# ARTICLES

# Cutting of Single-Walled Carbon Nanotubes by Ozonolysis

**Zheyi Chen,**[†] **Kirk J. Ziegler,**[§] **Jonah Shaver,**[‡] **Robert H. Hauge,**[*,†] **and Richard E. Smalley**[†]

*Center for Nanoscale Science and Technology, Department of Chemistry, Rice University, Houston, Texas 77005, Department of Physics, Rice University, Houston, Texas 77005, and Department of Chemical Engineering, University of Florida, Gainesville, Florida 32611*

*Received: December 23, 2005; In Final Form: April 13, 2006*

Cutting of single-walled carbon nanotubes (SWNT) has been achieved by extensive ozonolysis at room temperature. Perfluoropolyether (PFPE) was selected as a medium for cutting SWNT due to its high solubility for ozone ($O_3$). A mixture of 9 wt % of $O_3$ in $O_2$ was bubbled through a homogeneous suspension of pristine SWNT in PFPE, at room temperature. The intense disorder mode in the Raman spectra of ozonated SWNT indicates that extensive reaction with the sidewalls of SWNT occurs during ozonolysis. Atomic force microscopy (AFM) images of SWNT, before and after ozonolysis, provided a measure of the extent of the cutting effects. Monitoring of the evolved gases for both pristine and purified SWNT indicates $CO_2$ was produced during the ozonolysis process with a dependence on both system pressure and temperature. During heating, FTIR analysis of gases released indicated that carbon oxygen groups on the sidewalls of SWNT are released as $CO_2$. SWNT was found to be extensively cut after an ozone treatment with a yield of ∼80% of the original carbon.

## Introduction

In the fast growing field of nanotechnology, single-walled carbon nanotubes (SWNT) are recognized as a new strong,[1] electrically[2] and thermally[3] conductive material. Since their discovery,[4,5] many synthesis[6,7] and purification[8−10] methods have been developed to produce clean SWNT with length ranging from several hundred nanometers to several millimeters. Due to their long length and chemical inertness, SWNT are not soluble in common solvents. To increase their solubility, processibility, and dispersity in other materials, short SWNT and a scalable cutting technology are needed. SWNT with lengths less than 100 nm are very important for many applications in nanoelectronics, biological systems for drug delivery, and nanocomposites.

In an earlier work, Liu[11] found that chemical "shortening" of SWNT by prolonged sonication in a mixture of concentrated sulfuric and nitric acids was effective. However, this is not an efficient cutting process, due to the high weight loss of SWNT. More recently, fluorination has become the preferred route to cutting. Gu[12] reported that the pyrolysis of sidewall-fluorinated SWNT at up to 1000 °C can cut them to lengths of 50 nm. Later, Ziegler[13] proposed the cutting strategy of combining sidewall fluorination with Caro's acid treatment. This is a two-step process that involved the breakage of carbon−carbon bonds on the sidewall followed by etching at these damage sites to create short SWNT.

As an alternative to fluorine, ozone, a strong electrophile,[14] may also serve as a cutting agent. Ozone was reported to attack and open C=C double bonds in many organic compounds using Criegee's mechanism for ozonolysis.[15] Ozonolysis of the highly π-conjugated fullerene ($C_{60}$) was found to produce an intermediate, fullerene ozonide ($C_{60}O_3$), followed by the formation of $C_{60}O$.[16] In another study, ozonolysis was found to occur at the end caps of SWNT using highly concentrated ozone.[17] Due to the geometrically strained curvature of SWNT sidewalls and the high reactivity of ozone toward C=C double bonds, there is a high probability that ozonolysis on the sidewalls of SWNT, especially for those with small diameters,[18,19] may lead to cutting of individual SWNT into short sections. Previous studies[19,20] on the ozonolysis of SWNT were performed in methanol at dry ice/acetone temperature. We have substituted perfluoropolyether (PFPE) for safety reasons and because both ozone and oxygen readily dissolve in PFPE. In this study, we show that reaction of ozone effectively cuts pristine SWNT in PFPE, at room temperature. We believe this process is a scalable, effective, and safe route to cut SWNT.
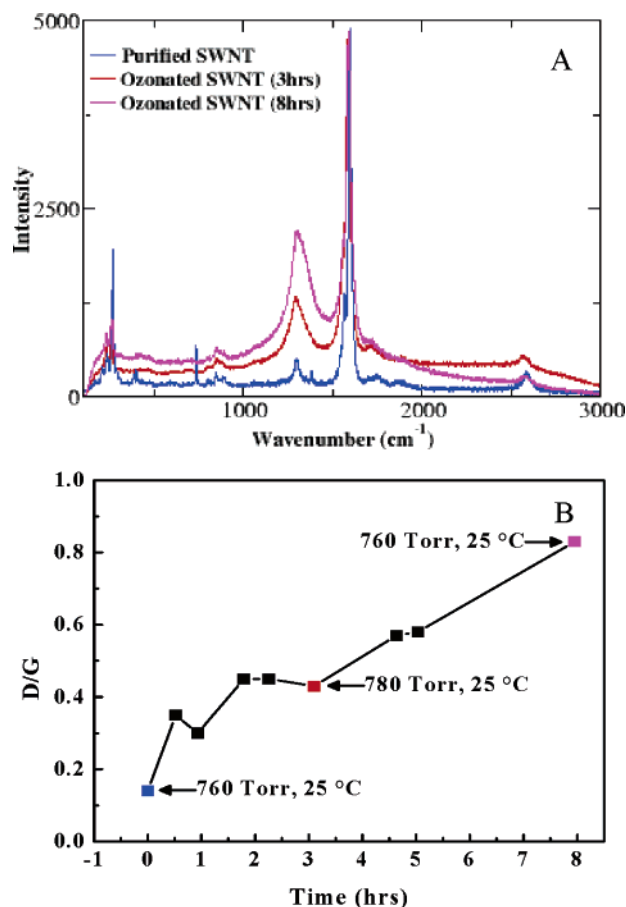
## Experimental Section

Pristine and purified SWNT produced from the HiPco[7,21] process were used throughout this study. At room temperature, a mixture of 9 wt % ozone (OzoneLab OL80W/FM500 wall mounted line of ozone generators) in $O_2$ was bubbled through a suspension (concentration of 1 g/L) of 0.2 g of pristine SWNT in 200 mL of PFPE (Galden HT-90) in a 250 mL three-neck flask for 1, 3, and 8 h, respectively. The SWNT suspension was homogenized with a high-sheer homogenizer, while the ozone/oxygen gases were bubbled through the suspension. Then, the ozone/oxygen flow was stopped and the suspension was purged by pure oxygen for 30 min to 1 h to remove residual ozone. The ozonated SWNT was then extracted with ethanol

* Corresponding author. Tel: 713-348-6384. Fax: 713-348-5320. E-mail: hauge@rice.edu.
† Department of Chemistry, Rice University.
‡ Department of Physics, Rice University.
§ University of Florida.

Cutting of Single-Walled Carbon Nanotubes by Ozonolysis

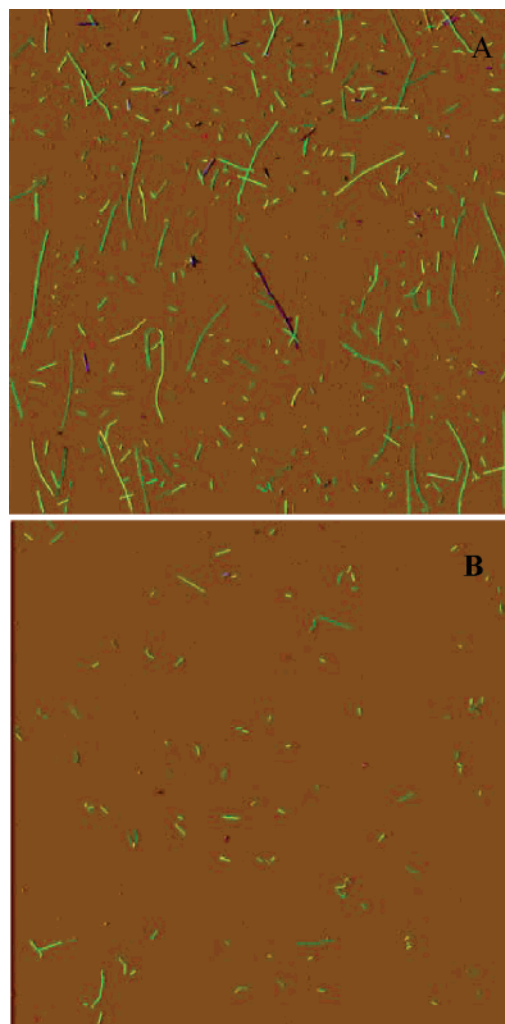*J. Phys. Chem. B, Vol. 110, No. 24, 2006* **11625**



**Figure 1.** (A) Normalized Raman spectra (780 nm excitation) of purified SWNT before (blue curve) and after ozonolysis for 3 h (red curve) and 8 h (purple curve). (B) D/G ratios after exposure to $O_3$ under different conditions.



**Figure 2.** (A) AFM image ($10\,\mu m \times 10\,\mu m$) of *n*-dodecylated SWNT before ozonolysis. (B) AFM image ($10\,\mu m \times 10\,\mu m$) of *n*-dodecylated SWNT after ozonolysis for 3 h.

(immiscible with the PFPE) in a separation funnel, where PFPE was drained away for distillation and reuse. Afterward, hexane and ethyl ether were added to the suspension to flock out the SWNT and to remove any residual PFPE. SWNT precipitates were then filtered with 0.2 $\mu m$ PTFE filter paper and vacuum-dried at a temperature close to the boiling point of PFPE (~90 °C).

Previous Fourier transform infrared (FTIR) spectroscopic studies of the oxidation and etching of SWNT with highly concentrated ozone have revealed that CO and $CO_2$ are produced during ozonolysis.[17] This implies that similar reactions may occur on the sidewalls of SWNT for SWNT suspended in a liquid. A series of studies were performed on pristine and purified SWNT respectively with a Thermo Nicolet 370 FTIR to monitor the existence and concentration of $CO_2$ and $O_3$ during the process. The temperature and pressure dependency of the reaction was also investigated. A dry ice/acetone trapping system was used to remove PFPE from the gas stream.

Raman spectroscopy was used to determine the extent of reaction with the sidewalls of SWNT. Raman spectra of the SWNT before and after ozonolysis are compared in Figure 1A. A typical Raman spectrum of the purified HiPco SWNT shows well-defined radial breathing modes (RBM), a disorder mode with very low intensity, and a high-intensity tangential mode, which indicates that the pristine SWNT have long-range one-dimensional structure with very few defects.[22] After ozonolysis, a much higher D/G ratio is observed, which implies the interrupted translational symmetry along the SWNT. This was also found by Wong et al.[19,20] Figure 1B shows the D/G ratios

after exposure to $O_3$ under different temperature and pressure conditions. In general, one sees an increase of the D band to G band ratio with continuous exposure to $O_3$.

Atomic force microscopy (AFM) was used to analyze the length distribution of SWNT before and after ozonolysis. A Birch reaction was carried out on pristine and ozonated SWNT to covalently bond *n*-dodecyl groups onto the sidewalls of SWNT to render them individually soluble in chloroform.[23] The SWNT suspension in chloroform was then spin-coated onto mica wafers for tapping-mode AFM imaging with a Digital Instruments Nanoscope IIIA. The length measurements were accomplished through image analysis using SIMAGIS software (Smart Imaging Technologies, Houston, TX). Typically, 500–1000 individual SWNT were counted to obtain meaningful results.

**Results and Discussion**

As described previously, ozonolysis of pristine SWNT was carried out in PFPE for 1 h, 3 h, and 8 h, respectively. Ozonolysis of 1 h and 3 h was carried out at room temperature and at 760 Torr. The 8 h ozonolysis was carried out at different temperatures and pressures. After ozonolysis (9 wt % $O_3$ in $O_2$) followed by alkylation, both pristine and ozonated SWNT are soluble in chloroform. Figure 2 shows typical AFM images (10 $\mu m \times 10\ \mu m$ scale) of pristine SWNT before (A) and after 3 h
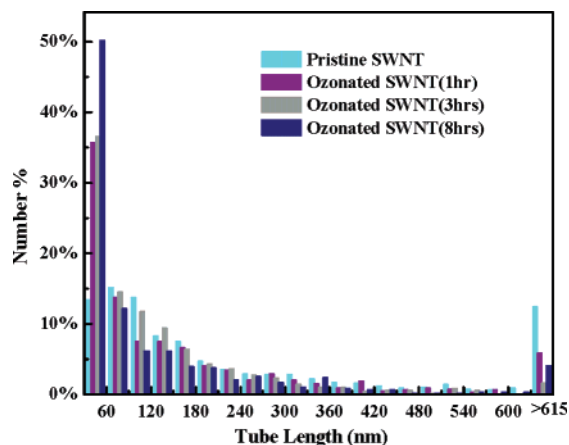
**Figure 3.** Number distributions of pristine SWNT and ozonated SWNT for 1 h, 3 h, and 8 h.

**TABLE 1: Medians and Carbon Yields of Pristine and Ozonated SWNT**

| sample | median by number (nm) | median by weight (nm) | final yield (%) |
|---|---|---|---|
| pristine SWNT | 146 | 614 | |
| cut SWNT by ozonolysis for 1 h | 92 | 371 | 88.5 |
| cut SWNT by ozonolysis for 3 h | 88 | 193 | 80.3 |
| cut SWNT by ozonolysis for 8 h | 59 | 324 | |

ozonolysis (B), in which the shortening of SWNT after ozonolysis can be easily seen. The histogram of SWNT with 30 nm bins, before and after ozonolysis, is shown in Figure 3. Before ozonolysis, SWNT produced in the HiPco process has a broad length distribution. After 1 h ozonolysis, the histogram showed a decrease in the percentage of longer SWNT and an increase in the percentage of shorter SWNT. Additional ozonolysis for 2 more hours caused an additional decrease in the percentage of longer SWNT relative to shorter SWNT. XPS results indicate a stoichiometry of $\sim C_7O$ after ozonolysis for 3 h. Temperature and pressure were adjusted during an 8 h ozonolysis. In comparison to 3 h ozonolysis, the number distribution exhibited not only a much higher percentage of short SWNT but also a higher percentage of longer SWNT. This inconsistency is suspected to be due to partial fluorination of SWNT, as discussed in the following section when ozonation is carried out at elevated temperature. Median lengths and yields after ozonolysis are summarized in Table 1. Both the length and number medians show a clear cutting effect with ozonolysis time. However, the length median after 8 h ozonolysis shows an unexpected increase due to the presence of a larger number of long SWNT. We believe that some SWNT are rendered inert to cutting due to the evolution of fluorine from the PFPE during its own reaction with ozone at the elevated temperature used during the course of the 8 h ozonolysis. Partial fluorination is indicated by a high weight increase, rather than a weight decrease as expected, 111% for the 8 h ozonolysis as compared to the yield of 88.5% for 1 h and 80.3% for 3 h exposures, respectively. The fluorination of SWNT is also indicated by much enhanced carbon–fluorine stretching modes for the 8 h ozonolysis, as seen in Figure 4. The calculated yield for the 8 h run is not included in Table 1 because of sample fluorination.

Infrared monitoring of the ozone and gases produced during the ozonolysis was carried out. In addition to ozone, only carbon
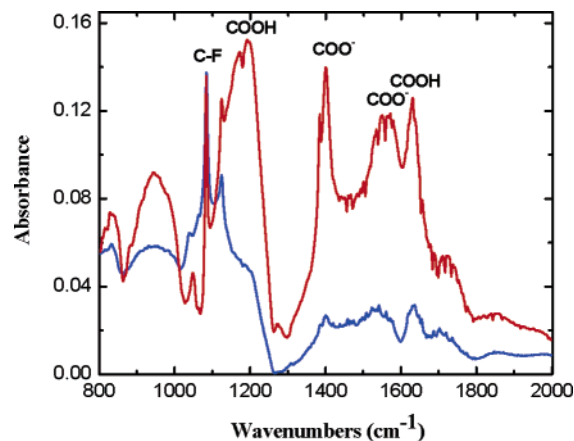


**Figure 4.** FTIR spectra of ozonated SWNT: for 3 h (red curve) and 8 h (blue curve).
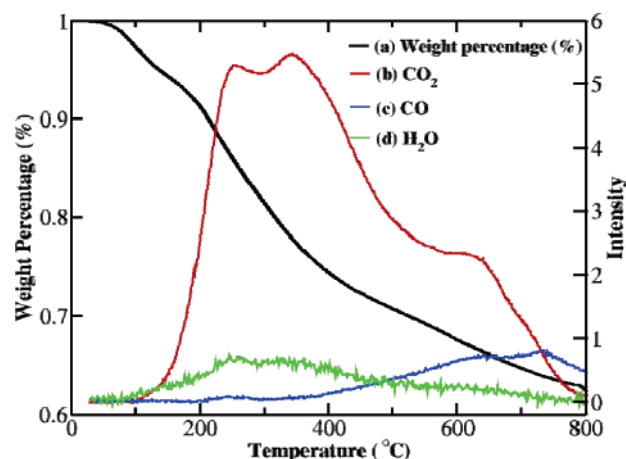


**Figure 5.** (a) Thermal gravimetric analysis (TGA) result of ozonated purified SWNT in $N_2$: weight percentage as a function of temperature (black curve); (b, c, d) FTIR spectra of the involved gas during TGA process. $CO_2$ (2300–2380 $cm^{-1}$), CO (2050–2250 $cm^{-1}$), and $H_2O$ (3400–3800 $cm^{-1}$).

dioxide was observed to be a product of the reaction. Table 2 gives changes in absorbance for ozone and carbon dioxide for different operating conditions. The data indicate that a small increase in pressure results in a large loss of ozone without a corresponding large increase in $CO_2$. This suggests a significant loss mechanism for ozone other than by reaction with SWNT. Most probably this is a SWNT-catalyzed conversion of ozone to oxygen. This effect is not observed when SWNT is not present. When the temperature of the reaction was raised, a more than doubling of the evolution of carbon dioxide was observed while the ozone decreased by less than half. This also suggests that even at 1 atm pressure a significant fraction of the ozone loss does not come from reaction with carbon and result in carbon dioxide evolution.

FTIR spectra from the 3 and 8 h ozonation runs are shown in Figure 4; the main features can be accounted for by assignment to various carbon oxygen species such as the ionized and nonionized carboxylic groups. Although sidewall epoxy bonding of oxygen is expected, it is difficult to clearly assign any features to an epoxy group. The sharp features near 1100 $cm^{-1}$ are attributed to C–F bonding that results from the release

**TABLE 2: Absorbance of $CO_2$ and $O_3$ in the FTIR Spectrum during Ozonolysis on Pristine SWNT**

| gas | absorbance intensity at 21 °C, 760 Torr | absorbance intensity at 21 °C, 800 Torr | absorbance intensity at 75 °C, 760 Torr |
|---|---|---|---|
| $CO_2$ (2300–2380 $cm^{-1}$) | 1.5 | 4.5 | 4 |
| $O_3$ (980–1086 $cm^{-1}$) | −2 | −22.5 | −2.5 |

Cutting of Single-Walled Carbon Nanotubes by Ozonolysis

*J. Phys. Chem. B, Vol. 110, No. 24, 2006* **11627**

of fluorine via oxidation of the PFPE solvent by ozone. This appears to occur to a greater extent at higher temperatures and is consistent with the observed weight gain for reaction at 75 °C.

Finally, as shown in Figure 5, heating the ozonated sample caused carbon dioxide and water to be evolved at temperatures below 400 °C, with the evolution of increasing amounts of CO above 400 °C. If one assumes that the weight loss from 100 to 800 °C is due largely to $CO_2$, the initial carbon-to-oxygen ratio in this 8 h sample is calculated to be 3.5; this value is somewhat lower than the ratio of 5 obtained from XPS. The actual value is probably better determined by the weight loss since XPS has difficulty providing quantitative information on light elements.

## Conclusions

In summary, we present a new cutting method for SWNT using PFPE as reactant medium. This ozone-based process appears to be a scalable, safe, and effective method for cutting SWNT.

## References and Notes

(1) Yu, M. F.; Files, B. S.; Arepalli, S.; Ruoff, R. S. *Phys. Rev. Lett.* **2000**, *84*, 5552

(2) Thess, A.; Lee, R.; Nikolaev, P.; Dai, H. J.; Petit, P.; Robert, J.; Xu, C. H.; Lee, Y. H.; Kim, S. G.; Rinzler, A. G.; Colbert, D. T.; Scuseria, G. E.; Tomanek, D.; Fischer, J. E.; Smalley, R. E. *Science* **1996**, *273*, 483.

(3) Hone, J.; Whitney, M.; Piskoti, C.; Zettl, A. *Phys. Rev. B* **1999**, *59*, R2514.

(4) Iijima, S.; Ichihashi, T. *Nature* **1991**, *363*, 603.

(5) Bethune, D. S.; Klang, C. H.; Vries, M. S. de; Gorman, G.; Savory, R.; Vazquez, J.; Beyers, R. *Nature* **1993**, *363*, 605.

(6) Tans, S. J. *Nature* **1997**, *386*, 474.

(7) Nikolaev, P.; Bronikowski, M. J.; Bradley, R. K.; Rohmund, F.; Colbert, D. T.; Smith, K. A.; Smalley, R. E. *Chem. Phys. Lett.* **1999**, *313*, 91.

(8) Chiang, I. W.; Brinson, B. E.; Huang, A. Y.; Willis, P. A.; Bronikowski, M. J.; Margrave, J. L.; Smalley, R. E.; Hauge, R. H. *J. Phys. Chem. B* **2001**, *105*, 8297.

(9) Zimmerman, J. L.; Bradley, R. K.; Huffman, C. B.; Hauge, R. H.; Margrave, J. L. *Chem. Mater.* **2000**, *12*, 1361.

(10) Xu, Y. Q.; Peng, H. Q.; Hauge, R. H.; Smalley, R. E. *Nano Lett.* **2005**, *5*, 163.

(11) Liu, J.; Rinzler, A. G.; Dai, H.; Hafner, J. H.; Bradley, R. K.; Boul, P. J.; Lu, A.; Iverson, T.; Shelimov, K.; Huffman, C. B.; Rodriguez-Macias, F.; Shon, Y.-S.; Lee, T. R. Colbert, D. T.; Smalley, R. E. *Science* **1998**, *280*, 1253.

(12) Gu, Z.; Peng, H.; Hauge, R. H.; Smalley, R. E.; Margrave, J. L. *Nano Lett.* **2002**, *2*, 1009.

(13) Ziegler, K. J.; Gu, Z.; Shaver, J.; Chen, Z.; Flor, E. L.; Schmidt, D. J.; Chan, C.; Hauge, R. H.; Smalley, R. E. *Nanotechnology* **2005** *16*, S539.

(14) Carles, J.; Fliszár, S. *Adv. Chem. Ser.* **1972**, 112, 35−49.

(15) Criegee, R. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 745.

(16) Heymann, D.; Bachilo, S. M.; Weisman, R. B.; Cataldo, F.; Fokkens, R. H.; Nibbering, N. M. M.; Vis, R. D.; Chibante, L. P. F. *J. Am. Chem. Soc.* **2000**, *122*, 11473.

(17) Mawhinney, D. B.; Baynebjim, V.; Jyzbetsivam, A.; Yates, J. T., Jr.; Liu, J.; Smalley, R. E. *J. Am. Chem. Soc.* **2000**, *122*, 2383.

(18) Lu, X.; Zhang, L.; Xu, X.; Wang, N.; Zhang, Q. *J. Phys. Chem. B* **2002**, *106*, 2136.

(19) Banerjee, S. ; Wong, S. S. *Nano Lett.* **2004**, *4*, 1445.

(20) Banerjee, S. ; Wong, S. S. *J. Phys, Chem. B* **2002**, *106* (47), 12144.

(21) Bronikowski, M. J.; Willis, P. A.; Colbert, D. T.; Smith, K. A.; Smalley, R. E. *J. Vac. Sci. Technol.* **2001**, *19*, 1800.

(22) Journet, C.; Maser, W. K.; Bernier, P.; Loiseau, A.; Lamy de la Chapelle, M.; Lefrant, S.; Deniard, P.; Lee, R. S.; Fischer, J. E. *Nature* **1997**, *388*, 756.

(23) Liang, F.; Sadana, A. K.; Peera, A.; Chattopadhyay, J.; Gu, Z.; Hauge, R. H.; Billups, W. E. *Nano Lett.* **2004**, *4* (7), 1257.