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Grafting of adipic anhydride to carbon nanotubes through a Diels-Alder cycloaddition/oxidation cascade reaction

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Abstract: Different reactions have been reported for the successful functionalization of carbon nanotubes (CNT). The Diels-Alder cycloaddition is recognized as a plausible chemical approach, but few reports are known where this strategy has been used. In this study, the functionalization was performed by 1,3-butadiene generated from 3-sulfolene under heating conditions in diglyme. This simple and easily scalable method resulted in functionalized CNT with mass losses of 10 - 23 % by thermogravimetric analysis (nitrogen atmosphere). The functionalization was also supported by acid-base titration, elemental analysis, temperature programmed desorption and X-ray photoelectron spectroscopy. The high content in oxygen detected on the CNT surface was assigned to anhydride formation due to a cascade oxidation of the alkene groups generated in the cycloaddition reaction. The complete evolution of the alkene leads to a grafting density of 4.2 mmol g^{-1} for the anhydride moiety. Ab-initio calculations in CNT model systems indicate that the Diels-Alder addition of butadiene is a feasible process and that subsequent oxidation reactions may result in the formation of the anhydride moiety. The presence of the anhydride group is a valuable asset for grafting a multitude of complex molecules, namely through the nucleophilic addition of amines.

1. Introduction

Carbon nanotubes (CNT) continue to attract great interest from the scientific community as a result of their unique electrical, mechanical and thermal properties. However, the application of CNT have been limited by the strong inter-tube interactions keeping them together in bundles and their poor interaction with other materials. Surface chemistry modification [1-4] has been used to manipulate their fascinating properties [5]. The wide application of the Diels-Alder reactions in the functionalization of fullerenes [6] motivated the use of this type of reaction for the functionalization of CNT. Although some theoretical studies on the Diels-Alder cycloaddition of butadiene to single wall carbon nanotubes (SWCNT) suggested that this reaction was not feasible, the same authors concluded in a subsequent study that the [4+2] cycloaddition of *o*-quinodimethane was a plausible process [7]. This was experimentally proved for the first time in 2004 by Delgado et al [8], when SWCNTs were reacted with *o*-quinodimethane generated from an appropriate sultine. Few years later (2007), Sakellarious et al [9] reported the same process using different precursors (benzociclobutenes). Zhang et al (2005) [10] reported the cycloaddition of several dienes to

2

fluorinated SWCNT and in 2006 Ménard-Moyon et al [11] performed the cycloaddition of 2,3-dimethoxy-1,3-butadiene to SWCNT, assisted by transition metals and pressure. The reaction of furan derivatives and cyclopentadiene with CNT and carbon nanofibers (CNF) was reported by Munirasu et al (2010) [12] and Zydziak et al (2011) [13] respectively. Despite the theoretical study performed by Lu et al (2002) [7] where the cycloaddition of 1,3-butadiene to CNT surface was considered unfavorable, the reaction of 1,3-butadiene occurs with CNF when the diene (1,3-butadiene) is generated *in situ* from 3-sulfolene (by sulfur dioxide extrusion) upon heating [14]. In the present work, we demonstrate that the functionalization of MWCNT with 1,3-butadiene generated from 3-sulfolene indeed takes place and we provide theoretical calculations that indicate that the cycloaddition of 1,3-butadiene to model CNT is mildly exothermic and consequently possible. The characterization of functionalized material by thermogravimetric analysis (TGA), potentiometric titration, X-ray photoelectron spectroscopy (XPS), temperature programmed desorption (TPD) and elemental analysis shows that the CNT are actually decorated with carboxylic anhydride groups. Under the preparation conditions reported, the original alkene undergoes a cascade oxidation process, to finally yield carboxylic anhydride groups.

2. Experimental Section

2.1. Functionalization of CNT

CNT were obtained from Nanocyl (NC 7000), diethylene glycol dimethyl ether (diglyme) and 3-sulfolene were purchased from Sigma-Aldrich.

The reaction of the CNT with 3-sulfolene was carried out in the presence of diglyme as solvent (60 mL). The reaction was studied at two different temperatures (100 ºC and 150 ºC), using CNT:3-sulfolene mass ratios (1:1 and 1:2) and different time periods (2, 4 and 7 days). After the reaction was concluded the modified CNT were filtered over a PTFE membrane (0.2 µm) and washed with ethanol. To ensure that unreacted material was removed, CNT were sonicated for 15 minutes in ethanol and filtered again. The obtained solid was then dried under vacuum overnight at 100 ºC.

A blank experiment was performed by heating the CNT in diglyme, at 100 ºC and 150 ºC, in contact with air, during 7 days. In a different experiment, CNT and 3-sulfolene were combined in a 1:2 mass ratio using diglyme as solvent and each mixture was heated at 100 ºC

3

and 150 ºC for 7 days, under nitrogen atmosphere. The same work-up procedure was used for the washing and drying processes.

2.2 Characterization techniques

3-Sulfolene was characterized by differential scanning calorimetry (DSC). The functionalized CNT were characterized by elemental analysis, TGA, TPD, XPS, and potentiometric titration. The DSC was conducted in a DSC20 Mettler oven with a Mettler TC11 controller, at a heating rate of 2 ºC min^{-1}, under argon atmosphere at a constant flow of 50 mL min^{-1}.

The elemental analyses of C, H, O, N and S were carried out in a LECO Truspec Micro CHNS microanalysis apparatus with a LECO Truspec Micro O accessory for O analysis. The C, H, S and N were determined from the amounts of C, H, S and N oxides produced in the combustion of a portion of the sample (1 mg of sample was used for each assay, with two repetitions). Oxygen was determined from the amounts of CO and CO_2 released in a pyrolysis at very high temperature, in a different portion of sample.

The TGA was performed on a Modulated TGA Q500 from TA Instruments. The samples (approximately 2 mg) were heated at 10 ºC min^{-1} under N_2 atmosphere or under air, at a constant flow of 50 mL min^{-1}.

The TPD analysis of the samples was conducted in a Micromeritics Autochem II chemisorption analyzer with a heating rate of 10 ºC min^{-1} under flowing argon (50 mL min^{-1}). The amounts of released CO and CO_2 were determined from the intensities of m/Z=28, and 44, respectively, monitored by an Omnistar mass spectrometer (Pfeiffer Vacuum).

For the XPS analysis, the samples were stuck on double-sided carbon adhesive tabs. XPS measurements were made in a SPECS spectrometer with a Phoibos 100 hemispherical analyser. The base pressure in the UHV chamber was about 1.0×10^{-7} Pa. The X-ray radiation source was non-monochromatic Mg Kα (1253.6 eV) at 100 W X-ray power and anode voltage of 11.81 kV. The photo-excited electrons were analysed in constant pass energy mode, using pass energy of 50 eV for the survey spectra and 10 eV (C1s, O1s) or 30 eV (S2p) for the high resolution core level spectra. Spectra were recorded at a take-off angle of 90 º. No binding energy correction was done because the samples did not exhibit any charging effects. CasaXPS software was used for data processing. The compositions in atomic percent (at. %) were determined from the survey spectra by considering the integrated peak areas (after corrections for the mean free-path of the outgoing electrons and the transmission function of the analyser) of the main XPS peaks of the different elements (C1s,

O1s, and S2p) and their respective sensitivity factors. Core level curve fitting in different components was performed using a Shirley background and a standard least squares algorithm. Each component was considered as a convolution of a Gaussian and a Lorentzian function (80:20).

In the potentiometric titration study, HCl (0.01 M) and NaOH (0.1 M) solutions were obtained from their respective 1 molar standard solutions (Fixanal®, Riedel de Haën®) using high purity water (electrical resistivity>18MΩ). The titrations were performed on a TIM850 titration Manager Titralab from Radiometer Analytical SAS. Titrations were carried out in duplicate for each sample under argon atmosphere. The CNT (100 mg) were suspended in 0.01 M HCl with 0.01 M NaCl (35 mL). The pH electrode was protected with dialysis tubing purchased from Sigma in order to prevent damage of the electrode and to ensure reproducible results. Before titration, the dialysis tubing was washed following the instructions provided by Sigma in order to remove glycerin, included as humectant and sulfur compounds. A reference test was run using the protected electrode and the aqueous HCl (0.01 M) solution was titrated with NaOH (0.10 M). Each sample was stirred for 30 min before NaOH addition (an initial portion of 2 mL followed by 0.01 mL min^{-1} until pH=11 was reached).

2.3. Theoretical calculations

Quantum chemical calculations were used to explore the energetic feasibility of Diels-Alder and related reactions on CNT. Calculations were done with the hybrid density functional Heyd-Scuseria-Ernzerhof (HSE) that has been widely used in extended carbon nanomaterials [15-17] together with the 6-31G(d,p) basis set [18]. All extended systems were computed with the Gaussian 09 [19] suite of programs with mono-dimensional periodic boundary conditions in vacuum and without vibrational corrections. Studies were performed on three single wall CNTs: (5,5), (9,0) and (10,0) (see Fig. 1).
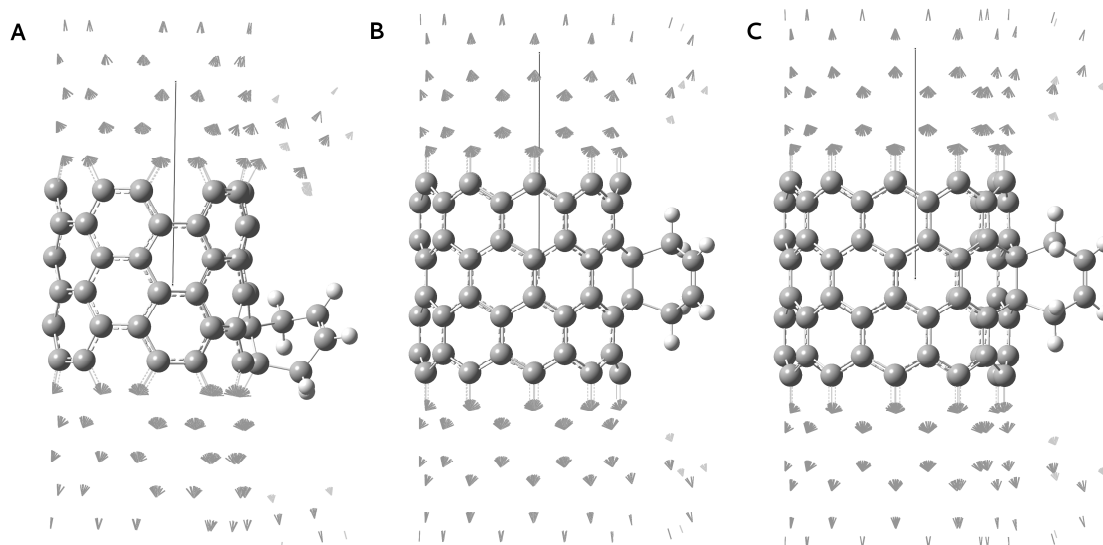
Fig. 1 - From left to right, cis-butadiene chemisorbed on (5,5), (9,0) and (10,0) CNTs with 60, 72 and 80 atoms. The ball and stick model represents the unit cell embedded by its periodic images.

3. Results and Discussion

3.1. CNT functionalization and DSC analysis

3-Sulfolene, a convenient precursor for 1,3-butadiene used in Diels-Alder cycloaddition reactions, is a solid material that releases the diene and sulfur dioxide on heating. The DSC analysis of 3-sulfolene (Fig. 2) shows the melting point of the solid at 73 ℃ and a maximum of thermal decomposition to generate 1,3-butadiene and SO_2 at 167 ℃.
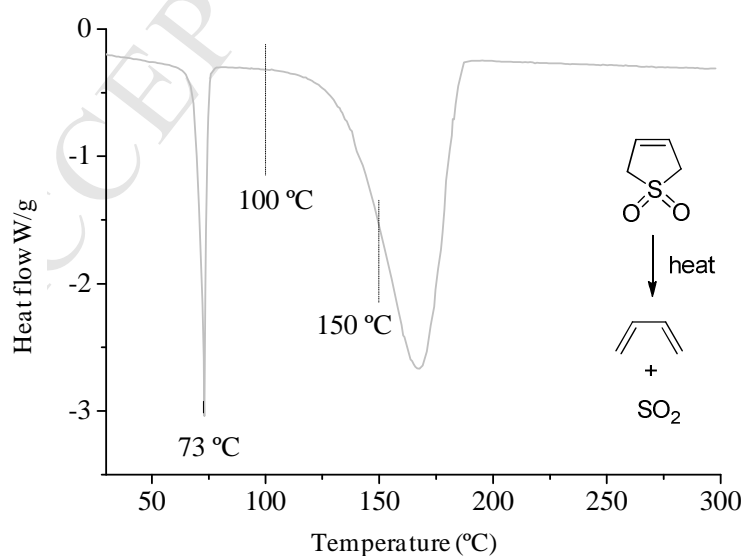

Fig. 2 - Thermal decomposition of 3-sulfolene recorded by DSC between 30 and 300 ℃.

As the concentration of 1,3-butadiene generated during the reaction depends on the temperature, the functionalization was studied at 100 ºC and 150 ºC. At 100 ºC a very slow thermal decomposition of 3-sulfolene is maintained throughout the reaction while at 150 ºC a fast evolution occurs. This may be reflected in the nature and extent of functionalization of the CNT surface. Besides the effect of temperature, the relative ratio of reagents and the reaction time were also investigated (Table 1).

Table 1. Experimental condition for the functionalization of CNT with 3-sulfolene and the weight (wt.) loss recorded by TGA in air and nitrogen atmosphere (atm.).

Exp.	Temp. (ºC)	CNT(g):Sulf.(g)	[Sulf.] (mol/dm^3)	Time (days)	Atmosphere	Wt. loss at 800 ºC in N_2 atm.(%)	Wt. loss at 500 ºC in air atm.(%)
1		1:1	0.14	2	Air	10.4	*
2		1:2	0.28		Air	11.9	*
3		1:1	0.14	4	Air	13.8	20.9
4	100	1:2	0.28		Air	18.1	*
5		1:1	0.14		Air	16.2	*
6		1:2	0.28	7	Air	23.0	32.1
6N		1:2	0.28		Nitrogen	*	6
Blank1		1:0	-		Air	*	5
7		1:1	0.14	2	Air	11.8	*
8		1:2	0.28		Air	11.7	*
9		1:1	0.14	4	Air	13.4	15.9
10	150	1:2	0.28		Air	14.3	*
11		1:1	0.14		Air	16.4	*
12		1:2	0.28	7	Air	17.4	23.9
12N		1:2	0.28		Nitrogen	*	9
Blank2		1:0	-		Air	*	9

Not determined

3.2. TGA analysis

The pristine CNT used in this work exhibited a high thermal stability at 800 ºC in nitrogen atmosphere with a weight loss of 0.7 %, attributed to residual contamination of amorphous carbon (Fig. 4A and 4C). Depending on the experimental conditions used for the functionalization reaction (Table 1), different weight loss values were obtained by TGA at 800 ºC (under nitrogen atmosphere) or at 500 ºC (in air). A plot of these values (recorded by TGA at 800 ºC in nitrogen atmosphere) against time of reaction is presented as supplementary data (Figure S1). As the reaction time increases, so does the extent of functionalization. This tendency was more evident for the CNT heated at 100 ºC when the

initial ratio of CNT:3-sulfolene was 1:2 (Exp. 2,4 and 6). Higher weight losses were obtained for CNT heated with 2 equivalents of 3-sulfolene at 100 ℃ for 4 and 7 days (Exp. 4 - 18 % and Exp. 6 - 23 %, respectively). Heating the reagents for two days resulted in similar weight losses (10.4 -11.9%) independently of the sulfolene:CNT ratio (1:1 or 2:1) or the temperature used to perform the reactions (100 ℃ or 150 ℃). At 150 ℃, the weight loss of the functionalized CNT was comparable when either one or two equivalents of 3-sulfolene were used.

This pattern for the weight loss by TGA, reflects the nature and extent of functionalization, and can be associated to the experimental conditions that were used. The rate of thermal decomposition of 3-sulfolene and the interaction of 1,3-butadiene and sulfur dioxide in solution with the CNT surface at 100 ℃ or 150 ℃ may be relevant factors in this process. The decomposition of 3-sulfolene into 1,3-butadiene and sulfur dioxide (both in the gas form under NTP conditions) was faster at 150 ℃ reducing their interaction with the solvent and with the suspended material. At 100 ℃, the much slower formation of 1,3-butadiene from 3-sulfolene results in an improved interaction with the solvent, prolonging the contact between the reactive species.

Relevant information was obtained from the TGA of the CNT heated for 7 days at 100 ℃ (Blank1) or at 150 ℃ (Blank2) (supplementary data, Figure S2). The moderate weight loss indicates that the solvent has only a marginal effect on the CNT surface, although more pronounced at 150 ℃.

Heating a 1:2 mixture of CNT and sulfolene for 7 days at 100 ℃ or 150 ℃ under a nitrogen atmosphere results in a weight loss, by TGA, comparable to that obtained in the blank experiments (supplementary data, Figure S3). This observation indicates that air plays a major role in the functionalization reaction but is not the sole ingredient, as in the absence of sulfolene air fails to interfere with the stable aromatic surface.

The samples of functionalized CNT obtained from experiments 3, 6, 9 and 12 were selected to be studied by TGA in air atmosphere. Figure 3 shows the thermogravimetric curve of pristine and functionalized CNT (Exp. 3, 6, 9 and 12) in N_2 and in air atmosphere. The main oxidation of pristine CNT (Fig. 3B and D) was initiated at 500 ℃ leading to 10.5 wt.% of residue (mainly metal oxides from the CNT synthesis). Before reaching 500 ℃, the pristine

CNT presented a weight loss of 2.2 % that may be related to oxidation of amorphous carbon on the surface. Both CNT modified at 100 ºC (CNT-Exp. 3 and 6) or at 150 ºC (CNT-Exp. 9 and 12) showed two main degradation steps between 200 and 500 ºC. The functionalized CNT-Exp. 3 and 6 showed a total weight loss at 500 ºC of 20.9 and 32.1 %, with a maximum degradation rate of the CNT at 613 ºC and 609 ºC respectively. The amount of residue obtained at 700 ºC was 9.4 % for CNT-Exp.3 and 6.9 % for CNT-Exp.6. The CNT-Exp. 9 and 12 showed a total weight loss at 500 ºC of 15.9 and 23.9 %, maximum degradation rate of the CNT at 638 ºC and 605 ºC and an amount of residue at 700 ºC of 10.1 and 9.0 % respectively. For all the samples the thermal stability was higher in inert atmosphere (Fig. 3A and C) with a main degradation step between 200 and 500 ºC and weight losses of 13 – 23 %.
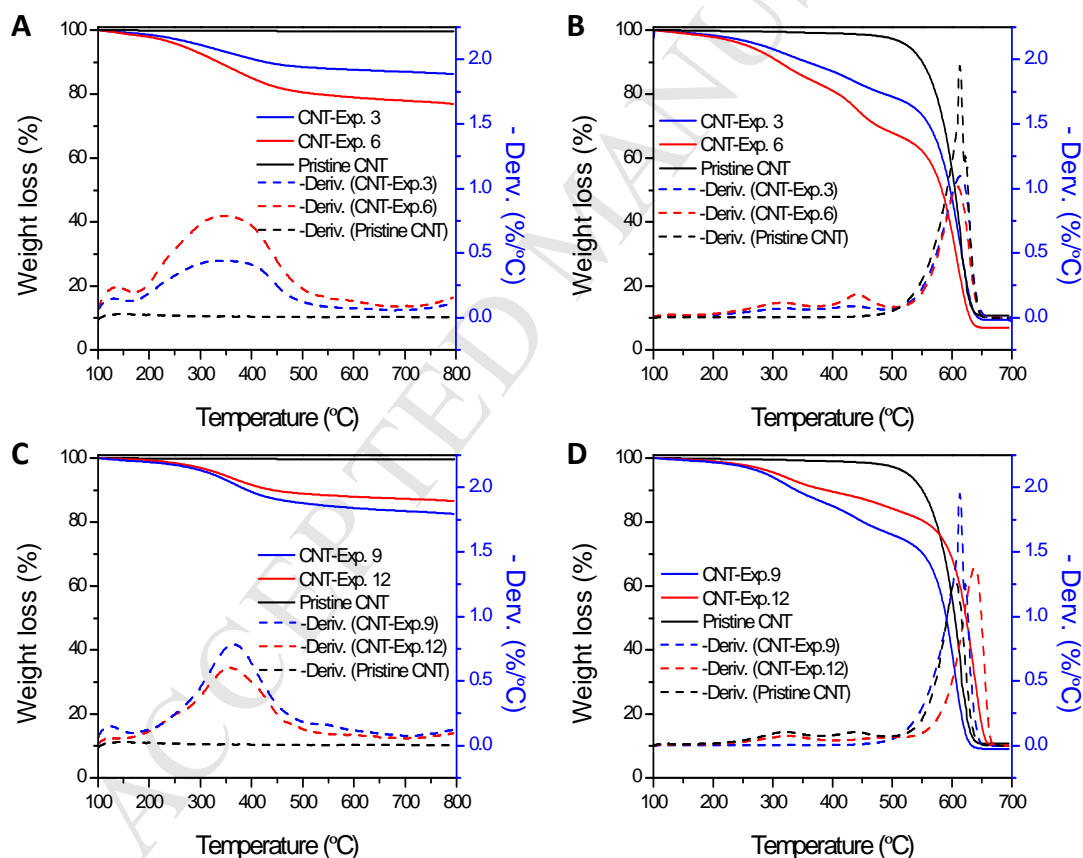

Fig. 3 - TGA curves (solid lines) and first derivative (dash lines) of functionalized and pristine CNT. The TGA experiments were performed in nitrogen (A and C) and in air (B and D) atmosphere.

3.3. Elemental Analysis

Table 2 shows the elemental composition (wt. %) of the pristine and functionalized nanotubes obtained in Exp. 3, 6, 9 and 12. The CNT prepared in Exp. 6 show the highest O/C ratio, followed by exp. 12. The results confirm the presence of sulfur, probably arising from sulfonation of the CNT surface due to the formation of sulfur trioxide and sulfuric acid in the reaction medium. The highest content in S was obtained for the CNT functionalized at 100 ℃ (Exp.3 and Exp. 6) reflecting the higher concentration of SO_2 retained in solution at lower temperature.

Oxygen is the major element incorporated on the nanotube, with a 23-41 fold molar excess over sulfur. The presence of hydrogen supports the Diels-Alder functionalization, where methylene carbon atoms are generated by the cycloaddition of butadiene.

Elemental analysis shows that the amount of residue detected after complete oxidation of the samples varies between 6.8 and 10.5 %, and this is in agreement with the results obtained by TGA in air atmosphere.

Table 2. Bulk composition obtained from elemental analysis.

Sample	C (wt. %)	H (wt. %)	O (wt. %)	S (wt. %)	Residue (wt.%)	O/C	S/C
Pristine CNT	88.34	0.32	0.7	-	10.6	0.008	-
Exp. 3	79.92	1.56	8.49	0.73	9.3	0.106	0.009
Exp. 6	77.69	2.14	14.29	0.93	6.8	0.184	0.012
Exp. 9	79.71	1.45	7.99	0.44	10.4	0.100	0.006
Exp. 12	77.98	1.80	11.15	0.55	8.5	0.143	0.007

3.4. Potentiometric analysis

Previous studies on the Diels-Alder functionalization of CNF with sulfolene resulted in material that exhibited an acidity increase relative to pristine CNF [20]. This observation, associated to a high amount of oxygen on the CNT surface prompted us to investigate the influence of functionalization on the acid-base properties of CNT. The acidity was determined by potentiometric titration following a method similar to that previously

10

described by Gorgulho et al [21]. A suspension of 100 mg of CNT in 35 mL of 0.01 M HCl was titrated with 0.1 M NaOH. The volume of NaOH determined for the last inflection point of the titration curve (Fig. 4) was used to calculate the number of H^+ equivalents present in 100 mg of CNT modified in experiments 3, 6, 9 and 12 (Table 3).

The titration curve (Fig. 4) for pristine CNT showed that the volume of NaOH necessary to reach pH 7 matches the amount required to titrate the pre-added HCl (reference test). However pristine CNT exhibit an inflection point at pH 3.3 that is probably due to the presence of aluminum carbide, previously identified as a contaminant in the Nanocyl CNT [22, 23]. This material may be formed during the industrial process used for the preparation of the CNT.
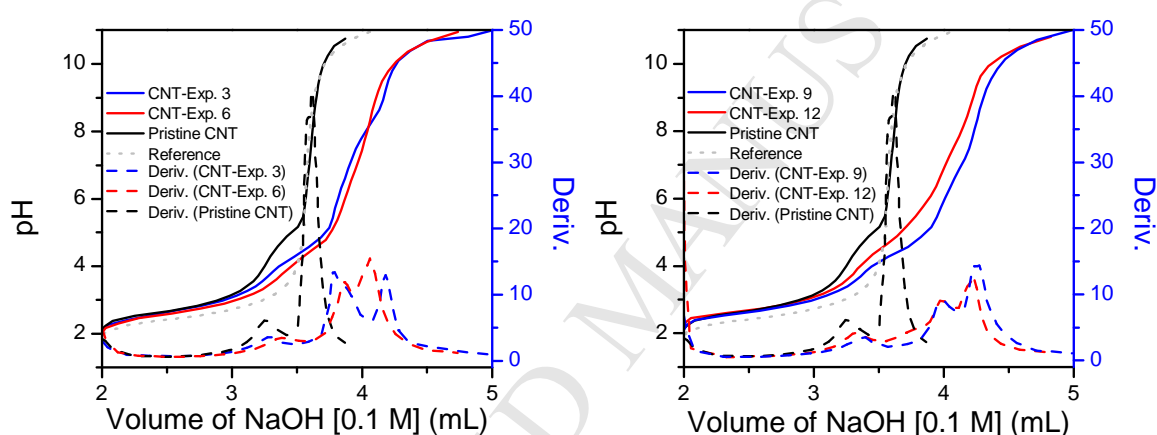

Fig. 4 - Titration curve of pristine CNT, functionalized CNT (CNT-Exp. 3, 6, 9 and 12) and reference test.

The increase in acidity of the functionalized CNT relative to pristine CNT was evident. A plausible source for this acidity may be the presence of sulfonic and carboxylic acids. The later could arise from oxidation of the original alkenes formed by Diels-Alder cycloaddition, promoted by the long heating periods in contact with air.

Table 3. H^+ equivalents quantified for 100 mg of sample using the last inflection point of the titration curve (see Fig. S4 in supplementary data).

Exp.	H^+ equiv. (mmol)	Volume of 0.1M NaOH (mL)
3	0.42	4.20 ± 0.03
6	0.41	4.10 ± 0.05

9	0.43	4.25 ± 0.05
12	0.42	4.20 ± 0.03
Pristine CNT	0.36	3.60 ± 0.03
Reference	0.36	3.60 ± 0.02

As mentioned before, the thermal decomposition of 3-sulfolene in 1,3-butadiene also releases sulfur dioxide. Kisamori et al [24] demonstrated that activated carbon fibers can catalyze the oxidation of SO_2 to SO_3 subsequently hydrated to H_2SO_4. The reaction of sulfur dioxide with water and oxygen can also be catalyzed by CNT [25] leading to sulfuric acid. The formation of SO_3 as a precursor of H_2SO_4 will allow the sulfonation of CNT under milder temperature conditions (100-150 ºC) when compared to the reaction conditions reported by Yu et al [26] (250-300 ºC). The presence of sulfuric acid in solution was detected for Exp. 6 and 12 by addition of benzyl amine. Benzyl ammonium sulfate was isolated and fully characterized. Elemental analysis allowed to determine that 2 moles of amine were associated with 1 mole of sulfuric acid. This observation further supports that the sulfur content of the modified CNT (detected by elemental analysis), may be due to sulfonation of the pristine CNT, present as sulfonic acid and in part responsible for the surface acidity.

3.5. TPD results

The CO and CO_2 TPD profiles for the CNT modified at 100 ºC and 150 ° C, presented in Fig. 5A) and B) respectively, are very similar for all the samples. The main feature of all the CO_2 release is a band with maximum at ~320-325 ° C. Apart from that, there is a small shoulder at low temperature (between 100 and 150 ° C) and a broad band at higher temperatures (between 450 and 800 ºC), showing a shoulder at 470-785 ° C for samples treated at 150 ºC. The CO release curves show a main band at ~340-360 ° C, a minor band at lower temperatures (~100-120 ° C), and a broad band at higher temperatures.

The main band at 320-360 ° C in both CO and CO_2 TPD profiles can be assigned to the decomposition of carboxylic anhydrides. These anhydride groups may result from the condensation reaction of two adjacent carboxylic acids either during the functionalization process or at lower temperatures, during the TPD experiment. Each carboxylic anhydride unit releases one molecule of CO_2 and one of CO. Indeed, for the four analysed samples, the main bands in the CO and CO_2 TPD profiles show similar areas, i.e., CO and CO_2 are released in an equimolar amount, as expected from the decomposition of carboxylic

anhydrides. The temperatures observed for the release of CO are higher by 20-40 ° C than those registered for CO_2 release, as generally reported in the literature for decomposition of carboxylic anhydrides [27]. The CO and CO_2 TPD profiles were deconvoluted independently. The amount of carboxylic anhydrides was calculated from the deconvolution of the lower CO_2 or CO TPD profiles and corresponds to 0.373 mmol g^{-1} for Exps. 3 and 9, 0.721 mmol g^{-1} for Exp. 6 and 0.563 mmol g^{-1} for Exp. 12 (see Table S2).

There is a small shoulder in the CO_2 TPD profiles between 100 ℃ and 300 °C, where individual (non-condensed into anhydrides) carboxylic acids would be expected to be released as CO_2. The remaining CO and CO_2 desorption signals can be assigned to minor quantities of lactone, quinone and other carbonyl groups, possibly arising from oxidation of the CNT edges (more reactive to oxidation than the basal planes). The possibility that these were pre-existing groups in the pristine CNT can be ruled out as blank TPD experiments of the pristine samples (not shown) yielded very low or no CO or CO_2 evolution in the whole temperature range studied.
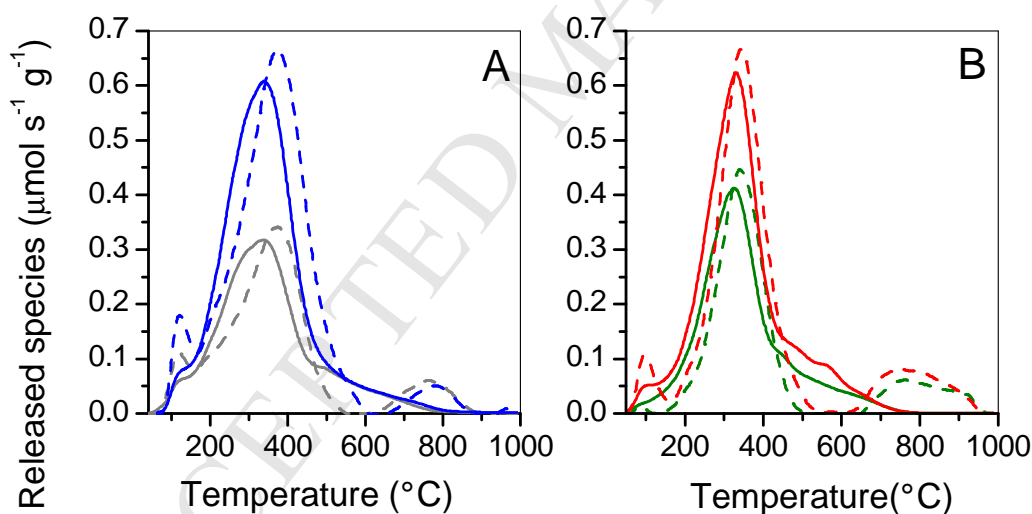

Fig. 5 - TPD profiles of samples prepared at A) 100 ° C, and B) 150 ° C. The released amounts of CO and CO_2 are shown in dashed and solid lines, respectively. The colour code is: CNT-Exp. 3 (grey), CNT-Exp. 6 (blue), CNT-Exp. 9 (green), and CNT-Exp.12 (red).

3.6. XPS analysis

3.6.1 Survey spectra

The low resolution survey spectra of the samples under study is presented in Fig. 6 and Table 4 shows the corresponding atomic composition. The results are quantified in atomic percentage (at. %) and in weight percentage (wt. %). The trends observed in the TGA experiments are in good agreement with the results of XPS analysis: CNT-Exp. 3 and 9, with similar C content, also show similar weight loss at 800 ºC, CNT-Exp. 12 and 6, with lower and decreasing C content show higher, increasing weight loss at 800 ºC. The highest oxygen content is observed for the CNT functionalized in CNT-Exp. 6. Treatments with higher CNT:sulfolene ratios (1:2 vs. 1:1) or longer reaction times (7 vs. 4 days) yield higher O/C ratios. The S/C ratios measured show a higher S surface content for CNT treated at lower temperature (S/C approximately 0.02 at 100 ºC *vs* 0.01 at 150 ºC).

The XPS characterization data supports the similarity of the surface composition of the CNT from the blank experiments (Blank 1 and Blank 2) and from the CNT:sulfolene reactions under nitrogen atmosphere (Exp. 6N and 12N). The CNT surface is only mildly affected by heating in air without sulfolene or by heating with sulfolene under nitrogen atmosphere. The combination of sulfolene and air is crucial for the chemical transformations occurring on the CNT surface. This can be explained if the reactive alkene function, created on the external layer of the CNT by Diels-Alder reaction, is rapidly oxidized in the presence of air. The apparent absence of Diels-Alder cycloaddition when the reaction is performed under nitrogen atmosphere (Exp. 6N and 12N) may be due to an equally fast retro-Diels-Alder, preventing the adduct to remain on the CNT surface. A fastest process, such as the oxidation of the newly formed double bond, would lead to a stable single bond, blocking the retro-Diels-Alder reaction.
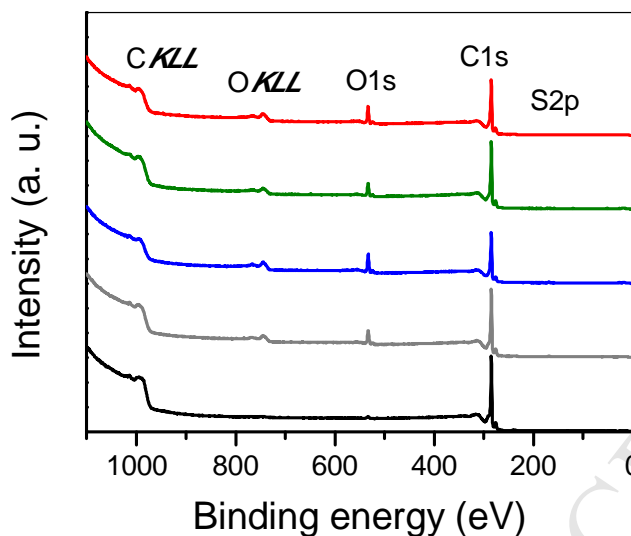
14

Fig. 6 - XPS survey spectra of pristine CNT (black), exp. 3 (grey), exp. 6 (blue), exp. 9 (green), and exp.12 (red).

Table 4. Surface composition calculated from XPS survey spectra.

Sample	C (at. %)	O (at. %)	S (at. %)	C (wt. %)	O (wt. %)	S (wt. %)	O/C (from wt.%)	S/C (from wt.%)
Pristine CNT	98.64	1.36	-	98.20	1.80	-	0.018	-
Exp. 3	91.03	8.36	0.61	87.70	10.73	1.57	0.122	0.018
Exp. 6	87.08	12.24	0.68	82.78	15.50	1.72	0.187	0.021
Exp. 6N	97.59	2.20	0.21	96.54	2.90	0.56	0.030	0.006
Blank1	98.02	1.98	-	97.38	2.62	-	0.027	-
Exp. 9	92.31	7.34	0.35	89.60	9.49	0.90	0.106	0.010
Exp. 12	88.81	10.86	0.33	85.27	13.89	0.85	0.163	0.010
Exp. 12N	96.72	3.12	0.17	95.47	4.10	0.43	0.043	0.005
Blank2	96.47	3.53	-	95.35	4.65	-	0.049	-

3.6.2 High resolution spectra

Figure 7 shows background-corrected, normalised, high resolution O1s core level spectra for the treated materials. All the bands have similar shape, although those corresponding to treatments at 150 ºC are slightly narrower and also slightly shifted to higher binding energies (BE) than those corresponding to treatment at 100 ºC. If the reaction proceeded as expected, and the CNT were decorated exclusively with carboxylic acids, the expected O1s band

15

would consist of two components at BE~532 eV (doubly-bonded oxygen in HO-C=O) [28] and ~534 eV (singly-bonded oxygen in HO-C=O) in 1:1 ratio. However, when the bands are deconvoluted into two components (see Fig. 7B), the former is higher than the latter. This excess of doubly-bonded oxygen can be explained by the presence of carboxylic anhydrides and/or of carbonyl groups and quinones from oxidation of the CNT.
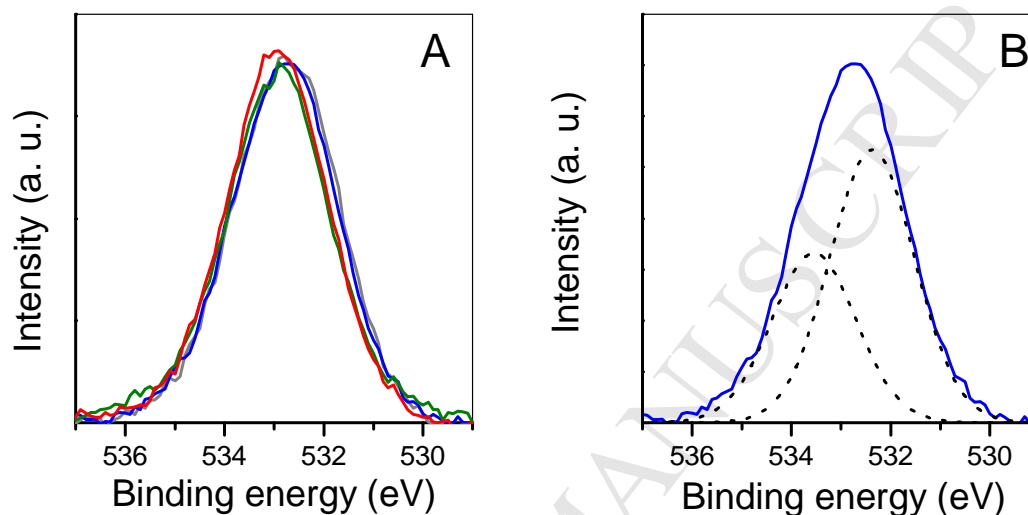

Fig. 7 - A) Background-corrected, normalized high resolution O1s core level XPS spectra of pristine CNT (black), CNT-Exp. 3 (grey), CNT-Exp. 6 (blue), CNT-Exp. 9 (green), and CNT-Exp.12 (red). B) Deconvolution of the spectrum for CNT-Exp. 6 into 2 components (dotted lines).

The high-resolution S2p core level spectra are shown in Fig. 8. The S2p spectra for samples obtained at the same temperature are similar. Those corresponding to higher temperatures are shifted by 0.5 eV to higher BEs and wider than those obtained at 100 ºC. The low signal-to-noise ratio makes deconvolution of S2p spectra not reliable. However, the position of the bands (~168.5-169.0 eV) suggests the presence of sulfonic acids [29].
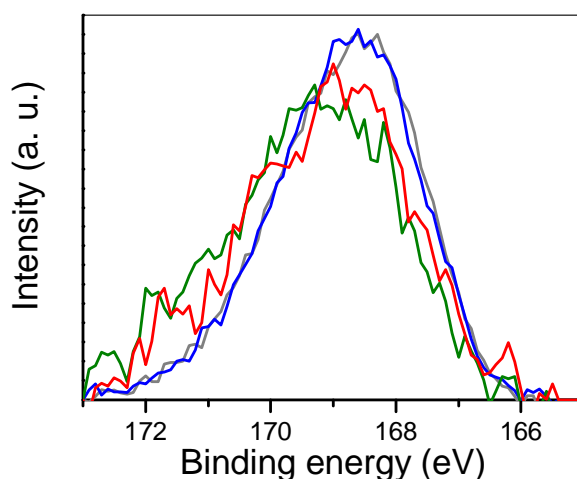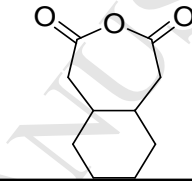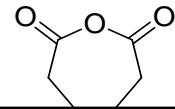
16

Fig. 8 - Background-corrected, normalized high resolution S2p core level XPS spectra of CNT-Exp. 3 (grey), CNT-Exp. 6 (blue), CNT-Exp. 9 (green), and CNT-Exp.12 (red).

3.7. Combined data analysis for Exp. 6

The characterization studies clearly indicate that Diels-Alder reaction is accompanied by extensive oxidation, induced by oxygen present in air. The functionalization conditions used in experiment 6 can be considered as the most convenient approach for the cycloaddition of butadiene to the CNT surface. Combining CNT and sulfolene in a 1:2 mass ratio and heating at 100 ºC for 7 days, resulted in the highest weight loss by TGA (23 % at 800 ºC under nitrogen atmosphere and 32 % at 500 ºC in air). A comparative analysis of the results obtained by the different characterization techniques is presented for this functionalized material.

The elemental analysis (Table 2) confirms that sulfur, absent in the pristine CNT, is present in the sample, arising from sulfonation of the CNT surface. A high content of oxygen (30-fold molar excess over sulfur) reflects a considerable extent of functionalization accompanied by oxidation. The presence of hydrogen supports the cycloaddition of butadiene. A similar trend is observed by XPS, where oxygen and sulfur were identified on the CNT surface. The results of the titration experiment show a low acidity for the functionalized CNT (0.05 mmol%) and this can be assigned to carboxylic and sulfonic acids formed by side-reactions. All the evidence suggests the presence of anhydride as the major functional group on the CNT surface. Theoretical calculations in model systems indicate that

17

the Diels-Alder addition of butadiene to the cyclohexene moiety grafted on the CNT after the first round of cycloaddition is a thermodynamically favoured process. The high amount of hydrogen determined by elemental analysis supports these findings as this may arise from a reaction of part of the alkene groups incorporated during the functionalization, with an additional molecule of butadiene, prior to oxidation. Figure 9 summarizes our proposal for the functional groups identified and quantified by elemental analysis and potentiometric titration of the functionalized CNT. The mmol % of each chemical group for CNT-Exp. 6 was calculated from the elemental composition (H, O and S) and the acidity was calculated by titration. The functional groups already present in the pristine CNT were not considered, as the percentage of hydrogen and oxygen used in the elemental analysis calculations was subtracted from the corresponding values for CNT-Exp. 6 (details in supplementary data).

	SO_3H	COOH		
From EA.	0.029	-	0.135	0.105
From titration	-	0.021**	-	-

CNT* The functional groups present in the pristine CNT were not considered as the H and O % was subtracted from the corresponding values for CNT-Exp. 6 in the calculations.

** H+ from COOH calculated from the total acidity of 0.05 mmol determined by titration, assuming that 0.029 mmol can be assigned to sulfonic acid (EA).

Fig. 9 - Functional groups identified for Exp. 6 by elemental analysis (EA) and potentiometric titration quantified in mmol %.

Deconvolution of the TPD CO_2 and CO desorption profiles (Fig. 10) shows that the major contribution arises from the anhydride functional group as these signals, at a desorption temperature in the 320-360 °C range, are generated in a 1:1 molar ratio. The remaining CO and CO_2 desorption signals can be assigned to minor quantities of carboxylic acid and also to lactone, quinone and carbonyl groups, possibly arising from oxidation of the CNT edges. The molar ratio of anhydride indicates that approximately 18 moles of this functional group are present, compared to 1-2 moles for each of the remaining groups. The relative amount of oxygen is in accordance with the XPS results and supports the observation that anhydride is

the major functional group present on the surface. This evidence, together with the low acidity of the functionalized CNT accessed by titration, indicates that adjacent carboxylic acids generate anhydrides under the reaction conditions used for the experiment.
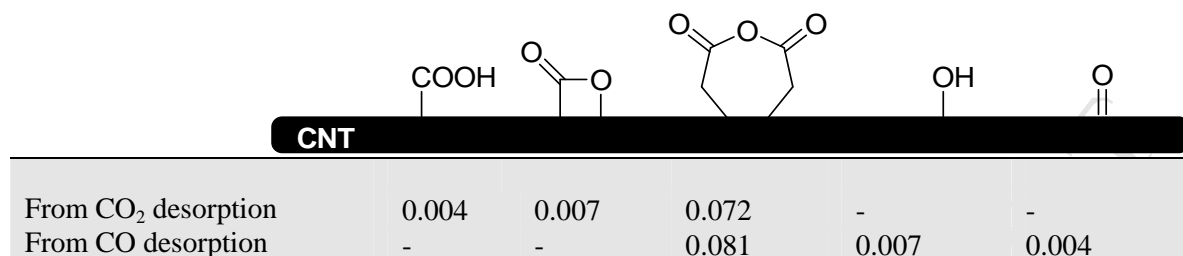

	COOH	O=C–O	anhydride (ring)	OH	O
From CO$_2$ desorption	0.004	0.007	0.072	-	-
From CO desorption	-	-	0.081	0.007	0.004

Fig. 10 - Functional groups identified for Exp. 6 by deconvolution of the TPD profiles and quantified in mmol %.

Figure 11 summarizes all functional groups that can be expected on the CNT-Exp. 6 surface and their abundance in mmol %. These values were estimated from elemental analysis, potentiometric titration and TPD data. The XPS results were not considered for these calculations as they correspond exclusively to a surface analysis that depends on the x-ray surface penetration. Nevertheless the XPS data fully supports the predominance of anhydride and the presence of minor amounts of sulfonic and carboxylic acids, carbonyl groups and lactones. The TPD was used to estimate the ratio of the functional groups detected from CO and CO$_2$ desorption.

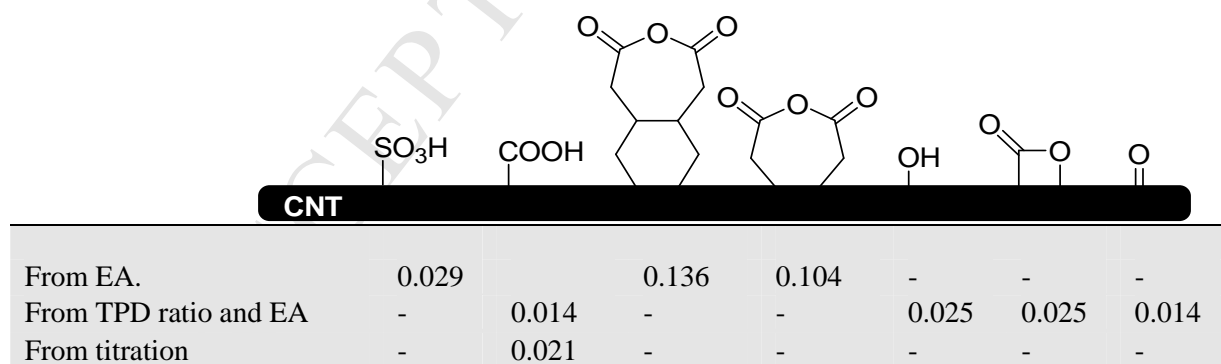|	SO$_3$H	COOH	anhydride (fused ring)	anhydride (ring)	OH	O=C–O	O
From EA.	0.029		0.136	0.104	-	-	-
From TPD ratio and EA	-	0.014	-	-	0.025	0.025	0.014
From titration	-	0.021	-	-	-	-	-

Fig. 11 - Functional groups (mmol %) identified for Exp. 6.

Among the different chemical moieties detected on the modified CNT surface, the anhydride functional group it is by far the most abundant. A grafting density of 4.2 mmol g^{-1} was calculated for this group, using the chemical composition presented in Fig 11 (supplementary

19

data). These values would also result in a predicted 36.3 % functionalization, comparable with the experimental weight loss of 32.2 % registered by TGA in air atmosphere.

3.8. Theoretical studies

A previous report on a (5,5) CNT system predicted that Diels-Alder reactions with CNT were endothermic by at least 2 kJ mol^{-1} [30]. In contrast, in our calculations, Diels-Alder reactions are thermodynamically feasible for the systems studied, with exothermic reaction energies: -1.1 and -2.1 kJ mol^{-1} for (5,5) and (9,0) respectively, and barely exothermic for others like the (10,0), with a reaction energy of -0.02 kJ mol^{-1}. This discrepancy is probably due to the different Hamiltonians used: we modelled a 1D periodic system [31, 32] while in the previous work [30] a finite section of a CNT was used. Chemical functionalization affects the frontier orbitals of extended Csp^2 systems, which are delocalized, and consequently better represented by a periodic Hamiltonian. On the other hand, finite models are better suited to calculate the energetics of isolated functional groups.

In order to get further insight, we used a periodic (9,0) CNT as a model system to explore the energetics of a number of other reactions, namely the chemisorption of 3-sulfolene, a second butadiene cycloaddition and different oxidation reactions. The chemisorption of 3-sulfolene was found to be slightly endothermic (0.7 kJ mol^{-1}), which indicates that the direct Diels-Alder cycloaddition of 1,3-butadiene to CNTs is more likely than 3-sulfolene chemisorption followed by rearrangement.

The Diels-Alder cycloaddition was found to be much more exothermic (-12 kJ mol^{-1}) on the double bond generated from a prior cycloaddition (**2**, Fig 12) than on a pristine (9,0) CNT (-2.2 kJ mol^{-1}), (**1**, Fig. 12), which shows that CNTs are not good dienophiles. The cyclohexene double bond can also be oxidized exothermically to give a cyclohexane epoxide (**4**, Fig. 12) (-6.9 kJ mol^{-1}). Under the experimental conditions that were used, the second and subsequent cycloadditions and the oxidation on the cyclohexene double bond may happen competitively. The predominant concentration of cyclic anhydrides observed experimentally indicates that oxidation ultimately may exhaust the alkene groups generated by the Diels-Alder cycloaddition. Different pathways to yield a cyclic anhydride can be envisaged. Fig. 12

20

summarizes a number of possible reaction intermediates with corresponding energetics from quantum chemical models (for simplicity, reactions were computed with respect to water and oxygen). Interestingly, the only reaction that was found to be endothermic (1.2 kJ mol^{-1}) was the cyclization step that transforms the dicarboxylic acid (**7**, Fig. 12) to the cyclic anhydride (**8**, Fig. 12). In contrast, the transformation from **2** to the cyclic anhydride form was found to be a much more exothermic process (-39.4 kJ mol^{-1}). Note that functional groups resulting of successive cycloaddition reactions, like compound **3**, are expected to be involved in similar oxidation processes, ultimately incorporating equivalent adipic anhydride moieties (**9**, Fig. 12).
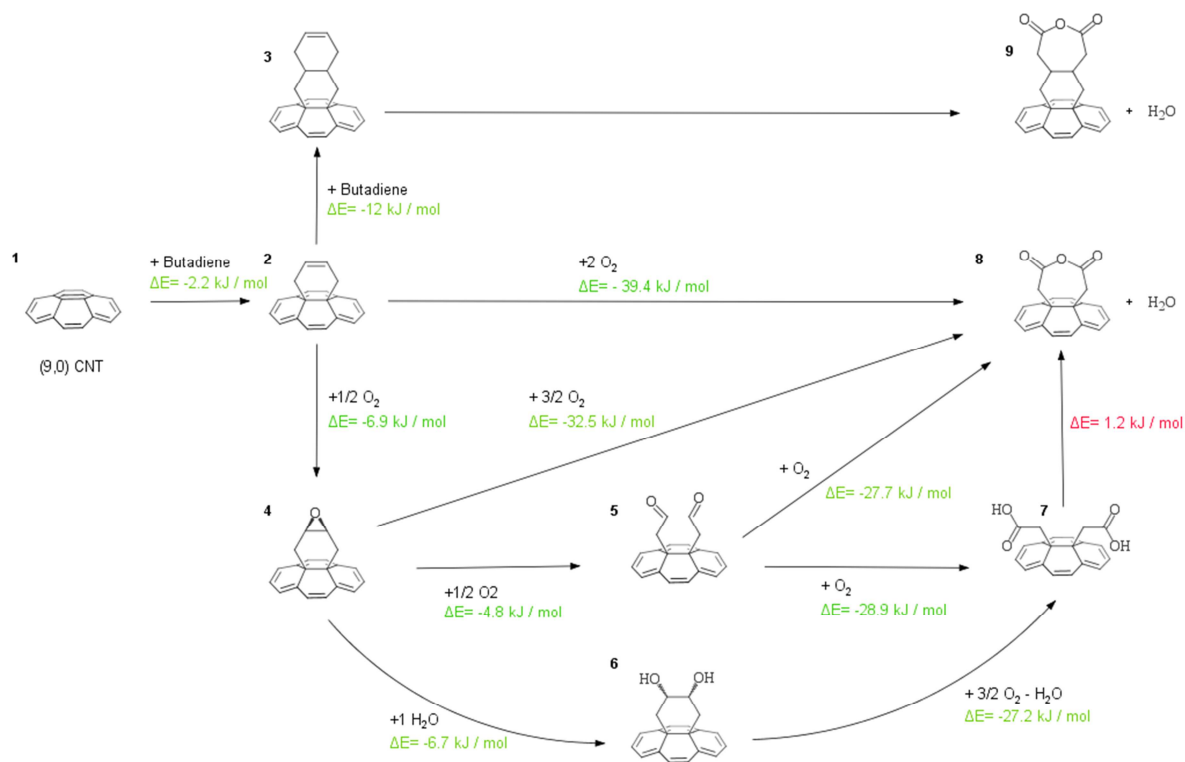

Fig. 12 - Diels-Alder cycloaddition, subsequent oxidation products and corresponding B3LYP/6-31G(p,d) energies for a periodic (9,0) CNT represented as a pyrene moiety. Negative energies, in green, indicate exothermic reactions while positive energies, in red, indicate endothermic reactions

4. Conclusion

In summary, this work presents a simple route to prepare CNT decorated with the anhydride function. The experimental evidence is consistent with a mechanism that involves an initial Diels-Alder cycloaddition to the CNT surface of butadiene generated *in situ* from sulfolene upon heating in diglyme. A cyclohexene ring is grafted on the nanotube wall and rapidly evolves either to the oxidized product, in the presence of atmospheric oxygen, or further incorporates a second butadiene unit. Both products present comparable thermodynamic stability, according to theoretical calculations. Oxidation proceeds until all the alkene groups are consumed, ultimately leading to the anhydride moiety in a chemical sequence predicted as highly exothermic. The oxidation process is crucial in order to stabilize the Diels-Alder adduct on the CNT surface. This is supported by the experimental observation that the highly conjugated carbon surface does not retain the cyclohexene unit when the reaction is performed under nitrogen atmosphere. Heating the CNT in air, but in the absence of sulfolene, resulted in a negligible oxidation extent.

The Diels-Alder reaction was performed under different experimental conditions: temperature of 100 ºC and 150 ºC, reaction time of 2, 4 and 7 days and CNT:sulfolene mass ratios of 1:1 and 1:2. A very good grafting density of anhydride was obtained when the reagents were combined in a 1:2 mass ratio and the diglyme suspension was heated at 100 ºC for 7 days.

Elemental analysis and XPS confirm that a high content of oxygen was incorporated in the carbon material and TPD further supports that most of the oxygen is in the form of anhydride groups. A minor contamination with sulfonic acids may arise from sulfonation, as sulfur trioxide and sulfuric acid are also formed as by-products. The reduced acidity of the functionalized material, as determined by potentiometric titration, also indicates a low concentration of sulfonic and carboxylic acids. Other minor contaminants such as phenols, ketones and lactones may also be formed (from XPS and TPD data) but the anhydride is by far the major component, present in approximately 18 fold molar excess over the remaining chemical groups and a grafting density of 4.2 mmol g^{-1}.

Quantum chemical calculations on periodic carbon nanotubes were used to explore the energetic feasibility of the different reactions to rationalize experimental observations.

Diels-Alder reactions on CNT were found to be weakly exothermic, which supports the presence of retro-Diels-Alder reactions, but subsequent reactions, such as direct oxidation or a second cycloaddition, involved much higher energies and are more likely. The overall transformation of a cyclohexene moiety to a cyclic anhydride was found to be the most exothermic process (-39.4 kJ mol^{-1}) which is coherent with the high concentration of these functional groups found in the experiments.

The Diels-Alder cycloaddition of butadiene to carbon nanotubes in the presence of atmospheric oxygen is a viable option for the production of anhydride-functionalized CNT. The anhydride group can be used as a reactive precursor for different derivatives, incorporated through nucleophilic addition namely using primary or secondary amines. Tailoring the properties of nanomaterials requires a judicious selection of the functional groups to be appended on their surface and the anhydride unit is a valuable asset for this purpose.

Acknowledgments

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