

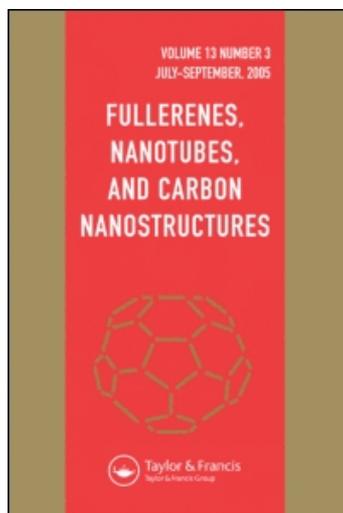
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Surface-to-Depth Analysis of Functionalized Multi-Wall Carbon Nanotubes (FMWCNTS)

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Abstract: Surface-to-depth analysis of functionalized multi-wall carbon nanotubes, FMWCNT was achieved by the use of high resolution x-ray photoelectron spectroscopy (XPS) and secondary ion mass spectrometer (SIMS). The pristine nanotubes were functionalized through various steps. These included i) treatment in nitric acid followed by dispersion in dimethylformamide (DMF) and ii) further modification by the linking molecule, 1-ethyl-3-(3-dimethylaminopropyl carbodiimide), (EDC) through covalent attachment. Pristine nanotubes dispersed in DMF, possessed an atomic percentage of oxygen up to 3%, which more than doubled after treatment in nitric acid. After the second functionalization step, the atomic percent of oxygen was lowered relative to nitrogen as some oxygen was possibly displaced by the anchored molecules of EDC. In addition positive ions of CHNH, N₂, CO, CH₃NH, C₂H₃O, and negative ions of O, OH, and CN were detected by SIMS. On SIMS depth profiling, the intensity levels of both OH⁻ and CN⁻ ions were found to be steady throughout the 180 sec etch duration, indicating good in depth chemical functionalization of the carbon nanotube structure. Preliminary studies on functionalization of carbon nanotubes by atmospheric pressure dielectric barrier discharges (APDBD) are also reported.

Keywords: Functionalized carbon nanotubes, SIMS, XPS, biomedical sensors, dielectric barrier discharge

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INTRODUCTION

Carbon nanotubes (CNT) (1) have been a subject of great interest and research for many applications such as composite materials, battery electrode materials, microfluidics, biosensors, field emission, interconnects, and so on. CNTs are of nano-dimensions and are important for nanofabrication and miniaturization. This material has an unusual ring-type structure and can form self-assembling nano-structures. It also exhibits unusual properties such as high Young's modulus, mechanical hardness, and flexibility; an electronic conductivity that can vary from metallic to insulating with exceptional current-carrying capacity, ballistic transport, extremely high thermal conductivity, and high optical polarizability. Its nano-dimensions with graphitic surface chemistry makes it ideal candidate for biochemical sensor application (2). In developing CNTs for biomolecular detection, they are usually functionalised in stages by various methods such as chemical covalent, noncovalent, defect, endohedral, and exohedral functionalization in order to increase their solubility, processibility, electron transport, and immobilization of biomolecules.

In recent years, nonequilibrium plasmas under atmospheric pressure have been developed as an effective means for surface modification of materials. Atmospheric pressure plasma/discharge (APP/D) processing of solid surfaces offers many advantages compared to vacuum plasma and wet chemical methods, including the absence of solvents, and expensive vacuum components, speed, room temperature treatment, and the capability to coat large size substrate. In spite of the industrial use of APP/D for treating polymers there are no reports on the APP treatment of carbon nanotubes. APP/D is particularly suitable for functionalization of aligned nanotubes, where wet chemical manipulation could damage and even destroy the highly desirable vertical alignment.

A preliminary study on the oxidation of CNTs using atmospheric pressure dielectric barrier discharge (APDBD) will be presented in this paper. A surface-to-depth analysis is performed based on XPS and SIMS techniques to probe various stages in the chemical and APP/D functionalization process of CNTs.

EXPERIMENTAL DETAILS

MWNTs with 10–30 nm diameter were synthesized by CVD process using acetylene as carbon source and Fe-Ni as catalyst. The growth temperature was approximately 750°C. The as grown MWNTs were rinsed with HCl and distilled water. The HCl treated product was composed of ~85%, 10% amorphous carbon, and 5% NiO, FeO, and Al₂O₃. These nanotubes are denoted as pristine nanotubes. MWNTs were further purified by refluxing

the pristine nanotubes at concentrated HNO_3 for 4 hr. The solid product was collected on a PTFE membrane (Millipore porous filter, $0.2 \mu\text{m}$) after diluting with deionized water until the filtrate pH became nearly neutral. These purified nanotubes are deemed as functionalized.

MWNT suspension was prepared by dispersing 10 milligrams in 10 mL of organic solvent *N,N*-dimethylformamide (DMF) with the aid of ultrasonic agitation. Moreover, 23 mg of EDC were added to 50 mg of functionalized multi-walled nanotubes and then dispersed in 10 ml of dimethylformamide (DMF). The solution was sonicated for 1–2 hr. Films were deposited on Si/Au substrate by the drop-dry technique.

The ESCA300 XPS machine equipped with the high resolution Scienta-ESCA300 spectrometer and Kratos XSAM 800 equipped with an energy analyser; Mg Ka x-ray source at 15 KeV and 20 mA was used for this study. The SIMS analysis was done with Mini SIMS, MC300 MkII, Millbrook Instruments having 1 amu resolution. An ISA Labram system was used for con focal micro Raman analysis with a wavelength of 514.53 nm. Double Gaussian product function was used for the curve deconvolution. The Bruker D8 x-ray diffractometer was used for powder XRD analysis.

RESULTS AND DISCUSSION

Chemical Functionalization

Nitric acid is the standard reagent for purification of nanotubes and has traditionally constituted the first step in many different purification schemes. It has been demonstrated that nitric acid removes the transition metal catalyst that is used in the production of carbon nanotubes together with amorphous carbon. However, it produces a significant destruction in the structure of carbon nanotubes and introduces $-\text{COOH}$ and $-\text{OH}$ groups at the defect sites, present at the nanotube ends and sidewalls.

The degree and depth of functionalization of multiwall carbon nanotubes are shown in SIMS spectra (Fig. 1), XPS spectra (Fig. 2), and Table 1. Following the acid purification/functionalization procedure, an EDC bifunctional linking molecule was used to activate certain sites for further biomolecular attachment. SIMS analysis detected the presence of positive ions of CHNH , N_2 , CO , CH_3NH , $\text{C}_2\text{H}_3\text{O}$, and negative ions of O , OH , CN , and N . The SIMS relative intensity ratio of $\text{CN}^-:\text{O}^-(\text{OH}^-) = 1:2$, is comparable with the XPS intensity ratio of $\text{N}1s:\text{O}1s = 3.45\%:6\%$. The O^- , OH^- , CN^- , and N^- ions from the surface to depth analysis were found to be steady through the 180 sec etch time duration. These detection levels of ions over relatively large depths of profiling are indicative of true surface-to-depth functionalization. The O^- and OH^- are most likely to be present due to the acid

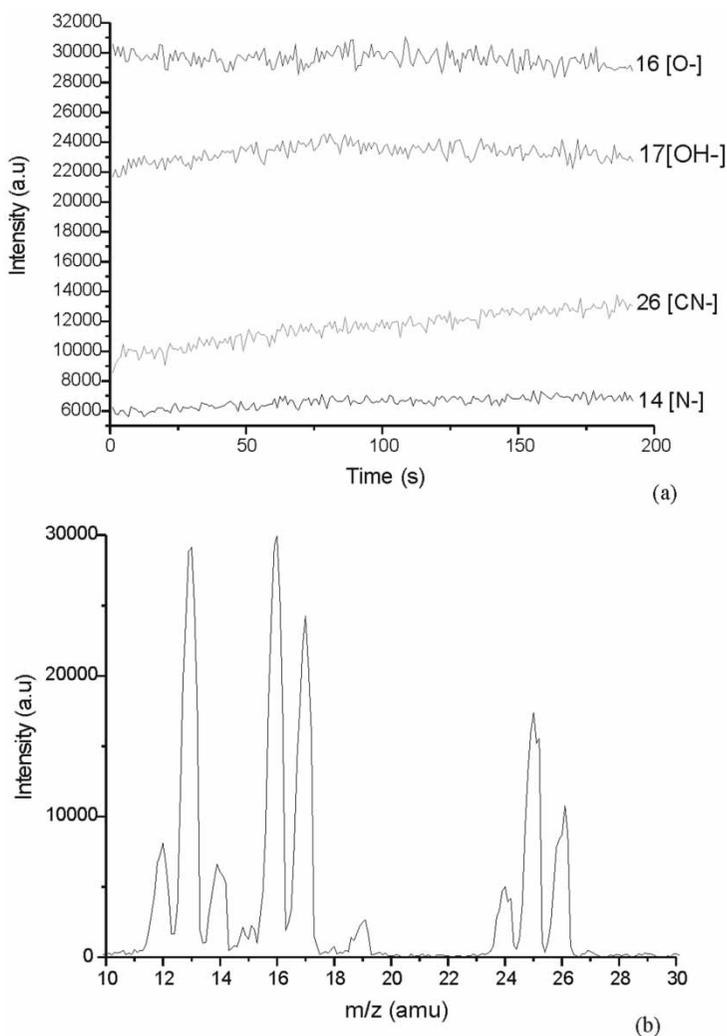


Figure 1. FMWCNT-EDC_DMF: (a) Intensity (a.u) of SIMS depth profile of O^- , OH^- , N^- and CN^- ions over 200 s scan duration, (b) Spectral intensity (a.u) versus mass-to-charge ratio (m/z) of the negative (-ve) ions.

treatment, while the N^- and CN^- are due to the second stage of the functionalization procedure used in the study.

XPS results presented in Table 1 indicate more than 100% increase (3.3–8.16%) in the oxidative group (O atomic % concentration) when pristine CNTs are compared to the acid treated ones. A very small amount of N (0.81%) was traced on the acid-treated CNTs dispersed in DMF solution.

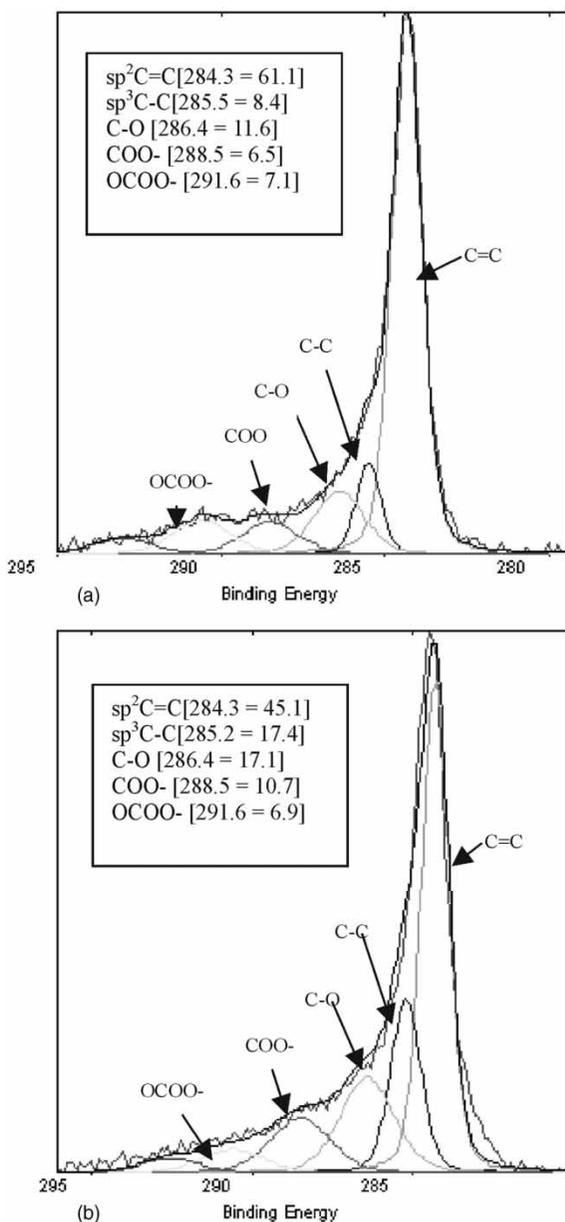


Figure 2. XPS analysis of (a) NFMWCNT in DMF before and (b) after atm. DBD treatment.

Table 1. The XPS atomic % composition of MWCNTs (F = functionalized, NF = nonfunctionalized)

	C1s (at. %)	O1s (at. %)	N1s (at. %)
Sample I-chemical (ESCA300 used)			
NF, MWCNT, DMF	96.7	3.3	—
F, MWCNT, DMF	90.3	8.16	0.81
F, MWCNT, EDC, DMF	90.55	6	3.45
Sample II-DBD (XSAM 800 used)			
NF, MWCNT	91.8	8.2	
DBD-F, MWCNT	71.8	28.2	

However, the N content rose to 3.45% upon subsequent treatment with the EDC bi-functional molecular linkage. These N atoms are likely from the EDC bi functional molecule.

The results from the described SIMS depth profiling suggest that the type of bonding between the N atoms of the EDC bifunctional molecules and the C atoms of CNT is a covalent bond, but the exact configuration/hybridization is not definite. Nitrogen and carbon atoms are both multivalent, each with a possibility of forming sp^1 , sp^2 , and or sp^3 hybridization, making a total of nine different configurations. The N atom of EDC has a probability of π -bonding configuration such as in a pyridine and pyridine-like bonding configuration with the C atoms of the CNT rings. The bonding configurations depend on the site (side-wall, defect sites or end termini) of the linkage bond formation of the N atom of EDC with the CNT atoms. The unterminated atoms of the CNT end termini have a possibility of bonding with N in its fourfold coordinate substitution sites as in $N_4^+-C_3^-$, N_4^+ , and N_3^0 bonding configuration and or its twofold coordinate sites (double bond unit having either two electrons in σ -bond, one π -bond electron and a non bonding pair electron, or a double bond unit with three σ -bond electrons, one π -bond electron and an anti-bonding π^* state). Thus it may be valuable to monitor the specific sites and the binding configurations for specific molecular immobilisation.

Atmospheric Pressure Dielectric Barrier Discharge Processing

One of the alternatives to chemical functionalization is the use of atmospheric pressure dielectric barrier discharges (APDBD). XPS analysis of DBD (setting = 120 cycles, 0.42 W, 20% speed) functionalized CNTs, showed incorporation of oxygen up to 20% atomic concentration (Table 1) compared to the pristine one (Sample II). The XPS deconvoluted peak of pristine MWCNT and DBD functionalized MWCNT are presented in

Fig. 2. In addition to functionalization it could be possible to use APDBD to remove surface impurities. The above XPS peak deconvolution of DBD treated sample suggests that the sp^3 C-C seems to increase, however this requires further investigation. The observed chemical shift following the DBD treatment in air atmosphere is about 1 eV. This could be due to the electronegative oxygen electron pull on the C atom of the CNT. The results from the Raman analysis indicated no significant change in the radial breathing mode peaks following DBD treatment. This suggests that (at the DBD settings used) there was no damage to the nanostructure of the CNT.

A complementary XRD pattern of the pristine MWCNT is shown in Fig 3. This profile is typical of a well-crystallized carbon material with a possible contribution from the catalytic metallic element following CNT synthesis. The detected pattern assigned to the CNT crystal planes of [002], [100], [111], and (101) could also be assigned to graphene crystal (4).

CONCLUSIONS

Surface-to-depth analysis of both chemical functionalized and DBD functionalized multi-wall CNT is shown to be useful for characterization of nanotubes at various stages in the functionalization procedure to ascertain the nature and degree of modification and the exact bonding configuration. The atomic percent of oxygen was lowered relative to nitrogen as some oxygen was possibly displaced by the anchored molecules of EDC. Positive ions of CHNH, N₂, CO, CH₃NH, C₂H₃O, and negative ions of O, OH, CN, and N were detected. On SIMS depth profiling, the OH⁻ as well as CN⁻ were

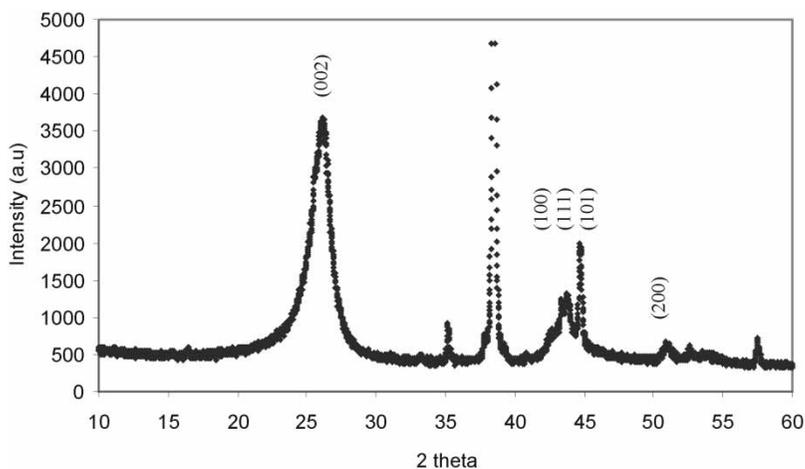


Figure 3. XRD pattern of pristine nonfunctionalized-MWCNT.

found to be steady all through the 180 sec scan time duration. The results from the Raman analysis indicated no significant change in the radial breathing mode peaks following DBD treatment. This suggests that (at the DBD settings used) there was no damage to the nanostructure of the CNT. Finally, the XRD diffraction profile is typical of a well-crystallized carbon material.

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