Temperature dependent evolution of the local electronic structure of atmospheric plasma treated carbon nanotubes: Near edge x-ray absorption fine structure study

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Near edge x-ray absorption fine structure (NEXAFS) spectroscopy has been employed to obtain the temperature dependent evolution of the electronic structure of acid treated carbon nanotubes, which were further modified by dielectric barrier discharge plasma processing in an ammonia atmosphere. The NEXAFS studies were performed from room temperature up to 900 °C. The presence of oxygen and nitrogen containing functional groups was observed in C K edge, N K edge, and O K edge NEXAFS spectra of the multiwalled carbon nanotubes. The N K edge spectra revealed three types of π* features, the source of which was decisively identified by their temperature dependent evolution. It was established that these features are attributed to pyridinelike, NO, and graphitelike structures, respectively. The O K edge indicated that both carbonyl (C═O), π*(CO), and ether C−O−C, σ*(CO), functionalities were present. Upon heating in a vacuum to 900 °C the π*(CO) resonances disappeared while the σ*(CO) resonances were still present confirming their higher thermal stability. Heating did not produce a significant change in the π* feature of the C K edge spectrum indicating that the tabular structure of the nanotubes is essentially preserved following the thermal decomposition of the functional groups on the nanotube surface. © 2006 American Institute of Physics. [DOI: 10.1063/1.2260821]

I. INTRODUCTION

Carbon nanotubes (CNTs) have been the focus of intensive research interest mainly because of their rich electronic and mechanical properties, which may be tuned by functionalizing the sidewalls. Several methods such as chemical,1 electrochemical,2 polymer wrapping,3 and plasma treatment4–8 have been applied to modify the CNT surface. We have recently developed an alternative route, which is efficient, cheap, does not require solvents, and is capable of functionalizing large size substrates. The approach consists of nanotube exposure to plasma created by atmospheric dielectric barrier discharge. We have demonstrated this technique by successfully functionalizing multiwalled carbon nanotubes (MWNTs) with oxygen. In air we found CNT optimal functionalization within a few seconds (<5 s) at a discharge power of 0.5 W.7

Nitrogen is the most widely used atomic species for producing n-type CNTs in situ8 and modifying their surface chemistry.9,10 A recurring problem though has been to characterize the nature of surface groups on these functionalized tubes. The main difficulty is to identify the large number of possible local structures such as graphitelike (N atoms replacing C atoms in graphite layers) pyridinelike, pyrrolic, cross-linked sp3 structures, and gaseous N2 present in the material.10–18 The near edge x-ray absorption fine structure (NEXAFS) and electron energy loss spectroscopy (EELS) are sensitive to local electronic structure and are a few of the promising methods to study such a system.19–22

NEXAFS spectroscopy is analogous to EELS in that they both determine aspects of the unoccupied electronic structure of samples by core level excitation. However, EELS has a poorer spectral resolution (1 eV instead of 0.1 eV for NEXAFS) and causes increased radiation damage to sensitive molecules, owing to the use of an electron beam for excitation. In a number of comparative studies researchers have found good agreement in the overall shape of C K edge spectra, but the NEXAFS exhibited a number of structures, which were not resolved by the EELS.23,24

In this paper we present the electronic structure of acid treated MWNTs, which were further modified using atmospheric pressure dielectric barrier discharge (APDBD) treatment in ammonia atmosphere. The acid treatment served several purposes: (i) it purifies, disentangles the nanotubes, and introduces oxygen groups on their ends and sidewalls25 and (ii) it introduced oxygen groups that act as activation centers for attracting N atoms. We found that the chemically activated CNTs after treatment in DBD-NH3 atmosphere attracted higher N concentration compared to their nonactivated counterparts.26 The origin of this behavior can be found in the electron capturing nature of the functional groups. The amine chemical groups can donate electrons to the oxidized nanotube surface. The ability to introduce amine related groups on CNT surface via plasma treatment is interesting because it provides a basis for covalent immobilization of biological systems.27,28 From an in situ NEXAFS analysis, after high temperature annealing in vacuum, we were able to provide precise structure assignments and evaluate their thermal stability.
II. EXPERIMENT

MWNTs made by thermal chemical vapor deposition (CVD) process were obtained, after washing in HCl, from Sun Nanotech Co. Ltd., People’s Republic of China. They have average diameters of 10–30 nm and average length of 1–10 \( \mu m \) and sample purity of 85%. Acid-oxidized MWNT samples were prepared by refluxing the as received material in concentrated HNO\(_3\) for 4 h at 80 °C. The nanotubes were suspended in organic solvent \( N,N\)-dimethylformamide (DMF) and sonicated for 2 h to allow even dispersion. Then they were deposited onto a Au coated Si substrate and allowed to dry under an infrared lamp, producing a thick layer. These nanotubes have an oxygen concentration of 8.2 at. % and a nitrogen concentration of 1.7 at. %, which originate from the acid treatment and the sonication in DMF, respectively.\(^9\) The obtained MWNTs were treated in an AP-DBD chamber yielding an energy surface density in the order of 10\(^2\)–20\(^2\) \( \mu J/cm^2 \) for 2.5 s. Ammonia vapor was introduced to the APDBD chamber through an influx of \( N_2 \) gas to the ammonia solution (\( \sim \)35% NH\(_3\)). The nitrogen gas bubbled through the ammonia solution creating a vapor of ammonia. We avoided the direct introduction of ammonia gas due to its high toxicity. Details of the atmospheric plasma procedure can be found elsewhere.\(^7\) The nitrogen content in the resulting APDBD MWNTs was increased to a value of 5.5 at. % and the oxygen to 11.5 at. %.

The NEXAFS measurements were carried out at the SuperESCA beamline of the Elettra Synchrotron Radiation Facility (Trieste, Italy). The Si sample with the CNTs (5 \( \times \) 5 mm\(^2\)) was fixed on a Ta sample holder on the top of a 2 mm hole and inserted in the ultrahigh vacuum NEXAFS experimental chamber. The sample was subjected to rapid thermal annealing cycles of 2 min to temperatures up to 900 °C. The incidence angle of photon (\( h \)) was fixed at 55° from the surface normal (magic angle=54.7°). The data were acquired using surface sensitive total-electron yield (TEY) mode and were normalized to the signal from a gold-covered grid recorded simultaneously. The angle of incidence (the angle between the surface sample and the x-ray beam) of the light beam was kept at 55°. After subtracting the respective ionization jumps\(^15,29\) at both C K and N K edges, the resulting spectra were decomposed into several Gaussian peaks. In particular, the \( \sigma^* \) areas were fitted by asymmetric Gaussian peaks.

III. RESULTS AND DISCUSSION

Figure 1(a) presents the C K edge NEXAFS spectra of a functionalized sample at various annealing temperatures. All spectra were normalized at the maximum height for comparison purposes only.\(^30\) Three features are recognized in the C K edge spectra: (i) a sharp preedge peak at around 285.5 eV, known as \( \pi^* \) peak; (ii) two additional peaks (C2 and C3) appear in the range of 287–290 eV; and (iii) a broader resonance at photon energy, above 292 eV associated with vari-ous \( \sigma^* \) and \( \sigma^* + \pi^* \) transitions. The preedge resonance at 285.5 eV (C1) is due to transitions from the C 1s orbital to the unoccupied \( \pi^* \) orbitals ideally originating from \( sp^2 \) (C=\( \equiv \)C) sites.

![Figure 1](image)

The ratio of \( \pi^* \) (C1) to \( \sigma^* \) intensity is raised with the increase of annealing temperature [Fig. 1(d)] implying that at higher temperature the main participation is from \( sp^2 \) C hybrids. As the temperature increased the peak C1 increased at the expense of \( \sigma^* \) resonances. The peaks C2 (288.2 eV) and C3 (289.4 eV) can partially be assigned to \( \pi^* \) C=\( \equiv \)O (resonates in the approximate range of 287–289 eV) and \( \sigma^* \) C=O transitions (resonates in 289–291 eV) of the oxygen related functionalities introduced on the MWNT surface through the HNO\(_3\) acid treatment and APDBD processing. Recently, Banerjee et al.\(^{31}\) and Kuznetsova et al.\(^{32}\) found CO related features in the same energy range on ozonized and acid treated carbon nanotubes. Furthermore \( \pi^* \) (C=\( \equiv \)O) resonances at 288.2 eV have been observed for benzoic acid.\(^{32}\) For formic acid the \( \pi^* \) (C=O) is at 286.8 eV and for acrylic acid and propionic acid the \( \pi^* \) (C=\( \equiv \)O) resonances occur at 288.8 eV. Bearing in mind the electron capturing nature of the O and N functional groups there might be contributions from amide (CONH\(_2\)) groups within the 287–290 eV region.\(^{33}\) Resonances due to \( \sigma^* \) (C–H) dangling bonds occur at energies close to those of \( \sigma^* \) (C–O) bond. So the identifi-
culation of complete bonding states in this region (287–290 eV) is extremely complex due to large number of possible configurations.

Upon thermal treatment, the C2 and C3 features diminished drastically. Thus the C2 and C3 peaks can be readily assigned to oxygen and nitrogen functionalities since they decompose upon heating. Two representative deconvolutions, at room temperature and 750 °C, are shown in Figs. 1(b) and 1(c), respectively. For simplicity, the peaks C2 and C3 are considered as one peak. It is clear from the fitting that the oxygen and nitrogen surface groups \( \text{C2} + \text{C3} \) decreased significantly at 750 °C. Also all \( \sigma^* \) transitions are reduced with temperature.

More direct information about CN bonding can be extracted from the N K edge. In Fig. 2(a), the N K edge NEXAFS spectra of the nitrogenated CNT sample are shown at various annealing temperatures. Three \( \pi^* \) peaks at 399.5, 400.5, and 402.0 eV are prominent at the N K edge and they are denoted as N1, N2, and N3, respectively. The interpretation of these three absorption peaks is not yet established, mainly due to the complexity of the bonding structure in nitrogenated CNTs.\(^{10,34,35}\) The widely accepted assignment considers that N1, N2, and N3 are related to nitrogen in pyridinelike, molecular nitrogen, and graphitelike bonding environments, respectively.\(^{10,35}\) This correlation is based on the comparison with the resonance positions from standard carbonaceous materials.\(^{10}\) The relative intensity of each peak (N1, N2, and N3) referred to the total intensity N1 + N2 + N3 is shown in Fig. 2(c) as a function annealing temperature. One representative peak fitting at room temperature is shown in Fig. 2(b).

The relative intensity of the peak N1 increases whereas the intensity of peak N2 decreases significantly with the increase of annealing temperature. The relative peak intensity of peak N3 did not show any well-defined trend. We assigned peak N1 to C—N bonds as mentioned by several authors.\(^{10}\) The peak N3 could be due to substitutional nitrogen in graphite domains. The increase of the relative intensity of peak N3 at higher temperatures indicates the formation of graphitelike structure with the annealing temperature. As the temperature increases, the N is driven out of the films, which causes the more graphitelike structure. The above assignment for N1 (pyridinelike) and N3 (graphitelike) is consistent with measurements based on model systems, which contain both pyridine- and graphitelike structures.\(^{19}\) It was shown that pyridinelike structures have a lower binding energy than graphitelike structures by about 3 eV. This energy difference is very close with the energy difference between N1 and N3 (2.5 eV) confirming our assignment.

It appears that peak N2 corresponds to most unstable bonding configurations. Previously the peak N2 was assigned to intercalated nitrogen.\(^{36}\) We suggest that in our case this peak is related to the NO bonds rather than unbounded nitrogen. This peak clearly related to the C2 + C3 peak at the C K edge. Also the NO absorption on catalyst powder was found in the same energy region by Revel et al.\(^{37}\) After 650 °C the relative intensity of N2 decreases significantly, because of the removal of N-oxidic species.

With annealing at 900 °C the degree of graphitelike
structures increases due to the outdiffusion of nitrogen from the nanotube surface. This is also supported by the narrowing of the $\sigma^*$ states at the $N$ K edge. Therefore we conclude that three $\pi^*$ features in the $N$ K edge spectrum correspond to pyridinelike, NO, and graphitelike structures, respectively.

In Fig. 3(a), the O K edge NEXAFS spectra of the MWNT sample are shown at various annealed temperatures in the energy region from 520 to 560 eV. The room temperature spectra contain two characteristic peaks: (i) one at 534 eV, which is assigned to a $\pi^*$ C=O transition, and (ii) a broader asymmetric peak at 543 eV, associated with $\sigma^*$ C=O resonances. Figure 3(b) demonstrates that the intensity ratio of $\pi^*$ to $\sigma^*$ peak decreases with temperature. At 900 °C the $\pi^*$ (CO) peak disappears, while with the $\sigma^*$ (CO) is still prominent. This suggests that single bonded C–O–C species such as ether-type species are more thermally stable than species containing $\pi^*$ carbonyl orbitals. This observation is in accordance with previous nanotube study, where $\pi^*$ (C=O) features disappeared first upon heating, followed by the disappearance of $\sigma^*$ (CO) spectral features.

IV. CONCLUSIONS

A temperature dependent NEXAFS spectroscopy was employed to study the evolution of the electronic structure of acid treated MWNTs, which were further modified using DBD plasma treatment in ammonia atmosphere. The presence of oxygen and nitrogen containing functional groups was observed in C K edge, N K edge, and O K edge NEXAFS spectra of the MWNTs. The N K edge spectra revealed the presence of three types of local nitrogen $\pi^*$ bonding configurations in the energy region 398–403 eV. Through their temperature dependent evolution they were identified as pyridinelike, (N1), NO(N2), and graphitelike (N3) structures, respectively. The nitrogen substituted graphitelike structure (N3) became dominant by the annealing at 900 °C. The O K edge indicated that both carbonyl (C=O), $\pi^*$ (CO), and other C–O–C, $\sigma^*$ (CO) functionalities are present. Upon heating in a vacuum to 900 °C the $\pi^*$ (CO) resonances disappeared while the $\sigma^*$ (CO) resonances were still present confirming their higher thermal stability. Heating to remove the oxygen and nitrogen functional groups did not produce a significant change in the $\pi^*$ feature of the C K edge spectrum indicating that the tabular structure of the nanotubes is essentially preserved following the thermal decomposition of the functional groups on the nanotube surface.

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