

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.⁵ 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 physi-sorbed to the parent and unoxidized SWCNT scaffolds.

There are several reports in the literature⁴ 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.⁶), and workup 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 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

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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 $^{\circ}\text{C min}^{-1}$ for 50 min under an N_2 atmosphere to remove solvent. The samples were then heated from room temperature to 900 at 10 $^{\circ}\text{C min}^{-1}$ under an N_2 atmosphere.

Catalyst Removal⁷. As received HiPco SWCNTs⁸ (1 g) were heated to 225 $^{\circ}\text{C}$ 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 to 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^{4a}. 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). *Caution! This process uses a highly reactive mixture of acids; strong exothermic reactions are possible. Extreme caution should be used during the procedure. All oxidation reactions should be done in a fume hood and appropriate safety equipment should be worn, including a lab coat, rubber smock, thick rubber gloves, safety glasses, and a full face and neck shield.* Concentrated nitric acid (50–70%, 50 mL) was measured into a graduated cylinder followed by careful addition of oleum (35 mL). The acid mixture was slowly added to the SWCNT flask to avoid increasing the temperature of the mixture above 65 $^{\circ}\text{C}$, which could over-oxidize the d-SWCNTs. The temperature (30, 40, or 65 $^{\circ}\text{C}$) was maintained, and the mixture was stirred for 2 h followed by quenching over ice. The material was filtered over a polycarbonate membrane (0.45 μm), and the solid was rinsed with water.

The SWCNTs were then resuspended in a minimal amount of methanol and then precipitated in ethyl ether (250 mL) followed by vacuum filtration over the same membrane. The resuspension and precipitation was repeated until the methanol/ether filtrate was neutral as determined by pH paper. The resulting US-SWCNTs were dried at room temperature and analyzed.

Base Treatment of the US-SWCNTs⁶. The US-SWCNTs were added to a polypropylene Erlenmeyer flask (200 mL) with a Teflon stir bar along with aqueous NaOH solution (8 M, 50 mL). The mixture was heated to 100 $^{\circ}\text{C}$ and stirred under a nitrogen atmosphere for 48 h. The mixture was then filtered over a Teflon membrane (0.45 μm). The red filtrate was neutralized with HCl (12 M) and allowed to settle for 48 h, and the brown solid was collected by filtration. The black US-SWCNT solid filter cake was rinsed with deionized water (50 mL). The black filtrate and solid were analyzed without further treatment.

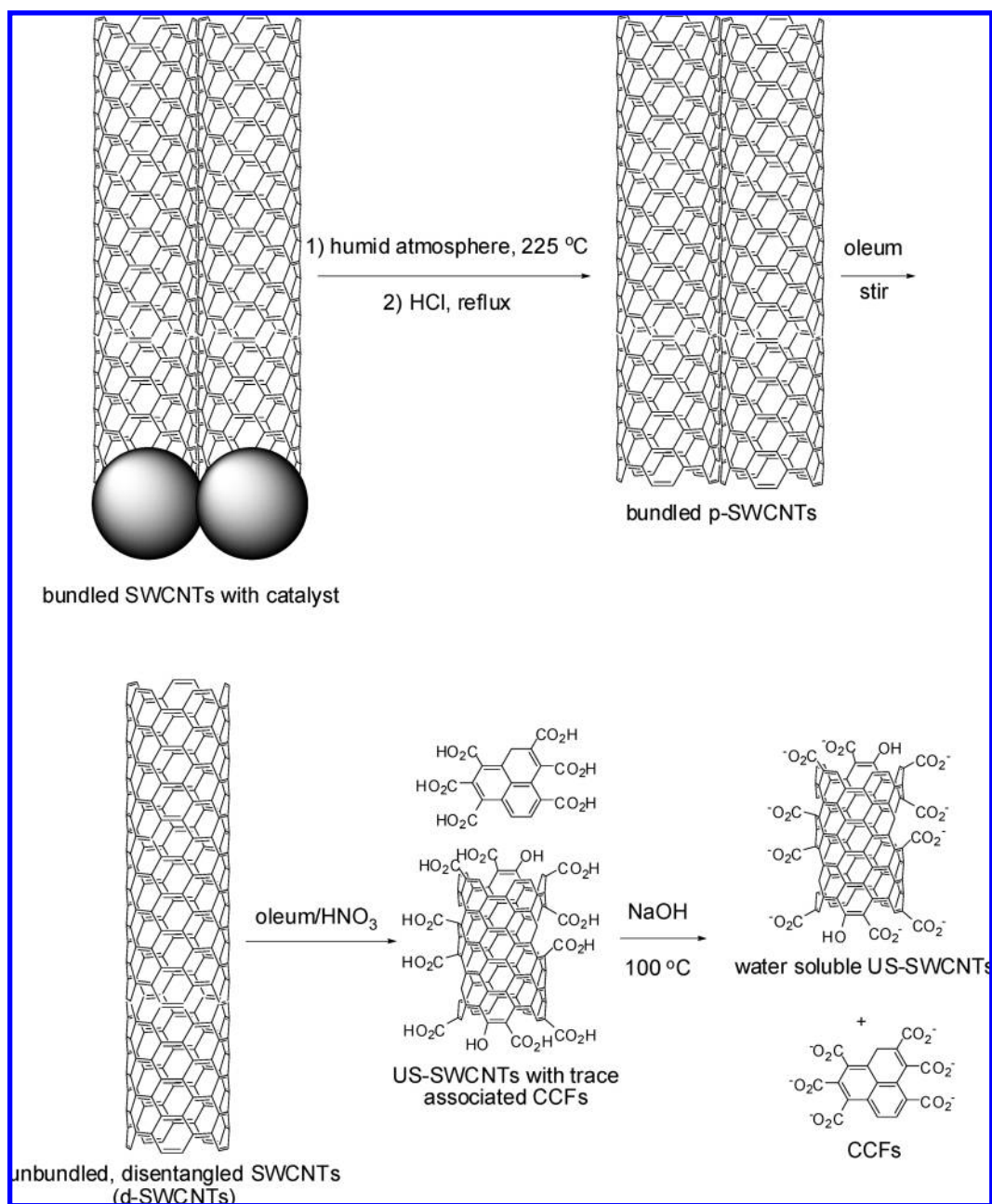
Results and Discussion

The purification procedure used on the SWCNTs is a two-step process.⁷ As-received HiPco SWCNTs⁸ are heated in a humid environment which oxidizes amorphous carbon and small fullerenes 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 fitted 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,⁹ potassium,¹⁰ higher temperatures,¹¹ or microwaves.^{12a} SWCNTs display unique behavior when subjected to microwave radiation^{12b} 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.^{4a} 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

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Scheme 1. As-received HiPco SWCNTs Purified (p-SWCNTs) to Remove the Catalyst and Amorphous Carbon^a

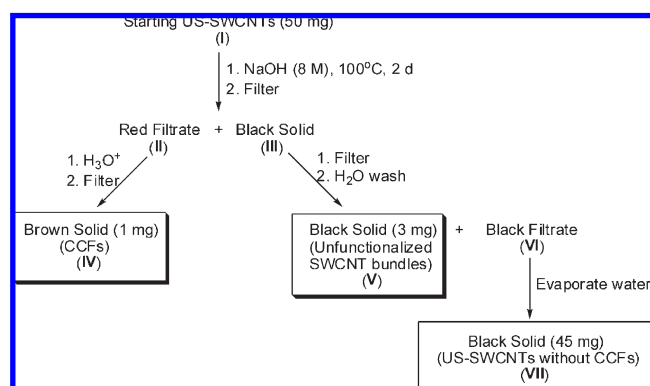
^a The p-SWCNTs were disentangled to form d-SWCNTs and oxidized to yield US-SWCNTs, which were then heated with 8 M aqueous NaOH. The US-SWCNTs were isolated by filtration with the CCFs in the resulting filtrate. Water-soluble US-SWCNTs were present in the second black filtrate after the filter cake was washed with DI water.

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^{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).^{4a}

Scheme 2 shows a summary of the Salzmänn-like purification process flow where the Roman numerals are assigned to each isolated fraction from the process. Following the protocol of Salzmänn 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.⁶ It was suggested that the basic conditions reduce the π – π interactions between the CCFs and nanotubes. Hence, the base treatment might allow the CCFs to be easily

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Scheme 2. Treatment Protocol Used on the US-SWCNTs That Were Isolated after the Oleum/Nitric Acid Oxidation

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.^{4a} 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 sp³-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

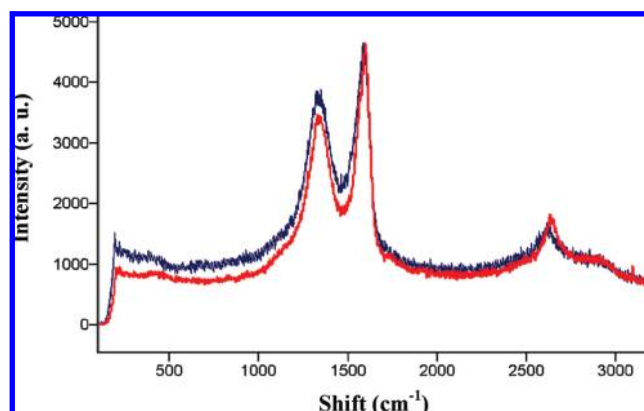


Figure 1. Raman spectra (633 nm, solid sample) of US-SWCNTs (I) before (blue) and after (VII) base treatment (red). The SWCNT material isolated after base treatment retained a high degree of sp³ carbons, confirming the presence of functional groups.

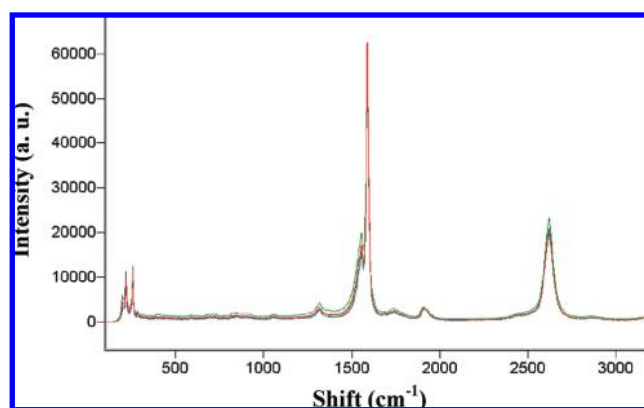


Figure 2. Raman spectra (5 scans overlaid) of the insoluble SWCNTs (V, 3 mg) collected after the second treatment with base.

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 sp³ carbons after base treatment. This suggests that the CCFs were not the only possible source of sp³ carbons in the material.

Raman analysis of the insoluble black solid (V) (Figure 2) revealed that it contains a small amount (3 mg or 6 wt %) of pristine SWCNTs that had likely remained bundled and hence unfunctionalized through the disentanglement process. This demonstrates that the disentanglement step is critical to provide exposed surface areas for the reaction, and the lack of a disentanglement step could be a major source of unfunctionalized nanotubes in others' protocols. In our process, however, there is only a small fraction of nanotubes remaining bundled and thus shielded from the oxidation.

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 CO₂

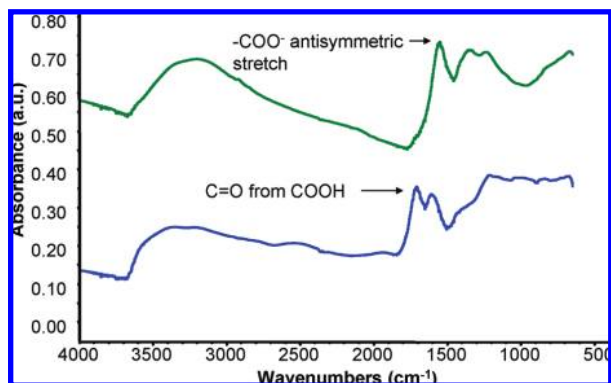


Figure 3. FTIR of US-SWCNTs before (I) (blue) and after (VII) (green) base treatment. The carboxyl peak is absent after base treatment.

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 ($\sim 1700\text{ cm}^{-1}$) and appearance of the peak at $\sim 1570\text{ cm}^{-1}$ indicative of formation of carboxylate salts.¹⁴ In addition, as recently disclosed by Fan et al., heating of exfoliated graphite oxide with 8 M NaOH at $80\text{ }^{\circ}\text{C}$ may facilitate deoxygenation;¹⁵ therefore, it is possible that some deoxygenation occurred when the based-treated US-SWCNTs were heated. Since the US-SWCNTs (VII) 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 VII 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.^{4b} The samples were heated to $200\text{ }^{\circ}\text{C}$ at $20\text{ }^{\circ}\text{C min}^{-1}$ and held for 60 min to remove any solvent and, then, heated to $900\text{ }^{\circ}\text{C}$ at $10\text{ }^{\circ}\text{C min}^{-1}$ 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 $\sim 40\text{ wt } \%$, 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

Table 1. XPS Results for SWCNTs During Various Stages of Oxidation

SWCNT sample	C1s (%)	O1s (%)	N1s (%)
p-SWCNTs	95	5	< 1
d-SWCNTs	87	13	< 1
US-SWCNTs before base treatment (I)	67	32	1
US-SWCNTs black filtrate (VII)	57	40	3
brown solid from red filtrate (CCFs) (IV)	64	36	< 1

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 US-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 $\sim 1:1$ with poorly defined peaks (Figure 4A), and the fluorescence is characteristic of the CCF material obtained by Salzmann et al.⁶ 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).^{2g} After oxidation, the US-SWCNTs are much shorter, with an average length $< 100\text{ nm}$ (Figure 5B–D).¹⁶ SWCNTs become shorter as the oxidation temperature is increased as shown in the images below of US-SWCNTs oxidized at 30 , 40 , and $65\text{ }^{\circ}\text{C}$. There are a few examples of US-SWCNTs that are $> 100\text{ nm}$ 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 ($< 1.5\text{ nm}$ in height), blue are small bundles ($> 1.5\text{ nm}$ in height), and red are non-SWCNT features. The average tube length was

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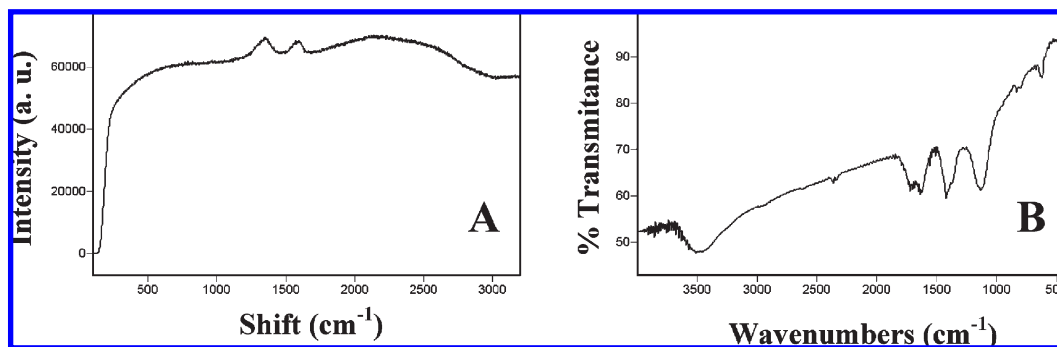


Figure 4. (A) Raman spectrum (633 nm) of the brown solid (IV, presumably CCFs) collected from the neutralized red filtrate after the base treatment of the US-SWCNTs. The material is more like graphite oxide than SWCNTs due to the high intensity of the D-band. (B) FTIR of the brown solid (IV) from the neutralized red filtrate. The FTIR spectrum was found to have characteristic hydroxyl, carboxyl, and carbon double bond stretches.

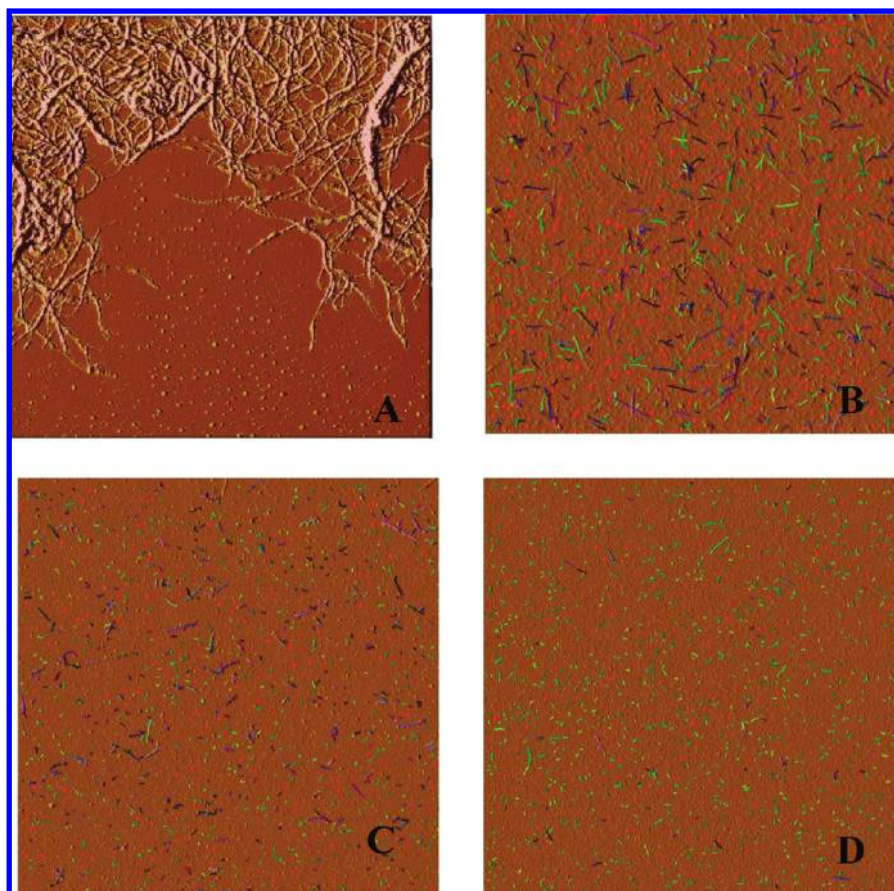


Figure 5. AFM analysis (spin coated onto freshly cleaved mica in DMF) by amplitude of (A) p-SWCNTs showing characteristic bundling and (B–D) US-SWCNTs oxidized at 30, 40, and 65 °C, respectively. Green features are individual SWCNTs, blue are small bundles, and red are non-SWNT features. The average tube length was found to be (B) 98, (C) 34, and (D) 33 nm. The picture edge lengths are (A) 10 and (B–D) 5 μm .¹⁵

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>.