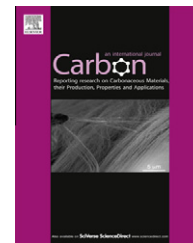


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New insights into the functionalization of multi-walled carbon nanotubes with aniline derivatives

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ABSTRACT

Multi-walled carbon nanotubes (MWCNT) were functionalized with a variety of chemical groups by reaction of *p*-substituted anilines (R-Ph-NH₂) in the presence and absence of isopentyl nitrite used for the *in situ* generation of diazonium species. All materials were characterized by X-ray photoelectron spectroscopy, thermogravimetry and infrared spectroscopy. In the presence of isopentyl nitrite, the extent of functionalization was high and nearly independent on the amount of isopentyl nitrite and on the aniline substituents (R = F, Cl, I, NH₂, NO₂, OH, COOH, COOEt and Et). Unexpectedly, the functionalization of MWCNT with anilines bearing electron withdrawing groups was also observed in the absence of isopentyl nitrite. In the case of OH-Ph-NH₂, the reaction leads to MWCNT with the highest degree of functionalization and this can be considered as a new and efficient methodology for CNT functionalization with phenol groups. The overall reaction mechanism is discussed for both reaction conditions: confirmation of a radical chain mechanism was obtained for the reaction performed in the presence of isopentyl nitrite, while the formation of stabilized dipolar intermediate species seems to be involved in the absence of isopentyl nitrite. The materials with the highest degree of functionalization showed very good dispersions in acetonitrile even after 1 month.

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1. Introduction

Carbon nanotubes (CNT) became a subject of increasing interest in different fields of materials chemistry, mostly due to their unique combination of properties [1–3]. The major obstacles to their use in a large variety of applications are their hydrophobicity and chemical inertness, which leads to low solubility in most solvents [4]. Moreover, CNT have tendency to aggregate and create agglomerates held together by van der Waals interactions [5]. Chemical functionalization is needed to overcome all these barriers, and to allow for eas-

ier handling, compatibility with other materials, as well as modulation of their electronic and mechanical properties [3,4,6]. Surface modified CNT can be used in many fields, such as transistor fabrication [7], optoelectronics [8], biological tagging [9], composite materials [10], bioenergetic applications [11] and catalysis [12].

Approaches for CNT modification include covalent and noncovalent functionalization of the sidewalls or edges/ends and defects, and the endohedral filling of the CNT cavity [13]. Oxidation of the edges/ends and defects of the graphitic sheets is one of the most studied methods of anchoring of

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chemical moieties at their surface [14]. However, this type of functionalization leads to high level of defects in the CNT structure, which can significantly modify its electrical and mechanical properties. The sidewall functionalization is less aggressive in terms of the CNT structure and consequently it is chosen when the electronic properties have to be kept [15]. One of the most important methods for the sidewall surface modification is the diazonium coupling to CNT since this method is versatile, scalable, low cost and provides high functionalization degrees with good conjugation characteristics [16]. This reaction can be carried out using an aniline derivative and an alkyl nitrite or using a pre-formed diazonium salt in organic or aqueous solvents. Notwithstanding the importance of this type of CNT sidewall functionalization, its mechanism is still under debate. The most accepted route is based in the Gomberg–Bachmann mechanism, in which the reaction occurs via electron transfer from CNT into the diazonium species, releasing N_2 and forming a reactive aryl radical that reacts with CNT to form arene bonds [17].

Generically, the functionalization of multi-walled carbon nanotubes (MWCNT) has been less investigated comparing to SWCNT, since they are less reactive, more difficult to disperse and to be compatible; however upon functionalization of the outer wall, the inner walls can be protected, assuring the maintenance of the initial properties. In the particular case of the diazonium coupling method, it has been mostly developed for single-walled carbon nanotubes (SWCNT) and in the case of MWCNT a low degree of functionalization was obtained [18]. Consequently, extension and optimization of this methodology to multi-walled carbon nanotubes is a key step either in the development of functionalization methods for MWCNT and in the elucidation of the reaction mechanism. We have studied the functionalization of MWCNT through oxidation followed by silylation reaction with functional organosilanes [19], and we are now interested in milder methods, which lead to less defects in the CNT structure, in order to develop novel chromophore–carbon nanotube hybrids through covalent and conjugated bonds. These materials can be used as photoactive nanohybrids for light harvesting and medical applications, such as photo dynamic therapy (PDT) [20].

In this paper, a variety of different aniline derivatives (R–Ph– NH_2) bearing functional groups with different electronic properties R = F, Cl, I, NH_2 , NO_2 , OH, COOH, COOEt and Et, were used to functionalize MWCNT through diazonium coupling reaction. Starting from the standard protocol which generates *in situ* the diazonium reactive species, [17] the influences of the electronic properties of substituents of the aniline derivatives and of the radical initiator – isopentyl nitrite – on the functionalization reaction were studied by performing the reaction in dimethylformamide with different ratios of radical initiator to the aniline precursors. With this study we endeavor to get insights into the derivatization mechanism associated with one of the most used methods for CNTs sidewall functionalization, now applied to MWCNTs. The functionalized MWCNT were characterized by X-ray photoelectron spectroscopy (XPS), thermogravimetry (TG) and Fourier transform infrared spectroscopy (FTIR). Complementary dispersibility tests of the functionalized MWCNT were also performed in several solvents.

2. Experimental

2.1. Reagents and solvents

All reagents and solvents were purchased from Aldrich, Merck and Fluka and used as received without further purification. CNT were commercially obtained from Nanocyl S.A., ref[®] NC3100 thin MWCNT. According to the supplier, they have an average diameter of 9.5 nm, length of 1.5 μm and >95% C purity. In the functionalization reactions were used: 4-fluoroaniline (98% Aldrich), 4-chloroaniline (98% Aldrich), 4-iodoaniline (98% Aldrich), 4-aminoaniline ($\geq 99\%$ Aldrich), 4-nitroaniline ($\geq 99\%$ Aldrich), 4-hydroxyaniline ($\geq 98\%$ Aldrich), 4-aminobenzoic acid (>98% Fluka Analytical), ethyl 4-aminobenzoate (>98% Sigma–Aldrich), 4-ethylaniline (>98% Sigma–Aldrich), isopentyl nitrite (97% Sigma–Aldrich), and *N,N*-dimethylformamide (DMF, 99.8% AnalaR NORMAPUR).

2.2. Preparation of materials

Pristine multi-walled carbon nanotubes (sample denoted as MWCNT) were functionalized using different experimental conditions described as follows.

2.2.1. Method 1

This method is based on the procedure of Dyke et al. [17] in a typical reaction, 100 mg of MWCNT are dispersed in DMF (30 mL) with sonication during 10 min. Then 15 g of aniline derivative (about 0.12 mol) is added to the reaction medium which is left under argon and heated. Then, 7.5 mL isopentyl nitrite (radical initiator) is added to the reaction slowly, in a molar ratio of 0.5 to aniline precursor. The reaction mixture is kept under stirring for 48 h at 80 °C; the resulting materials are denoted as R@MWCNT_1, where R = F, Cl, I, H_2N , O_2N , OH, HOOC, EtOOC and Et.

2.2.2. Method 2

A modification of method 1 was carried out with different ratios of radical initiator (isopentyl nitrite) to the aniline derivatives. Typically, 100 mg of MWCNT are dispersed in DMF (30 mL) with sonication during 10 min. Then, 15 g of aniline precursor (about 0.12 mol) is added to the reaction medium which was left under argon and heated. Addition of isopentyl nitrite was performed, slowly, to the reaction in different ratios to aniline derivatives: 0.3 for HOOC–Ph– NH_2 (4 mL) and 1.2 for EtOOC–Ph– NH_2 and I–Ph– NH_2 (20 mL). The reaction mixture is kept under stirring for 48 h at 80 °C; the resulting materials are denoted as R@MWCNT_2[z] where z = molar ratio of isopentyl nitrate to aniline derivative and R = I, HOOC and EtOOC.

2.2.3. Method 3

No radical initiator was used in this methodology. In a typical reaction, 100 mg of MWCNT are dispersed in DMF (30 mL) and 15 g (0.12 mol) of aniline derivative is added to the reaction medium which is kept under stirring in argon atmosphere for 48 h at 80 °C to obtain materials R@MWCNT_3, where R = F, Cl, I, H_2N , O_2N , OH, HOOC, EtOOC and Et.

In all cases, obtained black materials were dispersed in DMF, filtered through 0.2 μm polyamide membrane filters

(NL16 Whatman) and purified by reflux in clean DMF for 1 h and filtered again by the previous procedure, extensively washed with DMF and with diethyl ether and finally dried under vacuum at 120 °C overnight. The scheme of reactions and resulting products is shown in Fig. 1.

2.3. Physical–chemical characterization

X-ray photoelectron spectroscopy (XPS) analyzes were performed with collaboration of Centro de Materiais da Universidade do Porto (CEMUP, Porto, Portugal) in a VG Scientific ESCALAB 200A spectrometer using non-monochromatic Al K α radiation (1486.6 eV). The measurement was carried out using pellets of the materials. Binding energies were calibrated relative to the C1s peak at 284.6 eV. The raw XPS spectra were deconvoluted by curve fitting peak components using the software XPSPEAK 4.1 with no preliminary smoothing. Symmetric Gaussian–Lorentzian product functions were used to approximate the line shapes of the fitting components after a Shirley-type background subtraction. Atomic ratios were calculated from experimental intensity ratios and normalized by atomic sensitivity factors.

The thermogravimetry (TG) measurements were obtained in a STA 409 PC device from NETZSCH. All samples (typically 5–7 mg) were heated under nitrogen flow (200 cm³/min) to 900 °C at a rate 10 °C/min.

Fourier transform infrared spectra (FTIR) of the materials were collected with a Jasco FT/IR-460 Plus spectrophotometer in the 400–4000 cm⁻¹ range with a resolution of 4 cm⁻¹ and 32 scans. The spectra were obtained in KBr pellets containing 0.2% weight of MWCNT.

Dispersibility tests were performed at room temperature (18–22 °C) in several solvents (acetonitrile, toluene, water). Typically, 1 mg of material was dispersed in 8 mL of solvent and sonicated for 10 min; the dispersions were photographed after 15 min, 1 h, 1 day and 1 month.

3. Results and discussion

3.1. Materials prepared by method 1

The chemical characterization of the original and functionalized MWCNT surfaces was performed by XPS. The atomic percentages of relevant elements are summarized in Table 1 and the corresponding high resolution spectra are presented in Figs. 2 and 3.

In the pristine MWCNT the C% is 99.0% and O% is 1.0% indicating a residual oxidation of the surface of the carbon nanotubes (Table 1). After functionalizations by method 1, the surface C% decreased relatively to that of pristine MWCNT in agreement with the functionalization degree. In the case of substituted anilines R–Ph–NH₂ where R = F, Cl, NH₂, OH, the resulting materials showed carbon percentages in the range 94–95%, namely of 93.5, 95.1, 95.3, 93.9, respectively. In the case of the materials HOOC@MWCNT_1 and NO₂@MWCNT_1 the C% were 91.7% and 90.4%, respectively, and the highest decrease of C% can be related to the introduction of two or three heteroatoms; with materials with R = COOEt and R = Et the C% (93.4 and 97.4%, respectively) are slightly higher relatively to the previous tendency which can be justified by the inclusion of an alkyl chain during the functionalization, with the concomitant increase of C%. Furthermore, taking into account the carbon percentages and the type of attached functional groups, it can be concluded that the degree of functionalization is similar for all the materials, and independent of the electronic properties of the functional group of the aniline derivatives.

The C1s high-resolution spectrum of the original MWCNT (Fig. 3) was deconvoluted into six bands: a main peak at 284.5 eV assigned to the graphitic structure (sp²); a peak at 285.9 eV attributed to carbon–carbon single bonds of defects on the nanotube structure (sp³); a peak at 287.3 eV related to carbon–oxygen single bonds in alcohols, phenols and ethers (C–O); a peak at 288.9 eV due to carbon–oxygen double

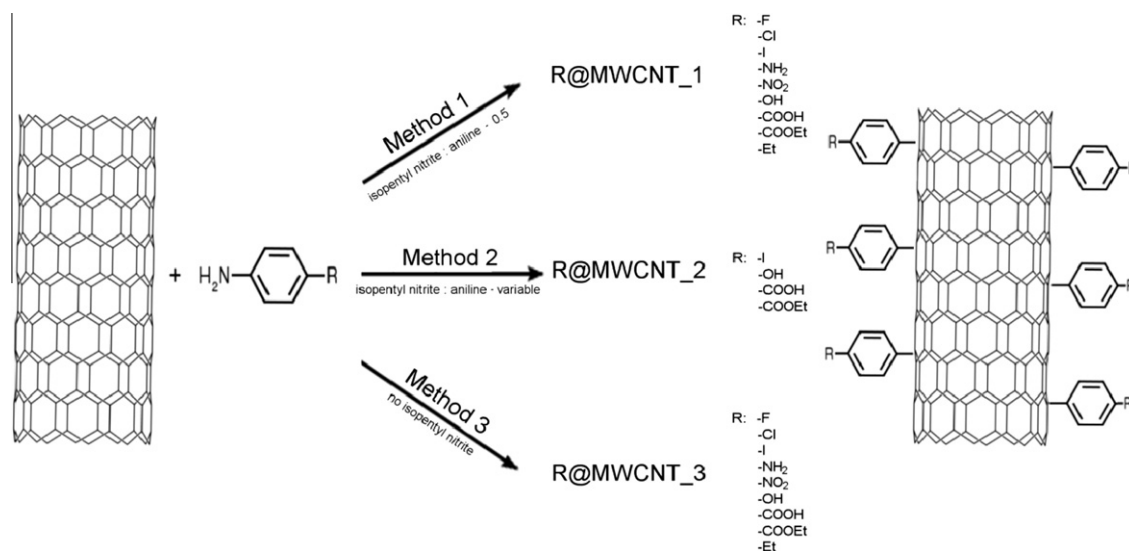


Fig. 1 – Reaction scheme of MWCNT functionalization with aniline derivatives.

Table 1 – The surface atomic percentages of relevant elements calculated from XPS high resolution spectra.

Sample	At%					
	C1s	N1s	O1s	F1s	I3d5	Cl2p
MWCNT	99.0		1.0			
F@MWCNT_1	93.5	0.9	2.1	3.5		
F@MWCNT_3	96.4	0.3	2.5	0.8		
Cl@MWCNT_1	95.1	0.3	1.8			2.9
Cl@MWCNT_3	97.8	0.2	1.9			0.2
I@MWCNT_1	a	a	a		a	
I@MWCNT_2[1.2]	91.2	1.1	3.0		4.7	
I@MWCNT_3	a	a	a		a	
H ₂ N@MWCNT_1	95.3	2.8	1.8			
H ₂ N@MWCNT_3	97.8	0.7	1.5			
O ₂ N@MWCNT_1	90.4	3.7	5.9			
O ₂ N@MWCNT_3	98.3	0.4	1.4			
HO@MWCNT_1	93.9	1.5	4.6			
HO@MWCNT_3	81.2	1.9	17.0			
HOOC@MWCNT_1	91.7	0.9	7.4			
HOOC@MWCNT_2[0.3]	93.1	0.8	6.1			
HOOC@MWCNT_3	97.9	0.4	1.7			
EtOOC@MWCNT_1	93.4	1.1	5.5			
EtOOC@MWCNT_2[1.2]	93.1	0.5	6.4			
EtOOC@MWCNT_3	98.6	0.2	1.2			
Et@MWCNT_1	97.4	1.1	1.6			
Et@MWCNT_3	98.3	0.4	1.3			

a This could not be determined due to I₂ release.

bonds in ketones and quinones (C=O); a peak at 290.4 eV assigned to carbon–oxygen double bonds in carboxylic acids, carboxylic anhydrides and esters (–COO) and a peak at 291.9 eV, attributed to the π – π^* shake-up satellite peak from the sp²-hybridized carbon atoms [19,21].

From the analysis of the high resolution spectra in the C1s region of functionalized materials (Fig. 2), it can be observed that, upon functionalization with halogen substituted anilines, there is a large increase of the relative intensity of the band at 286.0 eV and a slightly higher intensity of the band at 291.4 eV, confirming the introduction of C–C and C–halogen bonds. No significant changes of the C1s profile were observed with the other materials.

The broad band in the O1s region of the pristine MWCNTs was deconvoluted into two peaks (Fig. 3): a more intense peak at 532.2 eV, attributed to oxygen double bonded to carbon (O=C) from quinone, ketone and aldehyde moieties and a second peak at 533.9 eV due to oxygen single bonded to carbon (O–C), attributed to ether and phenol groups. Since oxygen atoms in carboxylic acids and esters have both single and double bonds, they contribute to both the aforementioned component peaks [22]. After functionalization by method 1, an increase in the oxygen content was observed for all the materials relatively to the original MWCNT (Table 1). Relative increases in the O% in the range 0.6–1.1% were observed when functional groups without oxygen atoms were introduced. Moreover, much larger increases were observed for materials functionalized with oxygen functional groups, with O% higher than 4.6%: for R = NO₂, OH, COOH and COOEt, the

O% were 5.9, 4.6, 7.4 and 5.5, respectively (Table 1), which can be explained by the types of functional groups attached. The introduction of oxygen groups onto the MWCNTs surface was also corroborated by the significant changes observed in the O1s high resolution spectra (Fig. 2), particularly in the relative proportions of the two previously referred peaks. In the case of HO@MWCNT_1, the C=O band intensity is much smaller than that of the C–O band, confirming the introduction of phenol or phenoxy groups; in the case of O₂N@MWCNT_1, only one band was observed at 532.9 eV, confirming the introduction of a NO₂ group, which overlaps the other two peaks; in the case of HOOC@MWCNT_1 and EtOOC@MWCNT_1, the two bands have equivalent areas due to the introduction of both C=O and C–O groups.

No nitrogen was detected in the original MWCNT as expected. However, upon functionalization by method 1 all the materials show the presence of nitrogen to some extent (Table 1): when the R group of the aniline derivatives does not contain nitrogen, the N% fall in the range of 0.3–1.5%, what is an unexpected result, but for materials with nitrogen functionalities, R = NH₂ and NO₂, the observed nitrogen percentages were 2.8% and 3.7%, respectively. The N1s XPS spectrum of material O₂N@MWCNT_1 (Fig. 3) shows two distinct bands at 400.0 and 406.1 eV; the first is due to an amine group and the second can be assigned to NO₂ groups. In N1s XPS spectrum of H₂N@MWCNT_1, the observed band was deconvoluted in two bands with BE at 398.7 and 400.1 eV (more intense peak). The two bands indicate that two slightly different amine groups are present in the MWCNT surface

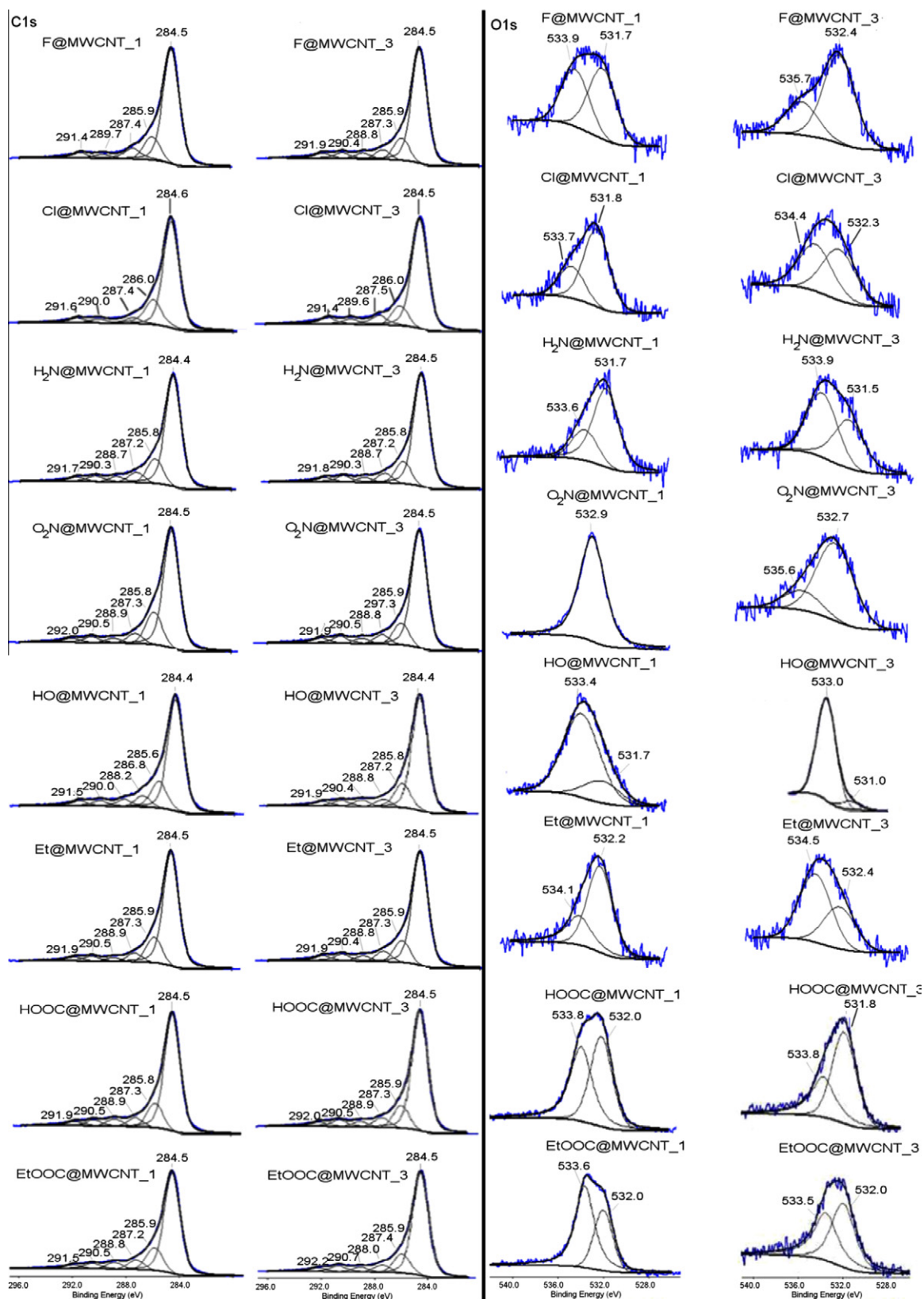


Fig. 2 – High-resolution XPS spectra in the C1s and O1s regions, with the corresponding fits for materials R@MWCNT_1 and R@MWCNT_3.

[23]. Similar N1s spectra were observed for materials with R = OH, COOH and COOEt.

The presence of halogen peaks in the high resolution spectra of R@MWCNT_1 R = F, Cl and I with atomic percentages in

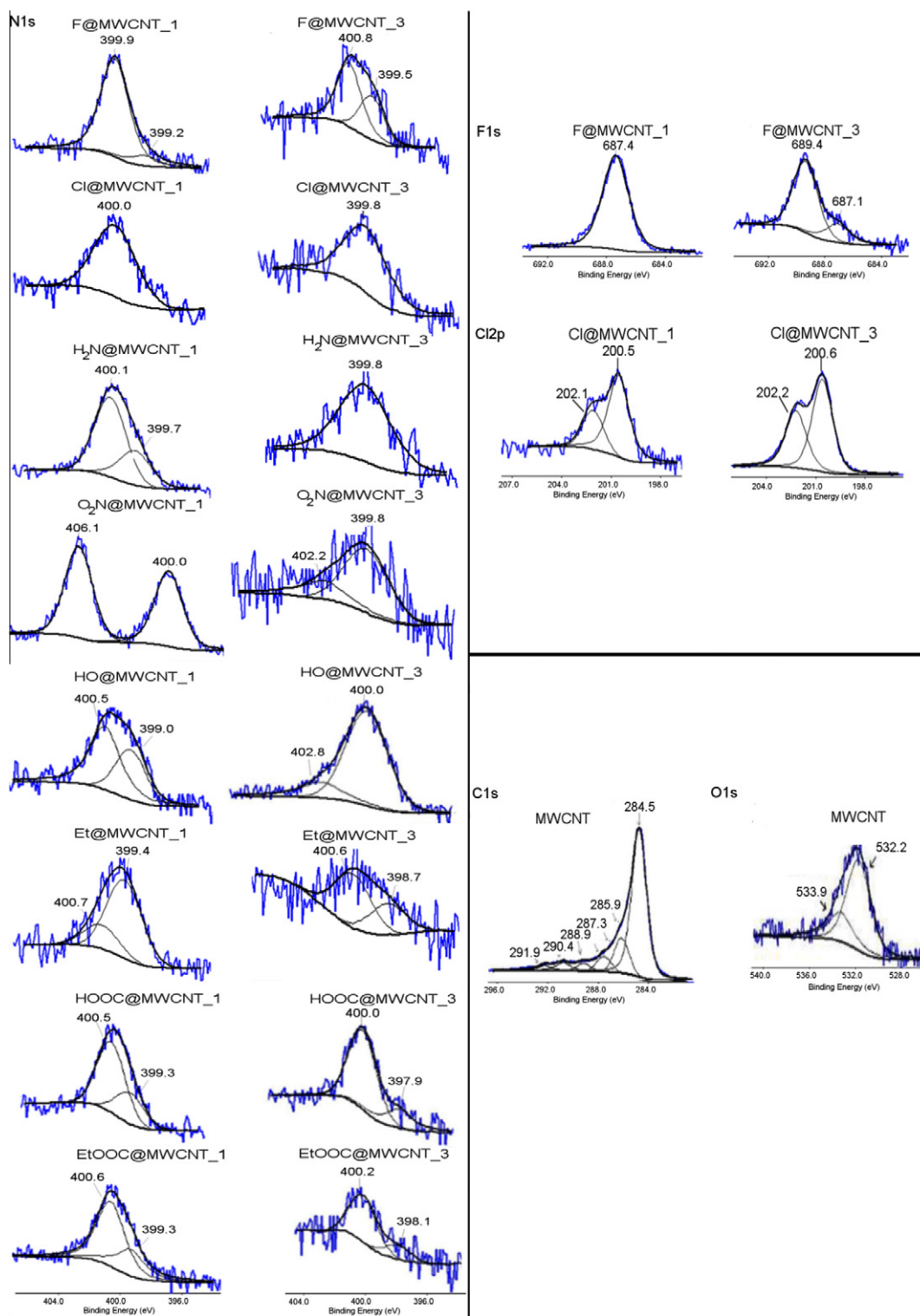


Fig. 3 – High-resolution XPS spectra in the N1s, F1s and Cl2p regions with the corresponding fits for materials R@MWCNT_1 and R@MWCNT_3 and XPS characterization of original MWCNT with C1s and O1s high resolution spectra.

the range 3–5% confirm the introduction of these functionalities onto MWCNT surface. The high-resolution XPS spectrum in the F1s region (Fig. 3) showed one peak at 687.4 eV for F@MWCNT_1 assigned to C–F bond. The high-resolution XPS spectrum in the Cl2p region (Fig. 3) was deconvoluted into two peaks: at 200.6 and 202.2 eV, which can be assigned to

C–Cl (Ph–Cl) bond. [24] In the case of iodine functionality it was only possible to analyse the sample resulting from method 2, I@MWCNT_2[1.2], since release of I₂ was observed during analysis of other iodine samples. In this particular sample, the I3d5 region shows a band at BE 620.9 eV, due to C–I bond.

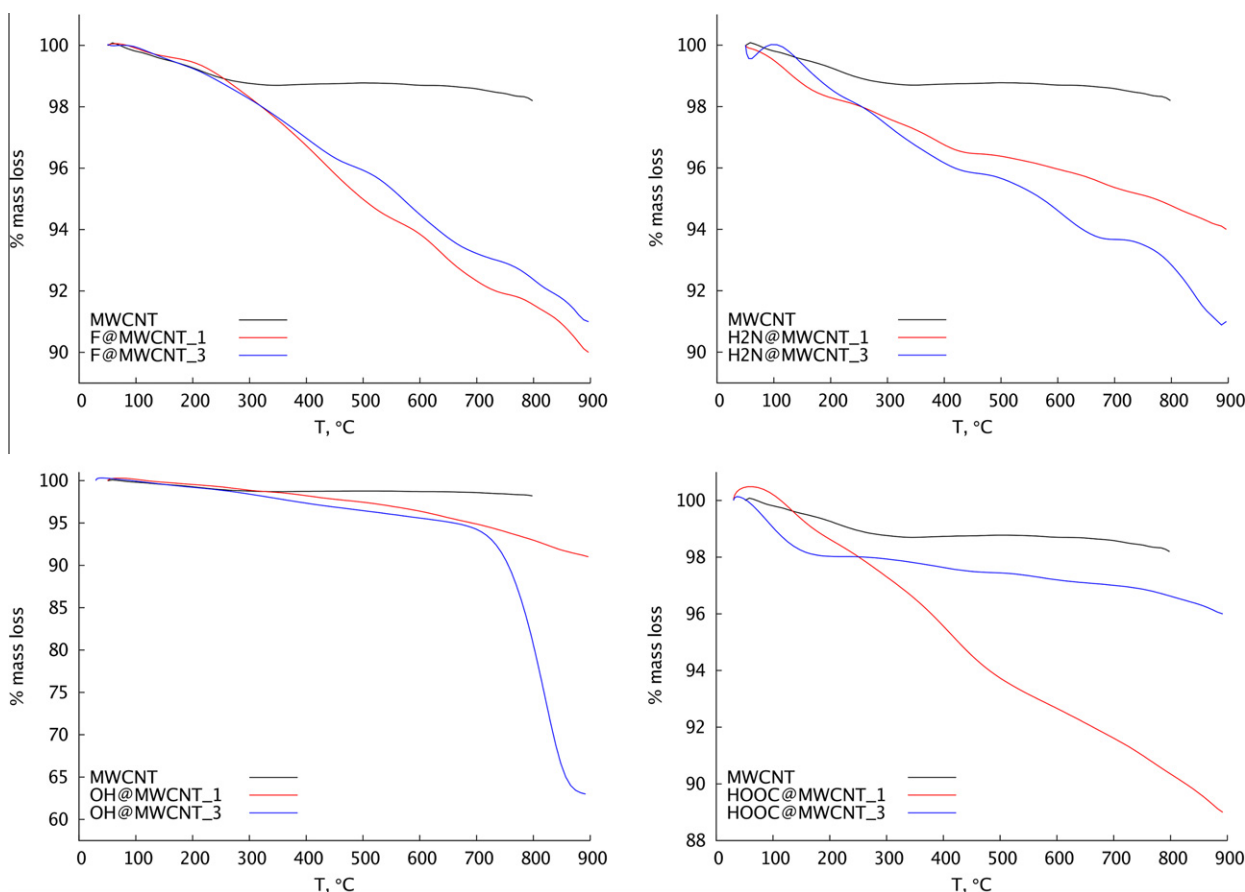
Table 2 – Total mass loss% obtained by TGA for original and functionalized materials.

Sample	% Total mass loss
MWCNT	2
F@MWCNT_1	10
F@MWCNT_3	9
Cl@MWCNT_1	8
I@MWCNT_1	9
I@MWCNT_2	11
I@MWCNT_3	22
H ₂ N@MWCNT_1	6
H ₂ N@MWCNT_3	9
O ₂ N@MWCNT_1	11
O ₂ N@MWCNT_3	6
HO@MWCNT_1	9
HO@MWCNT_3	37
HOOC@MWCNT_1	11
HOOC@MWCNT_2	12
HOOC@MWCNT_3	4
EtOOC@MWCNT_1	11
EtOOC@MWCNT_2	10
EtOOC@MWCNT_3	2
Et@MWCNT_1	9
Et@MWCNT_3	3

The XPS spectra confirm that all the functionalities were introduced onto the MWCNT surface upon functionalization by method 1; considering the surface atomic percentages of relevant elements, summarized in the Table 1, it can be stated that similar degrees of functionalization were obtained for the different aniline derivatives used. This result is the opposite of the work previously published by Bahr and Tour [25] who concluded that the reaction was not successful for some aniline derivatives, namely with R = –COOH and –OH groups. These results also suggest the occurrence of a competing mechanism to the Gomberg–Backman mechanism in the case of method 1, as indicated by the introduction of O and N percentages for all the materials.

TGA analyses were also used to confirm the functionalization of the materials; the total mass loss percentages are presented in Table 2, and the thermograms of pristine MWCNT and of materials R@MWCNT_1 and R@MWCNT_3 are shown in Fig. 4 for R = OH, COOH, NH₂ and F, as examples; the TGs for other materials are shown in Fig. S1, Supplementary material.

Fig. 4 shows that the pristine MWCNT are thermally stable in nitrogen until 900 °C: the small % of mass loss in the temperature range of 100–900 °C results from the decomposition of the few oxygenated surface groups in defects of the MWCNT structure. Consequently, the % of total mass loss in the functionalized materials can be related to the decomposition of surface attached moieties.

**Fig. 4 – Thermograms of pristine MWCNT and functionalized materials by method 1 and method 3 for R = F, NH₂, OH and COOH.**

In the case of materials R@MWCNT_1 (Table 2 and Fig. 4) the total mass losses are in the range of 8–11%; the observed small differences can be related to the masses of the functional groups, 11% for R = NO₂, COOH and COOEt, the material Cl@MWCNT_1 shows a total mass loss percentage of 8% which is consistent with a published result [18], and only for H₂N@MWCNT_1 the total mass loss was 6%. These results are consistent with XPS data and confirm that the extent of functionalization of all materials is independent of the functional group.

3.2. Materials prepared by method 2: influence of the amount of radical initiator

In order to study the influence of radical initiator on the functionalization of MWCNTs with aniline derivatives, a modification of the previous methodology was performed – method 2, in which different ratios of isopentyl nitrite to aniline derivatives are used relatively to method 1.

The molar ratio of isopentyl nitrite to 4-substituted aniline was increased from 0.5 in method 1 to 1.2 M equivalents for anilines with R = EtOOC and I; the opposite was also tested, in which the molar ratio of isopentyl nitrite was decreased to 0.3 for aniline with R = COOH; the corresponding XPS atomic percentages and TGA mass losses are shown in Tables 1 and 2.

For material EtOOC@MWCNT_2[1.2] the C1s atomic percentages by XPS are very similar to those of the corresponding material obtained by method 1 (93.1% and 93.4%, respectively) as well as for O1s and N1s atomic percentages. Also similar mass losses were observed in TGA, 10% and 11% for method 1 and method 2, respectively (Table 2 and Fig. 4). The iodine substituted material I@MWCNT2[1.2] cannot be compared by XPS (see above); however the TGA also shows identical mass losses of 9% and 11%, for method 1 and method 2, respectively. These results suggest that an increase in the amount of isopentyl nitrite does not lead to an increase in the degree of functionalization. Furthermore, HOOC@MWCNT_2[0.3] synthesized with 0.3 M equivalents of isopentyl nitrite relative to aniline precursor also show irrelevant differences relatively to material HOOC@MWCNT_1.

Taking into account that the amount of radical initiator is not important for the functionalization efficiency of MWCNTs and considering the possibility that concurrent mechanism is taking place (presence of nitrogen in the functionalized materials, see above), the functionalization methodology was also carried out in the absence of the radical initiator.

3.3. Materials prepared by method 3: absence of radical initiator

The functionalization of MWCNT by method 3 (absence of isopentyl nitrite) was performed with the same aniline derivatives used in method 1. The XPS and TG data are collected in Tables 1 and 2. Some facts can be highlighted by comparing the data from the different methodologies and aniline derivative substituents.

The degree of functionalization of materials R@MWCNT_3, as accessed by XPS and TG analyses is highly dependent on the nature of the R groups of the substituted aniline. Although

unexpectedly, some degree of functionalization was observed, except for materials with R = Et, COOEt and COOH, where the TG mass losses were inexistent or negligible (in the range of 2–4%) and the corresponding XPS spectra are very similar to that of pristine MWCNT.

A different behavior is observed in the case of halogen functionalized materials, where high surface carbon atomic percentages and low halogen atomic percentages contrast with high TGA mass loss percentages (9% and 22% for material F@MWCNT_3 and I@MWCNT_3, respectively); also, relatively high oxygen atomic percentages are observed for these materials. The high resolution XPS C1s peaks are different from those of materials functionalized by method 1, but also from the original MWCNT (only five peaks are observed) (Fig. 2). Two peaks can be observed in the deconvoluted XPS F1s spectrum of F@MWCNT_3, at 687.1 eV and 689.4 eV, indicating the presence of fluorine in two different environments [24]. These results may be explained by the introduction of the functionality through a mechanism where the loss of halogen and nitrogen atoms takes place.

The material H₂N@MWCNT_3 shows low O and N surface atomic percentages and high carbon percentages, but the TGA mass losses suggest a high level of functionalization, since it is 9% for H₂N@MWCNT_3 (higher than material H₂N@MWCNT_1); material O₂N@MWCNT_3 shows somewhat lower C% and a mass loss percentage of 6%. The loss of a NO₂ group also occurs to some extent, and the N1s spectrum (Fig. 3) also shows a small peak at 402.2 eV, attributed to cationic nitrogen atom [23].

The material OH@MWCNT_3 is a special case of functionalization by method 3, where an extraordinary decrease in the C% occurred (from 99.0% to 81.2%), rather higher than that observed with method 1 (from 99.0% to 93.9%), and also a high atomic percentage of oxygen is registered, 17%. The high resolution O1s spectrum (Fig. 2) shows an intense peak at 533.0 eV, which confirms the presence of C–O bonds. The surface N% is 1.9% and the nitrogen chemical environment is different from other materials, since the band observed in the N high resolution XPS spectrum was deconvoluted in two peaks: one at 400.0 eV, due to an amine group, and another at 402.8 eV, which can be assigned to cationic nitrogen.

Fig. 5 summarizes the surface atomic C% for HO@MWCNT, HOOC@MWCNT and EtOOC@MWCNT obtained by methods 1, 2 and 3. It can be confirmed that, in the case of HO@MWCNT the highest extent of functionalization was obtained with

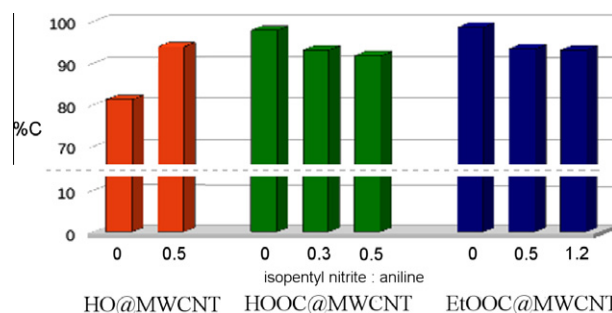


Fig. 5 – Comparison of C% vs ratio of radical initiator used in methods 1 to 3 for materials HO@MWCNT, HOOC@MWCNT and EtOOC@MWCNT.

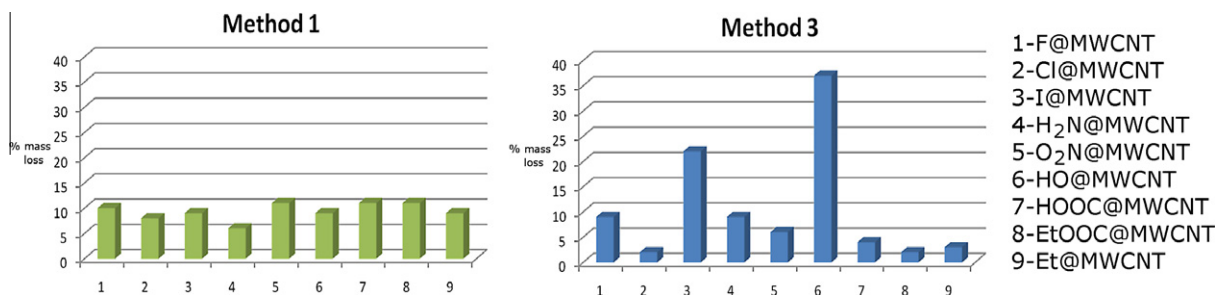


Fig. 6 – Comparison of total TG mass loss by methods 1 and 3 for the different functional groups.

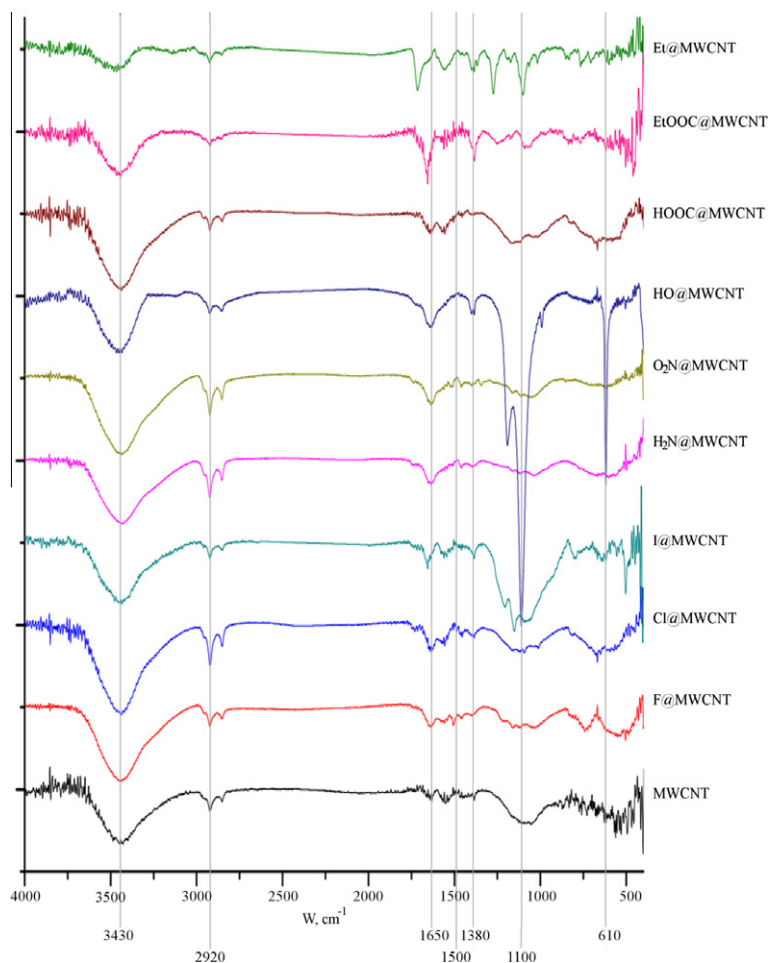


Fig. 7 – FTIR spectra of R@MWCNT_1 materials.

material HO@MWCNT_3 (absence of isopentyl nitrite), in comparison to HO@MWCNT_1 (where radical initiator was used in the reaction media).

Contrary to what was observed in the thermograms of materials R@MWCNT_1 and R@MWCNT_2 which were similar to each other (Figs. 4 and 6), in the case of materials functionalized by method 3 – R@MWCNT_3, there are significant differences between the thermograms of the various functionalized materials. In Fig. 6 it is possible to compare the total mass losses observed with methods 1 and 3 for the different functional groups, where it can be seen that high degrees of functionalization are observed with method 3 for ani-

lines with R substituents with high electron withdrawing and resonance properties, namely F, NH₂, OH. These data also confirm that a new mechanism occurs in method 3, where some loss of the original functional groups is occurring.

3.4. FTIR characterization

All materials were characterized by FTIR, and Fig. 7 shows the spectra of materials R@MWCNT_1; similar spectra were observed for materials obtained by method 2.

Due to the presence of extensive π - π interactions in MWCNT, their FTIR spectra present very weak and poorly re-

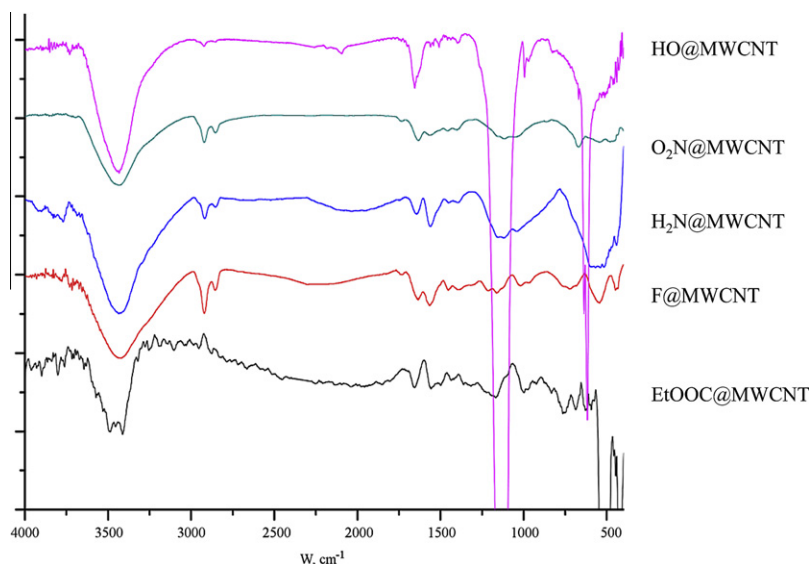


Fig. 8 – FTIR spectra of R@MWCNT_3 materials for R = OH, NO₂, NH₂, F and COOEt.

solved vibration bands. The bands observed in the original MWCNTs are assigned to the vibrations of the nanotubes structure and of carbon–oxygen groups from residual oxidation: the band at 1560 cm⁻¹, is assigned to C=C stretching vibrations of the aromatic carbon in non-graphitic domains [26], the band at 1100 cm⁻¹ has contributions from the skeletal C–C tangential motions (also observed in other carbon materials, such as C60) [26] and from some C–O stretching vibrations of oxygen groups. Finally, the band at 3400 cm⁻¹ corresponds to OH stretching vibrations from hydroxyl groups and residual adsorbed water.

The FTIR spectra of the functionalized materials show the CNTs characteristic vibration bands, as well as bands due to the functional groups attached to the surface of MWCNT, confirming the success of the functionalization. The introduction of functionalities leads to the disruption of the graphitic layer (no infrared bands are observed for graphite) and rupture of π – π interactions, which leads to more intense bands on functionalized materials than those detected in the spectra of the parent material.

Materials EtOOC@MWCNT_1 and HOOC@MWCNT_1 show characteristic bands at 1730 cm⁻¹ and 1680 cm⁻¹, respectively, that correspond to C=O stretching vibration and also peaks characteristic of OH groups at 3440 and 1395 cm⁻¹ due to OH stretching and bending vibrations, respectively.

For aliphatic chains, such as those present in Et@MWCNT and EtOOC@MWCNT, there are vibration bands in the regions near 2850 cm⁻¹ and 1300 cm⁻¹ characteristic of C–H stretching and bending vibrations, respectively.

With HO@MWCNT_1, characteristic bands appear in the regions near 3400 cm⁻¹ due to O–H stretching vibrations and at 1646 cm⁻¹, characteristic of O–H bending vibrations, as well as a more intense band at 1395 cm⁻¹ due to in-plane OH deformation vibrations, suggesting the presence of the phenol group. The intense peak at 1100 cm⁻¹ is assigned to C–O stretching and the peak at 616 cm⁻¹ can be due to the in-plane bending of the ring C–OH bond. The possibility that some groups may be attached to the carbon nanotube

through oxygen through a phenoxy bond cannot be excluded.

MWCNT functionalized with halogen groups (X@MWCNT, X = F, Cl and I) show intense bands for X-sensitive vibrations for *p*-substituted benzenes in the region near 1100 cm⁻¹ and C–X stretching and ring deformation vibrations at about 550 cm⁻¹.

The FTIR spectrum of O₂N@MWCNT_1 shows the characteristic bands in the region near 1650 and 1350 cm⁻¹, assigned to the asymmetric and symmetric stretching vibration of nitro group and in the region near 1120 cm⁻¹ from C–N stretching vibration. For material H₂N@MWCNT_1, new bands are observed in the regions 1200 and 1640 cm⁻¹, assigned to N–H rocking/twisting and scissors vibration, respectively.

The FTIR spectra of materials prepared by method 3 also confirm the presence of characteristic groups attached to the surface of carbon nanotubes (Fig. 8), or the low functionalization degrees observed for example for material COOEt@MWCNT_3.

3.5. Mechanistic considerations

Taking into account the characterization results of materials prepared by method 1 (reaction in DMF in the presence of isopentyl nitrite), some mechanistic considerations can be outlined. There are strong evidences that a chain mechanism is operating since the functionalization degrees were shown to be independent of the amount of isopentyl nitrite used, in the range of 0.3–1.2 M equivalents to the aniline substrate. Furthermore, the presence of isopentyl nitrite is essential for this reaction, because in its absence, a complete different reaction pattern was observed.

Another key point, is the fact that similar functionalization degrees were observed for the different substituted anilines, what is in accordance with the involvement of radical species within the mechanism. These observations are consistent with the main features of the classical Gomberg–Bachmann mechanism and the related further studies by Tour

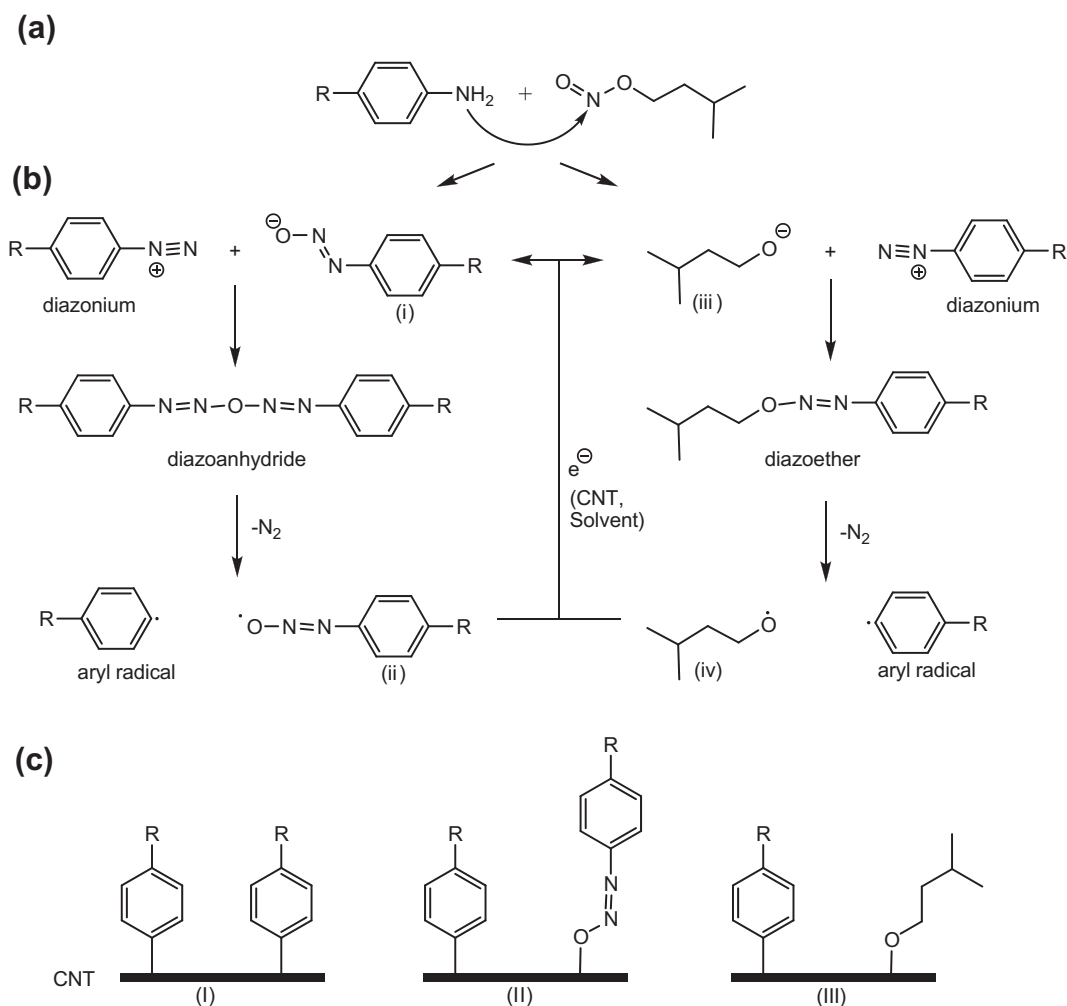


Fig. 9 – Proposed mechanism for MWCNT functionalization through method 1; (a) diazotization reaction; (b) formation of aryl radicals and of oxygen radicals that re-initiate the cycle; and (c) recombination of radicals with MWCNT.

et al. [17] and by Chenevier et al. [16]. For the reaction performed in this work, an adaptation of their mechanistic proposal is proposed in Fig. 9: the aniline derivatives attack nitrite group, giving the diazonium and diazotate species (i); the alcoxide (iii) can also be formed (a more detailed mechanism for the diazotization reaction is shown in Fig. S2, Supplementary material). The anionic species (i) and (iii) can react with the diazonium leading to diazoanhydride and to diazoether, respectively. These intermediates can undergo thermal decomposition with release of nitrogen and generation of an aryl radical that can react with carbon nanotube forming a carbon nanotube-radical structure. The latter species can subsequently react with another aryl radical, probably after delocalization, leading to structures of type (I) (Fig. 9 and Fig. S3, Supplementary material).

Our results also suggest the presence of other associated paths, since the incorporation of nitrogen and oxygen was observed (XPS data), even when the aniline substituent does not contain these elements. In order to explain this result and the evidences of a chain mechanism (in this case occurring in the absence of alkaline reaction medium [16]), we suggest that, upon heating and formation of an aryl radical, the simultaneous generation of oxygen radical species, (ii)

and (iv), can make the reaction to proceed, if these oxygen radicals can then abstract an electron from MWCNT or from other entity such as the solvent (DMF), thereby generating new diazotate or alcoxide species. These anions will further re-initiate the process by reacting with diazonium and, ultimately, generating another equivalent of the diazoanhydride or diazoether (Fig. 9a). The coupling of radicals, (ii) and (iv), with CNT radical can also occur, leading to structures of type (II) and (III) (Fig. 9c) that would explain the addition of nitrogen and oxygen from 0.6% to 1.5% (XPS data), when these functionalities are not in the R substituent of the anilines. Moreover, the radicals (ii) and (iv) could also react with the solvent, to form DMF radicals that can then couple with the MWCNT. Albeit we cannot exclude this possibility, it seems to be less probable attending to the high resolution XPS spectra in the N1s region, in which the band deconvolutions lead to two peaks with BEs that correspond to two different, but not cationic, amines.

In method 3, the carbon nanotubes directly react with *p*-substituted anilines of general structure (v) (Fig. 10a), when R is a halogen, amine, nitro or hydroxyl group, although leading to different C, N, O, X contents in the functionalized materials.

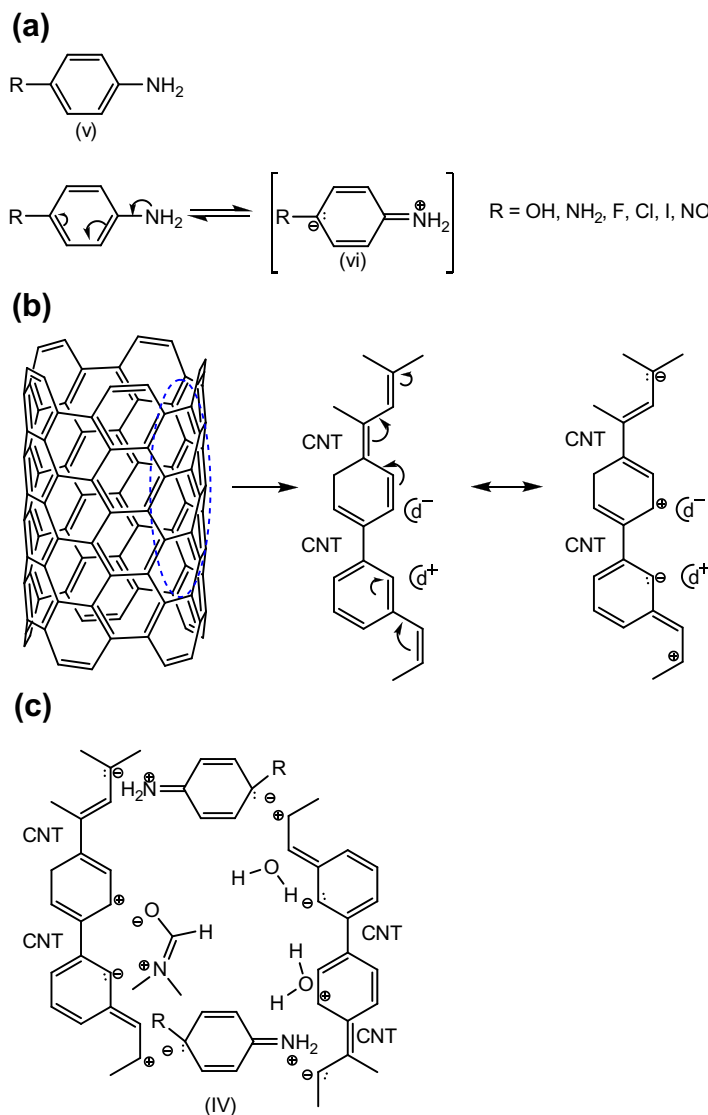


Fig. 10 – Proposed structure for a reaction intermediate in method 3: representation of a dipolar stabilized specie that can occur for a 4-substituted aniline with an electron withdrawing substituent.

When $R = F$, the TG mass loss is equivalent to that observed with method 1, although lower atomic surfaces F% and N% was observed, contrary to the O% which was high. The BEs in the F1s spectrum suggests two different fluorine environments what can indicate some direct binding of F to MWCNT. For amino and nitro derivatives similar reactivity pattern was observed. However, when $R = OH$ the highest functionalization degree was observed as indicated by the highest TG mass losses and the highest surface atomic O% relatively to all the obtained materials, including materials prepared by method 1. Hence, functionalization occurs, yet with loss of functional groups in more or less extent, depending on the R group.

Structures like (v) have the possibility to generate a relatively stable resonance structure in the zwitterionic form (vi) which is stabilized by the electron withdrawing and resonance characteristics of the R group. Due to electronic delocalization characteristic of the CNT structure, these dipolar structures can be further stabilized by electrostatic interac-

tions with the carbon nanotube wall and a particularly stable structure can be formed in the interspaces between two closed nanotubes (Fig. 10b). The structure (IV) in Fig. 10c is a schematic representation of a possible electrostatic network that can be occasionally formed; water molecules, present in the non-anhydrous reaction medium, can also play an important role in its stabilization as well as the polar solvent molecules (DMF). A concerted interaction between the carbon nanotube and the dipolar species can generate covalent bonds, justifying the observed results: some of the possible interactions (paths a–d) and resulting species (structures V–VIII) are schematically represented in Fig. 11.

The covalent attachment of R-aryl group with release of the amine entity can be explained through path (a), while the simultaneous removal of both R and NH_2 groups can be explained through path (b). In both paths, the introduction of hydroxyl groups in the CNT structure occurs in some extent. The results from reactions with fluoraniline, amino-aniline and nitro-aniline can mainly be explained by these two

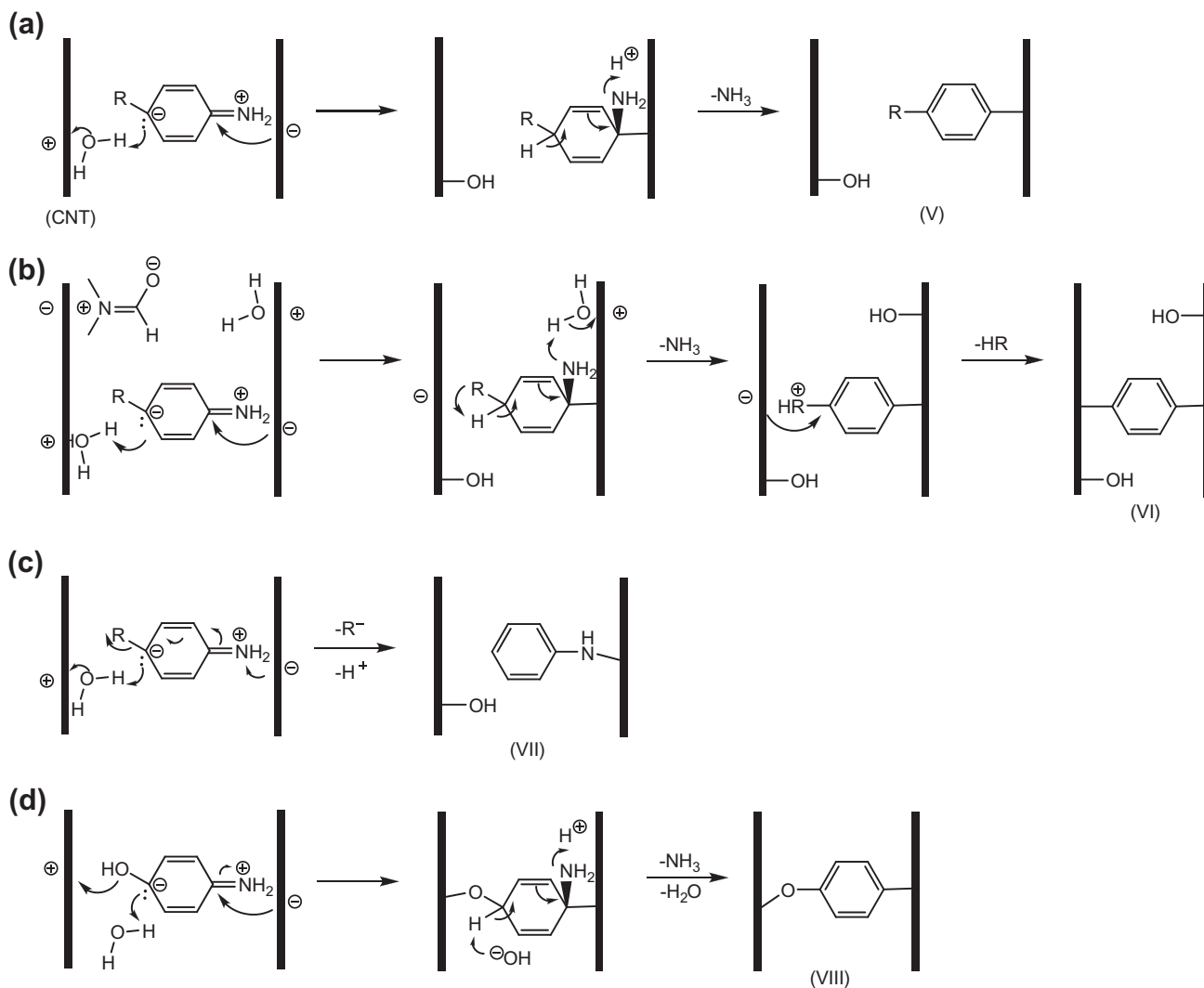


Fig. 11 – Possible pathways for covalent interaction of MWCNT and the stabilized dipolar intermediates.

paths, although, with some occurrence of path (c), which could also explain the binding of the aryl moiety to CNT through amine group, with release of R^- group.

In the case of $R = OH$, the high level of oxygen groups introduced can be explained by path (a). The TG for this material showed almost exclusively decomposition at high temperatures, confirming the presence of phenol groups; nevertheless, we cannot exclude the possibility that some functionalization occurred through phenoxy groups, if the reaction proceeds through path (d).

3.6. Dispersibility tests

A comparative study of the effect of the solvent used in dispersion of the materials was performed in acetonitrile, toluene and water. In all cases, the dispersion of the functionalized materials was better than that of pristine MWCNT, and the best dispersion for tested materials was obtained in acetonitrile. The control of the dispersibility after 15 min, 1 h, 1 day and 1 month shows that material dispersions are stable even after 1 month. As an example, the dispersibility of MWCNT and materials HO@MWCNT_1, HOOC@MWCNT_1,

EtOOC@MWCNT_1, I@MWCNT_1 and HO@MWCNT_3, in acetonitrile, after 1 month, are shown in Fig. 12. Good dispersions were also obtained for materials H₂N@MWCNT_1 and Et@MWCNT_1. A complete dispersibility study with time can be seen in Fig. S4, Supplementary material.

In water the dispersion was good for materials HOOC@MWCNT_1 and EtOOC@MWCNT_1. The poorest dispersion was observed with toluene and material I@MWCNT_1 (Fig. S5, Supplementary material).

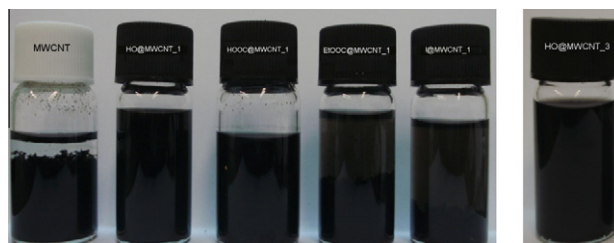


Fig. 12 – Dispersibility of MWCNT and materials HO@MWCNT_1, HOOC@MWCNT_1, EtOOC@MWCNT_1, I@MWCNT_1, respectively, in acetonitrile after 1 month.

4. Conclusions

Functionalization of MWCNT by *in situ* generation of diazonium species was performed in DMF with *p*-substituted anilines with groups R = F, Cl, I, NH₂, NO₂, OH, COOH, COOEt and Et and using isopentyl nitrite as radical initiator (methods 1 and 2). Combination of XPS and TGA data showed that it was possible to functionalize MWCNT with good functionalization degrees, although in lower extent when compared with SWCNT. Furthermore, the FTIR spectra of the functionalized materials showed the characteristic bands of each aniline substituent, confirming that the functional groups are attached to the surface of carbon nanotubes and that functionalization was successfully.

The experimental conditions used lead to equivalent degrees of functionalization for all the tested aniline derivatives, albeit different amounts of radical initiator were used. These results gave evidence that the diazonium coupling to MWCNT reaction occurs by a chain mechanism based in the classical Gomberg–Bachmann mechanism. Furthermore, the presence of some amounts of nitrogen present in functionalized materials was also possible to rationalize using the same mechanism.

MWCNT functionalization also occurred in the absence of radical initiator (method 3), when anilines with electron withdrawing groups (R = halogen, amine, nitro or hydroxyl) were used; in some cases with surprising very good yields: material HO@MWCNT_3 exhibited the highest degree of functionalization among all materials prepared by methods 1–3. The proposed reaction mechanism was based in the formation of dipolar intermediate species stabilized by interactions with carbon nanotube, leading to binding and loss of functional groups in different extent. This is an important result as can be considered as a new and efficient method for the preparation of sidewall OH functionalized MWCNTs.

All the functionalized MWCNT materials exhibited very good dispersibility properties for long time periods, especially in acetonitrile.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.carbon.2011.12.018.

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