

Article

Selective Grafting of Primary Amines onto Carbon Nanotubes via Free-Radical Treatment in Microwave Plasma Post-Discharge

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Abstract: A novel strategy to graft functional groups at the surface of carbon nanotubes (CNTs) is discussed. Aiming at grafting nitrogen containing groups, and more specifically primary amine covalent functionalization, CNTs were exposed under atomic nitrogen flow arising from an Ar + N₂ microwave plasma. The primary amine functions were identified and quantified through chemical derivatization with 4-(trifluoromethyl)benzaldehyde and characterized through X-ray photoelectron spectroscopy. The increase of the selectivity in the primary amines grafting onto CNTs, up to 66.7% for treatment of CNT powder, was performed via the reduction of post-treatment oxygen contamination and the addition of hydrogen in the experimental set-up, more particularly in the plasma post-discharge chamber. The analyses of nitrogenated and primary amine functions grafting on the CNT surface suggest that atomic nitrogen (N•) and reduced nitrogen species (NH• and NH₂•) react preferentially with defect sites of CNTs and, then, only atomic nitrogen continues to react on the CNT surface, creating defects.

Keywords: carbon nanotubes; atomic nitrogen; primary amine grafting; microwave plasma; XPS

1. Introduction

Since 1991 [1], carbon nanotubes (CNTs) have attracted worldwide interest among many researchers and engineers owing to their outstanding physical properties resulting from their one-dimensional structure. These unique mechanical, thermal and electrical properties allow for envisaging their use in many scientific and technological fields [2]. Offering in the same time a high aspect ratio and a low density, CNTs are ideal candidates as advanced filler materials in polymer composites [3]. An important parameter for producing nanocomposites with largely improved properties relies on the extent of dispersion of the individual CNTs. However, this task is particularly challenging since CNTs have a strong tendency to form agglomerates stabilized by numerous van der Waals interactions between CNT sidewalls [4]. These bundles, in addition to the CNT low solubility in water and organic solvent, constitute drawbacks for engineering of CNT in the majority of their potential applications.

The functionalization of CNT sidewalls is an effective way to prevent CNTs from aggregation in order to achieve better dispersion and stabilize the CNTs within a polymer matrix through interfacial interactions between CNTs and the host polymer [5]. The covalent grafting of functional groups onto CNT surface can be achieved through two general processes [6]. The functional groups can be grafted on the already existing defects in the nanotube lattice such as pentagon–heptagon pairs (or Stone-Wales defects), sp^3 hybridized defects or vacancies. The other way is the sidewall functionalization which consists of grafting chemical groups through reactions onto π -conjugated skeleton of CNTs. Since the reactivity of CNT sidewalls remains low, the direct sidewall functionalization of CNTs requires highly reactive species such as nitrenes, carbenes or radicals. However, for high degree of chemical functions grafting, the disruption of the π -conjugated become too important, involving the loss of CNTs properties, especially the electrical conductivity [7]. The majority of developed covalent functionalization of CNTs is carried out in organic solvent. Nevertheless, the CNT surface, being widely inert, needs rather harsh conditions for wet chemical functionalization that requires generally multistep time-consuming reactions, rarely resulting in a controlled process [8]. Moreover, intensive or long sonication processes, needed to disperse CNTs in the solvent, could not only cause damage to the sidewalls, but also cut the CNTs into short segments [9,10].

Alternative “dry” processes are also being developed such as the ball-milling of CNTs in reactive atmospheres for example [11]. This technique was used to graft different chemical groups at the ends of cup-stacked CNTs resulting in the decrease of the average length of CNTs.

The use of plasma discharges have also been proposed and developed for the solvent-free modification of the surface of CNTs. Considered as the fourth state of the matter, the plasma is an ionized gas constituting a highly reactive chemical environment and gathering free electrons, ions, radicals, ultra violet to visible radiation and excited neutral species [12]. The plasma treatment of CNTs can result in different types of surface modification depending on plasma type and the process. The inert argon (Ar) plasma produces an efficient etching and cleaning process of CNTs [13] and can

activate the surface of CNTs allowing the subsequent grafting of polymer [14,15]. The CNTs can be also coated with different plasma polymer films [16–20]. In function of the nature of the polymer grafted onto CNTs, different organic compounds such as aniline, phenol or 1-naphtol and inorganic pollutants such as Pb(II) or UO_2^{2+} can be removed from aqueous solution in contact with the formed CNT composites [21–23]. Besides being time efficient processes, the plasma treatments are also versatile techniques to tailor the CNT surface properties by the grafting of functional groups paving the way for subsequent chemical reactions like polymer grafting for example. The most common plasma treatments of CNTs consist of introducing them directly in the plasma discharge allowing to bind fluorine [24,25], oxygen [26–28] or nitrogen [29–32] containing functional groups. The excited species such as electrons, ions or radicals interact with the CNTs surface breaking the C=C bonds and promoting the grafting of functional groups on the created structure defects. Moreover, UV photons interact also with CNTs creating active sites on their sidewalls but they promote at the same time the defunctionalization of moieties grafted on CNTs [33]. However, the high energy particles bombardment and irradiation of CNTs in plasma discharge can also badly damage the graphene layers or even destruct CNTs [34–36]. A limitation of the power supplied to the plasma or a limited duration of the treatment can be applied to limit destruction of sidewalls. However, these limits greatly hinder achieving a suitable and controlled functionalization of CNTs. Another possibility is to avoid the functionalization of CNTs directly inside or close to the plasma, where the density of energetic ions and electrons is very high and, instead, placing the CNTs outside the discharge production zone to reduce the detrimental effects associated with ion bombardment and irradiation [33,37,38]. In this approach, radicals play a key role in grafting functional moieties onto CNT surface. The application of microwave discharge sources for the production of intense beams of atomic, radical or metastable species is well established [39]. The efficiency of this approach depends on the density of produced radicals. In this context, a surface wave discharge set-up was developed to achieve a high atomic nitrogen production through the homolytic dissociation up to 43% of molecular N_2 [40]. CNT pellet was treated in the post-discharge of Ar + N_2 microwave plasma, allowing the grafting of 10.6 atomic % of nitrogen containing functional groups [41]. In this set-up, the nanotubes are placed 40 cm from the discharge in contact with atomic nitrogen species that have enough mean lifetime to reach them contrary to other reactive species. High resolution photoelectron spectroscopy analysis showed that by exposing multi-wall CNTs to atomic nitrogen $\text{N}\cdot$ generated in the μ -wave plasma, nitrogen chemical groups were grafted onto the CNT surface altering the density of electronic states without alteration of the structure of CNTs [42].

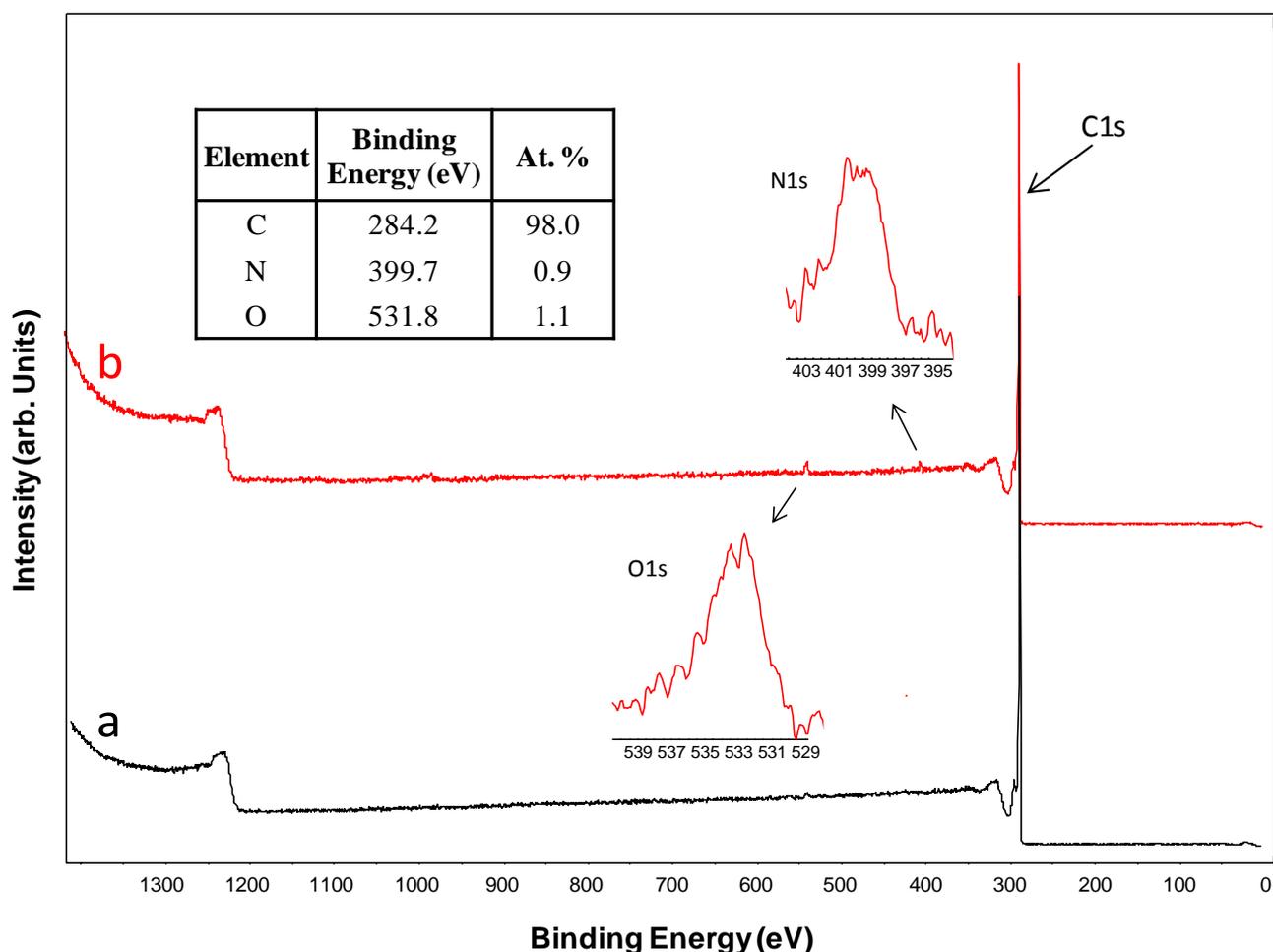
In the present work, Ar + N_2 microwave (μ -wave) plasma post-discharge treatment of CNT powder has been performed in order to incorporate amino groups on the surface of CNTs. Particularly, special attention has been drawn to the selectivity of the process, aiming at increasing the content of primary amines selectivity grafted on the nanotube surface. Higher selectivity has been reached by the reduction of oxygen contamination and the addition of hydrogen in the experimental set-up.

2. Results and Discussion

2.1. Treatment of CNT Powder

If the treatment of CNT pellets in the post-discharge allows a very efficient covalent functionalization reaction on CNT surface [42], the functionalization is not homogeneous because just the CNTs near the top surface of the pellets are exposed to the plasma. Indeed, atomic nitrogen can only interact with the nanotubes present on the upper surface of the sample. A mechanical stirring system of CNT powder has thus been developed with the aim of treating a large amount of CNTs. The CNT powder was stirred during the treatment allowing a permanent renewal of carbon nanotube accessible to the reactive atomic nitrogen flow. The treated CNTs were analyzed using X-ray photoelectron spectroscopy (XPS), a technique frequently used to determine the changes in the atomic content of CNTs after functionalization reactions [29,43,44]. The aim of this experiment was to determine whether nitrogenated groups were grafted homogeneously on the whole surface of the carbon nanotubes. Figure 1 shows the comparison of XPS survey spectrum recorded on CNTs and on N-functionalized CNTs.

Figure 1. X-ray photoelectron spectroscopy (XPS) spectra of (a) pristine carbon nanotubes (CNTs) and (b) CNTs exposed to atomic nitrogen in the Ar + N₂ microwave plasma post-discharge chamber.



A low intensity peak of nitrogen at 399.7 eV appears in the spectrum recorded on treated CNTs (Figure 1(b)). The relative concentration of N element is about 0.9 ± 0.1 at.%. The increase of O1s peak intensity at 532 eV is also observed, the oxygen relative atomic concentration is equal to 1.1 ± 0.3 at.%, which means an oxygen incorporation of about 0.5 at.% after CNTs treatment. XPS measurements were carried out on five different locations of the same sample, the slight standard deviation of the relative nitrogen atom concentration showed that the whole amount of CNTs was homogeneously treated. The total amount of grafted elements per CNTs is smaller when the treatment is performed in powder than in pellets probably due to the difference in the atomic nitrogen residence time at the surface of each carbon nanotube.

2.2. Origin of Oxygen Surface Contamination

As previously discussed, the μ -wave plasma post-discharge treatment allows the covalent grafting of nitrogen groups, but also the introduction of oxygen enriched groups on the carbon nanotube surface [42]. Oxygen contamination sources generally observed in plasma surface modification processes are most often the residual oxygen and water vapor present in the plasma [45]. However, unlike the grafted nitrogen content, a variation of the relative percentage of oxygen atoms between samples treated with identical plasma parameters was observed. Oxygen contamination can thus be provided from another source such as post-plasma reaction on the surface of carbon nanotubes. To shed some light on the origin of this contamination, freshly treated CNT pellets were put under atmospheric pressure either using argon or oxygen. The results from XPS analysis are presented in Table 1.

Table 1. Surface element content of CNTs pellets treated under same treatment plasma parameters and conserved under atmospheric pressure (a) in argon or (b) oxygen.

Element	Binding Energy (eV)	At. %	Element	Binding Energy (eV)	At. %
C1s	284.2	83.8	C1s	284.3	83.1
N1s	399.8	11.5	N1s	399.9	9.4
O1s	533.0	4.7	O1s	533.0	7.5

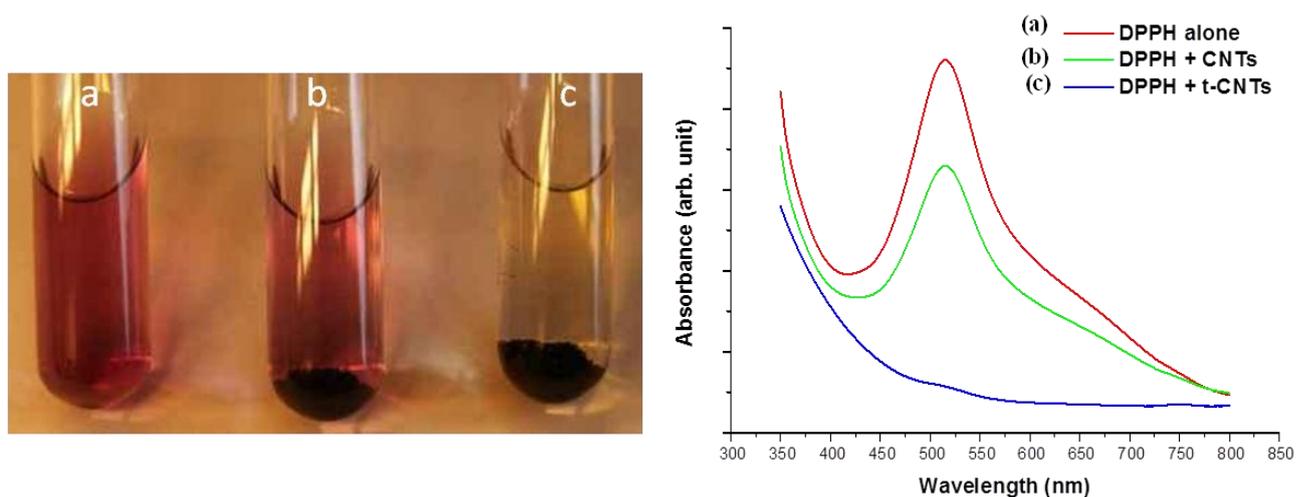
(a)

(b)

When the freshly treated nanotubes were placed under atmospheric pressure via oxygen, the relative concentration of grafted oxygen increased while nitrogen content was lower than when placed in argon. It seems thus that reactive species remain on the surface of CNTs after functionalization process, which can react with oxygen or water vapor present in ambient atmosphere. In order to explain this observation, we suggest that these reactive species are radicals remaining on the CNTs surface after plasma post-discharge treatment. Interestingly, the presence of a significant amount of radicals on the freshly treated CNTs surface has been clearly evidenced by chemical reaction with 2,2-diphenyl-1-picrylhydrazyl (DPPH). DPPH is widely used to test the ability of compounds to act as free radicals scavengers or radical hydrogen donors. In the presence of such species, DPPH turns from purple to pale yellow color corresponding to the reduced form of DPPH [46].

When freshly treated CNTs (t-CNTs) are contacted with the DPPH solution, the supernatant turns from purple to yellow color, while no evolution of the DPPH purple color is observed when it is added onto pristine CNTs. These observations were further confirmed by UV-visible absorption spectroscopy (Figure 2).

Figure 2. Qualitative assessment of the presence of radicals on the surface of freshly treated CNTs. Photograph and absorption spectrophotometric analysis of (a) 2,2-diphenyl-1-picrylhydrazyl (DPPH) solution alone, (b) DPPH solution in presence of pristine CNTs and (c) DPPH solution in presence of freshly treated CNTs (t-CNTs).



The molecule of DPPH is characterized as a stable free radical due to the delocalization of the spare electron over the aromatic molecule giving rise to the deep purple color, characterized by an absorption band in methanol solution, centered at a wavelength of about 520 nm. This absorption peak is conserved when the DPPH solution is added to pristine CNTs showing if any chemical reactions occurred. The observed decrease of peak intensity can be related to the decrease of DPPH concentration due to partial physisorption of DPPH aromatic rings on the graphitic CNTs surface. When DPPH solution is added to freshly treated CNTs, this characteristic absorption peak cannot be observed meaning that DPPH is under reduced form after reaction with free radicals present on the t-CNT surface. The DPPH solution was also added to CNTs treated one day earlier, no color change was observed showing that all remaining radicals did react under ambient atmosphere.

Taking into account these observations, one may assume that oxygen contamination of the treated CNT surface is partially due to post-plasma reaction between the radicals remaining active at the CNT surface and ambient air (O_2) atmosphere. Accordingly, all μ -wave plasma post-discharge treated CNTs were recovered samples under ambient atmosphere with argon gas for one hour right after the treatment.

2.3. Quantification of Primary Amine Functions Grafted on CNTs

In the μ -wave post-discharge plasma treatment, atomic nitrogen species interact with CNTs leading to covalent grafting of nitrogenated groups on their surface without damage to their structure. However, among these nitrogenated functions, primary amines have attracted our attention because they can be used as initiation sites for promoting lactone ring-opening polymerization yielding

polyester-grafted MWCNT nanohybrids [47]. The quantity of primary amine functions was determined after chemical derivatization with 4-(trifluoromethyl)benzaldehyde (TFBA) [38,48,49]. This technique was developed to selectively label surface functional groups of interest with molecules containing an element that is not present on the surface prior to the derivatization reaction. Elements like fluorine or iodine are most useful because they can be determined by XPS with very high sensitivity [50]. A treated CNT pellet was exposed to a TFBA saturated atmosphere and then analyzed by XPS (Table 2).

Table 2. XPS analysis of treated CNT pellet: relative content in [N] and [NH₂] and primary amine selectivity; ¹[N] = (N/C) × 100; ² determined using Equation (1); ³ ([F]/3[N]) × 100.

CNTs Elemental Composition				[N] (%) ¹	[-NH ₂] (%) ²	-NH ₂ Selectivity (%) ³
(at.%)						
C	N	O	F			
83.1	11.5	4.5	0.9	13.8	0.4	2.6

Even if the quantity of nitrogen groups is important (11.5 at.%), the amount of primary amines remains limited to 0.3 at.% at the surface of treated CNTs pellet. The -NH₂ selectivity value is thus limited to 2.6% which means that only one fortieth of nitrogen functions are primary amines. The quantity and the selectivity of primary amines are thus very low on the surface of CNT pellet treated under these parameters. After the treatment of CNTs powder, no significant traces of fluorine could be detected by XPS while 1 at.% of nitrogen was measured confirming the very low primary amine group selectivity. These observations can be explained knowing that the hydrogen source to yield amine functions is only constituted of residual water molecules and hydrogen traces present in the discharge tube and post-discharge chamber. A solution for reaching a selective -NH₂ grafting, is to introduce hydrogen gas in the plasma set-up.

2.4. Introduction of H₂ in the μ-Wave Plasma Discharge

Hydrogen gas was introduced at the top of the discharge tube together with argon and nitrogen gases. The hydrogen molecules are easily dissociated in the μ-wave plasma. A large majority of the molecules are thus transformed in atomic hydrogen H• [33], which can react with nitrogen species to form reduced nitrogen radicals in the plasma. Different quantities of hydrogen were introduced directly in the discharge tube, the flow varied from 0 to 56.5 sccm, which was the maximal flow allowed by the hydrogen mass flow controller. The values of relative quantity of the elements present onto the surface of the treated CNTs pellets, as derivatized by TFBA, were measured by XPS on every sample thus treated under increasing hydrogen flow in the discharge. An evolution of the elemental composition of the CNT pellet surface is observed with the increase of the hydrogen flow in the discharge chamber. The quantity and selectivity of primary amines in function of introduced H₂ flow are presented in Figure 3 as well as the evolution of nitrogen content.

With the increase of the hydrogen flow, the quantity of nitrogen atoms decreased, while the content in primary amine functions is enhanced, resulting in an increase of primary amine selectivity from 2.5% to 26% for the maximal hydrogen flow. It is interesting to note that the oxygen content decreases with the hydrogen flow as well (from 4.5 to 1.8 at.% when introduced H₂ content varies from 0 to 56.5 sccm). Different treatment mechanisms can explain this behavior. The used parameters allowed

reaching a dissociation rate of N_2 of 20% in the Ar + N_2 glow. However, the added hydrogen molecules are in majority dissociated in the plasma and this reaction completely modifies the plasma chemistry, which can limit the N_2 dissociation rate in atomic nitrogen. The passivation of the CNT surface by atomic hydrogen can also explain the limited grafting of nitrogen and oxygen atoms.

Figure 3. Quantity and selectivity of primary amines and nitrogen content in function of H_2 flow directly introduced in the discharge chamber.

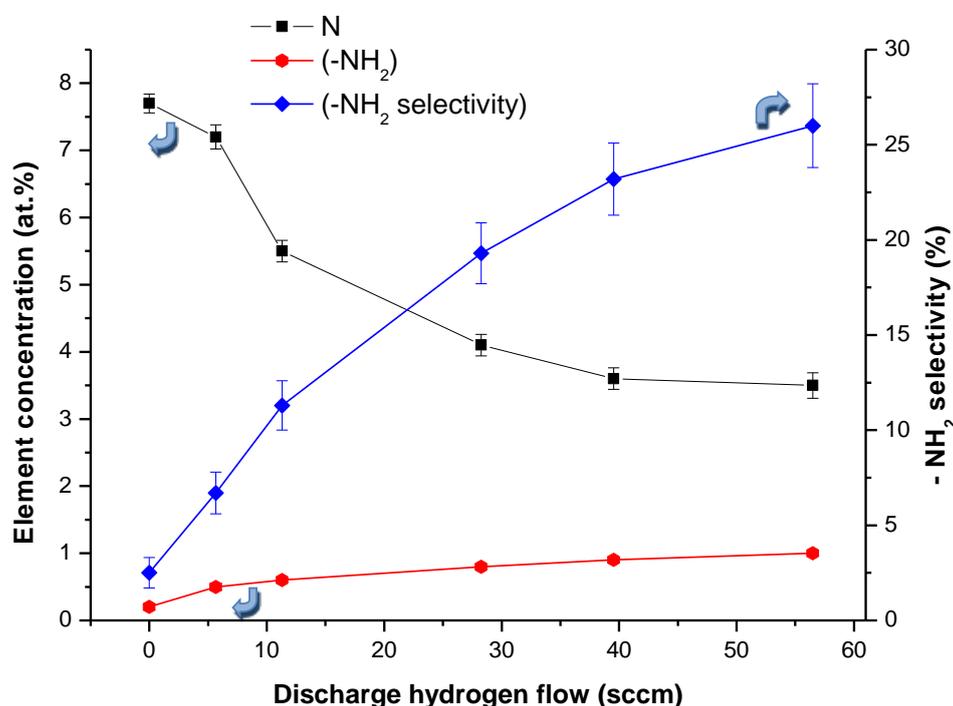


Figure 3 suggests that the grafting of primary amines tends to some saturation with the addition of hydrogen in the plasma chamber and the decrease of nitrogen content tends to stabilize it as well, at *ca.* 40 sccm of added hydrogen flow. These results demonstrate that the selectivity of primary amines grafting can be enhanced by the introduction of H_2 in the Ar + N_2 μ -wave plasma. The relative quantity of grafted $-NH_2$ groups tend to be equal to 1%, which is certainly a very acceptable value compared to data reported in the literature and for their use as further initiation sites for polymerization process. In a next step, the treatment of 0.5 g of CNT-powder was carried out with the addition of 56.5 sccm of hydrogen gas in the discharge tube for 2 h. After compression in pellet, TFBA derivatized CNTs were analyzed by XPS (Table 3).

Table 3. XPS analysis of CNTs in function of H_2 flow introduced in the μ -wave plasma discharge chamber: relative content in [N] and [NH₂] and primary amine selectivity; ¹ [N] = (N/C) \times 100; ² determined using equation 1; ³ ([F]/3[N]) \times 100.

H_2 (sccm)	CNTs Elemental Composition (at.%)				[N] (%) ¹	[-NH ₂] (%) ²	-NH ₂ Selectivity (%) ³
	C	N	O	F			
0	98.0	0.9	1.1	traces	0.9	traces	/
56.5	98.8	<0.2	0.6	0.4	<0.2	0.1	/

Evaluation of the quantity of nitrogen atoms grafted on the CNT-surface was not possible through XPS analysis since the nitrogen content proved to be much lower than the minimum nitrogen content detectable by XPS. However, under the same treatment conditions, but without any addition of hydrogen gas in the discharge chamber, the grafted nitrogen atoms were equal to *ca.* 1 at.%. Owing to their higher XPS sensibility after the TFBA derivatization process, the content in primary amine functions could be determined to be close to 0.1 at.%. In comparison with pristine CNTs, no variation in the oxygen content was observed. The quantity of grafted primary amines is thus reduced when hydrogen is added in the Ar + N₂ discharge tube. Even if this addition of H₂ in the μ -wave plasma allows an increase of quantity and selectivity in primary amine functions, the quantity of nitrogen (and primary amines) is reduced due to the passivation of the CNT surface by atomic hydrogen. As hydrogen cannot be detected by the XPS set-up, it was not possible to determine the grafted hydrogen content.

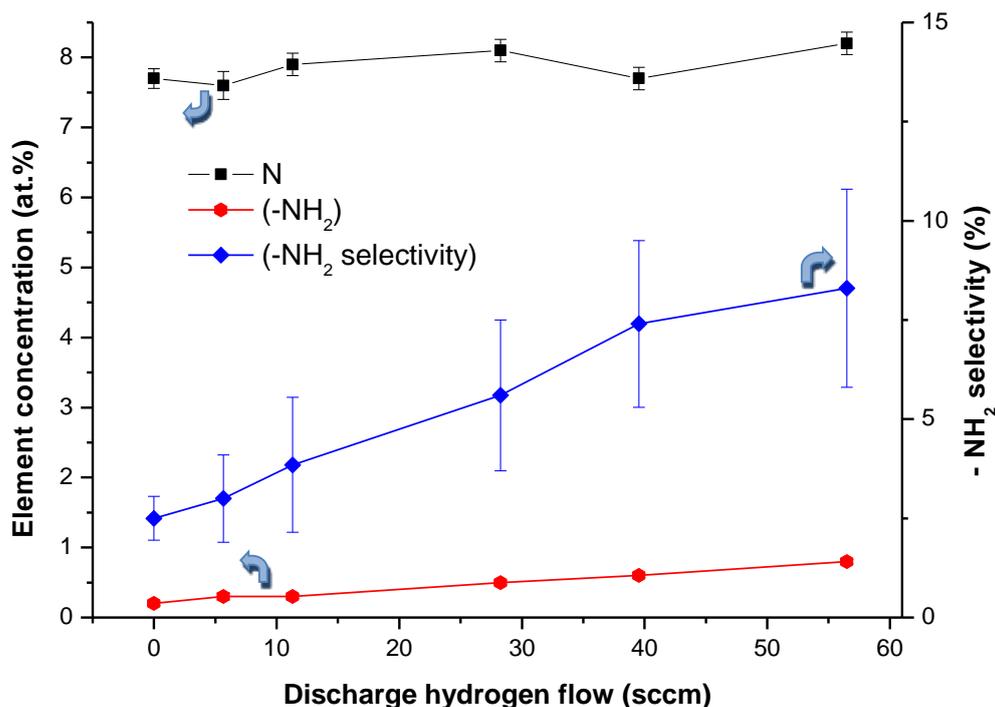
The introduction of hydrogen gas in the discharge tube during Ar + N₂ μ -wave plasma post-discharge treatment of CNTs therefore allows the increase in the selectivity of primary amines grafted on the CNT surface. However, the total amount of -NH₂ grafting is reduced due to atomic hydrogen passivation of CNTs. The extent of this passivation cannot be quantified and can impact the CNT properties if the creation of defects in the structure of carbon nanotubes becomes too significant. An alternative process can thus be proposed, that is the introduction of hydrogen gas directly in the post-discharge chamber during the plasma treatment of the CNTs.

2.5. Introduction of H₂ in the μ -Wave Plasma Post-Discharge

Hydrogen gas was directly introduced in the post-discharge chamber, instead of in the discharge tube, to avoid the formation of high atomic hydrogen content, which can react instead of other radicals, resulting in the passivation of CNT surface as previously observed. In this strategy, no changes occur in the Ar + N₂ μ -wave plasma allowing the preservation of the N₂ high dissociation rate of 20% in the used standard plasma parameters. It was expected that the interaction of carbon nanotubes with atomic nitrogen in hydrogen atmosphere could result in an increase of both quantity and selectivity of primary amine grafting. Different quantities of hydrogen gas were introduced in the post-discharge chamber, the flow varied again from 0 to 56.5 sccm. The values of relative quantity of the elements present on the surface of the treated CNTs pellets, as derivatized by TFBA, were measured by XPS on every sample thus treated, under increasing hydrogen flow, in the post-discharge (Figure 4).

With the addition of hydrogen directly in the discharge, there was no evolution of the grafted nitrogen content, which remained relatively constant around 7.9% regardless of the addition of the H₂ flow in the post-discharge chamber. However, the total primary amine content increased continuously from 0.2% to 0.8%, resulting in an enhancement of the -NH₂ selectivity from 2.5% to 8.3%. The relative percentage of oxygen atom also decreases when the hydrogen flow is introduced in the post-discharge chamber (from 4.5 to 3.2 at.% when introduced H₂ content varies from 0 to 56.5 sccm). In contrast to the treatment of CNTs in the post-discharge of the Ar + N₂ + H₂ μ -wave plasma, the quantity and the selectivity in primary amines does not saturate at higher hydrogen flow values and increase continuously.

Figure 4. Quantity and selectivity of primary amine groups and nitrogen content in function of H₂ flow introduced in the post-discharge chamber.



The treatment of 0.5 g of CNT-powder was thus carried out with the addition of 56.5 sccm of hydrogen gas in the post-discharge chamber. The CNTs were treated for 2 h using standard plasma parameters and, after their compression in pellet, they were derivatized with TFBA. XPS results are represented in Table 4.

Table 4. XPS analysis of CNTs in function of H₂ flow introduced in the μ -wave plasma post-discharge chamber: relative content in [N] and [NH₂] and primary amine selectivity; ¹ [N] = (N/C) \times 100; ² determined using equation 1; ³ ([F]/3[N]) \times 100.

H ₂ (sccm)	CNTs Elemental Composition (at.%)				[N] (%) ¹	[-NH ₂] (%) ²	-NH ₂ Selectivity (%) ³
	C	N	O	F			
0	98.0	0.9	1.1	traces	0.9	traces	/
56.5	96.1	1.0	0.9	2.0	1.0	0.7	66.7

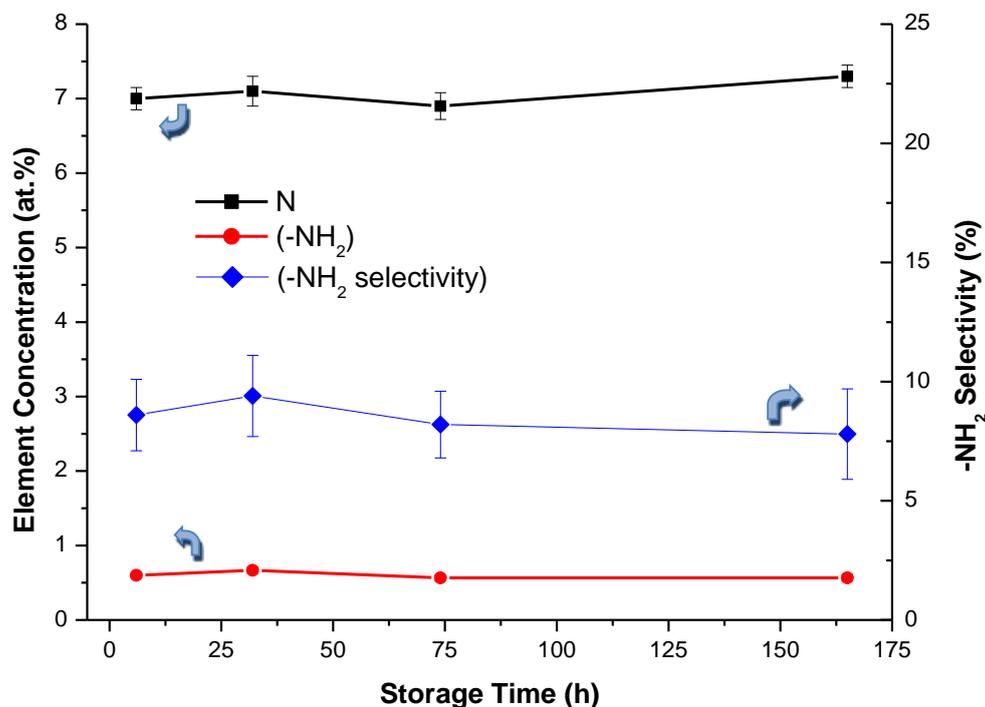
As in the case of pressed CNT-pellets, the quantity of grafted nitrogen atoms remains identical to the value obtained after the treatment of CNT-powder without addition of hydrogen. The quantity of oxygen also presents the same behavior with a slight decrease from 1.1 to 0.9 at.% with addition of hydrogen. However, the quantity and the selectivity of primary amines are very different compared to the CNT pellet treatment. In fact, the measured quantity of -NH₂ is equal to 0.7% resulting in a selectivity as high as 66.7%, which means that 2/3 of grafted nitrogenated groups are constituted by primary amine functions. A quantity of grafted -NH₂ of 0.7% is certainly high enough to initiate the polymerization of lactone for example [51]. Moreover, the low content of elements grafted on the CNTs during the μ -wave

plasma post-discharge treatment, 1 at.% of nitrogen and 0.3 at.% of oxygen, should limit the damage to their conjugated structure allowing the preservation of their physical properties.

2.6. Stability of Primary Amines Grafted on CNTs

A major concern when primary amines are grafted on a surface is their long term stability, commonly referred to as “ageing”. For example, the density of primary amine functions grafted on a polymer surface via plasma treatment can decrease by more than 50% with time [52] due to post-plasma oxidation that converts amines into amides [53] and due to an important thermodynamically driven reorientation of amine functions into the polymer bulk [50]. It was thus important to verify if primary amines grafted on CNTs can undergo this ageing process. A treatment of the CNT pellet was carried out using standard plasma parameters with introduction of hydrogen flow of 56.5 sccm in the μ -wave plasma post-discharge chamber. This treated CNT-pellet was divided in four parts, which were derivatized by TFBA after different storage times under ambient atmosphere (Figure 5). No evolution in either quantity or selectivity in grafted primary amines with storage time has been observed attesting a good stability of these functions.

Figure 5. Time-evolution of the surface-compositions of treated pressed CNTs pellets with storage time under ambient atmosphere.



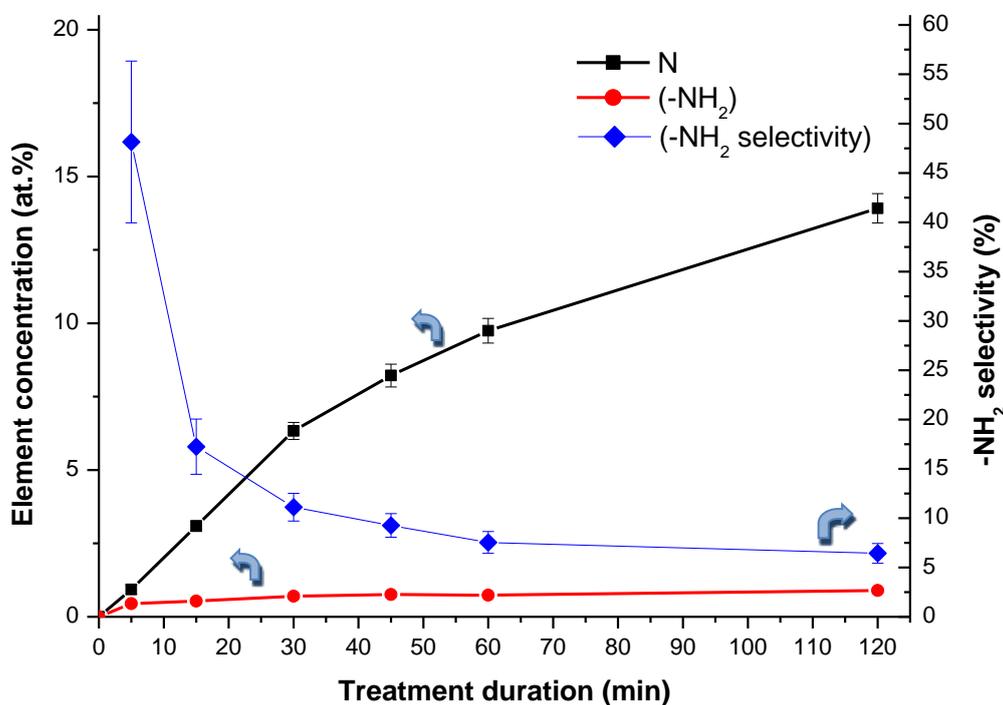
In order to take such stability into account, it may be suggested that primary amine functions could be stabilized by a delocalization of the nitrogen non-bonding electron pair into the aromatic rings of the graphene structure of the carbon nanotubes. This effect can be compared to the resonance delocalization observed in aniline.

2.7. Influence of Treatment Time on Nitrogen and $-NH_2$ Functions Grafting

The time of the μ -wave plasma post-discharge treatment is one important parameter in determining the quantity of grafted elements on the surface of the CNTs. The evolution of the nitrogen content and primary amine functions quantity (and selectivity) was studied in function of the treatment time. Both CNT powder and pellet has been studied in order to control the influence of the surface area that interacts with reactive species. In both experiments, the treatment was carried out with standard plasma parameters and with introduction of hydrogen (56.5 sccm) in the post-discharge during the process for a time ranging from 0 to 120 min.

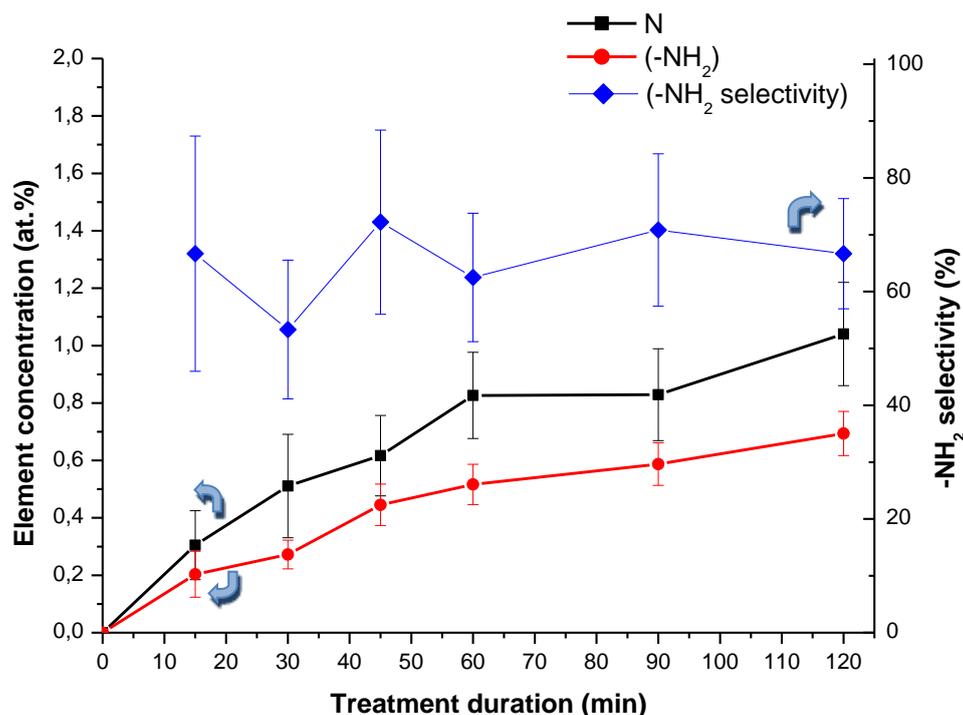
Saturation in the content of grafted primary amine is observed after a few minutes of treatment of the CNT pellet while the nitrogen content increases with the reaction time. The resulting primary amine selectivity presents a sharp decrease from 48.1% to 11.1% between 5 and 30 min and then slightly decreases at longer treatment times (Figure 6).

Figure 6. Evolution of nitrogen content and primary amines quantity and selectivity on CNT pellet with increasing treatment time.



The results obtained after treatment of 0.5 g of the CNT powder are presented in Figure 7. In the case of the CNT powder treatment, the content in nitrogen and primary amines changes in the same proportion with the treatment time. The selectivity in grafted primary amines remains relatively high and constant at *ca.* 66%.

Figure 7. Evolution of nitrogen content and primary amine quantity and selectivity on CNT powder with the treatment time.



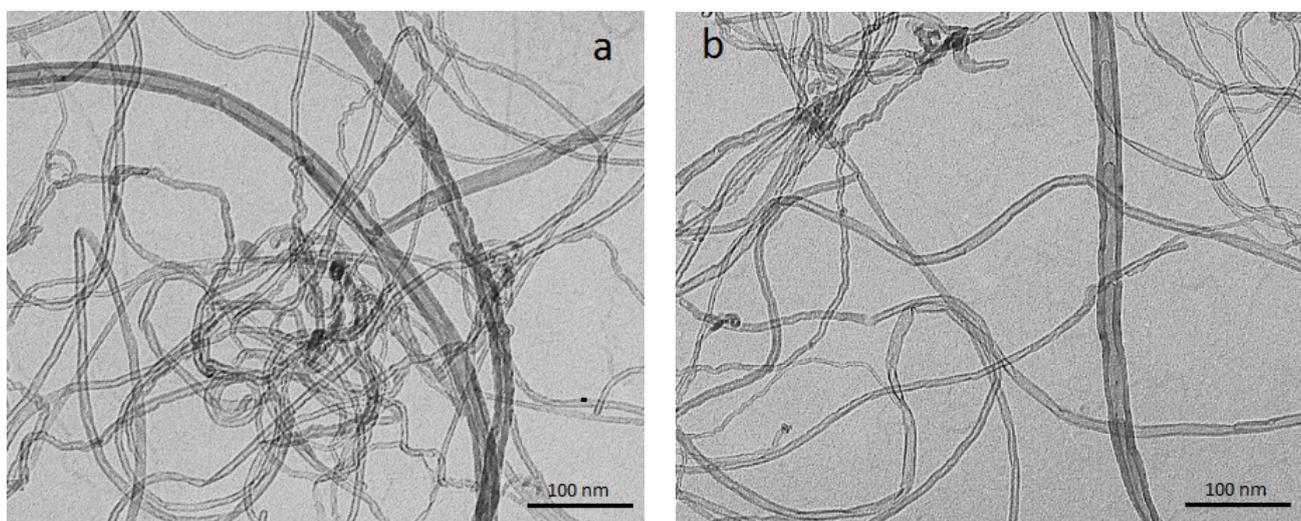
Two different trends in the evolution of the content in nitrogen and primary amines can be observed for CNT-powder and pellets. In Figures 6 and 7, we can observe that the primary amine selectivity, after 5 min of the CNT pellet treatment, is in the same range as the value recorded after 2 h of treatment of CNT powder ($48 \pm 9\%$ and $66 \pm 19\%$, respectively). It is known that the covalent functionalization of carbon nanotubes is performed preferentially onto defects present along the nanotube structure [54]. One hypothesis can be extracted from these results: at the beginning of the treatment, atomic nitrogen $N\cdot$ and reduced nitrogen radicals such as $NH\cdot$ and $NH_2\cdot$ react with structural defects of CNTs. This first part of the treatment consists of a functionalization via defect-side chemistry. When all defects are saturated, the process continues via a sidewall functionalization where reactive species create new defects on the surface of CNTs. However, during this second phase, it can be suggested that only atomic nitrogen displays enough reactivity to create new defects. The difference of reactivity between these radical species would explain the decrease of primary amine selectivity during pellet treatment with atomic nitrogen continuing to graft nitrogenated functions on CNTs while the interaction with $NH\cdot$ and $NH_2\cdot$ species, and thus primary amines grafting, would be reduced. In fact, we have demonstrated that molecular hydrogen cannot react with the nitrogen radicals present on the surface of the CNTs and, thus, the grafting of atomic nitrogen does not allow the incorporation of primary amine functions. In the case of the CNT powder, the overall surface is by far too important for treatment time to reach the sidewall functionalization phase. Moreover, carbon nanotubes are permanently stirred up, resulting in a limited residence time of the active species for any given CNT, which does not trigger the creation of new defects by the atomic nitrogen. In the case of CNT pellet treatment, it seems that nitrogen radicals already begin to create defects in the CNT lattice after 5 min while the quantity of primary amine groups has almost reached the maximum value observed for the CNT powder treatment (0.60 and 0.66 at.% for treatments of CNT pellet and powder respectively).

The functionalization of 0.5 g of acid treated CNT powder, which presents a high density of defects, was carried out using the same μ -wave plasma post-discharge treatment conditions. A higher quantity of nitrogen is grafted ($[N] = 2\%$) with a selectivity in primary amine functions around 60% indicating the influence of the structural defects on the efficiency of the CNT amino-functionalization.

2.8. Structure of CNTs after μ -Wave Plasma Post-Discharge Treatment

The effect of μ -wave plasma post-discharge treatment of CNT powder, treated in presence of H_2 , on the structure of CNTs was investigated with transmission electron microscopy (TEM). TEM images of CNTs before and after primary amine grafting are presented and compared in Figure 8. No difference of the CNT morphology can be observed between untreated and plasma post-discharge modified samples. The integrity of the CNT structure does not appear modified after the surface grafting of amine groups. It is worth noting that high resolution TEM analysis have also been studied and revealed that the surface morphology of CNTs treated in the post-discharge of $Ar + N_2$ μ -wave plasma was not altered [42].

Figure 8. Representative TEM images of CNTs (a) before and (b) after μ -wave plasma post-discharge treatment for 2 hours with introduction of H_2 in the post-discharge chamber.



3. Experimental Section

The multi-walled carbon nanotubes (CNTs) used in this work were industrially produced by Nanocyl S.A. (Nanocyl[®]-7000), via a catalytic carbon vapour deposition (CCVD) process. Carbon nanotubes have a purity of min. 90% carbon. These nanotubes are characterized by an average outer diameter of 10 nm, corresponding to *ca.* 9–10 concentric layers. The average length is *ca.* 1.5 μ m.

The CNTs were treated in the post-discharge of an $Ar + N_2$ microwave plasma sustained through a surface wave launched in a quartz tube via a surfaguide supplied by a 2.45 GHz microwave generator. Hydrogen gas can also be introduced either in the discharge or in the post-discharge chamber. The experimental set-up was described elsewhere in detail [40]. It is important to note that the discharge tube and the post-discharge chamber are separated by a diaphragm playing two-roles in the post-discharge treatment. Firstly, the separation between the plasma set-up and the post-discharge protects the samples

placed in the post-discharge from irradiation of high-energy particles from μ -wave plasma. Moreover, the average distance of 40 cm between the end of the discharge tube and sample holder promotes the interaction of nanotubes with atomic nitrogen species that have enough mean lifetime to reach them contrary to other reactive species.

The used plasma parameters for all treatment of CNT pellets and powders were identical allowing the comparison between results. The pulsation time and the period were laid down to 225 μ s and 900 μ s respectively and the average discharge power was set to 400 W. The pressure in the discharge and the post-discharge chamber were fixed to 36 Torr and 3 Torr respectively. The CNT pellets were placed on a sample holder like schematically represented in a previous paper [41]. For the treatment of powder, the CNTs were placed in a crucible directly mounted on a vibrating speaker membrane in the post-discharge chamber. The CNTs were stirred permanently during the treatment which is limited to 2 h to avoid overheating of the microwave generator. The treatment time was set at 45 min for treatment of CNT pellets and 2 h for CNT powder, while the quantity of treated CNTs powder was fixed at 0.5 g. To avoid the dispersion of the CNT powder in the post-discharge chamber, the Ar flow has been reduced leading to a flow ratio of Ar to N₂ of 14:1. This decrease of the Ar flow influences the N₂ dissociation in the plasma discharge, actually equal to 18%, the half value obtained with optimal plasma parameters [40].

XPS analyses were performed on a VG-ESCALAB 220iXL spectrometer under a pressure typically around 10–10 Torr. The XPS data were collected using monochromated Al K α radiation at 1,486.6 eV, survey spectra were recorded with a 50 eV pass energy 150 W electron beam power, as well as the high resolution spectra in the regions of C1s, N1s, O1s and F1s with a 20 eV pass energy. Elemental composition was inferred from photoelectron peak areas using the respective photoionization cross-section calculated by Scofield [55] and corrected by the electron inelastic mean free path and the transmission function of the spectrometer analyzer [56]. XPS analysis measures the kinetic energy and the number of electrons that escape from the top (\sim 10 nm) of the material being analyzed. It is important to note that since carbon nanotubes present an average diameter of *ca.* 10 nm, XPS results arise from the average analysis of the volume of the first CNTs layer and not of the extreme surface of the nanotubes. The element quantification values obtained from the XPS analyses were normalized in relation to the quantity of carbon element. The normalized values are represented with square brackets, [N] for nitrogen for example. All samples were analyzed at minimum three different places.

The derivatization reaction was performed by exposing pressed CNT pellets to 4-(trifluoromethyl) benzaldehyde (TFBA) vapor in a chamber at 3 Torr pressure and room temperature. The aldehyde group of TFBA reacts exclusively with primary amine functions, as shown by Chevallier *et al.* [57]. Primary amine concentration is derived as follows:

$$[-NH_2] = \left[\frac{F}{3} / (C - 8F/3) \right] \times 100\% \quad (1)$$

where [NH₂] is the percent of carbon atoms carrying primary amines, F and C are the fluorine and carbon atomic concentrations determined by XPS after the reaction with TFBA. F/3 corresponds to the number of –NH₂, 8F/3 represents the amount of carbon introduced with TFBA molecules. The [–NH₂]/[N] (or F/3N) ratio is considered as a measure of –NH₂ groups grafting selectivity, namely the relative concentration of N atoms bonded in primary amines (in % of N). The latter is therefore particularly useful for comparing samples with different [N] values and determining the selective

primary amination efficiency of treatment. The time of exposition of each sample to TFBA agent was fixed to 12 h after a kinetic study of $-\text{NH}_2$ derivatization [58].

Concerning the test used to detect radical species on CNTs, a solution of DPPH in methanol with a concentration of 5×10^{-7} M was prepared and 20 mL of this solution was added into test tubes containing each 20 mg of pristine CNTs and freshly treated CNTs.

TEM observations were performed on a Philips CM200 apparatus using also an acceleration voltage of 100 kV. The CNTs were sonically dispersed in ethanol and a drop of the solution was deposited onto the TEM grid.

4. Conclusions

Surface treatment of CNTs in the Ar + N₂ μ -wave plasma post-discharge is an original way to readily functionalize one step CNTs with nitrogenated functions. In particular, the results attest the efficient and selective grafting of primary amines on the surface when H₂ is added in the post-discharge chamber, without damaging the CNT structure. Although often underestimated, the influence of the atmosphere on the grafted elements on CNTs after plasma post-discharge treatment has been highlighted. The grafted primary amines proved stable over time. The increase of the primary amines selectivity grafting on CNTs powder has been performed via the reduction of oxygen contamination and the addition of hydrogen in the experimental set-up. The preliminary analyses of the nitrogenated functions and primary amines grafting on the CNTs surface seemed to indicate that atomic nitrogen (N•) and reduced nitrogen species (NH• and NH₂•) first react with the CNTs defect sites, then only atomic nitrogen continues to react on the CNT surface creating defects.

The introduction of primary amines on the nanotube surface by μ -wave plasma post-discharge treatment facilitates access to a large number of functional exploitations through the consecutive transformation of the amine functions. Among others, this provides the possibility to anchor groups for further initiation of polymerization reactions, in order to produce nanohybrids in which the CNT bundles can be disaggregated which is of interest for reinforced polymer composites. In this field, our proposed functionalization method provides a flexible and efficient route to covalently link CNTs to the polymer matrix which can result in improved mechanical performance without a decrease in the electrical properties. Another interesting aspect of our process is that the primary amine functions are directly grafted on the CNT surface with links between the function and the graphitic sidewall. This direct link between primary amine functions and CNT would be important in photovoltaic applications [59].

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