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Chemical oxidation of multiwalled carbon nanotubes

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ABSTRACT

The effect of oxidation on the structural integrity of multiwalled carbon nanotubes through acidic (nitric acid and a mixture of sulfuric acid and hydrogen peroxide) and basic (ammonium hydroxide/hydrogen peroxide) agents has been studied. In order to purify the as-received material, a non-oxidative treatment (with hydrochloric acid) was also applied. Electron microscopy and thermogravimetric analysis clearly revealed that the nitric acid-treated material under reflux conditions suffered the highest degree of degradation, such as, nanotube shortening and additional defect generation in the graphitic network. Basic oxidative treatment led to the complete removal of amorphous carbon and metal oxide impurities but the structural integrity was found to be intact. X-ray photoelectron spectroscopy was employed to confirm the different functionalities produced for each oxidation agent, whereas titration measurements determined the relative concentration of carboxylic functions onto the graphitic surface. Moreover, a general relationship between the chemical treatment and the amount of non-graphitic carbon was established by means of Raman spectroscopy measurements. The possibility of controlling the required amount of functionality, carboxylic and hydroxyl, via these oxidation procedures is discussed.

1. Introduction

Carbon nanotubes (CNTs) have raised much interest during the recent years due to their inherent extraordinary electrical and mechanical properties [1]. For some of the potential applications of this carbon allotrope, highly purified material is necessary, whereas the chemical inertness of the graphitic network presents a major challenge when it comes to composite material fabrication. The oxidation of CNTs either by wet chemical methods [2–9], photo-oxidation [10,11], oxygen plasma [12], or gas phase treatment [13] has gained a lot of attention in an attempt to purify and also enhance the chemical reactivity of the graphitic network. Typically, through the above harsh treatments, the pristine CNTs can be effectively purified and oxygen-containing groups, mainly carboxyl and hydroxyl, have been found to decorate the graphitic surface. The presence of oxygen-containing groups facilitates the exfoliation of CNT bundles, and increases the solubility in polar media [2,3]. This, in turn, affects the processing of CNTs and increases the possibility of further modification/functionalisation depending on application [14,15]. Concerning the use of CNTs as reinforcements in composite materials, the incorporation of oxygen-containing functionalities onto the graphitic surface is a very crucial step for the enhancement

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of interfacial adhesion. As a result, the unique mechanical and electrical properties of CNTs can be transferred to the properties of CNT-based composites.

The effects of the commonly used acid and/or air oxidation at elevated temperature on CNT surface morphology have been well documented in previous studies. Independent studies by Hu et al. and Martinez et al. [5,6] have found that treating single-wall CNTs with hot nitric acid leads to an efficient elimination of metal impurities and amorphous graphitic platelets. It is interesting to note that during that treatment, intercalation process of nitric acid molecules into the CNT bundle structure was found to take place [16], which is accompanied by bundle exfoliation and etching of the carbonaceous material. This process leads to the formation of additional amorphous carbon nanoparticles covering the remaining smaller bundles of CNT. In order to eliminate amorphous carbon, the nitric acid-treated material has to be annealed to 900 °C [6].

Concerning the oxidation reaction of sulphuric acid/hydrogen peroxide mixture (piranha) with CNTs, Ziegler et al. [7] have shown that the one-dimensional nanostructures can be cut in a controlled manner under specific conditions. At high temperatures, piranha was found to attack existing damage sites, generating vacancies in the graphene sidewall, and consume the oxidized vacancies to yield shorter nanotubes. Increased reaction time results in increasingly shorter tubes. However, significant sidewall damage also occurs as well as selective etching of the smaller diameter nanotubes. On the other hand, room-temperature piranha treatments showed the capability of attacking existing damage sites with minimal carbon loss, slow etch rates, and little sidewall damage.

The detailed observation and analysis of Zhang et al. [8] showed that the defects on CNTs, original or newly created, play a crucial role in the oxidation process. Following the defect-generating and defect-consuming steps, they explored the possible oxidation reactions and predicted the intermediate and final products. The presence of defects on CNT surface not only affects the structural stability of oxidized material but also determine its electronic properties. For instance, the wet oxidation experiment of Kovtyukhova et al. [17] showed that the disruption of the conjugated network of the tubes leads to an appreciable increase of the resistivity of about three-orders of magnitude.

On the other hand, there is very little information on the structural alteration of graphitic material under basic oxidative treatments. Recently, Kim et al. [18] have treated MWCNTs with an ammonium hydroxide/hydrogen peroxide mixture and showed that the resulting composite with epoxy as matrix had enhanced electrical conductivity due to the minor damages of the graphitic sidewalls.

In the present work, we perform a systematic study of the chemical oxidation of MWCNTs treated by various reagents that possess different degrees of oxidation power. In addition, a comparative study of acidic and basic oxidative treatments on the structural integrity of CVD grown MWCNTs, is made. Regulation of the amount of oxygen onto the CNT sidewalls is a prerequisite for building certain functional nanoscale structures and devices under special conditions. To modify the CNT surface, we treated the pristine material with concentrated HCl [19], hot nitric acid [20], piranha mixture [21,22] and ammonium hydroxide/hydrogen peroxide mixture. Treated MWCNTs were compared with the pristine material with purity above 80 wt%. Oxidised MWCNTs were tested by X-Ray photoelectron spectroscopy in order to quantify and qualify the nature of oxygen present on the MWCNT surface. The characterisation of the oxidised MWCNTs was completed by thermogravimetrical analysis, Raman spectroscopy and scanning/transmission electron microscopy (SEM/TEM) and showed the prospect of building the desirable oxygen-containing functionality onto the MWCNT surface under controlled conditions.

2. Experimental section

MWCNTs synthesized by CCVD of purity around 80% and of diameter ranging between 10 and 20 nm were employed in this study. The specific batch was provided by Nanocyl (Belgium). Purification and chemical oxidation of MWCNTs was carried out with four different agents using chemicals supplied by Aldrich.

Treatment 1: In this step the as-received MWCNTs were treated with hydrochloric acid, which is an established method for the removal of impurities. One grams of MWNCT was placed in a 500 ml round bottom flask and 200 ml of HCl was added. The mixture was stirred using magnetic stirrer for 2 h, then diluted in water, filtered, washed with deionised water and then dried in vacuum at 40 °C overnight.

Treatment 2: 0.3 g of the as-received MWCNTs were dispersed in 25 ml of the nitric acid (65 wt%) in a 100 ml round bottom flask equipped with a condenser and the dispersion was refluxed under magnetic stirring for 48 h. After that, the resulting dispersion was diluted in water and filtered. The resulting solid was washed up to neutral pH, and the sample was dried in vacuum at 40 °C overnight.

Treatment 3: 0.3 g of the as-received MWCNTs was dispersed in 25 ml of the piranha (mixture of sulphuric acid 96 wt% and hydrogen peroxide 30 wt% in ratio 70:30) in a 100 ml round bottom flask equipped with a condenser and dispersion was kept for 5 h. After that, the resulting dispersion was diluted in water and filtered. Then the resulting solid was washed up to neutral pH and the sample was dried in vacuum at 40° C overnight.

Treatment 4: 0.3 g of the as-received MWCNTs was dispersed in 25 ml of the mixture of ammonium hydroxide (25 wt%) and hydrogen peroxide (30 wt%) in ratio 50:50 in a 100 ml round bottom flask equipped with a condenser and the dispersion was heated to 80 °C and kept for 5 h. After that, the resulting dispersion was diluted in water and filtered. Then the resulting solid was washed up to neutral pH and the sample was dried in vacuum at 40 °C overnight.

The modified CNT material was quantitatively analyzed by titration to determine the COOH concentrations on the surface of the treated CNTs. In a typical experiment, the carboxylated CNTs were added into a 25-ml 0.04 N NaOH solution and stirred for 48 h to allow the solid CNT material to equilibrate with the NaOH solution. The mixture was titrated with a 0.04 N HCl solution to determine the excess NaOH in the solution and the concentration of the carboxylates on CNTs.

The XPS experiments were carried out in an ultra high vacuum system equipped with a SPECS LHS-10 hemispherical electron analyzer. A constant analyzer pass energy of $E_p = 36$ eV and the unmonochromatized Al Kα (1486.6 eV) line were used in all XPS measurements. The full width at half maximum of the C1s XPS peak, was 1.1 eV. The XPS core level spectra were analyzed with a fitting routine, which can decompose each spectrum into individual mixed Gaussian–Lorentzian peaks after a Shirley background subtraction. The determined standard deviation in XPS core level peak positions is about ±0.05 eV. The scanning electron microscopy observations were made on a Leo 1530 FESEM, Gemini scanning microscope. The dispersions of the MWCNTs in dimethylformamide were placed on mica substrates. All specimens were sputtered with gold before imaging. The transmission electron microscopy observations were made on a JEM-1011 microscope. The dispersions of the MWCNTs in dimethylformamide were casted on carbon grids. Thermogravimetrical studies were performed on a TGA2950 (TA instruments) under nitrogen at 10 °C/min in temperature range from 30 to 650 °C. Raman spectra were recorded using a microscope equipped triple monochromator combined with a peltier cooled charge couple device detector system. The spectra were acquired in the back-scattering geometry, while for excitation the 514.5 nm line of an Ar^+ laser was focused on the sample by means of an 80× objective at a power of ~2 mW, measured directly before the sample. The phonon frequencies were obtained by fitting Lorentzian lineshapes to the experimental peaks after background substraction.

3. Results and discussion

As already mentioned [2–9], acidic oxidative treatment to the CNT material may cause major alteration in its structural properties. Especially, pristine CNTs synthesized by the CVD method exhibit significant lack of conjugation and some precaution should be taken for the purification/surface modification of the material. The presence of dangling bonds at the as-produced material results in a graphitic network with a higher defect density [23]. This may lead to an appreciable etching of the carbon material even under moderate oxidation conditions. In order to transfer the optimum properties of MWCNTs to their composites, the main challenge is the preparation of highly purified material with no appreciable structural damage.

3.1. *Colloidal stability of CNT suspensions*

As is well known [24], CNTs have a strong tendency to agglomerate due to their nano size and their respective high surface energy. However, the grafting of chemical functionalities on the CNT surface, such as carboxylates, imparts negative charges and, therefore, creates the electrostatic stability required for a colloidal dispersion. This is indeed confirmed since all chemical treatments applied, with the exception of HCl, were found to improve the dispersion stability (Fig. 1) of CNTs in dimethylformamide and many common polar media, such as ethanol, methanol, isopropanol and water.

3.2. *Electron microscopy*

Scanning and transmission electron microscopy was used to detect possible morphological changes on MWCNT specimens depending on the severity of each treatment. As shown in Fig. 2a, no changes in the morphology are detected in the case of non-oxidative treatment with HCl. The tubes do not seem to be harmed at all, as the average length of each nano-object ranges above 1 μm long. After oxidation with strong oxidants such as nitric acid (Fig. 2b and f) and piranha (Fig. 2c), some bundles appear exfoliated and curled. Especially in the case of nitric acid-treated material, severe fragmentation (the average length was estimated to be ~700 nm) of the CNT structure takes place as clearly indicated in Fig. 2f. In addition, a major alteration of the structural integrity of CNTs is observed. Thus, the treatment of CNTs with strong oxidizing agents causes severe etching of the graphitic surface of the material, leading to tubes of shorter length with a large population of disordered sites. The above observations are in full agreement with the Raman spectroscopic results presented below. The presence of a large amount of oxygen-containing functionalities at the defect sites support the colloidal stability of the acid-treated material in polar media.

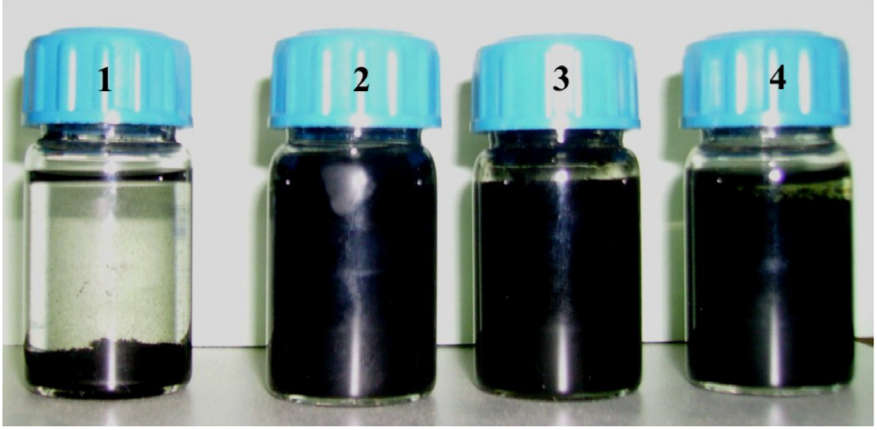

Fig. 1 – Pictures of the dispersion of the MWCNTs (0.2 g) in DMF (12 ml). 1-HCl-treated MWCNTs; 2-nitric acid-treated MWCNTs; 3-piranha treated MWCNTs; 4-MWCNTs after non-acidic treatment. Samples were kept for 100 days. MWCNTs were dispersed in DMF by sonication for 2 min.

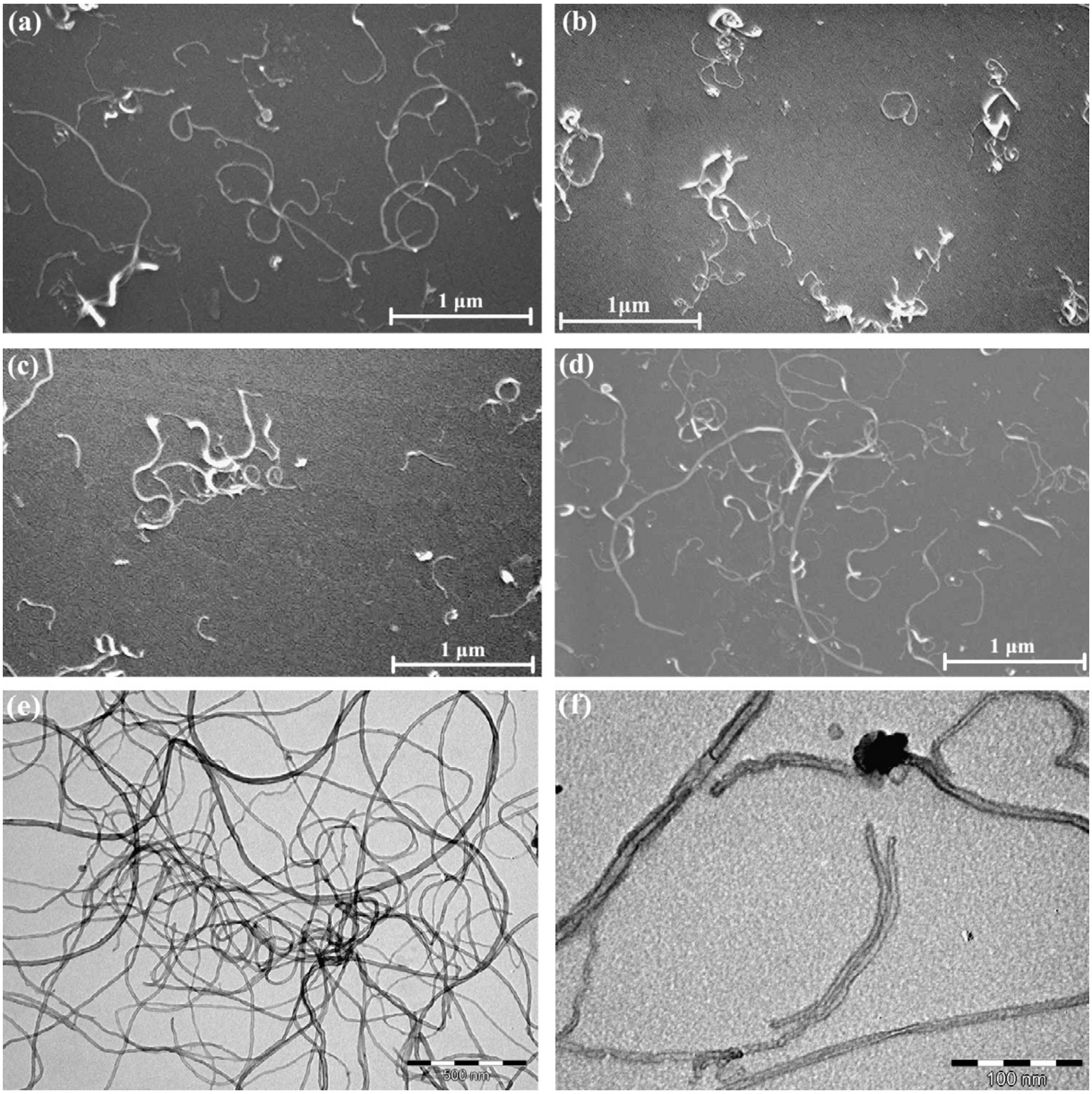

Fig. 2 – SEM images of the treated MWCNTs at two different magnifications: (a) after purification with HCl; (b) after nitric acid oxidation; (c) after oxidation with piranha; (d) after oxidation with ammonium hydroxide and hydrogen peroxide mixture; TEM images after modification with (e) ammonium hydroxide and hydrogen peroxide mixture and (f) after nitric acid.

Concerning the basic oxidative treatment (ammonium hydroxide/hydrogen peroxide mixture), no visible changes in the morphology of CNTs are detected and the corresponding images (see Fig. 2d and e) seem to be similar with those of the HCl-treated material. This is a clear indication that the basic treatment is not destructive for the tubes, while at the same time, highly purified material is produced (*vide infra*).

3.3. *XPS analysis*

With reference to functionality grafting, XPS is one of the surface analytical techniques, which can provide useful information on the nature of the functional groups and also on the presence of structural defects on the nanotube surface. In Fig. 3, the XPS C1s and O1s peaks of the as-received CNTs and after treatment with HCl are presented. Deconvolution of the C1s peak of the as-received MWCNTs (Fig. 3.1a) showed a main peak at 284.1 eV, attributed to the graphitic structure in agreement with recent photoemission studies on MWCNTs [25]. Moreover, a peak at 285.5 eV was attributed to defects on the nanotube structure [25–27], whereas the peaks at 286.7, 288.3 and 290 eV, correspond to carbon atoms attached to different oxygen-containing moieties [28]. Finally, the π–π^* transition loss peak was detected at 291.5 eV. Deconvolution of the XPS O1s peak (Fig. 3.2a) confirmed the presence of some carboxylic and hydroxyl functions onto the CNT surface at 533.2 eV (0.74 at.%) and 531.9 eV (1.19 at.%), respectively. The total oxygen amount on the as-received sample was 3.87 at.%. Furthermore, oxygen related to the iron oxide catalyst (529.5 eV and 1.19 at.%) and physically adsorbed oxygen/carbonates were detected at 530.7 eV (0.75 at.%). So, it can be concluded that the impurity of the as-received MWCNTs in-

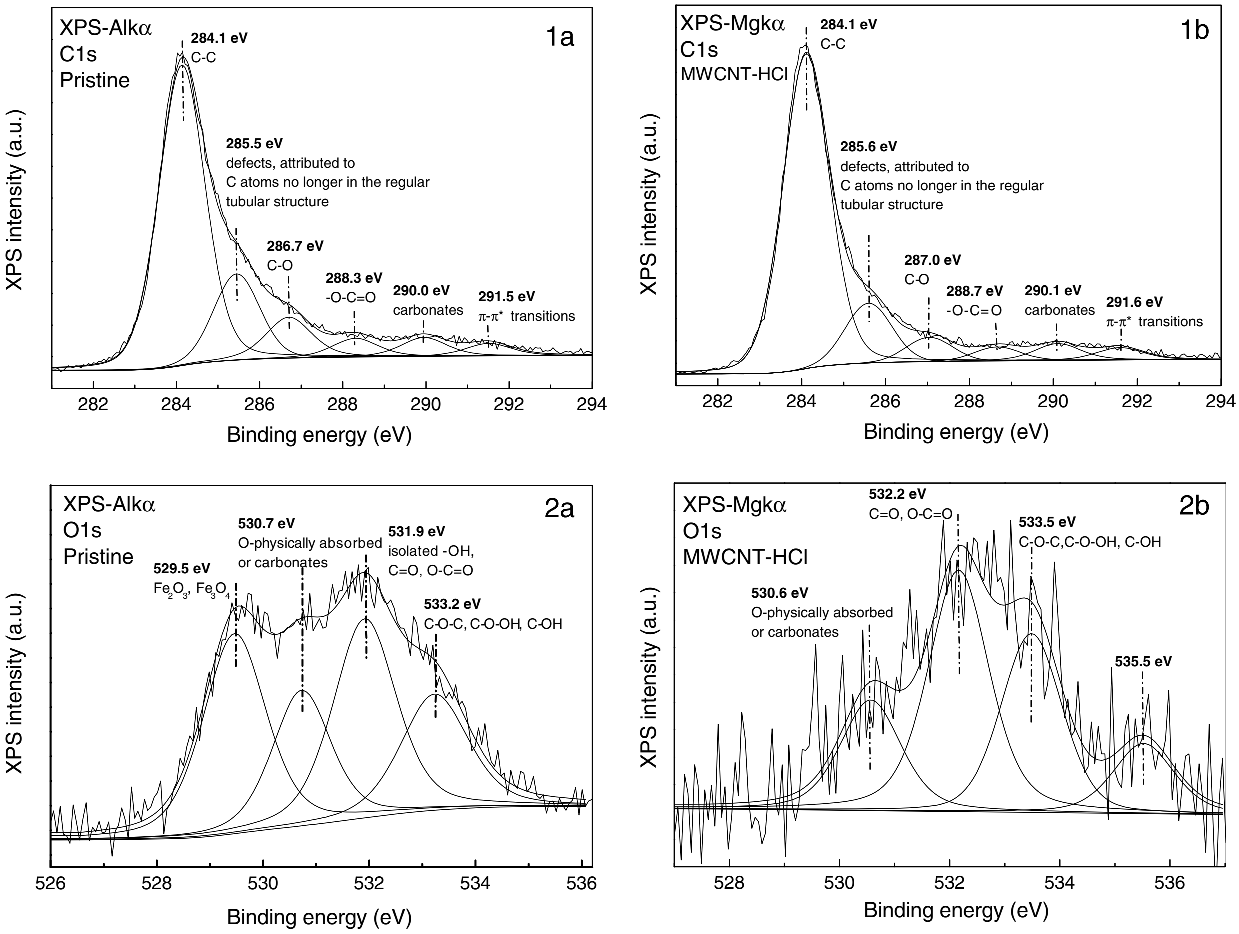

Fig. 3 – Deconvolution of the (1) XPS C1s and (2) O1s peaks of the MWCNTs: (a) as-received and (b) treated with HCl.

cludes the catalyst particles and graphitic platelets which amounts to about 17 at.%.

Study of the HCl-treated MWCNTs (Fig. 3.2b) showed significant decrease of the oxygen amount (1.58 at.%) on the surface of the MWCNTs as compared to the as-received nanotubes. The HCl is not an oxidation agent, and therefore we can safely assume that the amount of the oxygen found on MWCNTs was produced during the chemical vapour deposition process. The difference between the oxygen amount, related to the carbon in the as-received specimen and that after HCl treatment is mainly due to the oxygen bonded to the disordered carbon. As is evident, such kind of carbon species can be successfully removed from the MWCNT sample with the HCl treatment. A decrease of the oxygen amount is observed in all the O1s components from total oxygen, such as carboxylic (0.45 at.%), hydroxyl (0.65 at.%) and molecular oxygen or carbonates (0.29 at.%), while the peak attributed to the oxygen of metal oxides is not observed any more. This implies that oxygen species-originated from metal nanoparticles and chemical functionalities attached to the disordered carbon structures – were removed away during the filtration process. The deconvolution of the C1s spectrum of the HCl-treated MWCNTs (Fig. 3.1b) also revealed an increase of the graphitic carbon layer up to 73 at.% with simultaneous decrease of the defect peak from 17 to 13 at.%. A decrease was also observed to the peak related to the hydroxyl functionalities.

The total amount of oxygen (at.%) on the surface of MWCNTs as detected by XPS measurements for each treatment is given in Fig. 4. As is evident, there is a clear increase of oxygen content on the walls of CNTs for all treatments attempted here. The oxygen functionalities depend on the oxidation conditions and the overall amount of oxygen increase with increasing power of the oxidation agents. The increase of surface oxygen per type of oxidation treatment follows the trend: hydrochloric acid < ammonium hydroxide/hydrogen peroxide < piranha < refluxed nitric acid. The last column in Fig. 4 is related to the physically adsorbed oxygen and water content. Regarding defect presence at carbon sites, our experiments showed that the treatments with ammonia hydroxide/hydrogen peroxide mixture and piranha do not lead to production of additional defects on the outer walls of MWCNTs, as compared to the HCl-purified specimens (13 at.% for HCl and piranha treatments vs. 14 at.% for the NH_4OH/H_2O_2 treated sample). It is obvious that in the aforementioned cases oxidation seems to proceed to available defect sites without necessarily creating additional defects. However, in the case of the MWCNT sample treated with refluxed nitric acid a significant increase of the carbon defects up to 22 at.% is observed. In this case, the oxidative treatment not only “attacks” the carbon defect sites but also is responsible for the significant shortening of the nanotubes (see Fig. 2b) and thus the creation of additional defects that can be further oxidised.

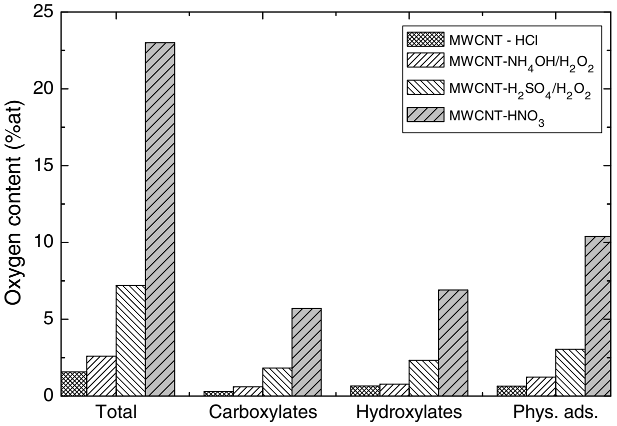

Fig. 4 – Oxygen content (at%) on the MWCNT walls after treatment with different oxidation agents.

3.4. *Titration analysis*

A direct acid–base titration technique using NaOH was performed to determine the concentration of surface groups [29]. In Table 1, the mmol of acidic oxygen-containing surface groups per gram of CNT material are given as a function of chemical treatment. The titration experiments demonstrate that an increase in severity of the oxidation results in an increase in the concentration of acidic surface sites, from 1.8 mmol/g on pristine tubes to 3.7 mmol/g on nitric acid-treated material. These results are in full agreement with the XPS data (Fig. 4).

3.5. *Raman spectroscopy*

Raman spectroscopy is a very valuable tool for the characterization of carbon-based nanostructures. The Raman spectra of pristine and treated MWCNTs excited with the 514.5 nm laser line are shown in Fig. 5. Each of them consists of three characteristic bands, namely the D-band at ~1338 cm^{-1}, the G-band at ~1572 cm^{-1} and the D′ at ~1608 cm^{-1}. The D-band is a disorder induced feature arising from double resonance Raman scattering process from a non-zero-center phonon mode [30–32]. The D band is usually attributed to the presence of amorphous or disordered carbon in the CNT samples. The carbon structural disorder is due to the finite or nanosized graphitic planes and other forms of carbon, such as rings along with defects on the nanotube walls, vacancies, heptagon-pentagon pairs, kinks and heteroatoms. It is important to mention that no systematic study has yet been carried out to differentiate the various contributions to the D band intensity. The G-band originates from in-plane tangential stretching of the carbon-carbon bonds in graphene sheets. The D′ band which is a weak shoulder of the G-band at higher frequencies is also a double resonance feature induced by disorder and defects. Also, it should be stressed that the radial breathing modes are too weak to be observed due to the large diameters of the tubes.

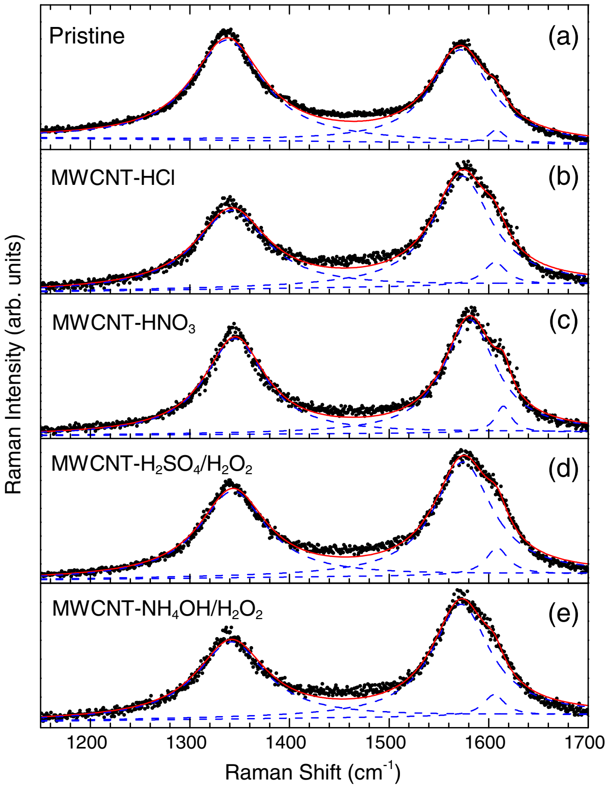

Fig. 5 – Raman spectra of MWCNT samples after treatment with different agents.

Firstly, we studied the effect of a non-oxidative treatment of CNTs to the vibrational contributions discussed in the previous paragraph. In Fig. 5a and b, the Raman spectra of pristine and hydrochloric acid-treated MWCNTs in the 1100–1700 cm^{-1} frequency range are presented, respectively. It is obvious that a reduction of the D-band intensity has occurred after non-oxidative treatment. By integrating the areas of the D and G peaks for both samples, a significant enhancement (~50%) of the corresponding ratio I_G/I_D (Table 2) was estimated. Thus, we can conclude that washing with hydrochloric acid leads to an appreciable elimination of graphitic nanoparticles. Hence, the HCl-treated tubes can be employed as a reference material for the Raman study of CNTs after oxidative treatments.

The spectra obtained after treatment of MWCNTs with the oxidative agents are shown in Fig. 5c–e. The intensity ratio of G to D-band (Table 2) in the spectrum of piranha treated sample is the same with the one of HCl-purified material, which is

Table 1 – Relative concentrations of carboxylic groups after titration

Sample	Pristine	HCl	HNO_3, reflux	H_2SO_4/H_2O_2	NH_4OH/H_2O_2
mmol/g	1.8	1.0	3.7	2.0	1.6

Table 2 – I_G/I_D intensity ratios for the treated MWCNTs

Sample	Pristine	HCl	HNO_3, reflux	H_2SO_4/H_2O_2	NH_4OH/H_2O_2
I_G/I_D	0.81	1.23	1.01	1.23	1.29

indicative of similar defect population in both cases. In contrast, the I_G/I_D ratio decreases sharply in the case of nitric acid treatment (Table 2), which supports the destruction of the graphitic integrity and the subsequent formation of small graphitic fragments. This is in full agreement with the SEM results in which cut tubes are produced after the refluxed nitric acid oxidation. Moreover, the increased carbon defect population observed by XPS gives an additional support to the Raman findings. The as-produced defect sites on the sidewalls and the tips of CNTs are more sensitive in extreme oxidizing conditions leading to adducts with enhanced oxygen content (see Fig. 4).

Regarding the ammonium hydroxide/hydrogen peroxide mixture treated MWCNTs an enhancement of the I_G/I_D ratio is evident from Table 2. Since this treatment does not produce additional sidewall defects (see section above on XPS results) we can safely conclude that this non-acidic treatment purifies the material effectively.

3.6. *Thermogravimetric analysis*

It is well known that different structural forms of carbon can exhibit different oxidation behaviour depending each time on the available reactive sites. For example, disordered or amorphous carbons tend to be oxidised at around 500 °C [33], because of their lower activation energies for oxidation or due to the presence of a large number of active sites. On the other hand, a well graphitized structure starts to oxidize at a relatively higher temperature between 600 and 700 °C, depending on type of CNTs [34,35].

The thermogravimetric experiments conducted on the as-received, HCl-treated and oxidized MWCNT samples are presented in Fig. 6 and, as expected, the thermal degradation of MWCNTs is a multistage process. The first stage, up to a temperature of 150 °C, a weight loss of approximately 1% is detected for the highly hydrophilic nitric acid-treated MWCNTs, which corresponds to the evaporation of the adsorbed water. The second stage – from 150 to 350 °C – is attributed to the decarboxylation of the carboxylic groups present on the MWCNT walls [36]. Thermal degradation in the range between the 350 °C and 500 °C may be explained by the elimination of hydroxyl functionalities, attached to the MWCNT walls [37]. Finally, at the temperatures higher than 500 °C, the observed degradation corresponds to the thermal oxidation of the remaining disordered carbon [33]. It is worth adding that the highest stability observed is exhibited by the non-acidic oxidation process, which has a plateau in weight loss up to 650 °C or higher. The lack of degradation for the MWCNTs treated by the ammonium hydroxide/hydrogen peroxide mixture indicates the absence of disordered carbon in the sample. This finding is in agreement with the XPS and Raman results and allows us to conclude that this specific treatment is the most effective for both purification and mild oxidation of the as-received material. However, it must be stressed that the amount of total oxygen (2.6 at%) present in the NH_4OH/H_2O_2 treated CNTs might be relatively low for a number of applications where strong interfacial bonding/thermodynamic wetting of the reinforcing medium is required.

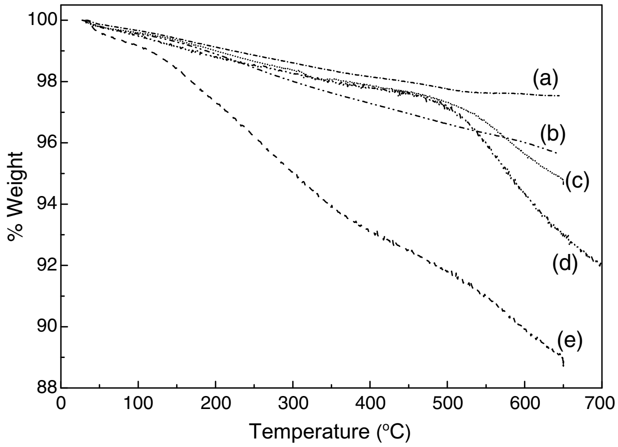

Fig. 6 – TGA curves of the MWCNT samples: (a) MWCNT–NH_4OH/H_2O_2, (b) MWCNT–H_2SO_4/H_2O_2, (c) MWCNT–HCl, (d) as-received and (e) MWCNT–HNO_3.

4. Conclusions

Chemical oxidation of MWCNTs with reagents of different oxidation power was studied. The reference sample was hydrochloric acid-treated MWCNTs which contains very low amount of graphitic nanoparticles bearing oxygen functionalities. The oxidative reagents used were a non-acidic mixture of ammonium hydroxide/hydrogen peroxide, a piranha solution and refluxing nitric acid. All prepared samples form permanent suspensions in common polar media, which is necessary for better manipulation of the material and use in the fabrication of novel composites. After each treatment, the functionalization yield, namely the density of carboxyl and hydroxyl functional groups on the graphitic network, was quantified by means of XPS and titration measurements. Oxidation with nitric acid under extreme conditions (reflux) increases the defect population/formation on the CNTs due to length shortening, as verified by XPS and Raman spectroscopy. Application of a piranha solution showed much lower oxygen content compared to nitric acid oxidation and the absence of additional defects on the graphitic surface. Use of non-acidic treatments such as the mixture of NH_4OH and H_2O_2, facilitates the complete removal of disordered carbon from the MWCNT specimens as confirmed by thermogravimetric analysis.

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