Cutting, Solubilizing and Size-Sorting of Single-Wall Carbon Nanotubes

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ABSTRACT

The fluorination of purified HiPco single-wall carbon nanotubes (SWNTs) to a stoichiometry CFx ($x \leqslant 0.2$) followed by pyrolysis of the partially fluorinated SWNTs up to 1000 °C was found to have "cut" the nanotubes to a range of short lengths (average < 50 nm). The pyrolysis process was monitored in-situ with TGA-FTIR. The "cut" nanotubes have been characterized by Raman, ATR-IR, EDAX and AFM measurements. Short bundles composed of strongly interacting individual nanotubes were found in the "cut" nanotube sample. Solubilization of the "cut" nanotubes was achieved by derivatizing them either through re-fluorination or by refluxing in dilute nitric acid. Such derivatized "cut" SWNTs form a stable suspension in alcohol solvents such as ethanol or isopropanol, through which the size exclusion chromatography (SEC) separation of these short SWNTs bundles was conducted. AFM analysis was used to characterize the fractions from the SEC and the statistical length distribution was obtained. The short lengths and specific reactivities of the *cut-SWNTs* should lead to novel applications in fields such as microelectronics, drug delivery media and composite materials.

Keywords: nanotubes, cutting, fluorination, solubilizing, size-sorting.

1 INTRODUCTION

Since their discovery in 1991[1], carbon nanotubes (SWNTs) have been found to possess very attractive mechanical, electrical, optical properties due to their 1D geometry and related unique electronic structures [2-4]. These properties suggest their potential applications in wide ranges such as polymer composites, nanoscale electronic devices, electrochemical devices, hydrogen storage materials, field emission devices, sensors and probes[5], etc. Also, the closed structure of the capped SWNTs makes them perfect nanoscale capsules to be used as delivery media in medical applications or to create hybrid materials by introducing substances into their cavities [6]. However, for certain applications above, SWNTs with specific length are required. In other research work, short SWNTs were obtained by chemical eching using H2SO4/HNO3 [7, 8]. We have developed a process which cuts the single-wall carbon nanotubes to an average length <50 nm [9]. In this process, the purified single-wall carbon nanotubes were first partially fluorinated to a stoichiometry CF_x ($x \leqslant 0.2$). Then, by pyrolyzing the partially fluorinated nanotubes (*F-SWNTs*) up to 1000 °C in an argon atmosphere the fluorine was driven off the sidewall of the nanotubes in the form of CF_4 or COF_2. This left behind the chemically cut nanotubes (*cut-SWNTs*). Characterization with spectroscopic and microscopic methods indicated that the *cut-SWNTs* were composed of short nanotube bundles. When re-fluorinated to stoichiometry C2F, the *cut-SWNTs* gained comparable solubility in isopropanol to that of the Fluorotubes [10]. By refluxing the *cut-SWNTs* in 1M HNO3, the *cut-SWNTs* were found to be functionalized with quinone or carboxylic groups on the ends and sidewall, so that they formed fairly stable suspensions in ethanol. The isopropanol suspension of the fluorinated *cut-SWNTs* was then passed through a size exclusion chromatography (SEC) column using controlled pore glass (CPG) as the supporting material to test the size-sorting effect. The fractions were collected and analyzed with AFM to gain statistical results of the length distribution. Primary length separation effects were found with this method and a more detailed study of column parameters is ongoing.

2 EXPERIMENTAL

The SWNTs samples used in this study were produced by the HiPco process [11]. The average diameter of the nanotubes produced by this method is ~ 1.0 nm. The SWNTs were purified to remove the amorphous carbon and catalyst Fe particles before fluorination. The fluorinating reagent was a gaseous mixture of helium diluted F_2 which was passed over the SWNTs samples at a controlled flow rate during the reaction process. The *F-SWNTs* with a stoichiometry of CF_x ($x \leqslant 0.2$) were produced by controlling the conditions of the fluorination such as reaction temperature, fluorine exposure time and fluorine concentration in the reagent mixture. The *F-SWNTs* were then pyrolyzed in an argon atmosphere. A thermogravimetric analysis (TGA) apparatus coupled with an FT-IR spectrometer was used to monitor the pyrolysis in-situ. The sample was heated at a rate of 10 °C / min. to 1000 °C. The gaseous species released from the sample during the pyrolysis were led into the FT-IR spectrometer and their concentration variations were plotted versus time and/or temperature.

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AFM examination of the *cut-SWNTs* was carried out by dispersing the nanotube samples in an aqueous surfactant solution (1% Sodium Dodecyl Sulfate, SDS) with ultrasonic assistance. The dispersion was then deposited onto a silicon wafer for AFM imaging.

The *cut-SWNTs* were re-fluorinated with 10% fluorine in helium at 150 °C for ~ 8 hours to achieve the atomic F/C ratio 1:2. The fluorination conditions had to be carefully controlled to avoid damaging the *cut-SWNTs*. Such re-fluorinated *cut-SWNTs* formed stable suspensions in isopropanol, similar to the behavior of the Fluorotubes.

The *cut-SWNTs* were also refluxed in 1M HNO3 solution for ~ 24 hours. After rinsing thoroughly with water, the nanotube samples were recovered by vacuum filtering and vacuum oven dried. The HNO3 treated *cut-SWNTs* were characterized with ATR-IR to determine the functionalization types. They were then dispersed in ethanol with ultrasonication.

Primary size-sorting tests were carried out by size exclusion chromatography. Simple glass column setup with controlled pore glass (CPG, pore size ~3000 Å) as supporting material and isopropanol as fluent was used. The isopropanol suspension of the fluorinated *cut-SWNTs* was passed through the column 10 – 20 cm in height. The fractions were collected at ~ 15 minates intervals. The colored fractions were then deposited on the same silicon wafer for AFM analysis.

3 RESULTS AND DISCUSSION

The stoichiometry of the partially fluorinated SWNTs was determined based on the weight gain during the fluorination and the EDAX elemental analysis of the *F-SWNTs*. We have been able to prepare *F-SWNTs* with atomic F/C ratio 1:3, 1:5, 1:10. Even lower F/C ratio could be achieved by defluorinating the Fluorotubes with hydrazine [12]. An approximate F/C ratio of ~ 1:20 was obtained in this way.

The TGA results of the pyrolysis are shown in Figure 1. The percentage weight loss curve indicates that the overall weight loss during the process was ~ 45% and the time derivative percentage weight loss curve shows that there were two main weight loss steps. According to the heating program, the first weight loss step occurred between ~ 300 °C and ~ 560 °C and the second weight loss step occurred at temperatures over 560 °C. After isothermal heating at 1000°C for one hour, the weight loss curve has almost leveled out at ~ 55%, showing that the defluorination of the *F-SWNTs* did not lead to complete destruction of the nanotubes even at 1000 °C.

The TGA coupled FTIR spectrometer collected information about the gaseous species released from the sample at various steps during the pyrolysis that account for the weight loss. There were mainly three gaseous species released at various time periods: CF_4, COF_2 and CO_2 (the origin of some of the oxygen could be as impurity from the argon used in the experiment). The chemigrams in Figure 2 profile the variation of the relative concentration of each species versus time during the pyrolysis. According to the chemigrams, CO_2 and COF_2 were released from the sample within the temperature range of 300 °C and 560 °C, and CF_4 started evolving from the sample at a higher temperature,

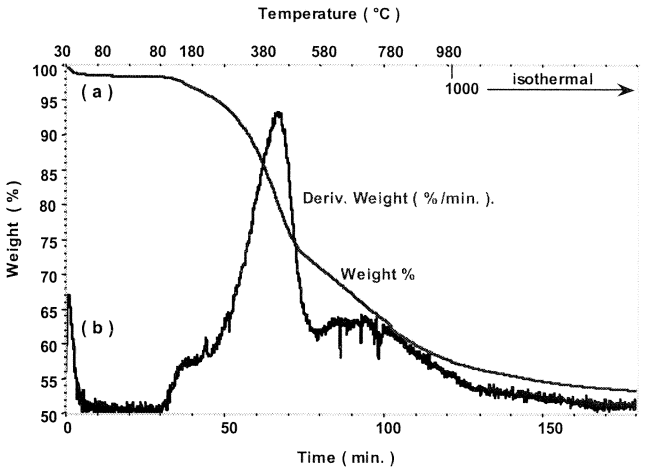

Figure 1: TGA of the F-SWNTs (stoichiometry ~C_5F) during pyrolysis in argon atmosphere. (a): weight percentage (%); (b): Derivate weight percentage (% / min.).

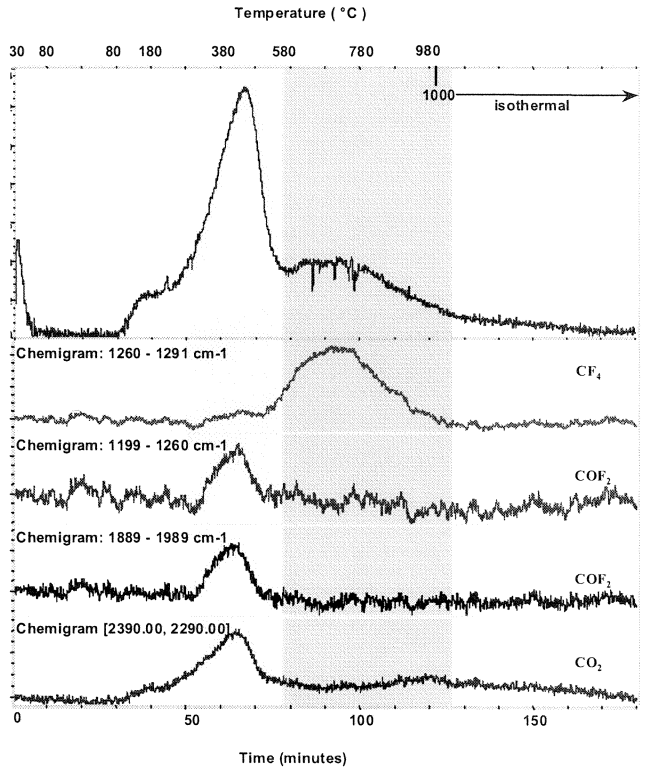

Figure 2 Correlation of the TGA derivative weight percentage curve and the chemigrams of the gaseous species released from the F-SWNTs during pyrolysis in argon atmosphere.

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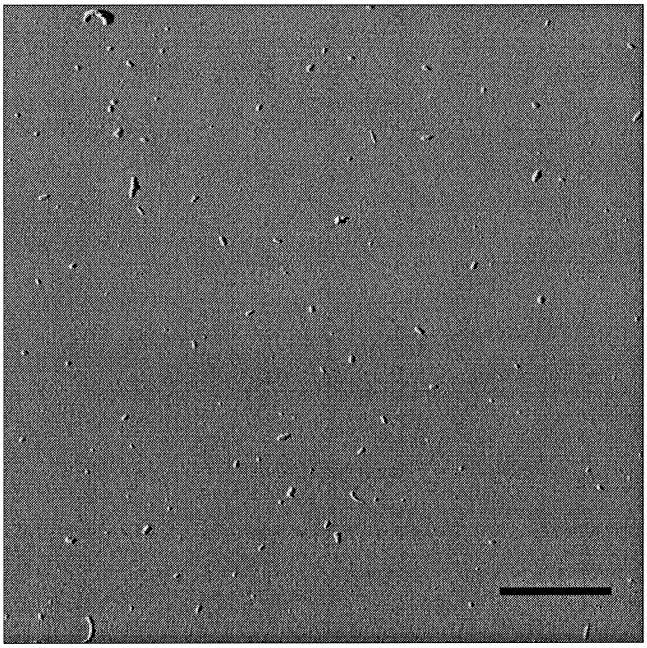

Figure 3 AFM image of the cut-SWNTs.
(Scale bar: 1 μm)

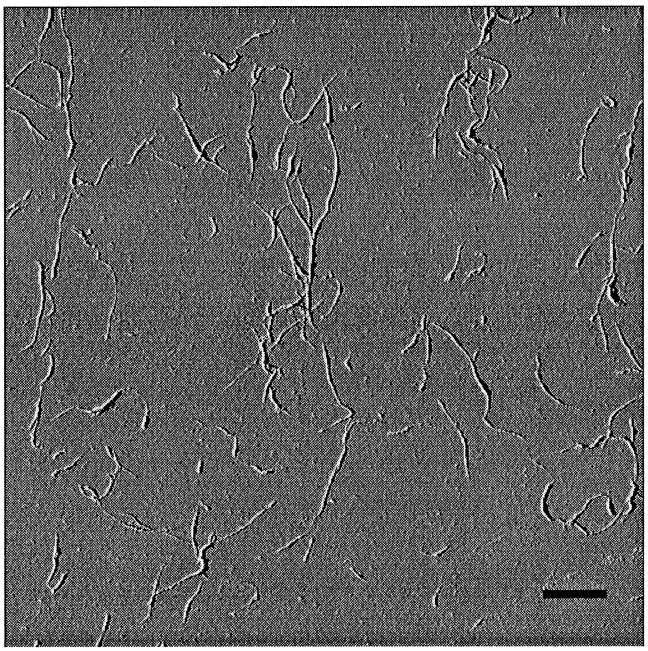

Figure 4 AFM image of the F-SWNTs.
(Scale bar: 1 μm)

560 °C. At that temperature, the release of CO_2 and COF_2 has already been completed. By putting together the chemigrams and the TGA curve on the same time scale, it can be seen that the two gas evolution steps are consistent with the two weight loss steps by TGA. Thus, the thermal defluorination of the *F-SWNTs* occurs in two steps: first, the evolution of CO_2 and COF_2 between ~ 300 °C and ~ 560 °C and second,

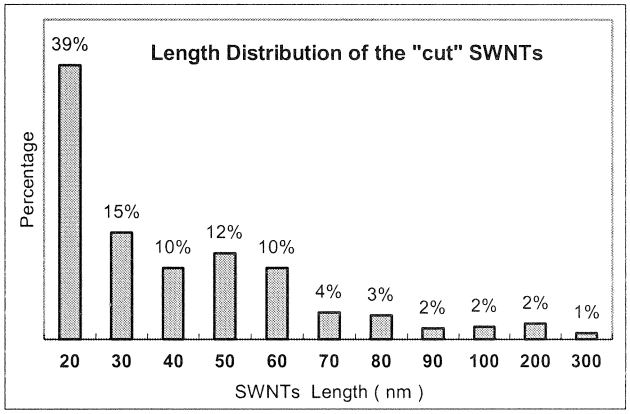

Figure 5 Length distribution of the cut-SWNTs.

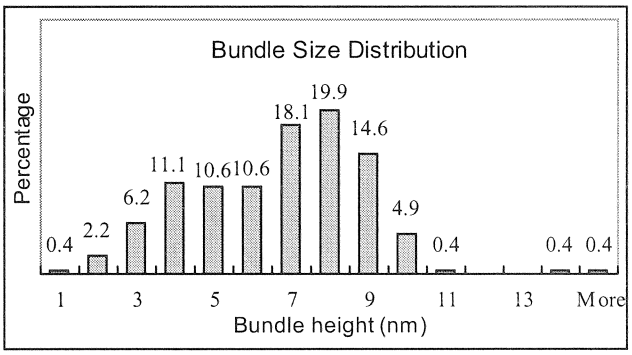

Figure 6 Bundle size distribution of the cut-SWNTs.

the evolution of CF_4 at temperatures higher than 560 °C.

During the pyrolysis of the *F-SWNTs*, fluorine was driven off the nanotube structure and, the fluorine has taken a certain amount of carbon from the nanotube sidewall. However, the loss of carbon didn't cause complete destruction and degradation of the SWNTs. Instead, ~ 55% of the mass survived as pristine nanotubes, even up to 1000 °C in the heating process, as established by examining the residue from the pyrolysis.

A typical AFM image of the *cut-SWNTs* is shown in Figure 3. As a contrast, the image of the *F-SWNTs* before the pyrolysis was also collected, as shown in Figure 4. The shortening of the SWNTs after the pyrolysis is apparent. The length distribution of the *cut-SWNTs* is shown in Figure 5. According to the AFM measurement, the average length of the cut-SWNTs bundles is ~ 40 nm. In contrast, most of the F-SWNTs are longer than 1 μm as shown in Figure 4. AFM height analyses indicate that the average bundle size (i.e. the diameter of nanotube bundles) is ~ 8 nm of the F-SWNTs and is ~ 6 nm of the cut-SWNTs (Figure 6).

The mechanism of the cutting is not clear yet, The distribution pattern of the fluorine atoms along the sidewall of the SWNTs was believed to determine the cutting effect. According to the STM study of fluorinated SWNTs [13], the fluorine atoms tend to arrange around the circumference of

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the nanotube and form band-like fluorinated areas along the nanotube sidewall. In the case of partially fluorinated SWNTs, the transition between the fluorinated and nonfluorinated bands typically remains quite abrupt and orthogonal to the SWNT axis. One would expect that the pyrolysis would only affect the fluorinated part of the SWNTs and leave behind the intact parts of the SWNTs, resulting in the cut, short SWNTs.

The re-fluorination and dilute HNO3 refluxing process have proved to be a successful way to incorporate the cut-SWNTs into alcohol solvents so that size-sorting of these short Nanotubes could be accessible.

SEC has been used to purify carbon nanotubes by separating out the impurities [14] and to sort the pristine nanotube bundles with lengths ranging from several hundred nanometers to over 10 μm [15]. Our primary testing on length separation of the cut-SWNTs by SEC was promising. By varying column heights, the difference in average length of nanotubes from separate fractions could be ~ 40 nm. Although there haven't been distinct boundaries between fractions and there were many factors influencing the yield, SEC will be an the effective and practical technique for the size-sorting of the cut-SWNTs.

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