrared (FTIR) data. The samples were heated in the thermogravimetric analyzer (TGA; Q50, TA Instruments) from room temperature (RT) to 200 at 20 °C min⁻¹ for 50 min under an N₂ atmosphere to remove solvent. The samples were then heated from room temperature to 900 at 10 °C min⁻¹ under an N₂ atmosphere.

Catalyst Removal

As received HiPco SWCNTs (1 g) were heated to 225 °C in an oven through which humidified air flowed for 18 h. The air was humidified by vigorous bubbling through water. The SWCNTs were then transferred and catalyzed in a Soxhlet apparatus in a glass frit thimble and heated to reflux with 6 M HCl until the rinse was clear and colorless and no soluble iron was visible. The SWCNTs were then transferred to a vacuum filter funnel fitted with a polycarbonate membrane (0.45 μm) and were rinsed with aqueous sodium bicarbonate and water to neutralize the acid without applying vacuum. The purified SWCNTs (p-SWCNTs) were collected by vacuum filtration and dried in the air at room temperature for instrumental analysis and further use.

Oxidation of the p-SWCNTs

The p-SWCNTs (100 mg) were stirred vigorously with a Teflon coated stir bar in oleum (100 mL) in a dry Erlenmeyer flask under a nitrogen atmosphere for 72 h to yield disentangled SWCNTs (d-SWCNTs).

Results and Discussion

The purification procedure used on the SWCNTs is a two-step process. As-received HiPco SWCNTs are heated in a humid environment which oxidizes amorphous carbon and small fullerences in the sample to carbon dioxide and also causes the carbon shell around the SWCNT metal catalyst to crack and expose the metal inside (Scheme 1). This method eliminates non-SWCNT carbon material in the sample, which could promote CCF formation. The SWCNTs were continually rinsed in a Soxhlet apparatus with 6 M HCl to remove the metal catalyst until the aqueous HCl in the Soxhlet was clear and colorless. The solid material was then transferred to a vacuum filter funnel filled with a polycarbonate membrane (0.45 μm). While on the vacuum filter funnel, without vacuum, the filter cake was washed with aqueous sodium bicarbonate to neutralize the solution, then filtered, and further washed with copious amounts of water. The resulting p-SWCNT material was dried at room temperature and ready for further use. Other methods to purify SWCNTs use nitric acid, potassium, higher temperatures, or microwaves. SWCNTs display unique behavior when subjected to microwave radiation which can alter the structure of the SWCNTs; therefore, the use of microwave purification was avoided. Nitric acid oxidizes the SWCNTs and was also avoided during purification.

The p-SWCNTs were then oxidized. The oxidation step begins by stirring the bundles of p-SWCNTs in oleum for 72 h which yields d-SWCNTs. This step is crucial to ensure that the bundles of SWCNTs are well dispersed for subsequent efficient and even oxidation throughout the material. When the SWCNTs are not thoroughly dispersed, oxidation will occur on the outside of the SWCNT bundles, leaving unreacted SWCNTs in the.

inner portions of the material. Efficient debundling of SWCNTs should be done in water-free sulfuric acid to ensure individual SWCNTs.4a,13 The d-SWCNTs were oxidized by carefully adding premixed nitric acid (50–70%) and oleum (100% sulfuric acid and 20% excess SO3) (10:7 v/v) to the d-SWCNTs in oleum with stirring for 2 h\(^\text{4a}\) at 30, 40, or 65 °C. The oxidized SWCNT mixture was quenched by pouring over ice and filtering to yield a filter cake. The solid material was dispersed in a minimal amount of methanol and then flocculated in ethyl ether before filtration. The methanol and ethyl ether treatment was repeated until the methanol–ether filtrate was neutral. The resulting product was oxidized US-SWCNTs as we described previously (Scheme 1).\(^\text{4a}\)

Scheme 2 shows a summary of the Salzmann-like purification process flow where the Roman numerals are assigned to each isolated fraction from the process. Following the protocol of Salzmann et al., the US-SWCNTs (I, 50 mg) were stirred in aqueous NaOH (8 M) at 100 °C for 2 d in a nitrogen atmosphere.\(^\text{6}\) It was suggested that the basic conditions reduce the \(\pi-\pi\) interactions between the CCFs and nanotubes. Hence, the base treatment might allow the CCFs to be easily

filtered from the US-SWCNTs; this process yielded a red filtrate (II). The isolated black solid (III) was then rinsed three times with water, and the black-colored wash (VI) was evaporated to afford VII (45 mg). Soluble US-SWCNTs were noted in VII, thus water solubilizing functional groups remained on the US-SWCNTs. Not all of the solid material went through the filter; less than 3 mg of the black solid (V) remained after three rinses with water. Unfunctionalized SWCNTs have hydrophobic properties and should not be soluble in aqueous solutions; therefore, the soluble US-SWCNTs retained functional groups. The base treatment was repeated on all of the SWCNT material (the combination of V and VII, 48 mg) that was collected after the initial filtration to ensure the complete removal of the CCFs. The resulting filtrate was a very pale yellow, confirming that the vast majority of CCFs had been removed in the first base treatment.

The initial red filtrate (II) was of great interest due to the possible presence of the CCFs. To neutralize the red filtrate (II) solution, HCl (12 M) was slowly added while stirring; bubbling and heating were observed during neutralization. The cloudy solution became clear while maintaining its red color and was allowed to settle for 2 d, after which a dark brown solid (IV) was observed in the flask and was then collected by filtration and analyzed. The collected brown solid (IV, 1 mg) was a small weight percent of the starting US-SWCNT material (I, 50 mg).

The fractions were characterized. Raman spectra of the p-SWCNTs show a disorder mode (diamondoid or D-band) with a very low intensity at 1350 cm$^{-1}$ (see the Supporting Information). Spectra of the US-SWCNTs (I and VII) show an increased intensity in the D-band that is attributed to the sp$^3$-carbons present on the US-SWCNTs after oxidation (Figure 1). The relative degrees of oxidation, or the D/G ratios, were determined by dividing the intensity of the D-band by the intensity of the tangential mode (graphitic or G-band) at 1590 cm$^{-1}$. It should be noted that Raman is not a quantitative tool to accurately determine the amount of functionalization of these US-SWCNTs. It is merely used for qualitative comparisons between samples, and at least five scans on different areas of the samples were completed for our assessment. There were subtle differences observed between the Raman D/G ratios before and after base treatment. This may be due to the removal of the trace CCFs by the base treatment and the subsequent loss of their fluorescence. The base-treated US-SWCNTs (VII) retained a high degree of sp$^3$ carbons after base treatment. This suggests that the CCFs were not the only possible source of sp$^3$ carbons in the material.

FTIR analysis of the US-SWCNTs before (I) and after (VII) base treatment illustrates that a hydroxyl peak is present in both cases, but the carboxyl peak is not present after base treatment (Figure 3). As a separate experiment, nonbased washed US-SWCNTs were heated to 100 °C under vacuum to determine if the heating induced CO$_2$
expulsion; the carbonyl peak was unchanged by FTIR in that experiment. However, when the US-SWCNTs were treated with 8 M NaOH for 2 d at room temperature, filtered and flocculated as previously, FTIR analysis indicated the loss of the carboxylic acid peak (~1700 cm⁻¹) and appearance of the peak at ~1570 cm⁻¹ indicative of formation of carboxylate salts. In addition, as recently disclosed by Fan et al., heating of exfoliated graphite oxide with 8 M NaOH at 80 °C may facilitate deoxygenation; therefore, it is possible that some deoxygenation occurred when the based-treated US-SWCNTs were heated. Since the US-SWCNTs were soluble in water after base treatment, solubilizing groups remained on the US-SWCNTs after removal of the CCFs, thus proving that the sidewalls of the US-SWCNTs are actually oxidized after the above-described oxidation method and not just coated with CCFs. The acidification of US-SWCNTs with 1 M HCl resulted in the restoration of the carbonyl peak (see the Supporting Information) indicating that most of the carboxyl functionality remains in VII after base treatment.

TGA of the p-SWCNTs and US-SWCNTs material was done in an inert environment to assess the amount of functional groups present in each product, resulting in a 17% weight loss for p-SWCNTs (see the Supporting Information). p-SWCNTs were also heated in air to determine the amount of metal catalyst remaining in the sample. SWCNTs are known to burn in air at elevated temperatures leaving the oxidized metal catalyst behind. The samples were heated to 200 at 20 °C min⁻¹ and held for 60 min to remove any solvent and, then, heated to 900 at 10 °C min⁻¹ under the same atmosphere. The TGA weight loss results show that p-SWCNTs contained <5% Fe when heated in air. The oxidized material (I) lost ~40 wt %, which correlates to the oxygen containing functional groups on the SWCNTs.

XPS was performed on SWCNTs to determine the percent of carbon, oxygen, nitrogen, and iron in the material at various stages of oxidation. A minimal amount of Fe was found in all samples. The p-SWCNTs have a small amount of oxidation due to the heating process involved in the purification. As the SWCNT material is further processed, the carbon content decreases and the oxygen increases (Table 1). The SWCNT-containing black filtrate isolated after base treatment (VII) showed a considerable amount of oxygen remaining on the US-SWCNTs. This further supports the idea that the US-SWCNTs sidewalls are actually oxidized and not coated with CCFs. The isolated solid (IV) from the red filtrate had a higher carbon to oxygen content than the US-SWCNTs. The XPS characterization illustrates that the nanotube material exposed to the oleum and nitric acid oxidation process was significantly oxidized.

The Raman spectra (633 nm excitation) of the brown solid CCFs (IV) collected after neutralization of the red filtrate showed that the material was highly fluorescent, the D/G ratio was ~1:1 with poorly defined peaks (Figure 4A), and the fluorescence is characteristic of the CCF material obtained by Salzmann et al. The ill-defined peaks are in the characteristic D- and G-band region described previously and suggest that the solid collected in the filtrate had a highly disordered graphitic structure.

The brown solid CCFs (IV) collected from the neutralized red filtrate were also analyzed by FTIR and found to have characteristic hydroxyl, carboxyl, and carbon double bond stretches at ~3400, 1721, and 1646 cm⁻¹, respectively (Figure 4B). The spectrum suggests that carboxylic acids and benzene rings are present, agreeing with the Raman data.

The SWCNT materials were further analyzed using tapping mode AFM. Images of the p-SWCNTs show that they are long ropes, as expected, due to their 0.5 eV nm⁻¹ van der Waals forces between neighboring nanotubes (Figure 5A). After oxidation, the US-SWCNTs are much shorter, with an average length <100 nm (Figure 5B–D). SWCNTs become shorter as the oxidation temperature is increased as shown in the images below of US-SWCNTs oxidized at 30, 40, and 65 °C. There are a few examples of US-SWCNTs that are >100 nm present in the images. If the US-SWCNTs were uncut, they would still remain hundreds of nanometers long. The images clearly illustrate that the US-SWCNTs have been oxidized to the point of causing them to be drastically shortened. Length analysis of the SWCNTs was performed with the AFM images using SIMAGIS Nanotechnology software version 3.0. Green features are individual SWCNTs (<1.5 nm in height), blue are small bundles (>1.5 nm in height), and red are non-SWCNT features. The average tube length was

<table>
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<tr>
<th>SWCNT sample</th>
<th>CIs (%)</th>
<th>OIs (%)</th>
<th>NIs (%)</th>
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<tbody>
<tr>
<td>p-SWCNTs</td>
<td>95</td>
<td>5</td>
<td>&lt;1</td>
</tr>
<tr>
<td>d-SWCNTs</td>
<td>87</td>
<td>13</td>
<td>&lt;1</td>
</tr>
<tr>
<td>US-SWCNTs before base treatment</td>
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<td>1</td>
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<tr>
<td>US-SWCNTs black filtrate (VII)</td>
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<td>40</td>
<td>3</td>
</tr>
<tr>
<td>brown solid from red filtrate (CCFs) (IV)</td>
<td>64</td>
<td>36</td>
<td>&lt;1</td>
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found to be (B) 98, (C) 34, and (D) 33 nm, cut at 30, 40, and 65 °C, respectively.

Summary

In conclusion, SWCNTs were aggressively oxidized and purified by treatment with base at elevated temperature. The resulting material was shown to have a reduced content of CCFs, with the data indicating that the CCFs represented less than 2 wt % of the starting material. The data also indicates that our oleum/nitric acid method of oxidation does in fact oxidize and shorten the sidewalls of the SWCNTs; not merely coat them with CCFs. The XPS data of the US-SWCNTs after base treatment shows that 40% oxygen content remained on the nanotubes, which explains their solubility in aqueous solution, and the majority of the addends are carboxylate salts after the base washing. The AFM images illustrate the significant shortening of the US-SWCNTs when using the nitric acid and oleum oxidation process. SWCNT chemistry can be specific to the source of SWCNTs used, and the resulting products can change dramatically with slight differences in oxidation medium and procedures. Researchers in the field are cautioned that deviations in the stated procedure will likely change the resulting SWCNT material. Further
investigations toward using purified US-SWCNTs in biological and materials systems are being pursued.

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**Supporting Information Available:** Raman and TGA thermogram of purified HiPco SWCNTs and ATR-IR spectrum of acidified base-treated US-SWCNTs. This material is available free of charge via the Internet at http://pubs.acs.org.