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Epoxidation and Deoxygenation of Single-Walled Carbon Nanotubes: Quantification of Epoxide Defects

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Sidewall functionalization of single-walled carbon nanotubes (SWNTs) has been studied extensively as a route to their separation, solubilization as well as subsequent reactivity. The simplest group of such reactions involves the addition of oxygen moieties to the sidewalls, including treatment with acid or wet air oxidation and ozonolysis. IR spectroscopic study of ozone treated SWNTs identified ester and quinone groups[1] as well as a band consistent with an epoxide. Theoretical calculations have suggested that the direct epoxidation of SWNTs may be accomplished by the reaction with highly reactive dioxiranes.[2] The authors suggested the facile formation of epoxy functionalized SWNTs (O−SWNTs) by this method, but there has been no experimental validation. Dioxiranes and peroxy-acids have been used extensively in organic chemistry for the epoxidation of electron-rich olefins and should be applicable to SWNTs.[3] In this regard, we have undertaken a study of the reaction of dioxiranes and organic peroxides with SWNTs to allow a comparison with the products from ozonolysis. An additional goal of this study was to develop methods to allow the quantification of the number of functional groups per SWNT. We have developed a catalytic method for the quantification of epoxide functional groups that has led to the surprising result that previously assumed "pure" SWNTs actually contain ca. 1 oxygen per 250 carbon atoms.

Epoxidation of SWNTs may be carried out by the reaction with either trifluorodimethyldioxirane, formed in-situ from trifluoroacetone and Oxone (potassium peroxymonosulfate, $KHSO_5$) in MeCN/H_2O,[4] or 3-chloroperoxybenzoic acid (*m*-CPBA)/CH_2Cl_2.[5] The resulting oxygenated SWNTs (O−SWNTs) have been characterized by Raman and FT-IR spectroscopy. As is expected, the Raman spectra for O−SWNTs show a dramatic increase in the D (disorder) band at 1290 cm^{-1} because of the chemical disruption of sp^2−hybridized carbon atoms in the hexagonal framework of the SWNT walls. The magnitude of the D band is increased further for the product from reaction with *m*-CPBA/CH_2Cl_2 in reflux condition. The ATR FT-IR spectra show no bands at 1250 and 1050 cm^{-1} characteristic of the ester groups observed during ozonolysis, but a band at 1210 cm^{-1} consistent with an epoxide moiety is seen.[6] Further evidence of covalent sidewall functionalization of SWNTs was evident from thermogravimetric analysis (TGA) in the 100−800 °C range. Epoxidized SWNTs show ca. 30% weight loss consistent with a C/O ratio of ca. 5:1−6:1. Thus, the spectroscopic analysis of the O−SWNTs formed using both acid peroxide or dioxirane is consistent with the epoxides. Furthermore, the present samples are spectroscopically similar to those obtained from the ozonolysis of SWNTs but without additional ester groups. However, the question of a technique to determine if the number of epoxide substituents is reagent specific still remains. Problems include the insolubility of O−SWNTs and the variability in lengths. Given the limitations of the spectroscopic quantification of sidewall substituents,[7] we suggest the development of a chemical approach based upon oxygen atom transfer from the O−SWNTs to a substrate for which quantification is readily obtained.

The use of transition metals as catalyst for the deoxygenation of organic epoxides is well established.[8] Given that we have demonstrated that the use of $MeReO_3$ (MTO)/H_2O_2 is suitable for the epoxidation of SWNTs,[9] we have investigated this catalyst for the quantification of the epoxide content in O−SWNTs. In the MTO system, deoxygenation occurs by an oxygen transfer reaction to a suitable substrate. We chose to use PPh_3 since the O-transfer to PPh_3 is enthalpically favorable and the amount of oxygen atoms transferred is readily quantified by ^{31}P NMR spectroscopy. Although de-epoxidation reactions with supported catalysts have been reported, unusually for such systems the present case employs a solution based catalyst (MTO) and both soluble (PPh_3) and heterogeneous (SWNT) reagents. Since the O-transfer reaction occurs in a two-step process from oxygenate to MTO and then MTO to PPh_3, the inhomogeneity of the reaction is not an issue.

A weighed sample of O−SWNT is placed in a Schlenk flask and thoroughly degassed with heating to remove adsorbed oxygen. A solution of MTO in toluene was added under inert atmosphere. Following that, a known amount of PPh_3 in toluene is added.[10] After the desired reaction time, the SWNTs are separated by centrifuge and washing with toluene. $^{31}P\{^1H\}$ NMR quantification is enabled by placing a small portion of the toluene decant in a NMR tube under N_2 containing C_6D_6 as the locking solvent. The relative integration of PPh_3 (−4.81 ppm) and $O{=}PPh_3$ (25.46 ppm) was determined. Knowledge of the PPh_3 and O−SWNT reagent starting mass allows for the quantitative measure of epoxide content, since the amount of $O{=}PPh_3$ formed is the same as the amount of epoxide removed (from the SWNT).[11] Thus, from the integration of the peaks in the $^{31}P\{^1H\}$ NMR spectrum, the percentage of PPh_3 consumed and the total percent mass loss from the sample is obtained and from this the C:O atomic ratio. Repetition of the measurement at different reaction times and MTO/PPh_3/O−SWNT ratios allowed for possible errors because of the presence of adsorbed O_2, leaks in the system, and insufficient reaction time.

As noted in the Introduction, the ozonolysis of SWNTs is proposed to result in epoxidation of the sidewall. On the basis of the catalytic deoxygenation, the oxygen content of batches of ozonated SWNTs under the same reaction conditions (Table 1) is constantly between C_6O and C_5O. The identity of the epoxide functional groups is further confirmed by comparing the oxygen content with SWNTs that have been reacted with the known epoxidation reagents as described above, see Table 1.

Raman spectra were obtained on samples before and after the de-epoxidation reaction. As can be seen from the spectrum of ozonated SWNTs before and after de-epoxidation (Figure 1), the disorder peak decreases significantly. This is consistent with removal of functionalization from the SWNTs and an increase in the overall short-range symmetry of the SWNT. The increase in the G′-band at 2600 cm^{-1} also confirms removal of functionalization, with a concomitant increase in the long-range symmetry of the SWNT.[12] Therefore, a large amount of functionalization (i.e.,

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Table 1. Oxygen Content of Various SWNT and O−SWNT Samples As Determined by Catalytic Deoxygenation

sample	approximate molecular formula
raw HiPCO	$C_{>123}O$
commercial purified	$C_{105}O$
cleaned SWNT (wet air oxidation)	$C_{250}O$
cleaned SWNT (SF_6)	$C_{35-43}O$
SWNT + ozone[a]	$C_{5-6}O$
SWNT + trifluorodimethyldioxirane[b]	C_9O
SWNT + *m*-chloroperoxybenzoic acid	C_5O

[a] Ozonation at room temperature for 3 h. [b] Formed in situ from trifluoroacetone.

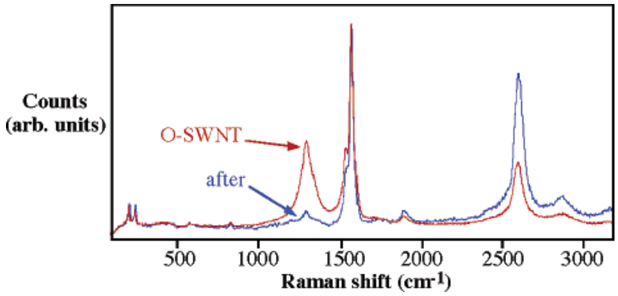

Figure 1. Raman spectrum (633 nm excitation) of ozonated O−SWNTs (room temperature for 3 h) before (red) and after (blue) deoxygenation with MTO/PPh_3.

epoxides) are being removed from the SWNT. The same changes in the spectral intensities are observed for O−SWNTs formed from epoxidation with trifluorodimethyldioxirane and *m*-chloroperoxybenzoic acid. The presence of the radial breathing modes (RBMs) at ∼230 cm^{-1} before and after deoxygenation indicates that the reaction does not effect the overall construction of the SWNT (i.e., it is still a tube). Each RBM is indicative of a certain chirality of SWNT; however, no inferences can be made about selective deoxygenation of any certain chirality even if there are observed changes in the RBMs. Since the MTO/PPh_3 system has been shown to be selective to only remove epoxides, any residual D band is presumably due to other sidewall functionalization and/or defects. Thus, we propose that epoxides represent the majority of functional groups added via both direct epoxidation and ozonolysis. Minor components are also present (possibly hydroxy or carbonyl groups), however, the extent of reduction of the D band and increase of the G′-band suggest that epoxides represent the majority of sidewall functionalization in ozonated SWNTs.

It should be noted that SWNTs used in devices and for physical measurements are routinely "purified" by an oxidative or oxidative/acid treatment to break up the graphitic carbon shell that encases the residual metal catalyst particles and remove the catalyst used in the growth of the SWNT, for example, acid based protocols including treatment with HNO_3/H_2SO_4 or $K_2S_2O_8/H_2SO_4$.[13,14] The presence of oxygen functional groups (including epoxides) added to the SWNTs during "purification" may possibly affect the overall electronic structure of a SWNT. Therefore, we have investigated the epoxide content of raw HiPco SWNTs as well as those after purification by acid treatment, wet air oxidation (wet Ar/O_2 (20%) atmosphere @ 225 °C), and treatment with O_2/SF_6.

As may be seen from Table 1, raw HiPco SWNTs appear to contain low epoxide content; however, it is difficult to get a consistent value because of the presence of significant metal catalyst content. There is also the possibility that oxidized large fullerenes are present, which would be more reactive than the SWNT. Contrary to expectations, the oxygen content is actually increased slightly upon purification with acid and increased greatly using the O_2/SF_6 method (Table 1). X-ray photoelectron spectroscopy (XPS) determined the overall oxygen content of O_2/SF_6 purified SWNTs to be between 2 and 5%.[15] The MTO/PPh_3 determined formula of $C_{43}O$ is equivalent to ca. 3 wt % oxygen, which is in good agreement with the XPS data.

Wet air oxidation of SWNTs results in the lowest epoxide content, and while our results do not suggest that additional epoxidation has occurred during the purification, the uncertainties associated with the measurements on raw HiPco cannot rule out some epoxide formation. It should be noted, however, that the presence of 1 epoxide per 250 carbon atoms is close to 1 epoxide per unit cell! The most surprising result of the present study is that supposedly purified SWNTs contain significant epoxide substitution. The fact that SWNTs previously presumed to be pure actually contain significant impurities suggest that these substituents may be carried over through subsequent sidewall functionalization and has implications for the accurate determination of their electrical, thermal, and mechanical properties. We propose that catalytic deoxygenation can be used as a method for analyzing a sample of SWNTs or as a further purification method.

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Supporting Information Available: Raman, IR, and $^{31}P\{^1H\}$ NMR spectra, MALDI-TOF MS. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Mawhinney, D. B.; Naumenko, V.; Kuznetsova, A.; Yates, J. T., Jr.; Liu, J.; Smalley, R. E. *J. Am. Chem. Soc*. **2000**, *122*, 2383.
(2) Lu, X.; Yuan, Q.; Zhang, Q. *Org. Lett.* **2003**, *5*, 3527.
(3) Murray, R. W. *Chem. Rev.* **1989**, *89*, 1187.
(4) To a MeCN solution (10 mL) of purified SWNTs (20 mg, 1.6 mmol) was added an aqueous Na_2EDTA solution (0.32 mmol). The resulting solution was cooled to 0 °C, followed by addition of trifluoroacetone (0.3 mL, 3.3 mmol). To this solution was added a mixture of sodium bicarbonate (0.40 g, 4.95 mmol) and Oxone (2.05 g, 3.3 mmol). The reaction mixture was stirred at 0 °C for 2 h then at room temperature overnight. After that, CH_2Cl_2 (20 mL) was added to the reaction mixture, and the mixture was filtered through a 0.2 μm PTFE membrane filter paper and dried in vacuo at 80 °C.
(5) *m*-CPBA (3-chloroperoxybenzoic acid, 77% max, 1.15 g, 6.6 mmol) was dissolved in CH_2Cl_2 (60 mL). After the solid has completely dissolved, purified SWNTs (40 mg, 3.3 mmol) were added, and the solution was stirred overnight. The reaction mixture was filtered through a 0.2 μm PTFE membrane filter paper and dried in vacuo at 80 °C.
(6) Creegan, K. M.; Robbins, J. L.; Robbins, W. K.; Millar, J. M.; Sherwood, R. D.; Tindall, P. J.; Cox, D. M.; Smith, A. B., III; McCauley, J. P., Jr.; Jones, D. R.; Gallagher, R. T. *J. Am. Chem. Soc*. **1992**, *114*, 1103.
(7) Zhang, L.; Zhang, J.; Schmandt, N.; Cratty, J.; Khabashesku, V. N.; Kelly, K. F.; Barron, A. R. *Chem. Commun*. **2005**, 5429.
(8) (a) Gurudutt, K. N.; Ravindranath, B. *Tetrahedron Lett.* **1980**, *21*, 1173. (b) Kim, S.; Kim, K. H. *J. Chem. Soc., Perkin Trans. 1* **1997**, 1095. (c) Alper, H.; Des Roches, D. *Tetrahedron Lett.* **1977**, *18*, 4155. (d) Zhu, Z.; Espenson, J. H. *J. Mol. Catal. A* **1995**, *103*, 87.
(9) Ogrin, D.; Barron, A. R. *J. Mol. Catal. A* **2006**, *244*, 267.
(10) HiPCO SWNTs (250 mg) were placed in a 250 mL Schlenk flask attached with an addition funnel. After evacuation for 30 min to remove any adsorbed O_2, a toluene (25 mL) solution of MTO (50 mg, 0.20 mmol) was added. PPh_3 (57 mg, 0.22 mmol) dissolved in toluene (25 mL) was added dropwise to the suspension over 15 min. The reaction was stirred overnight at 55 °C. The sample was centrifuged at 4000 rpm for 15 min, washed with fresh toluene (3 × 35 mL), and dried in air. A small portion of the toluene decant was transferred to a NMR tube under N_2. C_6D_6 (0.2 mL) was added as the locking solvent. The relative integration of PPh_3 (−4.81 ppm) and $O{=}PPh_3$ (25.46 ppm) was determined.
(11) To ensure that all oxygen atoms can be transferred, the reaction was carried out for the conversion of $C_{60}(O)_n$ to C_{60}, where the oxygen content of $C_{60}(O)_n$ was known by both MALDI-TOF MS and HPLC.
(12) Dresselhaus, M. S.; Pimenta, M. A.; Ecklund, P. C.; Dresselhaus, G. *Raman Scattering in Materials Science*; Webber, W. H., Merlin, R., Eds.; Springer-Verlag: Berlin, 2000.
(13) Rinzler, A. G.; Liu, J.; Dai, H.; Nikolaev, P.; Huffman, C. B.; Rodríguez-Macías, F. J.; Boul, P. J.; Lu, A. H.; Heymann, D.; Colbert, D. T.; Lee, R. S.; Fischer, J. E.; Rao, A. M.; Eklund, P. C.; Smalley, R. E. *Appl. Phys. A: Mater. Sci. Process.* **1998**, *67*, 29.
(14) Lian, Y.; Maeda, Y.; Wakahara, T.; Akasaka, T.; Kazaoui, S.; Minami, N.; Shimizu, T.; Choi, N.; Tokumoto, H. *J. Phys. Chem. B* **2004**, *108*, 8848.
(15) Gu, Z.; Smalley, R. E., personal communication.

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