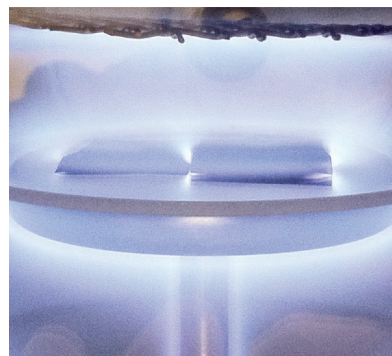


Thermal Stability of Plasma Generated Oxygenated Functionalities on Carbon Nanotubes

Nathan Hordy,* Jean-Luc Meunier, Sylvain Coulombe

Colloidal suspensions of functionalized carbon nanotubes (CNT nanofluids) have the potential to be used in a variety of applications, many of which require operation at elevated temperatures. In this study, we examine what effect exposure to an argon/oxygen/ethane RF glow discharge plasma has on the surface chemistry and structure of CNTs and what happens to the plasma-generated functionalities at high temperatures. An analysis performed using X-ray photoelectron spectroscopy and Raman spectroscopy indicates that longer and higher power plasma treatments decrease the sp² graphitic nature of the CNTs without increasing the degree of oxygen functional groups. Heating of the functionalized-CNTs up to 350 °C in air and 600 °C in argon, both lead to a substantial decrease in the surface oxygen concentration, which can be attributed to the decomposition of carboxylic functionalities at low temperatures (< 350 °C).



1. Introduction

Carbon nanotubes (CNTs) have become a material commonly produced and used in research laboratories around the world. Commercial applications have been contemplated from the beginning due to their extraordinary mechanical and electrical properties, although a number of challenges have hindered their transfer from the laboratory to large scale use.^[1] Amongst other challenges is the control of purity, chirality, and defect level, in addition to bundling and agglomeration. An increasing number of researchers have recently been focusing their attention on applications where some of these constraints are not as limiting and in some cases, actually seen as beneficial; the presence of

defects for functionalization is one example.^[2] CNTs are high surface-to-volume ratio nanostructures that can easily be used as scaffolding materials to construct compact and extremely high specific surface area micro/macro-structures for applications as wide-ranging as implants and heterogeneous catalysts.^[3,4] These CNTs can also be further functionalized through the grafting of surface moieties and/or the deposition of thin films or nanoparticles (NPs), creating opportunities for additional applications, such as hydrogen production,^[5] supercapacitors,^[6] and water purification.^[7] When CNTs are suspended within a base fluid, the resulting “nanofluid” is a broadband absorber of energy, with wide absorption capabilities covering technologically appealing ranges such as the visible, near IR, and medical ultrasounds (low MHz).^[8,9]

Recent development activities for these CNT suspensions focus on solar energy harvesting,^[10] biomedical imaging,^[11] NP-mediated heating,^[12] and cancer therapeutics.^[13] In these applications, the CNTs must be surface-treated to render them compatible with the surrounding

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environment, thus enabling efficient mechanical, electrical, thermal, and even solutal transfers. In addition, the surface functions must remain stable (or minimally altered) upon localized, as well as bulk heating.^[2] In previous works, we have shown that CNT-based nanofluids produced with plasma functionalized (F)-CNTs suspended in a variety of base fluids demonstrate unmatched stability over long periods of time (>10 months, our data), at temperatures far exceeding the typical $\sim 60^\circ\text{C}$ limit of surfactants (170°C in glycols, our data), and under repeated evaporation/condensation cycles.^[8,14,15] We postulated that this unmatched stability is the result of the high-temperature endurance of the plasma-generated oxygen moieties grafted onto the CNT surface. In this work, we present a systematic study of the effect of high-temperature exposure (100 to 600°C) to the stability of plasma-generated functionalities on CNTs.

2. Experimental Section

2.1. Carbon Nanotube Growth

The CNTs used in this study were grown directly from stainless steel 316 400 series mesh, using a thermal chemical vapour deposition (t-CVD) process developed in-house. In this growth process, the

stainless steel mesh are pre-cleaned in acetone and heated in argon (Ar) to 700°C within the t-CVD reactor. Acetylene (C_2H_2) is then injected for 2 min, following which the reactor is cooled to room temperature. Gas flowrates of 592 sccm and 68 sccm were used for Ar and C_2H_2 , respectively. Further details on the synthesis technique and growth mechanism of the CNTs can be found in Hordy et al.^[16] In this approach, the stainless steel mesh acts as both catalyst and substrate, meaning the CNTs that are produced are covalently bonded to the substrate and protrude radially from the grid bars of the mesh to create a semi-porous CNT forest with an average height of approximately $4\ \mu\text{m}$ (Figure 1A–B). All of the CNTs produced in this work are multi-walled (MW), and have on average a diameter of approximately 35 nm.

2.2. Plasma Functionalization

Following the synthesis, the CNTs are surface-functionalized using a low-pressure capacitively-coupled radio-frequency glow discharge sustained in an argon/oxygen/ethane gas mixture. The plasma reactor consists of a four-way stainless steel cross using NW-160 (14.9 cm ID) flanges (Figure 2). The top port is used to feed in the plasma gas mixture and ground electrode (coarse stainless steel wire mesh), the bottom port holds the live electrode, the rear port connects to the vacuum exhaust, and the front port provides optical access through a Pyrex window. The live electrode is powered by a

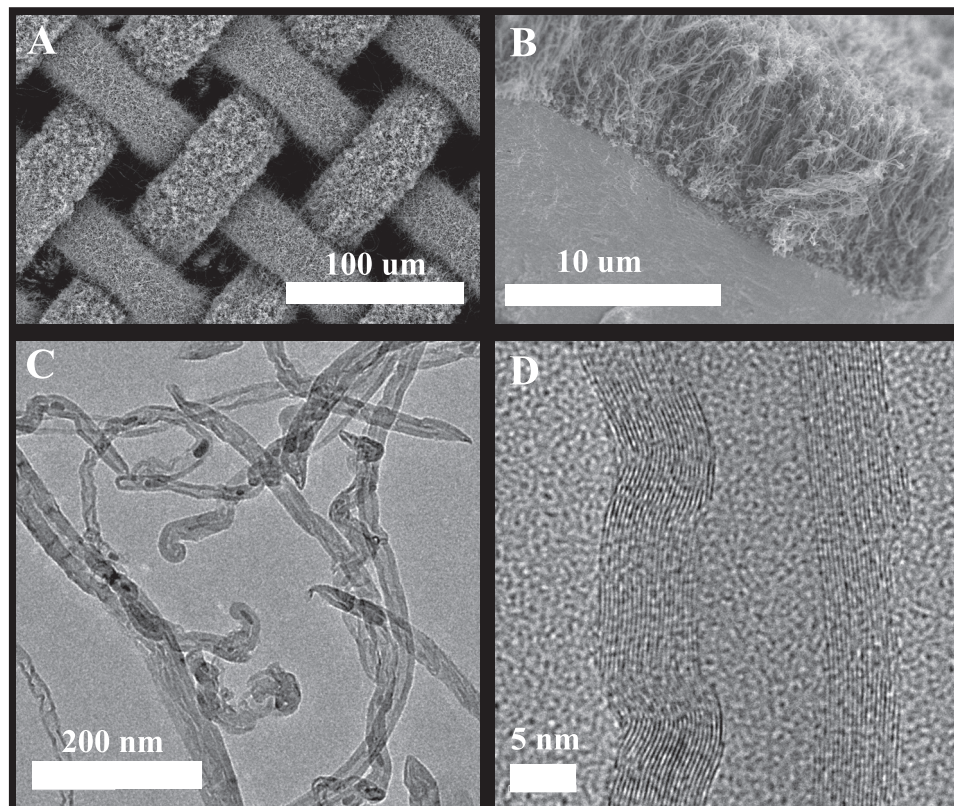


Figure 1. (A–B) SEM micrographs of a CNTs forest protruding directly from stainless steel substrate. (C–D) TEM micrographs of individual CNTs removed from the substrate.

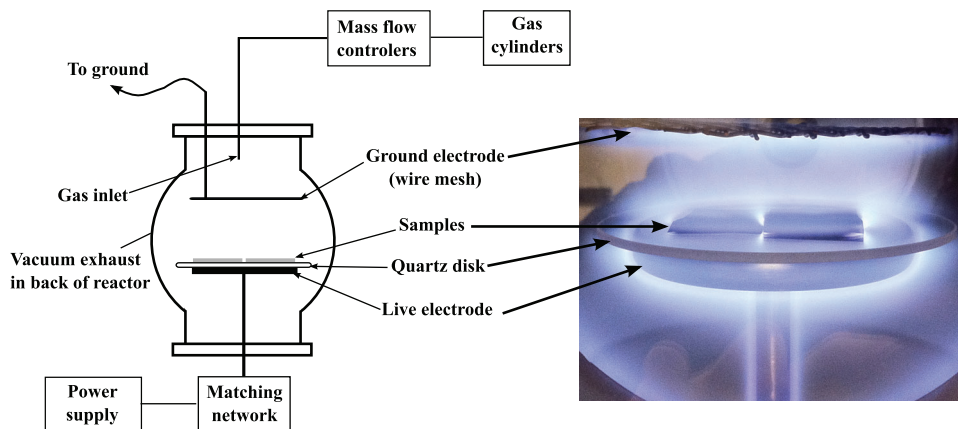


Figure 2. Schematic (left) and image (right) of the plasma functionalization setup.

variable duty cycle 13.56 MHz RF generator (Advanced Energy RF600A, VM-1000 matching network).

The CNT samples are placed on a quartz disk and loaded directly onto the live electrode (bottom, 10 cm diameter), after which the reactor is evacuated to the base pressure (approx. 10 mTorr) using a two-stage rotary vane pump (Alcatel, PASCAL Series 2005 SD). Once the base pressure is reached the reactor is then backfilled with an Ar/O₂/C₂H₆ gas mixture at flow rates of 250/5/1 sccm. The reactor pressure during plasma treatment is maintained at 2 Torr using an Intellisys throttling butterfly valve and an Adaptive Pressure Controller (NorCal Products). The inlet gas flow rates were controlled by Brooks 5850 E mass flow controllers and a Brooks 01545 Readout and Control Electronics indicator module. Unless otherwise stated, a treatment time of 2 min and a continuous RF power of 20 W were used.

2.3. Heat Treatment of CNTs

To study the thermal stability of the functionalities, both functionalized (F) and non-functionalized (NF)-CNT samples were heated to various temperatures in both an inert (Ar) and an oxygen-containing (air) atmosphere while still attached to the stainless steel substrate. This heating was done using the same t-CVD reactor that was used to grow the CNTs. For samples treated in air, the ends of the furnace were left open so that the samples could be exposed to the uncontrolled atmosphere of the laboratory. This was done instead of injecting purified air into the reactor as to simulate a real-world situation in which the CNTs would be exposed to an uncontrolled humid atmosphere at high temperatures. A slightly negative gauge pressure at the exit of the furnace tube, as a result of a vacuum trunk, ensured a flow of air in the reactor throughout the experiment. A heat treatment time of approximately 18 h was used for all experiments in air. The samples treated in Ar were heated in a custom designed t-CVD reactor equipped with vacuum components to ensure no oxygen was present during treatment.^[15] Complete oxygen removal was accomplished by purging the reactor at atmospheric pressure with Ar at a flow rate of 7 L min⁻¹ for 3 min, followed by pumping the chamber down to 20 mTorr. The chamber was then backfilled with Ar to atmospheric pressure at which time the reactor was heated to the desired temperature and held isothermally for 30 min. A flow rate of 250 sccm of Ar was used

throughout the heat treatment. After heating the furnace was cooled to room temperature before the samples were removed. A detailed description of how aqueous suspensions of CNTs were produced and how their stability was characterized is provided elsewhere.^[8]

2.4. Characterization Techniques

Visual characterization of the CNTs was conducted using a field emission scanning electron microscope (FE-SEM, Hitachi S-4700) and through transmission electron microscopy (TEM, Philips CM200). The graphitic structure of the CNTs was studied using a confocal Raman microscope (Bruker Senterra RamanScope), using a 633 nm HeNe laser (20 mW power), and a 50× objective mounted on an Olympus BX series optical microscope (9–18 cm⁻¹ resolution, 2 coadditions, 60 s integration time). Analysis of the surface composition before and after heat treatment was accomplished using an X-ray photoelectron spectrometer (Thermo Scientific K-alpha; calibrated to the Au 4f_{7/2} peak at 84.0 eV) with a monochromatized Al Kα photon source (hν 1486.6 eV). A perpendicular takeoff angle was used for both the survey (200 eV pass energy, 1 eV step size) and the high resolution (50 eV pass energy, 0.1 eV step size) scans, with a spot size of 400 μm. Data were collected and analyzed using the Thermo Scientific Avantage XPS software package. The Shirley/Smart method was used for background removal and any charging was corrected by calibrating the main C1s peak for graphitic carbon to 284.5 eV. The stability of the CNT nanofluids was quantified using an Evolution™ 300 UV-Vis spectrophotometer. All measurements were taken over the 400–700 nm range, at room temperature with the samples enclosed in Suprasil® quartz cuvettes with a pathlength of 1 cm.

3. Results

3.1. Identification of Surface Functional Groups by XPS

The surface chemistry of the F- and NF-CNTs was studied using XPS. As Figure 3A shows, before functionalization the

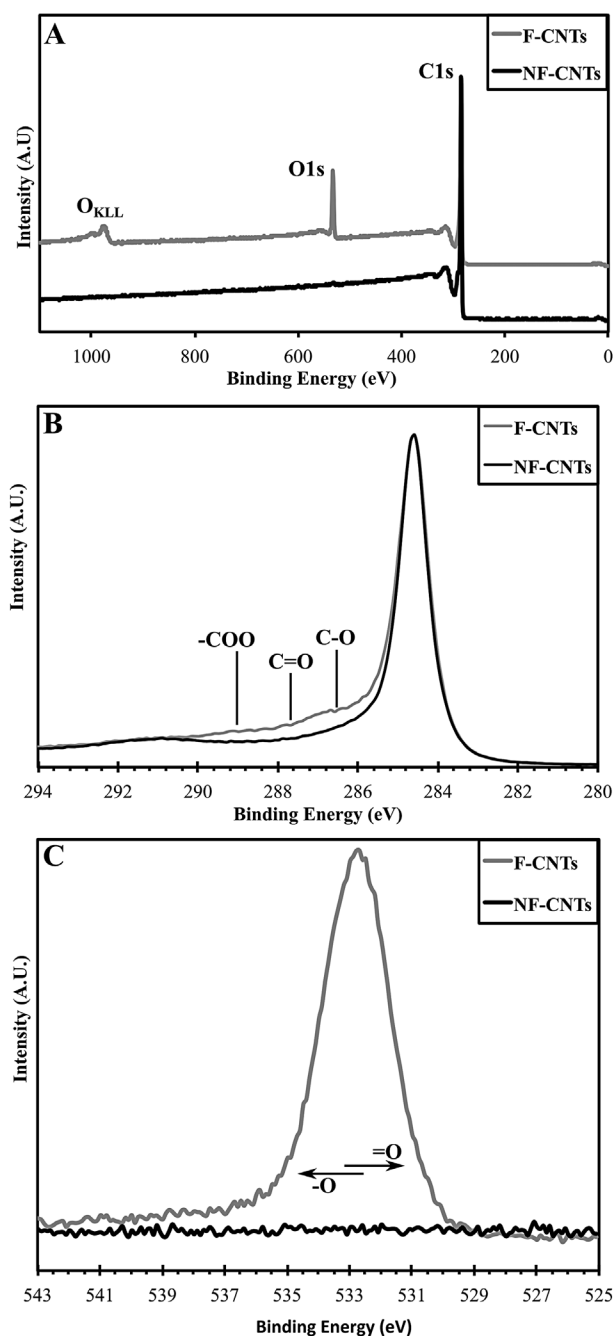


Figure 3. XPS survey (A), C1s (B), and O1s (C) spectra comparing F-CNTs and NF-CNTs. Approximate locations of various oxygen functional groups are also indicated.

CNTs were free of impurities (Fe, Cr, N, etc.) with only trace amounts of oxygen (<0.5 at.%) on the surface. After plasma treatment, a large peak at 532 eV appears, corresponding to approximately 10 at.% oxygen concentration. It should be noted that this 10 at.% does not correlate to a particular fraction of surface coverage nor can it be directly compared to other quantitative results found in literature, as factors such as penetration depth, take-off angle, and x-ray energy

all affect the measured result.^[17] Therefore, in this work quantification of atomic species and normalized measures of intensity will only be used to discuss trends between comparable samples.

High-resolution XPS spectra of the C1s and O1s peaks were acquired to provide a more detailed understanding of the types of functional groups present on the CNT surface (Figure 3B–C). Unfortunately, due to the highly asymmetric nature of C1s peak for CNTs, it is difficult to quantify specific types of carbon bonds related to the functionalization process.^[18] This asymmetry, which is a result of interaction with conduction band electrons,^[19] is clearly evident in Figure 3B, and is most likely enhanced by the defective sites within the graphitic carbon lattice.^[20–22] In addition, given the high energy environment of the plasma treatment, many different types of functional groups are present, making deconvolution of the C1s peak quite impractical.^[18] Therefore, instead of quantification through a peak fitting process, the regions in which functional groups are normally found in literature were identified and changes in the relative intensity of these areas were examined. For simplicity, the different possible carbon-oxygen functionalities for which binding energies occur in the same vicinity were grouped together. For the C1s peak this consisted of carbon singly bonded to an oxygen at approximately 286.0 to 286.3 eV (C*–O, phenols and ethers); carbon doubly bonded to an oxygen at approximately 286.8 to 287.6 eV (C=O, ketones and aldehydes); and carbon bonded to two oxygen atoms at approximately 288.1 to 289.1 eV (–C*OO, carboxylic, anhydride, and ester groups).^[23–27] A π - π^* shake-up characteristic of the aromatic carbons is also present at approximately 290.5 eV for all samples. Although the exact binding energy of these functional groups can vary, the order in which the type of functional groups appear is well established. Therefore the binding energies provided above and indicated with the various figures should be taken as approximate locations for the purpose of evaluating trends, rather than exact position of peaks.

With quantification of the functionalities not possible using the C1s peak, the other option is deconvolution of the O1s peak (Figure 3C). This has been attempted numerous times throughout the literature for various carbon-oxygen functionalities,^[18,22–31] unfortunately the results tend to differ quite significantly. As Brender et al.^[31] indicate, the number of components used to deconvolute the O1s peak vary study-to-study and can range from 2^[30] to 8.^[26] Given this, combined with the high amount of uncertainty always associated with peak fitting (Gaussian/Lorentzian ratios, asymmetry, FWHM, etc.), deconvolution of the O1s peak was not attempted. Instead, as with the C1s peak, well-established positions of functional group were used to evaluate trends. These moieties consist of oxygen doubly bonded to carbon with peak locations in the 531.0 to 532.8 eV range (O*=C, ketones, aldehydes, and carbonyls in

esters and anhydrides), where ketone linkages tend to be found at slightly lower binding energies than the other carbonyl functions; and the peak locations for oxygen singly bonded to carbon in the range of 532.2 to 533.9 eV ($-\text{O}-\text{C}$, phenols, ethers and single oxygen-carbon bonds in anhydrides and esters).^[18,26,30–32] The slight asymmetry observed at higher binding energies (>535 eV) may be a result of oxygen satellite peaks,^[31] or adsorbed water.^[23,25,26,33] Unfortunately the literature is not clear on the contributions from the oxygen atoms in the carboxylic functions. Some studies group both oxygen atoms in a combined peak at approximately 534.2 eV,^[23,25,27,29,33] while other separate them into their carbonyl (531.1–533.2 eV) and hydroxyl (533.2–534.5 eV) components.^[26,30–32] Zielke et al.^[23] suggest that due to the fact that the intramolecular proton exchange time is shorter than the relaxation time of excited species for carboxylic groups at room temperature, both components should be treated as one peak; however a detailed study on polymers containing only carboxylic groups suggests they should be separated into two peaks.^[32] Due to this uncertainty we will not interpret the location of the carboxylic peak(s) other than to suggest that if dehydration of two adjacent carboxylic groups were to form an anhydride, one would expect to see a shift to a lower binding energy (due to the conversion of the two hydroxyl groups into a single ether bond).^[30]

3.2. Structural Characterization by Raman Spectroscopy

The Raman spectra produced in this work for the NF-CNTs, F-CNTs, and heat-treated CNTs, all exhibit roughly the same features, which are typical for MWCNTs.^[34–36] When examining Figure 4 the features are clearly present over the ranges of 1 000 to 1 700 cm^{-1} and 2 300 to 3 300 cm^{-1} , while no peaks were observed below 1 000 cm^{-1} . Unfortunately, due to the large diameters (>2 nm) of the MWCNTs, the A_1 symmetrical radial breathing modes, which can normally be used to characterize the diameter and chirality of single walled- and double walled-CNTs,^[37] are not present here (would occur between 100 and 400 cm^{-1}). Deconvolution of the Raman spectra into the various components was achieved using the curve-fitting program of the OPUS 7.2 software (Levenberg–Marquardt minimization algorithm). Lorentzian line shapes were used for all the peaks except for the D' band, for which case a Gaussian line shape was employed. Lorentzian line shapes have been shown to provide good fits for the various Raman bands, particularly for disordered graphitic materials.^[38] In total, nine peaks were used to fit the first order and second order features. This particular combination of number of peaks and line shapes was chosen as it provided the best match for

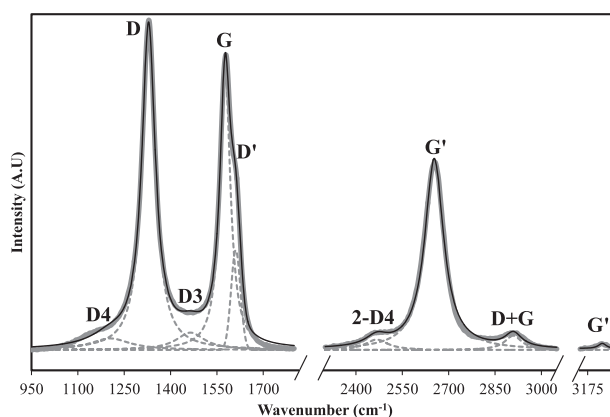


Figure 4. Raman spectrum of the CNTs with peak deconvolution measured using 1.96 eV excitation source.

the spectra and has provided a good fit for other MWCNT samples.^[34,39] The Raman shift, shape, and full-width half max (FWHM) of these bands are provided in Table 1.

It is important to note that as many of the bands are activated through a double resonance process, they exhibit dispersive behavior, meaning their position is dependent on the excitation frequency.^[40,41] All spectra reported in this work were activated using a 1.96 eV (633 nm) excitation source, as this energy has been shown to provides clear peaks for all the bands present for MWCNTs.^[35,41,42]

The peaks present between 1 000 and 1 700 cm^{-1} correspond to first order, single phonon, Raman features.^[34,43] The large peak present at approximately 1 578 cm^{-1} is present in Raman spectra of all graphitic (sp^2) carbons, and thus is labeled as the G band. This particular band originates from the in-plane bond stretching of sp^2 hexagonal carbon bonds (E_{2g} phonon at the Brillouin zone center).^[43,44] The second major peak seen at approximately 1 330 cm^{-1} has been well documented after the inducement of defects in sp^2 graphitic lattice, and thus is referred to as the D band (for defects or disorder).^[37] The presence of this D band is a result of the in-plane A_{1g} symmetric breathing mode involving phonons near the K zone boundary.^[38,45] A second disorder peak, named the D' band, can also be seen on the shoulder of the G band at approximately 1 612 cm^{-1} . Both of these disorder bands are activated through a double resonance process, with the D and D' bands associated with intervalley and intravalley scattering, respectively.^[40,41,46] Two other minor features, located between 1 100 to 1 300 cm^{-1} and 1 400 to 1 500 cm^{-1} (following the nomenclature first used by Sadezky et al.,^[47] these peaks are designated D4 and D3, respectively) were also identified during the deconvolution process. Although the presence of these two features has been documented for years, their origin is not as clear as the other bands.^[38,47] The feature present between 1 100 and 1 300 cm^{-1} (D4) has been

Table 1. Peak deconvolution for Raman spectra measured using 1.96 eV excitation source.

Peak Fit	Band Position [cm^{-1}]	FWHM [cm^{-1}]	Band Shape
D4	1 170–1 255	101–184	Lorentzian
D	1 327–1 332	44–60	Lorentzian
D3	1 458–1 475	72–145	Lorentzian
G	1 575–1 582	36–48	Lorentzian
D'	1 608–1 616	28–43	Gaussian
2-D4	2 461–2 476	35–114	Lorentzian
G' (2-D)	2 650–2 659	63–83	Lorentzian
D + G	2 904–2 918	43–81	Lorentzian
G'' (2-D')	3 217–3 232	22–42	Lorentzian

attributed to longitudinal optical (LO) modes,^[48,49] however given the varied results on whether or not this band (and its possible overtone located at approximately $2\,469\text{ cm}^{-1}$) is dispersive, its exact origin still needs to be confirmed.^[34,49] Additionally, a small peak (D3, peak between $1\,450$ to $1\,500\text{ cm}^{-1}$) must be inserted between the main D and G bands to complete the first order fitting. This region of higher than expected intensity is often seen, though not always identified, for various types of carbon materials. As the intensity of this feature is low with a very broad FWHM, it is not clear if it actually corresponds to a particular band such as amorphous carbon,^[50] caused by stacking defects of the graphitic layers,^[51] or if it is just an artifact left over from an incomplete background removal.

Second order, two-phonon Raman features, occurring at energies above $2\,400\text{ cm}^{-1}$ are also clearly present in Figure 4. The main peak at approximately $2\,655\text{ cm}^{-1}$ is the first overtone of the D band (located at $1\,330\text{ cm}^{-1}$).^[52] This band, which is also activated by a double resonance process, will be referred to as G' in this work (instead of 2-D), as this is common practice in literature relating to graphitic material due to the fact that it is symmetry-allowed and not caused by defects in the sp^2 structure.^[37] This same practice holds for the small G'' peak (first overtone of the D' band, sometimes referred to as 2-D' in literature) located at $3\,224\text{ cm}^{-1}$. The peak located on the lower frequency shoulder of the G' band at approximately $2\,469\text{ cm}^{-1}$, will be referred to as the 2-D4 band, as is most likely the first overtone of the D4 band,^[34,49] whereas the peak located on the higher frequency shoulder (approx. $2\,911\text{ cm}^{-1}$) is a result of a combination of the D and G modes (D + G).^[41]

All these peaks have been discussed extensively in the literature for various graphitic materials,^[37,38,41,43] as well as specifically for MWCNTs,^[34–36] unfortunately they are still often mischaracterized. It is also possible to obtain further analysis on these peaks through additional deconvolution,^[53,54] however as the focus of this work is on the plasma-generated functionalities and not the structure of the CNTs, no further deconvolution was

attempted. The fact that the D peak intensity is equal to or greater than the G band shows that the CNTs presented here contain a high number of defects in their graphitic structure. The result of some of these defects which distort the CNT wall structure, known as structural defects (caused by non-hexagonal rings^[55]), can be seen in the TEM analysis (Figure 1C–D). Other common defects, such as bond rotations (Thrower-Stone-Wales defects), also contribute to this D band Raman shift.^[56]

3.3. Effect of Plasma Parameters

It is well known that exposure of CNTs to an oxygen glow discharge results in the grafting of oxygen-containing functionalities to the surface of the CNTs.^[57] It is also known that control of the plasma parameters is crucial to avoid damage or etching of the CNTs.^[58–60] In previous studies we have shown that a small amount of oxygen (5 sccm) and ethane (1 sccm) in a primarily argon plasma is effective in functionalizing the CNTs without causing significant damage.^[15] In this work two of the most important parameters, namely the treatment time and RF power were examined to determine their effect on the surface chemistry and graphitic structure of the CNTs. As Figure 5 shows, neither increasing the treatment time or RF power had any effect on the amount of oxygen bound the surface of the CNTs. Initially, the NF-CNTs contained essentially no oxygen on the surface (0.4 at.%), however with just 1 min of plasma treatment, the total oxygen concentration increased to approximately 10 at.%. Longer plasma treatment times and higher RF powers did not serve to increase the total amount of oxygen on the surface, nor did it affect the functionalities that were produced (no change was seen in the C1s or O1s peaks; not shown).

Raman analysis for the various plasma conditions indicates that even though there is no change in the degree of functionalization of the CNTs, treatment time and RF power did affect the graphitic structure of the CNTs. To

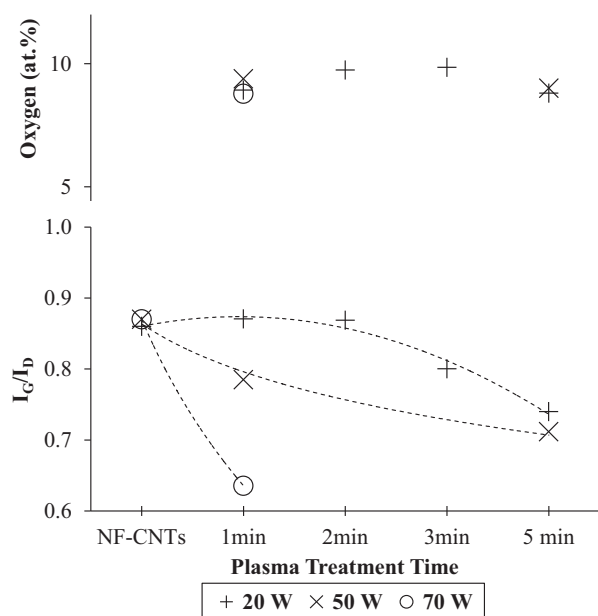


Figure 5. The effect of plasma treatment time and RF power on the XPS-derived surface atomic oxygen concentration (top), and the I_G/I_D peak intensity ratio (bottom). Trend lines added for visual clarity.

examine this effect, the I_G/I_D peak ratio was determined for the various plasma conditions. The use of this ratio was first proposed by Tuinstra and Koenig^[43] to determine the average crystallite size for graphite and has since been widely used to indicate the level of graphitization in various types of carbon. As it effectively characterizes the amount of disorder within the structure of the CNTs, this ratio is often used to demonstrate a change in defect level as a result of functionalization and heat treatment.^[42,45,61,62] In this work the intensity ratio of the G and D peak heights are presented instead of the ratio of peak areas, as suggested by Ferrari et al.^[38] for cases of large disorder, although the trends throughout this work remained consistent regardless which model (height or area) is employed. As Figure 5 shows, low RF power (20 W) did not have an effect on the I_G/I_D ratio at low treatment times (1–2 min), although as time increased (3–5 min) a slight decrease was found to occur. In addition, a decrease in graphitic order also took place after 1 min of treatment for RF powers of 50 and 70 W.

3.4. Thermal Stability of Functional Groups

To determine the thermal stability of the oxygen moieties produced by the plasma treatment, NF- and F-CNTs (while still attached to the stainless steel substrate) were heated in both an inert (Ar) and oxygen contacting (air) atmosphere and then analyzed after cooling to room temperature using

XPS and Raman spectroscopy. As Figure 6 shows the surface oxygen concentration of the F-CNTs, as determined by XPS, is significantly reduced after heating in both Ar and air, whereas it remains unchanged for NF-CNTs, except when heated in air above 350 °C. No measurable mass loss was found to occur for any of the CNT samples up to 600 °C in Ar and 450 °C in air, and SEM imaging (not shown) did not indicate any noticeable morphological changes. Heating to 500 °C in air did result in the complete oxidation of the CNTs, as is typical for MWCNTs.^[16,63] Degradation was also observed for heating of the CNTs to 650 °C in Ar, which can be attributed to the CNTs interacting with the stainless steel substrate, possibly resulting in carbide formation.^[64]

When examining the effect of heating on the F-CNTs (Figure 6), the same degree of oxygen-removal was seen when heating in an inert atmosphere for short period of time (Ar, 30 min) as for heating in an oxygen-containing environment for a long period of time (air, 18 h), up to 350 °C. This indicates that neither the heat treatment time nor the atmosphere (Ar or air) had a major effect on the stability of the oxygen moieties. Examination of the high-resolution C1s peak after the F-CNTs were heated in Ar shows a gradual decrease of intensity (Figure 7A), while the O1s peak shows a shift to lower binding energies in addition to the loss of intensity (Figure 7B). As expected, heating of the NF-CNTs to 600 °C in Ar had no effect on the surface oxygen concentration.

No change in the surface chemistry of the NF-CNTs was seen after heating in air up to 350 °C (Figure 6), however at higher temperatures (400 and 450 °C), a small increase to just over 2 at.% of oxygen occurs (Figure 6). As can be seen in Figure 8, little-to-no change occurs in the shape of the C1s

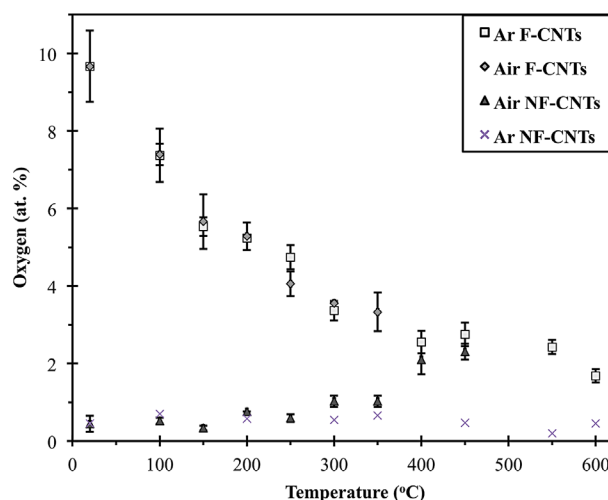


Figure 6. The XPS-derived surface atomic oxygen concentration after heat treatment in air (18 h) and argon (30 min) for both F-CNTs and NF-CNTs. Error bars represent ± 1 standard deviation.

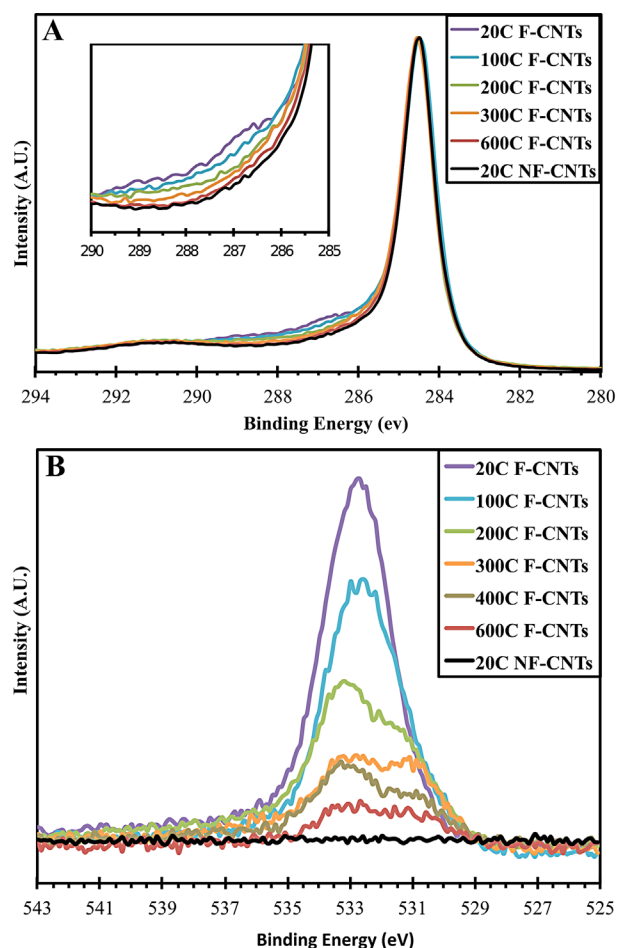


Figure 7. XPS C1s (A) and O1s (B) spectra for F-CNTs after heating in argon (30 min).

peak as a result of this oxidation, but the O1s peak is clearly increased in intensity from the NF-CNTs and shifted to lower binding energies from that for the F-CNTs at room temperature.

Characterization of the graphitic nature of the CNTs after heating in air for both F- and NF-CNTs resulted in a similar trend (Figure 9, using the I_G/I_D ratio as an indicator). No change in the I_G/I_D ratio occurs until 350 °C, after which the ratio decreases. Heating in Ar up to 600 °C did not result in any change in the I_G/I_D ratio for the NF-CNTs although a slight increase in the ratio did occur for the F-CNTs at 450 °C and above.

3.5. Nanofluid Stability

We have previously shown that F-CNTs are stable in suspension at temperatures as high as 170 °C in glycols.^[8] As a test on how the loss of functional groups at temperatures higher than 170 °C would affect stability

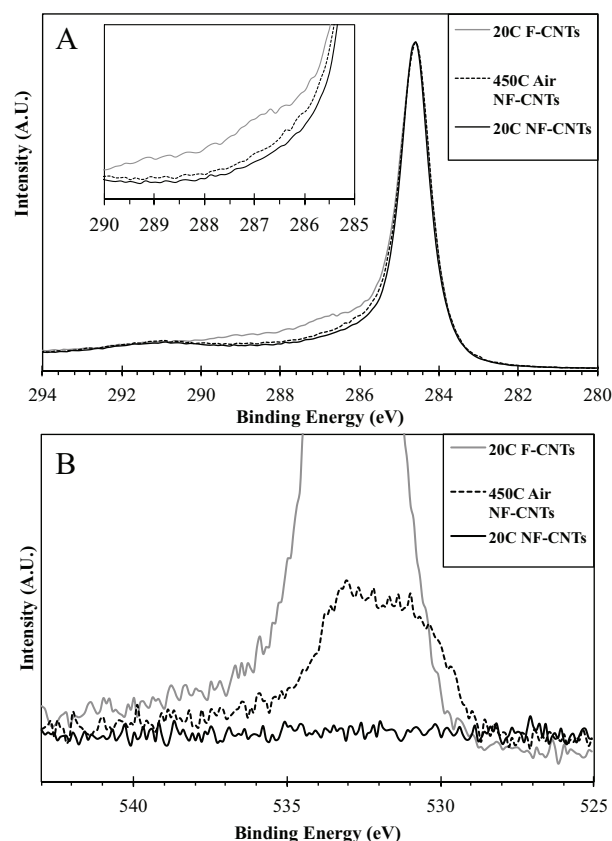


Figure 8. XPS C1s (A) and O1s (B) spectra comparing NF-CNTs after being heated in air (18 h) to non-heated F- and NF-CNTs.

(specifically, temperatures in the 200–600 °C range), aqueous suspensions were made at room temperature using the heated F-CNT samples. As Figure 10 and 11 shows, heating to 200 and 300 °C in Ar prior to suspension in water did not cause any decrease in stability of the CNTs, as measured after four weeks, while heating to 400 °C resulted in 23% agglomeration and heating to 600 °C lead to complete phase separation after 24 h.

4. Discussion

A high level of structural defects within the as-produced NF-CNTs can be directly seen in the TEM micrographs (Figure 1C–D) and indirectly observed from the strong disorder band present in the Raman spectra (I_G/I_D ratio < 1). A high level of defects is common in MWCNTs synthesized using t-CVD due to the fact the growth occurs under rapid, non-equilibrium conditions.^[56] The majority of intrinsic defects present in the CNT structure after growth can primarily be attributed to bond rotations and non-hexagonal rings, given that the formational energies of these defects are much less than for interstitial, vacancies,

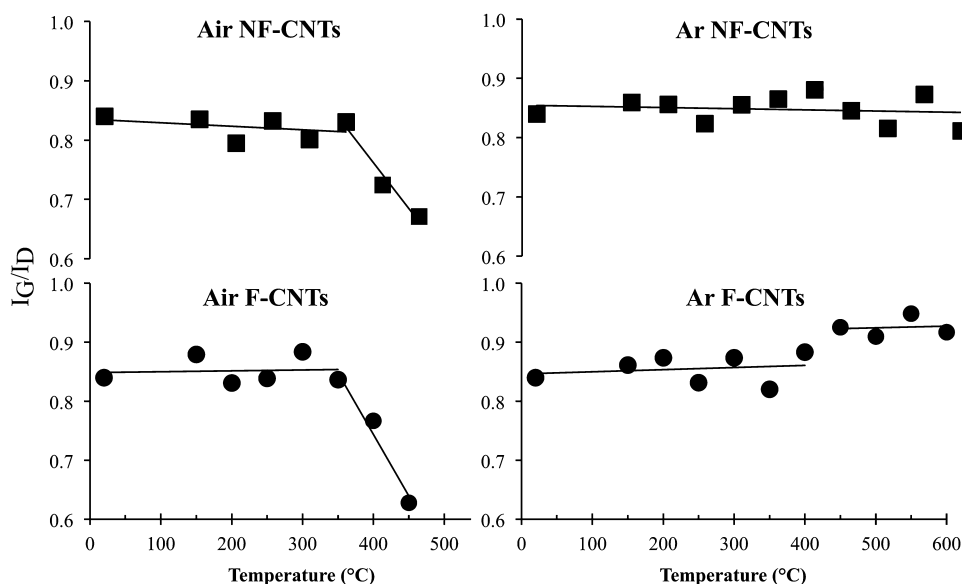


Figure 9. The I_G/I_D peak intensity ratio after heat treatment in air (18 h) and argon (30 min) for both F-CNTs and NF-CNTs. Trend lines added for visual clarity.

and sp^3 adducts.^[56] Although these defects most likely have a negative impact on the CNTs' mechanical and electrical properties, they provide prime locations to covalently bond oxygen moieties to the nanotube surface.^[65] Very short exposure to a low power oxygen-containing glow discharge (1 min, 20 W) was found to be sufficient to functionalize the CNT surface without inducing further damage on their structure (as shown by the unchanged I_G/I_D ratio), indicating the functionalization likely occurs through

bonding with existing defects and not through the creation of new ones. We postulate that the functionalization most likely proceeds through a defect bonding process, as reactivity along the sidewalls is low for MWCNTs due to their large outer diameters (on average approx. 35 nm). A larger CNT diameter results in less curvature and thus reduced strain on the graphitic matrix. Longer and higher power treatment did not lead to the grafting of additional oxygen moieties, as the porous 3-D network of CNTs (as opposed to a dense agglomerated powder) allowed for fast, unimpeded interaction between the defective nanotube surface and the plasma. Longer treatment times and higher plasma powers did however lead to an amorphization of the

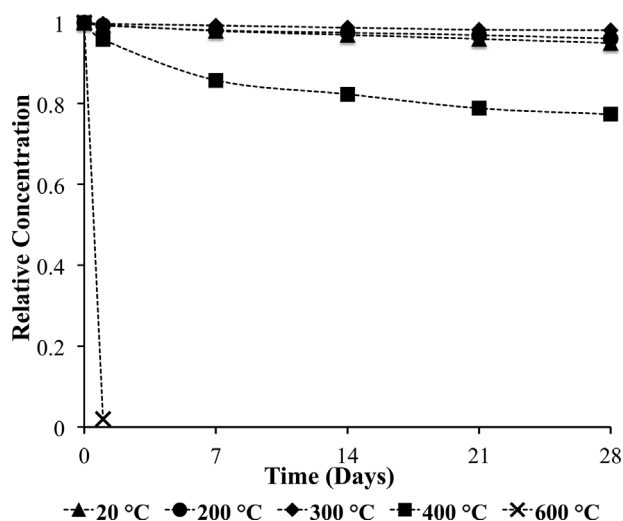


Figure 10. Relative concentration over time of the suspension made with the F-CNTs after heating, as determined by absorption spectroscopy. Trend lines added for visual clarity.

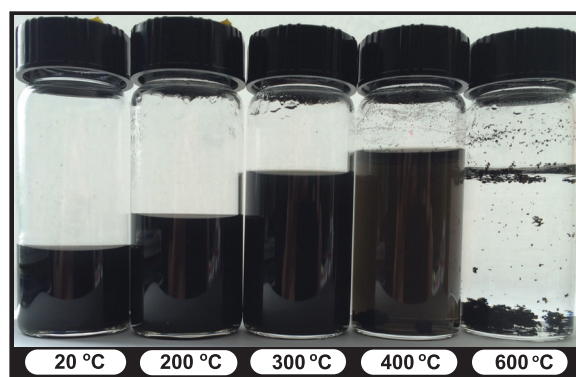


Figure 11. Aqueous based nanofluids produced after F-CNTs were heated in Ar. The photograph was taken after four weeks. Initial concentration of each was approximately 40 mgL^{-1} .

CNT lattice (up to a 25% decrease in the I_G/I_D ratio). This decrease in graphitic character of the CNTs as a result of prolonged and intense electron/ion bombardment is consistent with the literature for plasma treatment,^[61,66,67] and is also common during wet chemical functionalization of CNTs.^[65] Similar oxidation damage occurred during the heating of the NF-CNTs in air at high temperatures (400 and 450 °C), although a much smaller concentration of oxygen moieties were grafted to the CNT surface as compared to the plasma treatment (approx. 2.5 at.% compared to approx. 10 at.%). Examination of the O1s peak for the air-oxidized NF-CNTs (Figure 8B) shows a clear shift to lower binding energies from that of the plasma F-CNTs, indicating the formation of a higher degree of carbonyl-type bonds. These results are consistent with those found in the literature, as thermal oxidation of graphitic carbon is known to take place above 400 °C, induce damage in the graphitic structure,^[39,63] and result in the formation of primarily carbonyl type moieties.^[25] Unfortunately the NF-CNTs were too disordered prior to the plasma treatment to visually observe, via TEM, any substantial change in defect level as a result of the plasma treatment. It is also important to note that the plasma functionalization as well as the heating in air never resulted in an increase of the I_G/I_D ratio. Together with previously reported results (from thermal gravimetric analysis),^[16] this suggests that the CNTs are clean as one expects any amorphous carbon layer to be etched away under these conditions.^[62] This would also indicate that D3 peak found in the Raman spectra is not amorphous carbon and thus quantification of this peak for MWCNTs should not be used as an indication of purity, as suggested by Choi et al.^[50]

Following the plasma treatment, F-CNTs were heated in Ar and air in order to study the thermal stability of the oxygen moieties. It was found that regardless of the heat treatment time or atmosphere (Ar for 30 min or air for 18 h), heating to 350 °C results in the same decrease in surface oxygen concentration (from approx. 10 at.% down to approx. 3 at.%). This indicates that the heating duration of the F-CNTs (minimum 30 min) or the presence of oxygen while heating has little effect on the thermal stability of the functional groups. The large decrease in surface oxygen concentration (>60%) at relatively low temperatures (<350 °C) suggests that most of the moieties grafted to the CNTs surface are carboxylic groups, as these functionalities are the only ones which tend to decompose at these low temperatures.^[23,25,30,31,33] The mechanisms of oxygen removal over this temperature range are most likely through desorption of the carboxylic groups, and through the formation of acidic anhydrides caused by dehydration of adjacent carboxylic functions.^[30,31] The formation of additional anhydrides and the retention of ketone functions would explain the small shift to lower binding energies seen in the O1s peak (Figure 7B). Removal of other

oxygen moieties, such as anhydrides, aldehydes, phenols, and esters typically occurs at intermediate temperatures (300–600 °C), while the small percentage (<2 at.%) of remaining oxygen at 600 °C is most likely composed of ketone, quinone, pyrone, and ether groups. These XPS results do indicate a loss of oxygen beginning at lower temperatures than in previous studies.^[26,30,31,68,69] This may be due to the fact the heating was done at atmospheric pressure as opposed to under high^[31] and ultra-high vacuum,^[26,30,68,69] or that the CNTs used in this study were oriented within a porous 3-D network (see Figure 1A–B), as opposed to dense agglomerates,^[26,30,31,68,69] allowing for functional groups to easily desorb. Similar decomposition temperatures were seen by Rosenthal et al.^[18] with a porous network of plasma functionalized carbon nanofibers.

When the heated samples were studied by Raman spectroscopy, no significant change in the degree of graphitization of the F-CNTs was found to occur at temperatures below 400 °C, although a small increase (<10%) in the I_G/I_D ratio was seen at higher temperatures (400–600 °C). To the best of our knowledge this is the first study to examine the graphitic structure of the CNTs after the thermal removal of functional groups. These results suggest that desorption of the surface functional groups does not have a significant effect on the graphitic structure of the entire CNT (Raman signal penetration is >50 nm and thus encompasses the entire CNT structure^[20]), although the removal of oxygen moieties above 400 °C (in Ar) may result in some hybridization of disordered carbon back into a sp^2 lattice (only a small change of <10% in the I_G/I_D ratio was observed). Significant thermal annealing of sp^3 to sp^2 carbon generally occurs at temperatures above 600 °C, although small changes in the D and G peaks have been found to occur at temperatures as low as 400 °C.^[70] The decrease in the I_G/I_D ratio for both F- and NF-CNTs as a result of heating in air at 400 and 450 °C is due to thermal oxidation of the CNTs and not to removal of the functional groups.

Aqueous nanofluids produced using the heated samples provide an indication of how the loss of oxygen functional groups affects the stability of the F-CNTs when in suspension. As Figure 10 shows, no loss in stability was found to occur for the F-CNTs after heating to 200 and 300 °C. This indicates that even if some of the surface moieties are lost at high temperatures, stability can still be maintained. After heating in Ar to 300 °C, the surface oxygen concentration dropped by over 60% to 3.4 at.%, yet this was enough to maintain stability for four weeks at room temperature (no agitation). Heating further to 400 °C resulted in only an additional 8% drop in surface oxygen concentration (to 2.6 at.%), yet this corresponded to a 23% decrease in CNT concentration in the nanofluid as a result of agglomeration after four weeks, while heating to 600 °C (1.7 at.% oxygen remaining) resulted in complete phase

separation after 24 h. The type of functionalities remaining and not only the overall level of oxygen present should play an important role in the stability of the nanofluid, further studies are required to fully understand this phenomenon. The present characterization was made to provide indications of how F-CNT suspensions may respond when heated to high temperatures. However, given the important difference between heating in a liquid and heating in argon (or air), a direct comparison should not be made.

Suspensions of plasma-functionalized CNTs were shown to maintain a high level of stability even at high temperatures. This result can be attributed to both the growth and plasma processes providing a complementary technology platform. The t-CVD process generates a semi-porous forest of highly defective CNTs well anchored to the substrate, allowing for a full availability of the CNT surface to the plasma prior to any agglomeration. A very reactive and dry plasma environment then covalent binds a substantial amount of oxygen functional groups to the CNT defects, again maintaining the integrity of the CNT forest geometry and preventing agglomeration. Wet chemical treatments, such as boiling in harsh acids, do not lead to the same level of functionalization, as the CNTs in these wet methods tend to agglomerate before functional groups can be grafted on. In addition, wet functionalization techniques are generally complex, time-consuming, and difficult to scale up for industrial production.

5. Conclusion

Carbon nanotubes grown directly from a bulk stainless steel mesh were found to be free of impurities yet highly disordered. These defects nevertheless provide ideal locations for oxygen moieties to be grafted to the surface of the CNTs, without causing further damage to the graphitic lattice provided a low oxygen plasma treatment time and power was maintained. Low temperature heating (<350 °C) of the F-CNTs leads to a significant loss of oxygen moieties, indicating that a high level of carboxylic groups is added to the CNTs as a result of the plasma treatment. This loss of surface functionalities did not result in any decrease in stability when the heated F-CNTs were suspended in water, although heating at 400 °C and above did result in agglomeration.

Acknowledgements: The authors gratefully acknowledge the financial support provided by the *Natural Sciences and Engineering Research Council of Canada*, the *Fonds de recherche du Québec—Nature et technologies* and *McGill University*.

Received: October 7, 2014; Revised: November 4, 2014; Accepted: November 7, 2014; DOI: 10.1002/ppap.201400195

Keywords: carbon nanotubes (CNTs); plasma functionalization; radio frequency glow discharges (RFGD); thermal stability

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