

Nitric Acid Purification of Single-Walled Carbon Nanotubes

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Received: June 17, 2003; In Final Form: September 5, 2003

We report a systematic evaluation of the use of refluxing nitric acid as a purification treatment for electric arc-produced single-walled carbon nanotubes (SWNTs), by using a combination of thermogravimetric analysis (TGA) and near-infrared (NIR) spectroscopy. Nitric acid is the standard reagent for purification of SWNTs and has traditionally constituted the first step in many different purification schemes. It has been suggested that nitric acid removes the transition metal catalyst that is used in the production of the SWNTs together with amorphous carbon. Under all conditions, we find that nitric acid destroys SWNTs to produce amorphous carbon while reducing the amount of transition metal catalyst remaining in the sample. Thus, nitric acid is suitable for removing the catalyst from SWNT samples, but only at the expense of a significant destruction of the SWNTs.

Introduction

The purification of carbon nanotubes (CNTs) has attracted a great deal of attention because for some applications, such as their use in electronic devices and chemical and biological sensors, the CNTs must be of high purity. Single-walled carbon nanotubes (SWNTs) are usually contaminated with metal catalysts, amorphous carbon, and graphitic nanoparticles, and the presence of these impurities has hindered their application. A large number of purification methods have been reported, but refluxing nitric acid has probably been the treatment that has been employed most often, at least as the initial step in a purification; yet, there is very little quantitative information on the effects of this reagent on SWNTs.^{1–14}

Purportedly the major function of nitric acid treatment is to remove metal catalysts, perhaps together with some of the amorphous carbon.^{4,6,7} Because it is an oxidant, nitric acid may serve to oxidize the carbon atoms at the end of SWNTs. It was reported that refluxing or sonicating SWNTs in nitric acid opens the ends of the SWNTs¹⁵ and introduces carboxylic acid groups at the open ends and at defect sites of the SWNTs.^{1,11,16–21} Nitric acid treatment can also damage the walls of the SWNTs¹⁰ and thus produce carbonaceous impurities.⁴ In the presence of another strong oxidant like sulfuric acid, concentrated nitric acid can even cut the SWNTs into short pieces.¹ Nitric acid molecules or NO_x residues can intercalate the SWNTs² and lead to changes in the Raman spectra of SWNTs by doping.¹² The doping of the SWNTs induced by nitric acid treatment also leads to changes in the interband electronic transitions observable in the far- and near-IR spectra.²²

Dillon and co-workers reported the results of treating SWNTs with refluxing 3 M nitric acid over varying periods of time.³ They used transmission electron microscopy (TEM), thermogravimetric analysis (TGA), and Raman spectroscopy to characterize the SWNTs after nitric acid treatment and found that refluxing SWNTs in 3 M nitric acid for 4 and 16 h not only removed most of the metal catalysts, but also consumed a significant fraction of the nanotubes. This effect was magnified

when the treatment was extended to 48 h. Monthioux and co-workers studied the sensitivity of SWNTs to a series of chemical processing steps, some of which involved nitric acid; the SWNTs were mainly characterized by TEM.⁶ Very recently, Zhang and co-workers reported a systematic investigation of the effect of chemical oxidation on the structure of SWNTs produced by chemical vapor deposition (CVD). The oxidants used included 2.6 M nitric acid, concentrated sulfuric acid with concentrated nitric acid, and potassium permanganate.¹⁴ By using infrared spectroscopy and TEM, the authors found that dilute nitric acid works as a mild oxidant and introduces carboxylic acid groups only at those sites which contained defects before the nitric acid treatment. Despite the many high quality investigations of the effects of nitric acid on SWNTs, we are unaware of any studies that couple the yields of the SWNTs with a quantitative measure of product purity. Both pieces of information are necessary to assess the efficiency of a purification process.

The final purity of purified SWNTs has been evaluated by scanning electron microscopy (SEM),^{1,4,7,23–26} TEM,^{3,6,7,24} atomic force microscopy (AFM),^{25,27} TGA,^{3,7,24,25,28} and Raman spectroscopy.^{7,23–29} In some cases, the purity of the SWNTs was evaluated to be higher than 90%.^{3,9,23,26}

Recently, we reported a method to quantitatively evaluate the purity of as-prepared (AP-) SWNT soot by using solution phase near-IR spectroscopy (NIR), in which the SWNT purity was evaluated against a reference sample by using the region of the second interband transition (S₂₂, with spectral cutoffs of 7750–11 750 cm⁻¹) for semiconducting SWNTs (Figure 1).³⁰ This method is also applicable to the evaluation and optimization of SWNT purification procedures and allows us to investigate the effects of nitric acid treatment on SWNTs in a quantitative manner. In this paper, we report the evaluation of the effects of nitric acid treatment on electric arc-produced (EA-) SWNTs by using solution phase NIR spectroscopy. Because the use of nitric acid involves a compromise between the removal of impurities and the conversion of SWNTs into carbonaceous impurities, these experiments allow us to establish the optimum conditions for nitric acid treatment of EA-produced AP-SWNTs.

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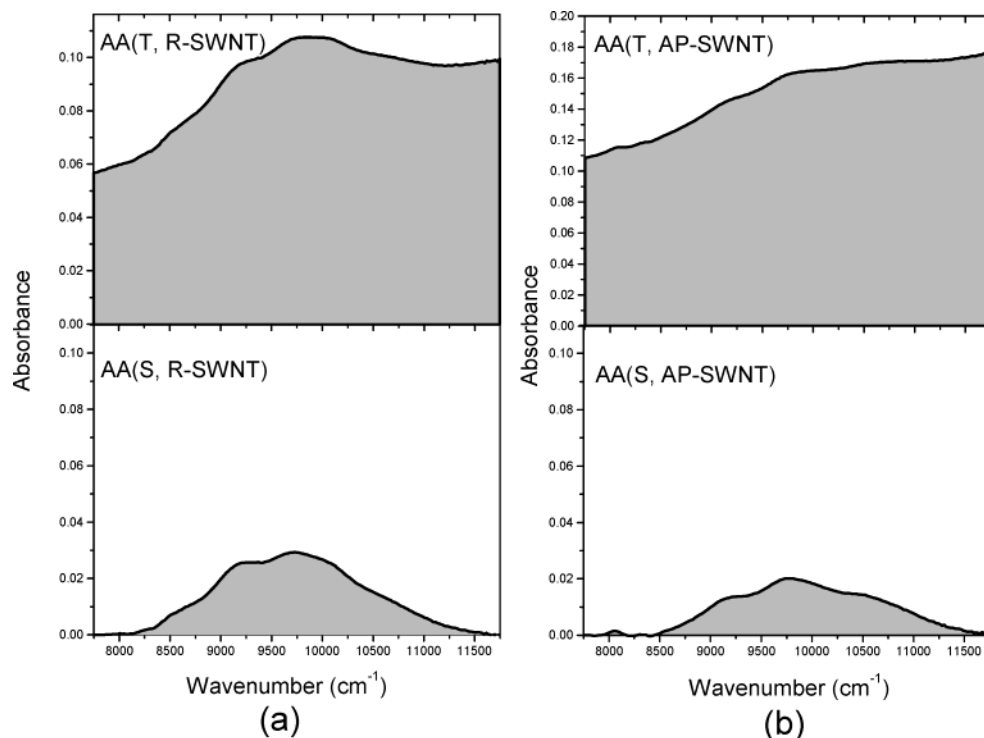


Figure 1. (a) Absorption spectrum of reference sample R-SWNT in DMF in the range of the S_{22} interband transition before (top frame) and after (bottom frame) baseline subtraction. The ratio of the areal absorptions (AA; note the change in terminology from our previous work³⁰ where this quantity was previously denoted A) in the bottom and top frames, $AA(S, R-SWNT)/AA(T, R-SWNT)$ is equal to 0.141. (b) Absorption spectrum of AP-SWNT sample in DMF before (bottom frame) and after (top frame) baseline subtraction. The ratio of $AA(S, AP-SWNT)/AA(T, AP-SWNT)$ is equal to 0.058. Thus, the content of SWNT in AP-SWNT is estimated to be 41% ($0.058/0.141$).

Experimental Section

The EA-produced AP-SWNTs were obtained from Carbon Solutions Inc. and used as received. All of the other reagents were purchased from Aldrich and used without further purification. Nitric acid solutions were prepared at the following concentrations: 2.8, 7.1, and 15.7 M (referred to as 3, 7, and 16 M, respectively). The NIR spectra of SWNTs in DMF solution were obtained on a Cary 500 Scan UV-vis-IR spectrometer. TGA data were recorded with a Perkin-Elmer Instruments, Pyris Diamond TG/DTA Thermogravimetric/Differential Thermal Analyzer, with a heating rate of 5 °C/min in air.

The general reaction scheme was as follows: 1 g of AP-SWNTs was refluxed in 150 mL of nitric acid. After refluxing, the mixture was cooled to room temperature, diluted with DI water, and filtered through a 1.2 μm pore-sized membrane. The product on the membrane was washed thoroughly with DI-water and dried at room temperature.

To understand the effects of nitric acid treatment on SWNTs, 1 g samples of AP-SWNTs were refluxed in 3 M nitric acid for 12, 24, and 48 h, in 7 M nitric acid for 6 and 12 h, and in concentrated nitric acid (16 M) for 6 and 12 h. The spectroscopic samples were prepared by sonicating the SWNT sample in DMF for 10 min with subsequent dilution to a concentration of ~ 0.01 mg/mL. The sonicated DMF solutions of the SWNTs were visually homogeneous. Figures 2 and 3 show the NIR spectra of the AP-SWNTs and the nitric acid treated SWNT samples.

Analysis

The content of SWNTs in an unknown sample should be evaluated by reference to a 100% pure SWNT sample. However, an analytically pure SWNT sample is not yet available and we

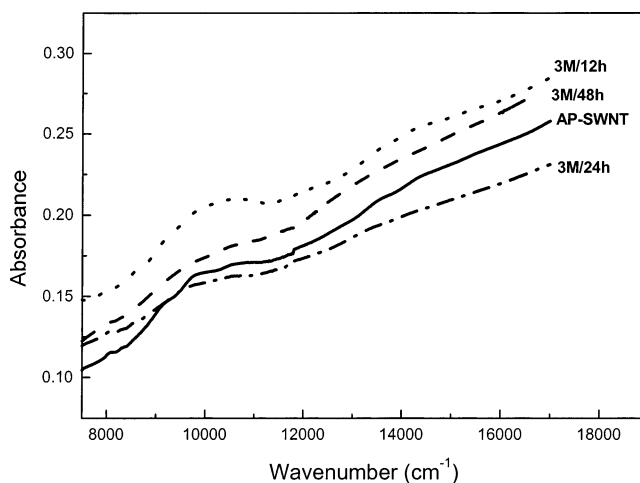


Figure 2. vis-NIR of AP-SWNT (solid line) and the products of 3 M nitric acid treated for 12 (dot line), 24 (dash-dot line), and 48 h (dash line).

choose a previously reported high purity sample as reference (R-SWNT = R2).³⁰ In what follows, the content of SWNTs in the R2 reference sample is set to 100% in order to analyze our results. By using the previously reported method,³⁰ the carbonaceous content of SWNTs (C-SWNT) in an arbitrary SWNT sample can be calculated from

$$C-SWNT = [AA(S, SWNT)/AA(T, SWNT)] / [AA(S, R-SWNT)/AA(T, R-SWNT)]$$

in which the areal absorption values (AA) are obtained by integration of the NIR spectra between the spectral cutoffs of 7750 and 11 750 cm^{-1} (chosen to capture the S_{22} interband transition). $AA(T, SWNT)$ and $AA(T, R-SWNT)$ are the total

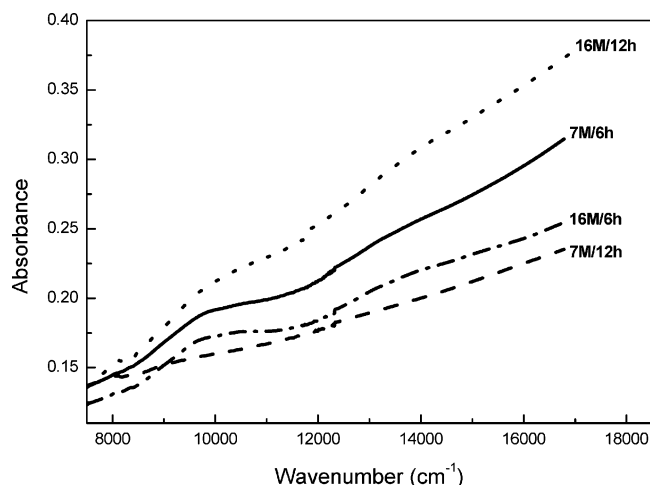


Figure 3. vis-NIR spectra of the products of 7 M nitric acid treated for 6 (solid line) and 12 h (dash line), and 16 M nitric acid treated for 6 (dash-dot line) and 12 h (dot line).

areas of the SWNT sample and R-SWNT under the full spectrum, whereas AA(S, SWNT) and AA(S, R-SWNT) are the areas of the SWNT sample and R-SWNT under the S_{22} absorptions after baseline correction, respectively (Figure 1).

The high-temperature TGA data (Figures 4 and 5) provides the weight percentage of metal (MET%) and this information together with the carbonaceous SWNT content (C-SWNT%) in the samples allows us to calculate the weight percentage of SWNTs (SWNT%) and carbonaceous impurities (CIMP%), within the assumptions of the model:

$$\text{SWNT\%} = \text{C-SWNT\%} (100\% - \text{MET\%})/100$$

$$\text{CIMP\%} = 100\% - \text{MET\%} - \text{SWNT\%}$$

Within the approximations discussed above, it is possible to construct a plot of the weight percentages of every component resulting from the nitric acid treatment (Figure 6).

Results and Discussion

Figures 4 and 5 show the TGA analyses of the AP-SWNTs and nitric acid treated products. The weight loss derivative curves ($-dW/dT$) directly reflect the occurrence of thermal events (such as the onset of burning) as a function of temperature. The TGA derivative curve of AP-SWNT shows two broad peaks that are assigned to amorphous carbon (around 350 °C) and SWNTs (around 425 °C).^{10,31} In the TGA curves of the nitric acid treated products, all of the peaks shift to higher temperatures due to the (partial) removal of the metal catalyst, and the SWNTs burned at about 540 °C.^{10,31}

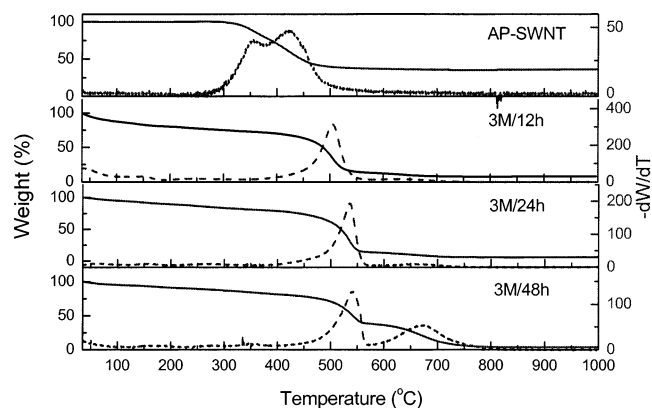


Figure 4. TGA data of AP-SWNT and 3 M nitric acid treated SWNTs. The solid lines are the weight versus temperature, and the dashed lines are weight loss derivative curves ($\mu\text{g}/\text{min}$).

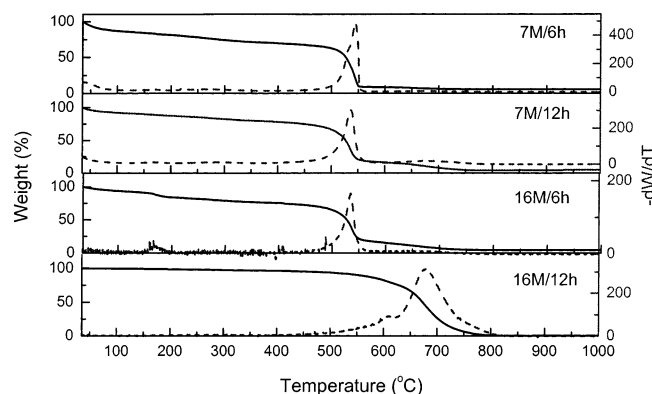


Figure 5. TGA data of 7 and 16 M nitric acid treated SWNTs. The solid lines are the weight versus temperature, and the dashed lines are weight loss derivative curves ($\mu\text{g}/\text{min}$).

The content of SWNTs in the AP-SWNT sample used as starting material in this study was found to be 41% by NIR analysis (Figure 1). Table 1 lists the SWNT content of the samples (within the assumptions of the analysis) and the yield of nitric acid treated SWNTs. It is found that the effect of nitric acid treatment on the SWNTs depends on both the refluxing time and the concentration of nitric acid. After refluxing AP-SWNT in 3 M nitric acid for 12 h, 69% of the starting material remained and the carbonaceous SWNT purity in the product was reduced to 36% from 41% in the starting material. The decrease in SWNT content indicates that even under the mildest conditions, treatment with nitric acid destroys SWNTs (see ref 32), and produces additional carbonaceous impurities in the sample. After refluxing AP-SWNTs in 3 M nitric acid for 24 h, the yield drops to 63% and the content of SWNTs is reduced

TABLE 1: Analysis of AP-SWNTs and Nitric Acid Treated SWNTs^a

sample	YLD %	C-SWNT% ^b	MET% ^c	SWNT% ^d	CIMP% ^e	metal weight loss (mg)	carbon weight loss (mg)
AP-SWNT		41	28.1	29	42		
3M HNO ₃ /12h	69	36	6.3	34	60	237	73
3M HNO ₃ /24h	63	20	4.6	19	76	252	118
3M HNO ₃ /48h	58	22	2.9	21	76	264	156
7M HNO ₃ /6h	65	31	4.2	30	66	254	96
7M HNO ₃ /12h	46	20	3.9	19	77	263	277
16M HNO ₃ /6h	28	24	3.4	23	73	272	448
16M HNO ₃ /12h	14	2	0.2	2	98	281	579

^a Based on an AP-SWNT starting sample of 1g (see Experimental Section). ^b SWNT carbonaceous purity is given by $\text{C-SWNT\%} = [\text{AA}(\text{S, SWNT})/\text{AA}(\text{T, SWNT})]/[\text{AA}(\text{S, R-SWNT})/\text{AA}(\text{T, R-SWNT})] \times 100\%$, in which $\text{AA}(\text{S, R-SWNT})/\text{AA}(\text{T, R-SWNT}) = 0.141$ (R-SWNT = R2). ^c MET% is the weight percentage of metal in the SWNT sample after correction for metal oxide formation. ^d SWNT% is the weight percentage of SWNTs in the sample. ^e CIMP% is the weight percentage of carbonaceous impurity in the sample.

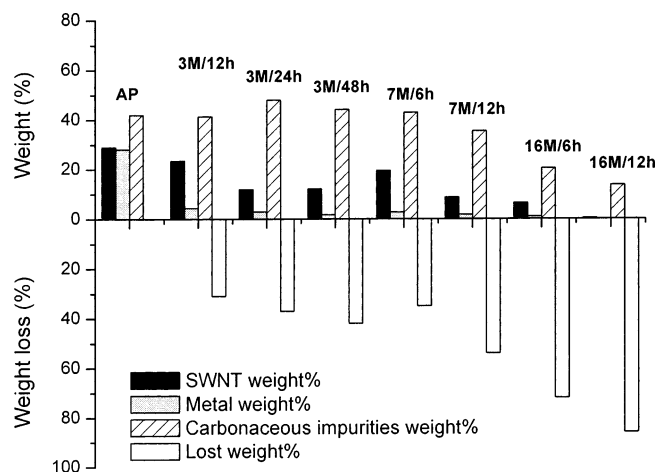


Figure 6. Mass balance of the normalized weight % of all components including SWNT, MET (metal), CIMP (carbonaceous impurities), and weight loss of the SWNT samples. SWNT weight% = C-SWNT% \times YLD%/100. Metal weight% = MET% \times YLD%/100. Carbonaceous impurities weight% = CIMP% \times YLD%/100. Lost weight% = 100% - YLD%. SWNT weight% + metal weight% + carbonaceous impurities weight% + lost weight% = 100%. The data of C-SWNT%, MET%, CIMP%, and YLD% are from Table 1.

to 20%. The content of SWNTs in the 3 M HNO₃/48 h product was similar to that of 3 M HNO₃/24 h product but with lower yield, which indicates the continued removal of SWNTs and carbonaceous impurities.

Refluxing in 7 and 16 M nitric acid provide harsher conditions than refluxing in 3 M nitric acid, and this is reflected in the yields of SWNTs obtained under these conditions: 65% (7 M HNO₃/6 h) and 28% (16 M HNO₃/6 h). Obviously, the application of 7 and 16 M nitric acid provides very strongly acid and oxidizing conditions so that a large amount of the SWNTs are consumed by the processing. The destruction of the SWNTs leads to the production of amorphous carbon (Figure 7), and this leads to a decrease in the fraction of SWNTs in the product. After treatment of the AP-SWNTs in 16 M nitric acid for 12 h the yield falls to 14% and the content of SWNTs is reduced to 2%. Hence, these latter conditions lead to virtually complete destruction of the SWNTs originally present in the sample (Figure 7).

The SWNT% remaining in the sample after 3 M HNO₃/12 h and 7 M HNO₃/6 h treatments is higher than that found in other samples. In this respect, these treatments represent purifications of the AP-SWNTs with respect to total impurities (metal and carbonaceous). However, the amount of metal remaining after the 3 M HNO₃/12 h and 7 M HNO₃/6 h treatments was slightly higher than was found in the other nitric acid treated SWNT samples.

As noted above, in its present state of refinement, the NIR analysis is only capable of providing the relative (carbonaceous) purities and thus provides an upper bound on the SWNT content. We have tested the results of the analysis in Table 1 and Figure 6, to a rescaling in which the reference value (R-SWNT) in the NIR analysis is multiplied by 1.5 (that is, [AA(S, R-SWNT)/AA(T, R-SWNT)] is set to 0.21 instead of 0.141),³⁰ and we find that the conclusions are unaffected.

As discussed above, nitric acid treatment consumes SWNTs and produces carbonaceous impurities under all conditions. Nevertheless, the nitric acid treatment is still useful as a first step in many purification schemes. With the ability to dissolve the metal catalyst, attack amorphous carbon, intercalate SWNTs, and break large particles, the nitric acid treatment can be a viable first step for SWNT purification. The key to achieving high

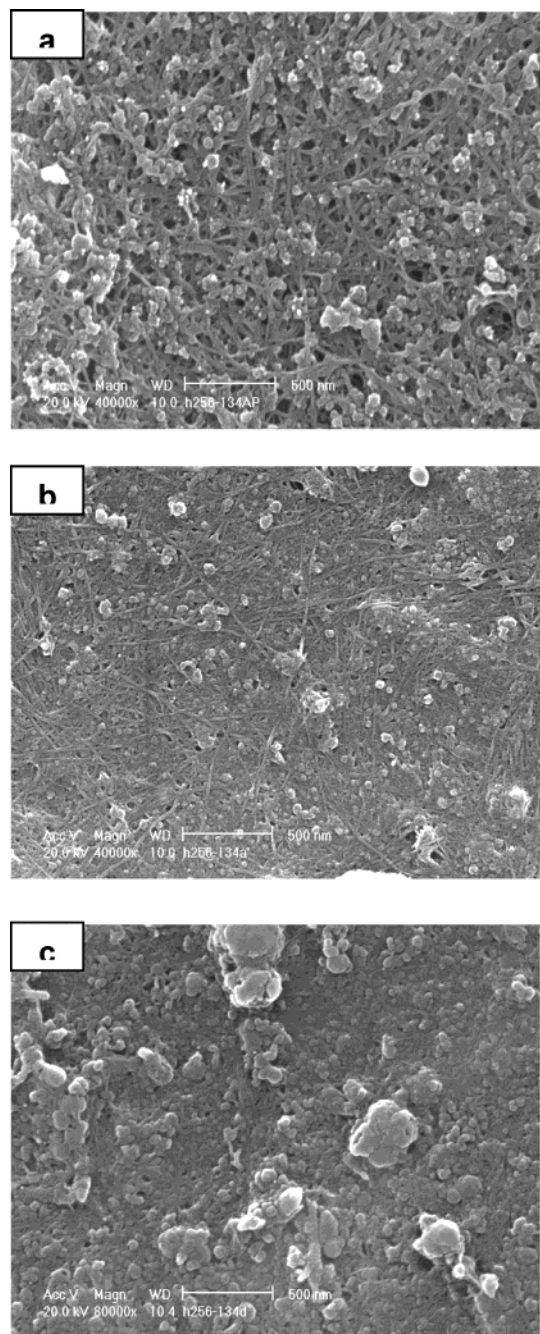


Figure 7. SEM images of products of AP-SWNT (a), 7M nitric acid treated for 6 h (b), and 16 M nitric acid treated for 12 h (c).

purity SWNTs is a subsequent process for removing the carbonaceous impurities that remain in the sample after nitric acid treatment. Many different chemical processes have been used as a post-nitric acid treatment. With respect to physical processes, however, simple filtration is ineffective due to the propensity of the carbon nanotubes to clog the filter pores. In this case the preferred method is cross-flow filtration which is known to give high purity material after nitric acid treatment.²⁴

In conclusion, we reported an evaluation of the effects of nitric acid treatment on SWNTs. The purity and yield of SWNTs after nitric acid treatment depends on the concentration of the nitric acid and the time of reflux; the 3 M HNO₃/12 h and 7 M HNO₃/6 h treatments were found to be most efficient.

Acknowledgment. This work was supported by the MRSEC Program of the National Science Foundation under Award No.

DMR-9809686 and by DOD/DARPA/DMEA under Award No. DMEA90-02-2-0216. Carbon Solutions, Inc. acknowledges NSF SBIR Phase I and II Awards No. DMI-0110221 from the Division for Design, Manufacture and Industrial Innovation.

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