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Infrared Spectral Evidence for the Etching of Carbon Nanotubes: Ozone Oxidation at 298 K

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Single-walled nanotubes (SWNTs) are an interesting new molecular form of carbon in the fullerene family, first reported by Iijima in 1991.[1] Intense research activity is now focused on these molecules[2] and many applications are envisioned.[2] It is necessary to understand the chemical processes and functionalization of SWNTs in order to pursue these applications. FTIR is one of the powerful techniques available to researchers to study these surface properties.[3] For example, we have recently used transmission FTIR to study the thermal decomposition of carboxyl and quinone functional groups formed by acidic cutting of the SWNTs.[4] These groups, located at the ends and at surface defect sites on the nanotubes,[2,5−8] block the entry ports for Xe adsorption on the interior of the SWNTs.[9] We report here FTIR spectroscopic studies of the oxidation and etching of SWNTs using ozone at 298 K, and the subsequent thermal stability of the oxygenated groups.

It has been shown through microscopy that reactions appear to begin at the end caps or kink sites of the SWNTs, followed by reaction at the rim sites that remain after the end caps and kink sites are etched away.[6,7,10] The enhanced reactivity of the end caps and kink sites, compared to the reactivity of the walls, can be understood by the increased strain at these sites causing a partial loss of conjugation.[8] In fact, forming a hole at the end cap by oxidation has been calculated to be much more energetically favorable (9 eV) than formation of holes on the walls.[11]

Ozonolysis is a common way to oxidatively break carbon−carbon double bonds at low temperatures.[12−14] Studies of the reaction of ozone with C_{60} and C_{70} have been reported in detail (see for example refs 15−17). However, the reaction of ozone with carbon nanotubes has been mentioned only briefly,[16,17] and no spectroscopic studies have been carried out.

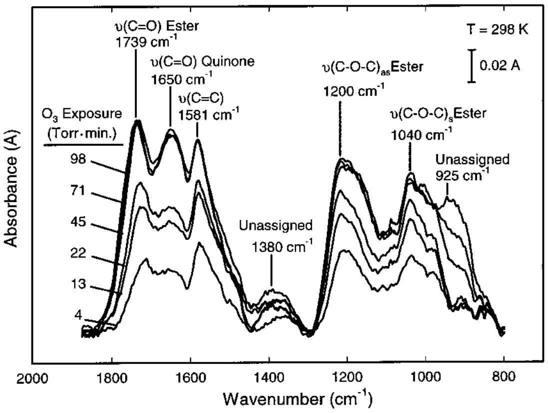

Figure 1. Infrared modes resulting from the ozonation of SWNTs. The background spectrum of the nanotubes before ozone exposure has been subtracted so that the changes can be more clearly observed. Both CO_2(g) and CO(g) are formed as well.

The SWNTs used in this study have a distribution of diameters near that of a (10,10) tube (13.6 Å).[18] The final sample consists of a mixture of open and closed-end SWNTs.[19] The samples were deposited via the drop/dry technique from a methanol suspension onto CaF_2 pressed into a tungsten grid clamped between electrical leads. This sample and a bare CaF_2 blank were then mounted in a stainless steel FTIR cell[20] used previously for transmission studies of powders and dispersed opaque materials.[21] The sample was heated to 373 K overnight in a vacuum (1×10^{-6} Torr after 16 h) to remove the solvent, followed by heating to 1073 K in a vacuum to remove most of the oxygen-containing functional groups on the original SWNT sample.[4] This heating revealed the IR-active phonon mode of SWNTs near 1580 cm^{-1}.[4]

The ozone was prepared at an initial purity of 97% (3% O_2) in a corona discharge-based trapping and purification system described elsewhere[22] and O_3(g) was transferred directly to the FTIR cell. The initial ozone purity in the FTIR system was determined to be ~70% O_3 (g) due to decomposition on the stainless steel walls of the apparatus.

Figure 1 presents the IR spectral changes of the SWNT sample caused by O_3 exposure at 298 K. The spectral bands that develop at 1739, 1200, and 1040 cm^{-1} are indicative of the production of ester groups. The band at 1650 cm^{-1} is assigned to the $C{=}O$ stretching mode of quinone groups, while the band at 1581 cm^{-1} is assigned to $C{=}C$ double bonds located near the newly formed oxygenated groups.[23,24] The origin of the bands at 1380 and 925

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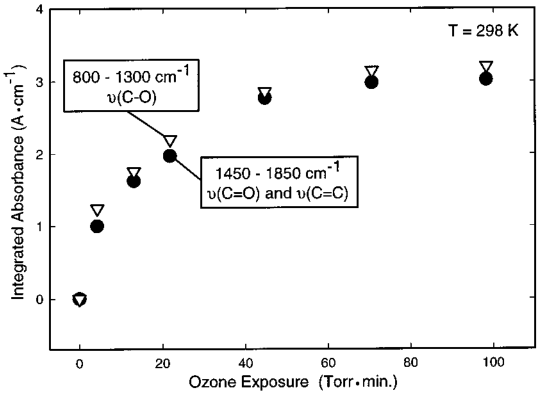

Figure 2. Rate of formation of oxygenated surface functionalities by ozonolysis. The dependence of the rate of C═O, C═C, and C−O functional group formation upon O_3 exposure to SWNTs.

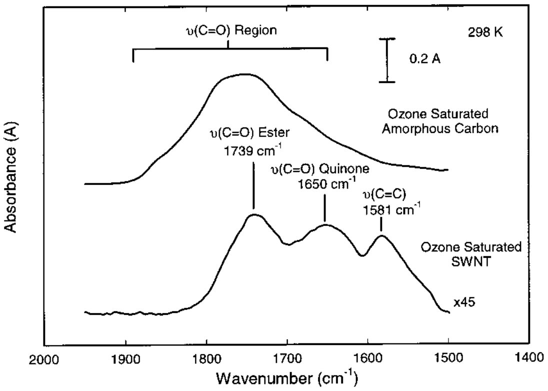

Figure 3. IR spectra showing the distinct carbonyl species formed on SWNTs. Comparison of FTIR spectra of ozonized SWNTs and amorphous carbon. The relative homogeneity of the oxygenated functional groups formed on the SWNT sample is demonstrated.

cm^{-1} is unknown at this time. CO_2 (g) and CO (g) (not shown) are formed during ozonation, revealing a carbon removal process. Also, no reaction was observed on the CaF_2 blank.

The progress of the reaction can be seen empirically in Figure 2, where each data point corresponds to the addition of fresh ozone. The initial rate of formation of oxygenated surface groups is very fast because the ratio of active sites to oxidized sites, S_a/S_{ox}, is large. However, the production of oxygenated species slows significantly after O_3 exposures in excess of about 60 (Torr•min) as S_a/S_{ox} diminishes. The rate of surface product formation diminishes after the ozone etches away the end cap sites and proceeds down the nanotube walls, where S_a/S_{ox} is constrained by the number of carbon atoms that make up the rim of the tube. This progression is in agreement with the TEM image of an ozone oxidized SWNT[16,17] and is consistent with theoretical predictions.[11]

Figure 3 compares the carbonyl infrared regions for SWNTs, and for amorphous carbon, both reacted with ozone to saturation. The amorphous carbon spectrum consists of one asymmetric, broad υ(C═O) band that is formed from the overlap of infrared modes arising from a variety of oxygen-containing surface functionalities that form on this inhomogeneous carbon surface. In contrast, the three sharper bands in the ozonized SWNT spectrum are a consequence of the more homogeneous structural character of the SWNT rims. This homogeneity constrains the formation of oxygenated species to a few distinct types.

Figure 4 shows the results of heating the ozonized tubes in the closed IR cell. The oxygenated functional groups begin to disappear near 473 K. By 873 K, almost all of the modes in this region disappear except for the unassigned band at 925 cm^{-1}. Also, CO_2 (g) is observed to form during heating. The addition and removal of these oxygenated groups does not appear to adversely affect the 1578 cm^{-1} SWNT phonon mode again (Figure 5). Since the phonon mode is the result of coupling within the carbon skeleton that makes up the SWNT walls, this indicates that the structural integrity of the nanotube walls has been maintained. This is most likely due to the ozonolysis reaction propagating from the ends of nanotubes rather than from the sides of the tube at wall sites.

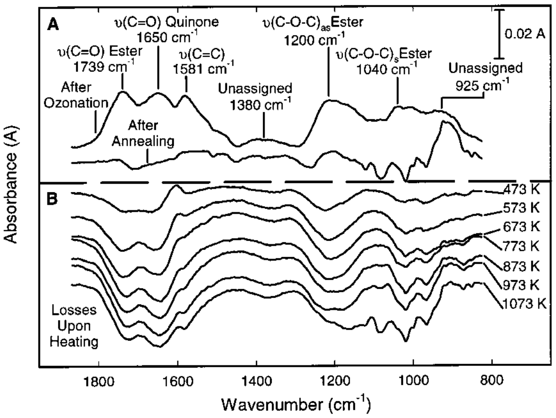

Figure 4. Thermal decomposition of the carbon−oxygen species formed by ozonolysis. Subtraction FTIR spectra demonstrating the loss of oxygenated groups due to heating the SWNTs in a vacuum. The difference spectrum collected after the final ozone exposure and the difference spectrum collected after heating in a vacuum to 1073 K are shown in panel A for reference. The difference spectra have the original SWNT spectrum before ozone exposure subtracted.

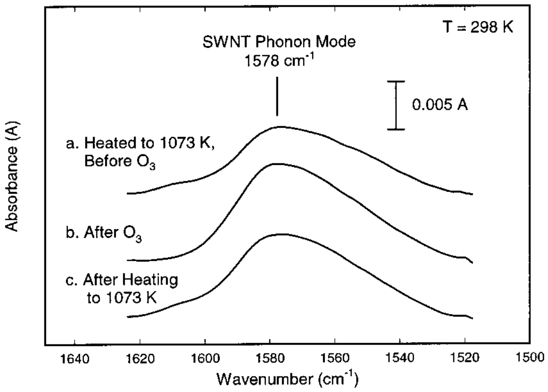

Figure 5. IR spectra of the (a) SWNT phonon mode before ozonation, (b) after ozonation, and (c) following the subsequent heating to 1073 K to remove the oxygenated groups. The retention of the phonon mode indicates that the structure of the nanotube walls has remained intact.

In conclusion, we have spectroscopically monitored the ozone reaction with SWNTs. This reaction produces two distinct surface-bound functional groups, esters and quinones, as well as gas-phase CO_2 and CO. The rate of formation of these species diminishes at higher O_3 exposures as the number of active sites on the SWNT diminishes. This is most likely due to the consumption of the end caps by ozone, subsequently constraining the number of active sites to the number of carbon atoms that make up the rim of the tube. The O_3-derived functional groups may be removed as CO_2 (g) by heating in a vacuum to 873 K, leaving the carbon nanotube walls intact.

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