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Thermal stability of oxygen functionalization in v-CNTs by low kinetic energy ion irradiation

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Abstract

Vertically aligned multiwalled carbon nanotubes synthesized by thermal catalytic chemical vapor deposition are irradiated with low kinetic energy oxygen ions to graft oxygen functional groups at their surface. Subsequently, the thermal stability of these functional groups is investigated by heating the sample progressively to 200, 300, 400 and 500 °C. X-Ray photoelectron spectroscopy (XPS) is used to analyze the atomic concentration and chemical configuration of the sample at each stage. Scanning and transmission electron microscopies are used to observe the morphology of the nanotubes after the thermal treatment. The solvent-free functionalization is carried out in 10 minutes reaching an oxygen atomic concentration of 17.2 at.%, with no impurities introduced. At the end of the thermal treatment, the relative oxygen content drops to 5.6 at.%. XPS analysis indicates four oxygen groups are produced by the ion irradiation: epoxide, hydroxyl, carbonyl and carboxyl groups, with the epoxides the least stable and the carbonyls the most stable. Combining low kinetic energy ion-implantation with a short post-anneal is shown to be an effective route to simultaneously control both sample oxygen content and the ratio of different oxygenated functional groups.

1. Introduction

Due to its unique properties the use of carbon nanotubes in electronic devices is a subject of huge interest in a vast number of scientific and technological fields [Quian 2020, Ghalandari 2020, Han 2019, Poudel 2018]. However, there are still limitations that impede the optimal application of carbon nanotubes at large scale. Frequently, carbon nanotubes are doped, functionalized, or conjugated with atoms, molecules and compounds in order to improve their properties [Muhulet 2018, Naqvi 2020, Merum 2017], notably their chemical reactivity due to their intrinsically inert surface. Grafting of oxygen groups at the surface of carbon nanomaterials is one of the most used functionalization for carbon materials, including carbon nanotubes [Tulli 2017, Adil 2020, Legrand 2016, Zuaznabar-Gardona 2020]. Oxygen groups grafted to the surface of carbon nanotubes affects their chemical and electronic properties, for example increasing surface chemical reactivity, decreasing hydrophobicity allowing solubilization in aqueous media, and transforming metallic carbon nanotubes to semiconducting [Malik 2016, Trulli 2017, Barinov 2009].

Oxygen functionalization of the carbon nanotubes can be performed using several techniques, the most commons being wet chemistry, simultaneous functionalization during the synthesis, photo-oxidation, plasma treatments and ion irradiation [Duch 2018, Rosca 2005, Grujicic 2003, Li 2008]. Among them, functionalization through oxygen ion irradiation has the advantage of being solvent-free, rapid functionalization times with easy control, site selective with the use of appropriate masks allowing fine tuning of the type and amount of grafted species [Bangert 2010]. Ion irradiation can be classified in two regimes: low kinetic energy ion irradiation (less than a few keV) and the high kinetic energy ion irradiation (from several keV to MeV) [Krashennnikov 2004, Kamimura 2005]. When a target is irradiated with low kinetic energy ions, most of the ions can directly interact with the sample, bonding to it (mainly at defect sites) and creating functional groups at the sample surface. Some other ions will create defects while crossing the sample, these defects can then serve as sites for further ions to create additional functional groups [Lehtinen 2010]. In order to fine tune the carbon nanotubes' properties for a desired application, the functionalization method must allow control of both the type and concentration of the functional groups. For example, carbon nanotubes with major concentration of carbonyl groups have superior electrocatalysis activity than nanotubes with other types of oxygen functional groups [Chen 2020]. In this perspective, low kinetic ion irradiation allows

controlled functionalization by adjusting the ions kinetic energy and ion dose irradiating the sample surface [Acosta 2019].

Heating is an important step in the integration of carbon nanotubes in different devices, during this step the nature and concentration of the functional groups of the carbon nanotubes may be accidentally modified. Due to their thermal stability, carbon nanotubes can be heated until 1200 °C if they are single wall nanotubes and until 2200°C if they are multiwall nanotubes without having significant changes in their structure [Yudasaka 2003, Kim 2004], heating below these temperatures may affect the functionalization of the carbon nanotubes without affecting their structure. Conversely, thermal treatments can be used to change type and concentration of the functionalities, for example, thermal heating is used to introduce defects on carbon nanotubes functionalized with oxo-groups to increase the electrocatalytic activity of CNTs to the oxygen reduction reaction [Chen 2020, Chen 2018]. Therefore, it is important to determine the thermal stability of functional groups grafted at the carbon nanotubes surface.

Here, vertically aligned carbon nanotubes (v-CNTs) synthesized by thermal catalytic chemical vapor deposition (referred to hereafter as v-CNTs), are functionalized with oxygen groups using low kinetic energy ion irradiation. The thermal stability of the oxygen functional groups grafted at the v-CNTs surface is investigated by heating progressively the sample to five different temperatures (200 °C, 300 °C, 400 °C, and 500 °C), the chemical configuration of the nanotubes surface is evaluated from the analysis of X-Ray photoelectron spectroscopy measurements after each stage of the sample: first on pristine v-CNTs, after the oxygen ion irradiation and after heating at each chosen temperature. The morphology of the nanotubes was examined by scanning and transmission electron microscopies.

2. Materials and Methods

2.1 v-CNTs synthesis

Thermal catalytic chemical vapor deposition was used to synthesize vertically aligned

multi-walled carbon nanotubes (v-CNTs) [Colomer 2011]. In brief, a multilayer of Si/Al/Fe was used as catalyst and Si wafers were used as substrates. First, an Al film (30 nm) was deposited on the Si wafers and after its oxidation, a 1.5 nm Fe layer was deposited and heated to 300 °C until Fe nanoparticles formation. Al and Fe layers were prepared using magnetron sputtering with a Quorum device. For the v-CNTs synthesis, the reactor was heated to 750 °C in atmospheric pressure under He flow (500 sccm). The catalyst was placed inside the reactor and H₂ flow (200 sccm) was introduced into the reactor for 20 min. After that, C₂H₄ flow (60 sccm) was introduced into the reactor, as the carbon source. At the end of the synthesis (25 min), a flow of He was used (500 sccm). The outer diameter distribution of the v-CNTs fluctuates between 10 and 40 nm.

2.2 v-CNTs oxygen functionalization

Oxygen functionalization of the v-CNTs was carried out with low kinetic energy oxygen ion irradiation, the functionalization method was already reported in a previous work [Acosta 2019]. The sample was mounted on a sample holder equipped with a resistive heater. Functionalization was performed in an ultra-high vacuum chamber system (PREVAC-541), the ion source was a Tectra Plasma source (TPIS) where microwave energy is used to create plasma from O₂, in the plasma ions (molecular ions and atomic ions), neutrals species, electrons, and UV photons are formed, the positive ions are extracted from the plasma using two grids located at the end of the plasma cup and brought to the target. The distance between the ion source and the target was about 12 cm. The v-CNTs were irradiated for 10 minutes with ions with kinetic energy of 1 keV, the current induced by the ion irradiation energy was 8 µA.

2.3 Thermal stability assays

In order to evaluate the thermal stability of the oxygen functional groups grafted at the surface of the v-CNTs after ion irradiation, the sample mounted on a sample holder equipped with a resistive heater, was heated in ultra-high vacuum. The temperature of the sample was raised to 200 °C, 300 °C, 400 °C and 500 °C progressively, the sample temperature was stabilized at each heating step for 15 minutes, after subsequently cooling to room temperature the X-Ray photoelectron spectra were recorded for each temperature.

2.4 Material characterization

The chemical composition of the v-CNTs surface was evaluated through X-ray photoelectron spectroscopy (XPS) using a VERSAPROBE PHI 5000 from Physical Electronics equipped with a monochromatic Al K α X-ray source. C1s and O1s core levels were recorded with an energy resolution of 0.6 eV. Both the sample heating and the ion irradiation were performed in the same ultra-high vacuum chamber, this chamber is connected to the XPS analysis chamber allowing in-situ measurements. XPS spectra were recorded at each step of the sample preparation, i.e. for pristine v-CNTs, after ion irradiation, and after the thermal assays at each temperature. The XPS spectra were recorded after the samples cooled down to room temperature. Deconvolution of the C1s core level spectrum allows determine the type and concentration of the oxygen functional groups at the v-CNTs surface before and after the resistive heating. The XPS data analysis was performed using the software CASA XPS.

The vertical alignment and morphology of the v-CNTs was evaluated before and after the thermal stability assays using a JEOL-JSM-7500F-Field Emission Scanning Electron Microscope operated at 15 kV for the SEM analysis and a for the TEM analysis.

3. Results and Discussion

XPS survey spectra identify the presence of only carbon and oxygen on the sample (Figure 1). The intrinsic oxygen concentration for pristine v-CNTs is ~1 at. %, related to oxidation during exposure to air. After oxygen ion irradiation (v-Ox-CNTs), this concentration increases to 17.2 at. %. This amount of oxygen grafted at the v-CNTs surface in 10 minutes of irradiation is high compared with other functionalization methods. After heating the sample to 200 °C, 300 °C, 400 °C and 500 °C the amount of oxygen decreases, as was expected, from 14.0 at. % when the sample was heated to 200 °C, dropping to 5.6 at. % when the v-CNTs were heated to 500 °C (Table 1).

Figure 1. v-CNTs XPS survey spectra showing the presence of carbon and oxygen in the sample.

v-CNTs sample stage	Carbon (at.%)	Oxygen (at. %)
Pristine	99.0	1.0
After oxygen ion irradiation	82.8	17.2
200 °C	86.0	14.0
300 °C	89.5	10.5
400 °C	92.2	7.8

Table 1. Relative atomic composition (at. %) of v-CNTs from XPS spectra. Treatment steps indicate 10-minute ion irradiation, followed by a progressive 15-minute heating initiating at 200 °C followed by 300°C, 400°C and 500°C.

The C1s and O1s core levels spectra were recorded at high energy resolution. The effect of the oxygen ion irradiation of the carbon nanotubes can be seen in the C1s spectra (Figure 2a), namely a widening in the left part of the spectra corresponding to photoelectrons ejected from C-O bonds, with higher binding energies than photoelectrons ejected from C-C bonds. The increased binding energy of these photoelectrons is attributed to the positive charge induced in the carbon atoms due to the bonding with the electronegative oxygen atoms, that change the electron screening of the carbon nucleus. Subsequent heating of the v-CNTs reduces this widening (Figure 2a), consistent with a decrease of C-O functionalities as the annealing temperature is increased.

Figure 2b shows the high resolution O1s spectra recorded. There is a clear increase in peak intensity after oxygen ion irradiation, followed by a decrease dependent on the annealing temperature. The peak is centered at 532.6 eV, due to the contribution of C-O functionalities (Mattevi 2009). The O1s peak changes in shape from a combined single peak to a double peak curve denoting desorption of one or more kinds of functional groups from the v-CNTs surface, this change in peak shape becomes more marked as the annealing temperature increases.

Figure 2. v-CNT high resolution C1s (a) and O1s (b) XPS spectra.

Besides obtaining the atomic composition of the samples, information about their chemical configuration can be obtained with X-Ray photoelectron spectroscopy by detailed analysis of the high resolution core level spectra. The analysis of both C1s and O1s were carried out by a least-squares fitting procedure using the software CASA XPS, O1s analysis is given in supplementary information. Figure 3 shows the C1s analysis for the pristine and oxygen ion irradiated v-CNTs. For the pristine v-CNTs only two components were used to reproduce the spectrum, one at 284.4 eV belonging to C-sp² atoms (C1) [Bittencourt 2011] and another at 290.9 eV assigned to photoelectrons losing kinetic energy due to π -plasmon excitations (C2) (Figure 3a). After oxygen ion irradiation (Figure 3b), five more components with the following binding energies were used to fit the spectrum. The first at 284.7 eV is assigned to photoelectrons ejected from C-sp³ atoms (C3), carbon atoms with sp³ hybridization due to the formation of defects induced by the irradiation with oxygen ions [Banhart 1999]. The other components were assigned to photoelectrons ejected from carbon atoms bonded with oxygen in the following configurations and binding energies, 285.9 eV attributed to C-O hydroxyl groups (C4), 286.7 eV assigned to C-O-C epoxy groups (C5), 287.6 eV assigned to C=O carbonyl functional groups (C6) and 289.1

assigned to COOH carboxyl functionalization (C7) [Bittencourt 2011, Acosta 2019].

Figure 3. C1s XPS analysis spectra of (a) pristine v-CNTs and (b) v-Ox-CNTs after oxygen ion irradiation.

Component assignments: C1 = C-sp², C2 = π -plasmon-excitations,
C3 = C-sp³, C4 = C-O, C5 = C-O-C, C6 = C=O, C7 = COOH.

Figure 4 shows the C1s analysis spectra recorded after heating at 200 °C (Figure 3a) and 500 °C (Figure 3b), we can clearly observe the change in the relative area of the components assigned to carbon bonded to oxygen (C4-C7) (values given in Table 2).

Figure 4. C1s XPS analysis spectra of v-Ox-CNTs heated at 200 °C (a), v-Ox-CNTs heated at 500 °C (b).
 Components assignment: C1 = C-sp², C2 = π -plasmon-excitations,
 C3 = C-sp³, C4 = C-O, C5 = C-O-C, C6 = C=O, C7 = COOH.

The C1s spectra recorded after each heating temperature were analyzed, the variation of the relative area, i.e. concentration, of the components used to fit the C1s spectrum was examined, they are compared in Figure 5 and shown in detail in Table 2. For the C-sp² component (Figure 5a), the large decrease from 96.5 % in v-CNTs pristine to 42.7 % in v-Ox-CNTs after oxygen functionalization clearly shows the irradiation breaking π -bonding, forming oxygen groups and C-sp³ defects. Upon heating at different temperatures, a partial ‘healing’ of the carbon nanotube structure occurs with the formation of new chemical bonds mainly in the C-sp² hybridization form, causing the increase in their relative concentration up to 62.1 % at the maximum temperature. The healing of C-sp² bonding on graphitic-carbon structures by increasing their temperature is a previously reported phenomenon [Krashennnikov 2007, Struzzi 2015, Scardamaglia 2015]. Oxygen ion irradiation creates C-sp³ related defects in the graphitic lattice with a relative concentration of 17.3 %, in agreement with early work by Banhart et al [Banhart 1999]. Although we expected the relative concentration of the C-sp³ component to decrease due to the healing of

the defects for increasing heating temperature, such behavior was not observed. The relative concentration of C-sp³ remains almost constant for all temperatures $\sim 17.0 \pm 2 \%$. It suggests a certain equilibrium between the C-sp³ defects that are being healed and the formation of C-sp³ defects due to the desorption of oxygen atoms when the nanotubes are heated.

The relative concentrations from the components assigned to oxygen functional groups in v-Ox-CNTs is detailed in Figure 5b. The change in relative concentration of these components gives information about their relative thermal stabilities. The C-O-C epoxy groups are the most unstable, and are completely eliminated after heating at 300 °C. This is followed by the carboxyl COOH groups whose relative concentration decreases considerably with temperature. These carboxyl groups are expected to fragment to generate C-O groups, which coupled with potential transformation of epoxy groups together explain the increase in the C-O relative concentration seen at 200 °C and 300 °C, which then decreases gradually at 400 °C and 500 °C. The most thermally stable functional group is the C=O carbonyl, which relative concentration remains almost constant.

In general, there is a decrease in the amount of oxygen functionalities grafted at the surface of the carbon nanotubes with increasing temperature, matching the drop in overall oxygen atomic concentration with increasing temperature. Nevertheless, even when the nanotubes were heated at 500 °C, a considerable number of oxygen functionalities remain in the surface of the nanotubes, with C=O carbonyl and C-O hydroxyl the most thermally stable and C-O-C epoxy group the least stable of all oxygen groups. The drop-off in total oxygen concentration is not sudden but shows a somewhat uniform decrease with temperature, a positive result showing that the application of a short post-implantation anneal allows good control of both total oxygen concentration and relative functional group concentration.

Figure 5. Relative concentration of the components in the C1s analysis spectra at each stage of the v-CNTs. C-sp² and C-Sp³ (a) C-O, C-O-C, COOH and C=O (b). Ion irradiation error bars: C-sp²: ± 4.0 , C-sp³: ± 3.2 , C-O: ± 2.6 , C-O-C: ± 0.9 , C=O: 1.3, COOH: ± 1.0 . Heated 200°C error bars: C-sp²: ± 4.9 , C-sp³: ± 4.3 , C-O: ± 2.2 , C-O-C: ± 1.0 , C=O: 0.9, COOH: ± 0.9 . Heated 300°C error bars: C-sp²: ± 2.8 , C-sp³: ± 2.5 , C-O: ± 2.2 , C=O: 1.4, COOH: ± 0.7 . Heated 400°C error bars: C-sp²: ± 3.9 , C-sp³: ± 2.9 , C-O: ± 1.0 , C=O: 1.2, COOH: ± 0.5 . Heated 500°C error bars: C-sp²: ± 3.5 , C-sp³: ± 3 , C-O: ± 1.2 , C=O: 1.0, COOH: ± 0.9 .

v-CNTs sample stage	Relative concentration (%)						
	C-sp ²	C-sp ³	C-O	C-O-C	C=O	COOH	Plasmon
Pristine	94.2 $\pm$ 1.2	0	0	0	0	0	3.8 $\pm$ 1.2
After Oxygen functionalization	42.7 $\pm$ 4.0	17.3 $\pm$ 3.2	6.3 $\pm$ 2.6	5.8 $\pm$ 0.9	4.1 $\pm$ 1.3	4.6 $\pm$ 1.0	1.9 $\pm$ 1.2
200 °C	45.0 $\pm$ 4.9	15.2 $\pm$ 4.3	9.6 $\pm$ 2.2	5.9 $\pm$ 1.0	2.6 $\pm$ 0.9	5.0 $\pm$ 0.9	2.7 $\pm$ 1.1
300 °C	51.0 $\pm$ 2.8	18.3 $\pm$ 2.5	10.7 $\pm$ 2.2	0	3.1 $\pm$ 1.4	3.3 $\pm$ 0.7	3.1 $\pm$ 1.9
400 °C	57.9 $\pm$ 3.9	18.7 $\pm$ 2.9	5.6 $\pm$ 1.0	0	5.0 $\pm$ 1.2	1.6 $\pm$ 0.5	3.4 $\pm$ 1.5
500 °C	62.1 $\pm$ 3.5	16.9 $\pm$ 3.0	4.5 $\pm$ 1.2	0	4.3 $\pm$ 1.0	3.4 $\pm$ 0.9	3.1 $\pm$ 1.6

Table 2. Relative concentration of the components in the C1s analysis spectra for v-CNTs at each stage of the sample.

The morphology of the aligned carbon nanotubes after heating at 500 °C was investigated by SEM and TEM microscopies (Figure 6). Figure 6a shows the macroscopic structure and the alignment of the v-Ox-CNTs by SEM microscopy, the density and the alignment of the nanotubes is not affected by the oxygen ion irradiation nor by the heating treatment. Figure

6b shows the TEM images of v-Ox-CNTs recorded at the final step of the heat treatment (500°C), the overall structure of CNTs was maintained after both, the oxygen ion irradiation and the heating treatment, with no significant degradation. This agrees with literature, changes in the diameter and the number of walls in CNTs is only observed after heating to typically 1400 °C (Yudasaka 2003). The inset of Figure 6b shows a mix of carbon nanotubes with both open and closed tips. Ion irradiation it is expected to result in open tipped nanotubes because is where the major of functionalization take place. The closed tips are thus likely due to the ‘healing’ effect of annealing resulting in oxygen desorption and structural rearrangement.

Figure 6. Electron microscopy of v-Ox-CNTs after heating at 500 °C. Scanning electron microscopy (a) shows that the overall structure of the nanotube film is maintained and the nanotubes are not amorphised by the irradiation or annealing steps. Transmission electron microscopy (b), the inset shows that both open and closed tips are present.

4. Conclusions

Low kinetic energy ion irradiation is a functionalization technique that permits the effective functionalization of vertically aligned carbon nanotubes with oxygen groups in a rapid, solvent-free and clean mode. Four different oxygen functional groups were identified by analysis of the C1s and O1s core level XPS spectra: epoxide, hydroxyl, carbonyl and

carboxyl groups. Annealing was used to study the thermal stability of each functional group, with epoxide groups the most unstable and carbonyl group the most stable. Furthermore, we show that the concentration of each functional group can be adjusted by the thermal treatment of the carbon nanotubes without damaging their overall structure owing to their thermal stability. As such the combination of low kinetic energy ion-irradiation followed by short time thermal anneals represents an excellent combination for oxygen functionalization of carbon nanotubes, allowing simultaneous control over both overall concentration and concentration of individual functional group types.

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