

Cambridge University Press

978-1-107-40891-3 - Materials Research Society Symposium Proceedings: Volume 887:

Degradation Processes in Nanostructured Materials

Editors: Mircea Chipara, Orazio Puglisi, Ralph Skomski, Frank R. Jones and Benjamin S. Hsiao

Excerpt

[More information](#)

---

## **Degradation Processes in Carbon Nanotubes**

Cambridge University Press

978-1-107-40891-3 - Materials Research Society Symposium Proceedings: Volume 887:

Degradation Processes in Nanostructured Materials

Editors: Mircea Chipara, Orazio Puglisi, Ralph Skomski, Frank R. Jones and Benjamin S. Hsiao

Excerpt

[More information](#)

---

Cambridge University Press

978-1-107-40891-3 - Materials Research Society Symposium Proceedings: Volume 887:  
Degradation Processes in Nanostructured Materials

Editors: Mircea Chipara, Orazio Puglisi, Ralph Skomski, Frank R. Jones and Benjamin S. Hsiao

Excerpt

[More information](#)

Mater. Res. Soc. Symp. Proc. Vol. 887 © 2006 Materials Research Society

0887-Q01-07

**Photo-oxidation of Single-walled Carbon Nanotubes.**B. Parekh, T. Debies<sup>1</sup>, C. M. Evans<sup>2</sup>, B. J. Landi<sup>2</sup>, R. P. Raffaele<sup>2</sup> and G. A. Takacs\*Department of Chemistry, Center for Materials Science and Engineering,  
Rochester Institute of Technology, Rochester, NY, 14623, U.S.A.<sup>1</sup>Xerox Corporation, Webster, NY 14580, U.S.A.<sup>2</sup>NanoPower Research Laboratories, RIT, Rochester, NY, 14623, U.S.A.**ABSTRACT**

UV- and vacuum UV-assisted photo-oxidation of single-walled carbon nanotube (SWNT) paper occurred with: (1) atmospheric oxygen pressure using low-pressure Hg lamps ( $\lambda = 253.7$  and  $184.9$  nm), (2) low oxygen pressure employing emission downstream from an Ar microwave plasma ( $\lambda = 106.7$  and  $104.8$  nm), and (3) high pressures of He in a rotating d.c. arc that was designed to produce a spectral continuum from He excimers ( $\lambda = 58 - 110$  nm). The photo-oxidized materials were characterized by x-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and Raman spectroscopy. UV photo-oxidation was demonstrated to be a controlled dry procedure for introducing oxygenated functional groups (C-O-C, C=O, O-C=O and O=C-O-C=O) on SWNTs.

**INTRODUCTION**

Previously, a number of methods have been used to oxidize carbon nanotubes (CNTs). Gas-phase oxidation in air at around  $750^\circ\text{C}$  leads to over oxidation often removing or severely damaging the CNTs in addition to reacting with amorphous carbon [1]. Liquid-phase oxidation, involving nitric and/or sulfuric acids, is mild and slow and produces high yields of oxidized CNTs [2] having a mixture of -C-O-, -C=O and -COO- functional groups as observed by x-ray photoelectron spectroscopy (XPS) [3]. Ozonolysis, both in the liquid [4] and gas phase [5 - 7], introduces oxygenated functionalities directly onto the sidewalls and not simply at the end caps or isolated defects [8]. Use of UV/O<sub>3</sub> in air with single-walled carbon nanotubes (SWNTs), shows by TGA and Raman analysis that ca. 5% of the carbons were functionalized and rapid initial oxidation occurs within 1 h of treatment which stops after 3 h probably due to exhaustion of active surface sites [9]. The UV/O<sub>3</sub> method is a dry technique that produces ozone *in situ* and, therefore, does not involve transport of reactive ozone to the reaction chamber from an electric ozonizer or liquid waste from solvent or a hydrolysis step. XPS analysis of the top 2 - 5 nm of the surface of multi-walled carbon nanotubes (MWNTs) shows that gas-phase UV and vacuum UV (VUV) photo-oxidation achieves oxygen concentrations up to 7.5 and 9.5 at% after treatment times of 4 and 2 h, respectively [10]. Curve fitting of the XPS C1s spectra reveals mainly the C-O-C functional group with the presence of C=O, O-C=O and O=C-O-C=O moieties [10].

In the present work, purified laser generated SWNT papers are photo-oxidized with UV and VUV radiation and studied with XPS, Raman and SEM microscopy.

Cambridge University Press

978-1-107-40891-3 - Materials Research Society Symposium Proceedings: Volume 887:  
Degradation Processes in Nanostructured MaterialsEditors: Mircea Chipara, Orazio Puglisi, Ralph Skomski, Frank R. Jones and Benjamin S. Hsiao  
Excerpt[More information](#)

## EXPERIMENTAL DETAILS

Synthesis of SWNTs was performed using an Alexandrite laser vaporization process, previously described in detail [11]. In summary, a graphite (1-2  $\mu\text{m}$ ) target was pressed at 20,000 psi and contained 3% w/w Ni (sub-micron) and 3% w/w Co (1-2  $\mu\text{m}$ ). The reaction furnace temperature was maintained at 1150 °C, with a chamber pressure of 700 torr under 100 sccm flowing Ar. The raw SWNT soot was purified by conventional acid reflux. The ratio of materials for refluxing was: 75 mg raw soot added to the acid solution (50 mL H<sub>2</sub>O, 12 mL concentrated HNO<sub>3</sub> (69-70 %), and 5 mL concentrated HCl (36.5-38.0 %)). The solution was brought to reflux at 120 °C for 14 h. The reflux solution was filtered over a 1  $\mu\text{m}$  PTFE membrane filter with copious distilled H<sub>2</sub>O to form the SWNT paper. The acid filtrate was discarded and subsequent washes (3x) with 50 mL acetone and 10 mL distilled H<sub>2</sub>O removed functionalized carbon impurities until the filtrate was clear. To complete the purification, the resulting paper from acid-reflux was thermally oxidized at 550 °C in the muffle furnace under stagnant air for 1 h.

Photo-oxidation of SWNT paper was studied using: (1) atmospheric oxygen pressure with low-pressure Hg lamps ( $\lambda = 253.7$  and 184.9 nm) [12], (2) low oxygen pressure with emission downstream from an Ar microwave (MW) plasma ( $\lambda = 106.7$  and 104.8 nm) [13], and (3) high pressures of He in a rotating d.c. arc that was designed to produce a spectral continuum from He excimers, He<sub>2</sub><sup>\*</sup>, ( $\lambda = 58$ -110 nm) [14 – 16].

A Physical Electronics Model 5800 XPS system provided elemental, chemical state and quantitative analyses of the top 2 – 5 nm of a sample's surface at an angle of 45° between the sample and analyzer.

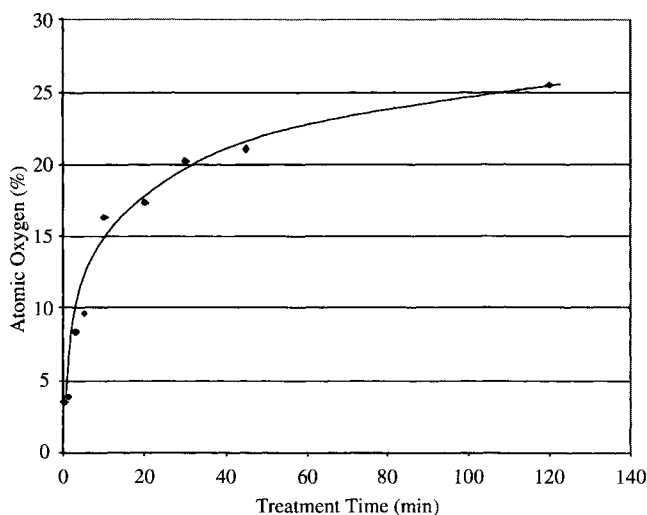
A Hitachi S-900 field emission SEM was used to analyze the surface morphology of the photo-oxidized SWNTs. The samples were applied directly to the brass stub using silver paint. The instrument operated at an accelerating voltage of 2kV and magnifications ranging from 5 – 70 kX.

Raman spectroscopy was performed at room temperature using a JY-Horiba Labram spectrophotometer with excitation energy of 1.96 eV. Sample spectra were obtained from 50 to 2800 cm<sup>-1</sup> using an incident beam attenuation filter to eliminate localized heating and subsequent sample decomposition.

## DISCUSSION

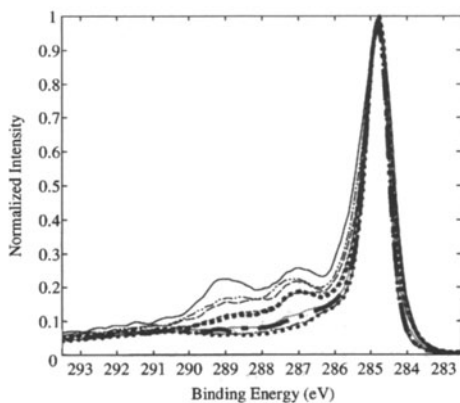
The oxygen concentration of UV photo-oxidized SWNTs increased rapidly initially with exposure time, but after 45 min, it slowed eventually reaching a value of 25.5 at% after 2 h of treatment time (Fig. 1). These nanoscale XPS measurements of the level of oxidation are larger than that reported for the % carbon functionalized as detected by microscale TGA data for UV/O<sub>3</sub> treatment in air of HiPco SWNT bucky paper (ca. 5%) [9] and infrared measurements of gaseous CO and CO<sub>2</sub> released following ozone treatment of closed end SWNTs prepared by laser ablation of graphite targets (5.5  $\pm$  2.5 %) [7]. XPS detection of the oxidation of MWNTs have been reported to have values up to 5 – 7.5 at% for UV photo-oxidation [10], KMnO<sub>4</sub>/H<sub>2</sub>SO<sub>4</sub> oxidation [17] and oxidation with a nitric/sulfuric acid mixture [3].

Cambridge University Press

978-1-107-40891-3 - Materials Research Society Symposium Proceedings: Volume 887:  
Degradation Processes in Nanostructured MaterialsEditors: Mircea Chipara, Orazio Puglisi, Ralph Skomski, Frank R. Jones and Benjamin S. Hsiao  
Excerpt[More information](#)

**Figure 1.** % O as a function of exposure time for UV photo-oxidized SWNTs

Figure 2 illustrates the overlapped C 1s XPS spectra obtained for the SWNTs exposed to different UV photo-oxidation treatment times. The spectra show a significant increase in the intensity of high binding energy peaks (~290-286 eV) associated with carbon-oxygen bonding. The peaks are assigned to species reported in the literature [18] and the areas are tabulated in Table I. Longer exposure time results in higher percentages of oxygen-containing functionalities as well as a reduction in C-C bonding.



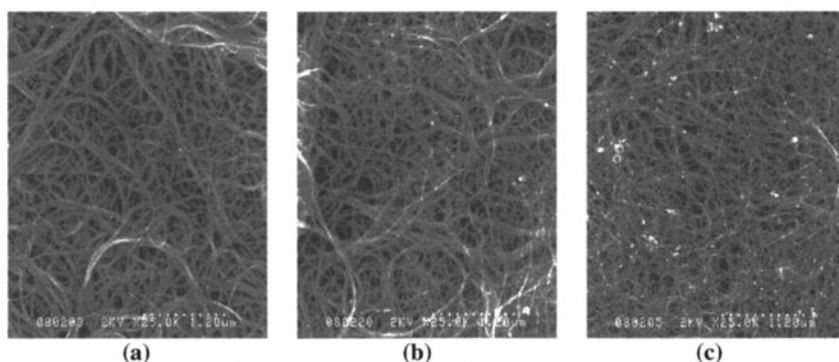
**Figure 2.** C 1s XPS Spectra for UV photo-oxidized SWNTs as a function of treatment time from 0 (....) to 120 min. (\_\_\_).

Cambridge University Press

978-1-107-40891-3 - Materials Research Society Symposium Proceedings: Volume 887:  
Degradation Processes in Nanostructured MaterialsEditors: Mircea Chipara, Orazio Puglisi, Ralph Skomski, Frank R. Jones and Benjamin S. Hsiao  
Excerpt[More information](#)**Table I.** Results of the Curve Fittings for C 1s Peaks of the UV Photo-oxidized SWNTs

B. E (eV)	Peak Area %									Assignment
	0 min	1 min	3 min	5 min	10 min	20 min	30 min	45 min	2 h	
284.8	51	51	45	43	52	51	46	45	39	C-C sp <sup>2</sup>
285.2	28	24	25	28	15	17	14	15	16	C-C sp <sup>3</sup>
286.0	8	11	12	14	9	9	12	11	14	C-O-C
287.3	4	4	6	7	11	10	12	12	11	C=O
288.6	3	3	4	3	7	7	9	10	11	-O-C=O
289.8	3	3	4	2	3	3	4	4	6	O=C-O-C=O
291.0	3	4	4	3	3	3	3	3	3	Energy Loss

Changes in the surface morphology were monitored using SEM and are shown in Fig. 3. For treatment times up to 45 min, there was little variation from the untreated SWNTs. However, beginning at ca. 45 min, changes became apparent in the bundle size of the SWNTs and the concentration of amorphous carbon. Additionally, changes in the Raman radial breathing mode (RBM) after 45 min suggest that the diameter distribution was altered, which is consistent with the presence of amorphous carbon shown in the SEM images. These results suggest that at longer exposure times the SWNTs may actually be consumed while at shorter times (< 45 min) there is controlled functionalization.

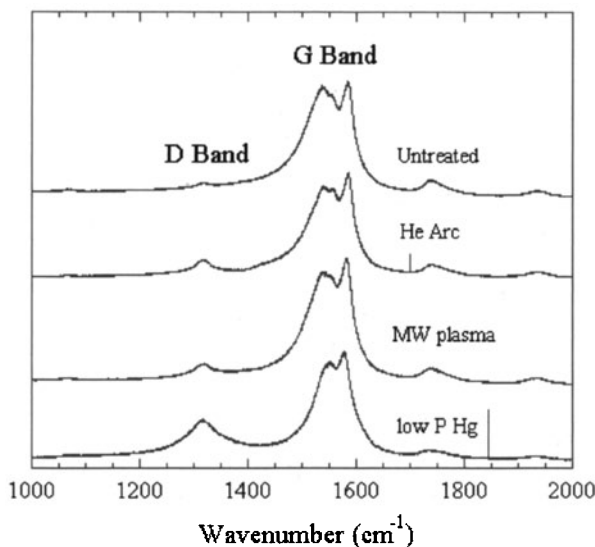


**Figure 3.** SEMs for SWNTs: treated for (a) 20 min, (b) 45 min and (c) 120 min of UV photo-oxidation. All SEMs are for a magnification =25 kX, sizing =1.20 μm.

Cambridge University Press

978-1-107-40891-3 - Materials Research Society Symposium Proceedings: Volume 887:  
Degradation Processes in Nanostructured MaterialsEditors: Mircea Chipara, Orazio Puglisi, Ralph Skomski, Frank R. Jones and Benjamin S. Hsiao  
Excerpt[More information](#)

Other photo-oxidation techniques, having different photon energies, also are being explored. Figure 4 shows the Raman spectra for a control sample and samples treated for 3 h with UV photo-oxidation (4.9 and 6.7 eV), 2.5 h of VUV photo-oxidation downstream from the MW Ar plasma (11.6 and 11.8 eV) and 5 min with the rotating He arc (11.3 – 21.4 eV) which resulted in O at% values of 4.7, 29.2, 15.8 and 14.0, respectively. The Raman spectra consist of a distinctive pair of broadband peaks at  $\sim 1580$  (G-band) and  $\sim 1340$   $\text{cm}^{-1}$  (D-band) corresponding to  $\text{sp}^2$  and defect-induced carbon stretching modes, respectively [19]. The D-band is caused by symmetry-breaking defects such as  $\text{sp}^3$ -hybridized carbon atoms, as well as, hetero-atoms, vacancies, heptagon-pentagon pairs, kinks or the presence of impurities [19]. The data shows that all three techniques of photo-oxidation increased the ratios of the intensities of the D:G bands as compared to the untreated sample with the largest increase for the sample treated using the UV low pressure Hg lamps.



**Figure 4.** Raman spectra taken at 1.96 eV for untreated SWNTs and SWNTs treated with He arc discharge, microwave Ar plasma and UV low pressure Hg lamps.

## CONCLUSIONS

Dry techniques, involving UV- and VUV- assisted photo-oxidation, successfully introduced oxygenated functional groups (C-O-C, C=O, O-C=O and O=C-O-C=O) on SWNT papers as observed by XPS spectroscopy of the top 2 -5 nm of the sample's surface. SEM and Raman spectroscopy provided complementary results which helped show that controlled functionalization occurred at short treatment times with UV photo-oxidation, while at longer treatment times, the bundles were eroded and the diameter

Cambridge University Press

978-1-107-40891-3 - Materials Research Society Symposium Proceedings: Volume 887:  
Degradation Processes in Nanostructured Materials

Editors: Mircea Chipara, Orazio Puglisi, Ralph Skomski, Frank R. Jones and Benjamin S. Hsiao

Excerpt

[More information](#)

distribution was altered. Higher levels of oxidation were achieved with SWNTs than MWNTs [10].

\*To whom correspondence should be addressed. Phone 585-475-2047.

Fax: 585-475-7800. E-mail address: gatsch@rit.edu.

## REFERENCES

1. T. Ebbesen, H. Hiura, H. Fujita and K. Tanigaki, *Nature* **367**, 519 (1994).
2. H. Hiura, T. W. Ebbesen and K. Tanigaki, *Adv. Mater.* **7**, 275 (1995).
3. Y. Xing, L. Liang, C. C. Chusuei and R. V. Hull, *Langmuir* **21**, 4185 (2005).
4. S. Banerjee and S. S. Wong, *J. Phys. Chem. B* **106**, 12144 (2002).
5. X. Lu, L. Zhang, X. Xu, N. Wang and Q. Zhang, *J. Phys. Chem. B* **106**, 2136 (2002).
6. O. Byl, J. Liu and J. T. Yates, Jr., *Langmuir* **21**, 4200 (2005).
7. D. B. Mawhinney, V. Naumenko, A. Kuznetsova, J. T. Yates, Jr., J. Liu and R. E. Smalley, *Chem. Phys. Lett.* **324**, 213 (2000).
8. D. B. Mawhinney, V. Naumenko, A. Kuznetsova, J. T. Yates, Jr., J. Liu and R. E. Smalley, *J. Am. Chem. Soc.* **122**, 2383 (2000).
9. L. Cai, J. L. Bahr, Y. Yao and J. M. Tour, *Chem. Mater.* **14**, 4235 (2002).
10. B. Parekh, T. Debies, P. Knight, K. S. V. Santhanam and G. A. Takacs, *Mat. Res. Soc. Symp. Proc.* (Degradation Processes in Nanostructured Materials) 2005 MRS Fall Meeting, this issue (2006).
11. B. J. Landi, R. R. Raffaele, S. L. Castro and S. G. Bailey, *Prog. Photovolt: Res. Appl.* **13**, 165 (2005).
12. U. Sener, A. Entenberg, B. Kahn, F. D. Egitto, L. J. Matienzo, T. Debies and G. A. Takacs, in: *Polyimides and Other High Temperature Polymers: Synthesis, Characterization and Applications*, K. L. Mittal (Ed.), Vol. **3**, 535 – 552, VSP, Utrecht (2005).
13. W. Dasilva, A. Entenberg, B. Kahn, T. Debies and G. A. Takacs, *Mater. Res. Soc. Symp. Proc.* **851** (Materials for Space Applications), 407 – 412 (2005); *J. Adhesion Sci. Technol.* **18**, 1465 – 1481 (2004).
14. G. A. Takacs, V. Vukanovic, F. Egitto, L. J. Matienzo, F. Emmi, D. Tracy and J. X. Chen, *10th IUPAC International Symp. on Plasma Chemistry (ISPC-10)*, Bochum, Germany, **1,4-29**, p. 1-6 (1991); G. A. Takacs, V. Vukanovic, D. Tracy, J. X. Chen, F. D. Egitto, L. J. Matienzo and F. Emmi, *Poly. Degrad. Stabil.* **40**, 73 (1993).
15. J. X. Chen, D. Tracy, S. Zheng, L. Xiaolu, S. Brown, W. VanDerveer, A. Entenberg, V. Vukanovic, G. A. Takacs, F. D. Egitto, L. J. Matienzo and F. Emmi, *Poly. Degrad. Stabil.* **79**, 399 (2003).
16. S. Zheng, A. Entenberg, G. A. Takacs, F. D. Egitto and L. J. Matienzo, *J. Adhesion Sci. Technol.* **17**, 1741 (2003).
17. S. Banerjee and S. S. Wong, *J. Am. Chem. Soc.*, **125**, 10342 (2003).
18. G. Beamson and D. Briggs, *High Resolution XPS of Organic Polymers*, John Wiley & Sons Ltd., Chichester, West Sussex, England, p.158 (1992).
19. A. Jorio, M. A. Pimenta, A. G. Souza Filho, R. Saito, G. Dresselhaus and M. S. Dresselhaus, *New Journal of Physics* **5**, 139.1 (2003).



Cambridge University Press

978-1-107-40891-3 - Materials Research Society Symposium Proceedings: Volume 887:  
Degradation Processes in Nanostructured MaterialsEditors: Mircea Chipara, Orazio Puglisi, Ralph Skomski, Frank R. Jones and Benjamin S. Hsiao  
Excerpt[More information](#)

Mater. Res. Soc. Symp. Proc. Vol. 887 © 2006 Materials Research Society

0887-Q06-01

### Photo-oxidation of Multiwalled Carbon Nanotubes

B. Parekh, T. Debies<sup>1</sup>, P. Knight, K. S. V. Santhanam and G. A. Takacs  
Department of Chemistry, Center for Materials Science and Engineering,  
Rochester Institute of Technology, Rochester, NY 14623, U.S.A.  
<sup>1</sup>Xerox Corporation, Webster, NY 14580, U.S.A.

#### ABSTRACT

MWNTs were photo-oxidized in quartz boats using low-pressure Hg lamps and emission downstream from Ar microwave plasmas which are primarily atomic line sources of 253.7 and 184.9 nm UV, and 106.7 and 104.8 nm vacuum UV (VUV) radiation, respectively. X-ray photoelectron spectroscopy (XPS) showed rapid oxidation during the first hour of UV treatment and then an increase that was directly proportional to the time of treatment up to 4 h where the oxygen concentration was 7.5 at%. VUV photo-oxidation resulted in an oxygen concentration up to 9.5 at% with exposure time for the initial 2 h of treatment. Beyond 2 h, the oxygen concentration decreased with VUV exposure due to a larger rate of de-oxidation than oxidation at the surface. Curve fitting of the XPS C1s spectra revealed mainly the C-O-C functional group with the presence of C=O, O-C=O and O=C-O-C=O moieties. SEM micrographs showed no apparent effect on the structure or appearance of the MWNTs as expected for surface modification. Gas phase photo-oxidation effectively functionalizes MWNTs without resulting in liquid waste from the traditional method of acidic oxidation.

#### INTRODUCTION

Gas-phase photo-oxidation of MWNTs were studied at 298 K with wavelengths from low pressure Hg lamps ( $\lambda = 184.9$  nm) and excited Ar atoms ( $\lambda = 106.7$  and 104.8 nm) downstream from a MW plasma which have sufficient energy to photo-dissociate gaseous oxygen and result in chemical modification of the surface. Earlier work reported in the literature focused on UV wavelengths (240 and 253.7 nm) photo-absorbed by the carbon nanotubes (CNTs) that did not change the surface composition but caused photo-desorption of O<sub>2</sub> [1] and changed the thermoelectric power [2, 3] while a UV/O<sub>3</sub> generator in air formed oxygenated functional groups on single-walled carbon nanotubes (SWNTs) [4].

#### EXPERIMENTAL DETAILS

The MWNTs, which were obtained in a powder form from Helix Material Solution, were produced by an electric arc method and characterized as > 95% pure and having a range of diameters and lengths from 60 - 100 nm and 0.5 - 40  $\mu$ m, respectively. The MWNTs were studied by placing the powder in a well of a quartz block. The UV and VUV experimental conditions and equipment are as reported in refs. [5] and [6].

The samples were analyzed with a Physical Electronics Model 5800 XPS that analyses the top 2 - 5 nanometers of a sample's surface with a take-off angle of 45° between the sample and analyzer. The quartz boat was positioned in a stainless steel sample holder so that the nanotubes were flush with the surface of the sample holder.

Cambridge University Press

978-1-107-40891-3 - Materials Research Society Symposium Proceedings: Volume 887: Degradation Processes in Nanostructured Materials

Editors: Mircea Chipara, Orazio Puglisi, Ralph Skomski, Frank R. Jones and Benjamin S. Hsiao

Excerpt

[More information](#)

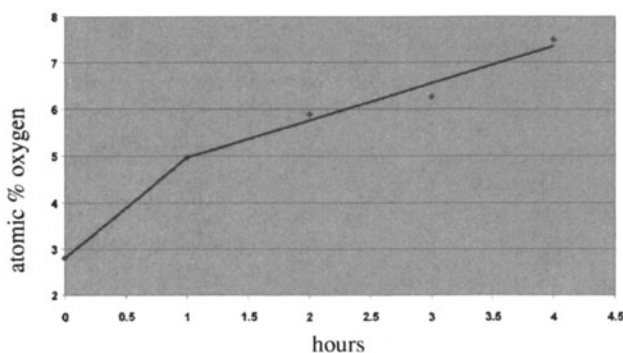
The quantitative analyses are precise to within 5% relative for major constituents and 10% relative for minor constituents. The samples were irradiated with monochromatic Al K $\alpha$  radiation (1486 eV) and charge neutralized with a flood of low energy electrons from a BaO field emission charge neutralizer which minimized radiation damage.

An Amray 3300 field emission SEM was used to analyze the surface morphology of the photo-oxidized MWNT powder in the quartz boats that were placed onto carbon adhesive tabs on Al stubs and coated with a thin conductive Au film of ca. 20 nm.

## DISCUSSION

The MWNTs contained only carbon and a trace amount of oxygen (ca. 2 at%). Photo-oxidation of MWNTs for 3.5 h with 253.7 nm radiation resulted in little effect on the chemical bonding as observed by the XPS C 1s and O 1s spectra consistent with the earlier work using the UV wavelengths of 240 and 253.7 nm [1-3].

When 253.7 and 184.9 nm radiation lamps were used, increasing oxidation of the MWNTs occurred as a function of exposure time up to 4 h where the O concentration was 7.5 at%. The data, which is plotted in Fig. 1, shows a linear relationship from 1 to 4 h of treatment with a correlation coefficient of r-squared = 0.96.



**Figure 1.** % O for MWNT samples as a function of exposure time to UV photo-oxidation.

The nanotubes exposed to VUV photo-oxidation contained an oxygen concentration up to 9.5 at% at 2 h of exposure time. As with the UV photo-oxidation results, most of the VUV photo-oxidation occurred within 1 h of treatment time. Beyond 2 h, the concentration of oxygen on the VUV photo-oxidized surface decreased and was equal to 4.2 at % at 4 h. SEM micrographs revealed no apparent effect on the structure or appearance of the UV (25kX, 1 $\mu$ m sizing bar) and VUV photo-oxidized MWNTs (100 kX, 300 nm sizing bar).

The C 1s spectra obtained from untreated samples were in good agreement with results reported in the literature [7, 8] and differed only slightly from the spectra obtained for the UV and VUV photo-oxidized nanotubes due to the low concentration of oxygen introduced by exposure. Figure 2 shows the C 1s spectrum for MWNTs treated for 3 h of