Functionalization of carbon nanotubes by atomic nitrogen formed in a microwave plasma Ar + N$_2$ and subsequent poly(ε-caprolactone) grafting

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Multi-walled carbon nanotubes (MWNTs) are placed under atomic nitrogen flow formed through an Ar + N$_2$ microwave plasma in order to functionalize covalently their side walls with nitrogen-containing groups. The MWNT surface analyzed by X-ray photoelectron spectroscopy shows the presence of amides, oximes and mainly amine and nitrile functions grafted in this way. In order to highlight the actual location of the amine functions grafted on MWNTs, they were considered as initiation species in ring-opening polymerization of ε-caprolactone using triethylaluminium as activator. The so-generated poly(ε-caprolactone) chains remain grafted on the MWNTs *via* amide bonds and form polyester islets along the nanotubes surface. TEM images of these MWNT surfaces grafted with poly(ε-caprolactone) show a good amino-sidewall distribution. This work demonstrates the side-wall amino-functionalization of carbon nanotubes readily achieved by microwave plasma with the possibility to reach within a short time period very high contents in nitrogen-based functions (~10 at.%).

Since their first observation in 1991, carbon nanotubes (CNTs)[1] have attracted the attention of many researchers around the world owing to their exceptional properties. Their excellent electrical and thermal conducting performances combined with their high toughness and transverse flexibility allow their use in a large range of applications like, for example, electronics components, chemical and biological sensors.[2] Offering at the same time a high aspect ratio (length-to-diameter) and a low density, this allotropic variety of carbon shows therefore strong application potential in reinforced composite materials, particularly by providing a three-dimensional conductive network through the polymer matrix with a low percolation threshold.[3] However, CNTs tend to form long bundles thermodynamically stabilized by numerous π–π interactions between the tubes. These bundles constitute a handicap in the majority of carbon nanotube applications. They exhibit very low solubility in water and organic solvents. In the case of their use as nanofillers, the homogeneous dispersion of CNTs in polymer matrices proves relatively difficult to achieve.[4]

The functionalization of nanotube sidewalls represents a solution in order to improve the interactions between CNTs and the solvent or the polymer matrix and, thus, to increase their dispersion ability. There are two main approaches for the surface modification of CNTs. One is the noncovalent functionalization used in several processes, such as ultrasonication,[5,6] addition of surfactants,[7,8] polymer wrapping[9,10] and the polymerization-filling technique (PFT).[11] One advantage of the noncovalent approach is that the structure of the nanotubes remains unaltered, thus their mechanical properties should not change but the forces between the wrapping molecules and the nanotubes surface might be weak and, thus, the efficiency of the load transfer might be low. Another approach relies on the covalent grafting of functional groups along the CNTs sidewalls. These functions are interesting to improve the interactions with the polymer matrix[12] and can be useful as anchoring sites for polymer chains.[9] The covalent bonding between CNTs and the polymer allows an optimal interfacial strength and thus a perfect load transfer to the CNTs to be achieved. However, in the majority of processes reported so far, such as chemical functionalization performed in solvent[13–15] or by ball milling,[16,17] only a very tiny fraction of the carbon atoms in the nanotubes get functionalized. Some targeted reactive functions, like amines, often require time-consuming and costly multistep reactions. Interestingly, a microwave-generated N$_2$ plasma has been very recently used as a source for incorporating nitrogen functional groups into SWCNTs *via* sidewall attachment.[18] But the production of atomic nitrogen was not highly efficient (dissociation rate limited to 5%).

This communication aims to describe an original way to readily functionalize in one step the surface of multi-walled carbon nanotubes (MWNTs) with nitrogenated functions and particularly with (reactive) amines, which can further initiate the polymerization of lactone monomers. Indeed, this two-step strategy combines a highly efficient microwave plasma functionalization and the covalent grafting reaction of *in situ* grown polyester chains. This process consists of placing a sample of carbon nanotubes under atomic nitrogen (N˙) flow obtained by molecular nitrogen dissociation in an Ar + N$_2$ microwave plasma (high dissociation efficiency of 40%). The treated samples were analysed by X-ray photoelectron spectroscopy (XPS, VG ESCALAB 220iXL) to determine the atomic percentages of elements and the nature of nitrogenated functions grafted on the MWNT surfaces. Interestingly, the location of the surface grafted amines (in fact

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mainly primary and possibly secondary amines) has been evidenced by transmission electron microscopy (TEM, Philips CM200) of *in situ* generated polyesters chains grafted/initiated from these reactive amines. Indeed, primary (and secondary) amines are known as very efficient initiator in ring-opening polymerization (ROP) of ε-caprolactone as activated by AlEt₃.[19]

In fact, the MWNTs are treated in the post-discharge of an Ar + N₂ microwave plasma sustained by a surface wave launched in a quartz tube *via* a surfaguide supplied by a 2.45 GHz microwave generator which can be pulsed. The gas flows (Ar and N₂) are regulated by mass flow controllers. The post-discharge is pumped by a rotary pump which maintains the pressure at several Torrs. The experimental set-up is shown in Fig. 1.

The MWNTs used in this work were produced by catalytic decomposition of acetylene on transition metal particles (Co, Fe) supported on Al_2O_3. The synthesis was carried out in a fixed-bed flow reactor at 700 °C. Purified MWNTs were obtained after dissolution of the support in boiling concentrated sodium hydroxide aqueous solution and dissolution of the catalysts in concentrated hydrochloric acid aqueous solution. The MWNTs are characterized by an average inner diameter of 5 nm and an average outer diameter of 15 nm, corresponding to 14–15 concentric layers. The average length is *ca.* 20 μm.

Firstly, before microwave plasma treatment, MWNTs were analysed by XPS. An XPS survey spectrum of these MWNTs reveals the presence of carbon (C1s centered at 284.4 eV), oxygen (O1s centered at 533.4 eV) and silicon (Si2p centered at 103.6 eV) on the sample outer surface. The peak quantitative analysis gives intensities of 5% in oxygen and 2% in silicon. The silicon peak energy is characteristic of silica (SiO_2) resulting from the chemical treatment used for the MWNT purification. The majority of oxygen (about 4%) is also due to silica, the MWNT surface is slightly oxidized as well.

Fig. 2 shows the XPS survey spectrum of MWNTs treated in the post-discharge of Ar + N₂ microwave plasma for 2 h under the following conditions: power = 400 W, argon flow = 1700 sccm, nitrogen flow = 50 sccm. These discharge parameters allow an optimal nitrogen dissociation rate (about 40%) to be obtained.[20]

Fig. 2 reveals the presence of carbon (C1s centered at 284.4 eV), oxygen (O1s centred at 532.9 eV), silicon (Si2p centered at 103.3 eV) and also the appearance of nitrogen (N1s centered at 398.9 eV) in comparison with the XPS spectrum of the pristine MWNTs.

Fig. 2 XPS spectrum of MWNTs treated with Ar + N₂ microwave plasma.

The peak quantitative analysis gives intensities of 8.3% in oxygen, 5.2% in silicon and 10.6% in nitrogen. The silicon and oxygen contents are higher than the values previously recorded for the untreated MWNTs. The nature and the percentage of the different nitrogenated functions grafted on the MWNT surfaces were obtained by N1s peak spectrum fitting.[21] The C1s spectrum fitting into different components related to nitrogen-containing groups was not considered because C–N and C–O species appear with analogous chemical shifts.

The N1s spectrum fitting (Fig. 3) shows the presence of four different nitrogen-based functions: amines (at 398.6 eV), nitriles (at 399.7 eV), amides (at 400.7 eV) and oximes (at 401.6 eV). A relative quantitative analysis gives an intensity distribution for these peaks equal to 3.9%, 3.7%, 2.2% and 0.8% respectively. Interestingly, the majority of nitrogenated functions are amines.

In order to precise the location of the amine functions grafted on MWNTs, it has been decided to take advantage of their presence to graft polyester chains in place (Fig. 4). Indeed primary (and possibly secondary) amines have been reported as highly efficient initiators of the ring-opening polymerization of ε-caprolactone (ε-CL).[19] For that purpose, triethylaluminium is added as an activator and the polymerization occurs *via* the so-called coordination-insertion mechanism. As a typical example, 20 mg of amino-functionalized MWNT were placed in two-necked vessel and suspended in 10 ml of ε-CL (99%) under nitrogen flow. The

Fig. 1 Scheme of Ar + N₂ microwave plasma.
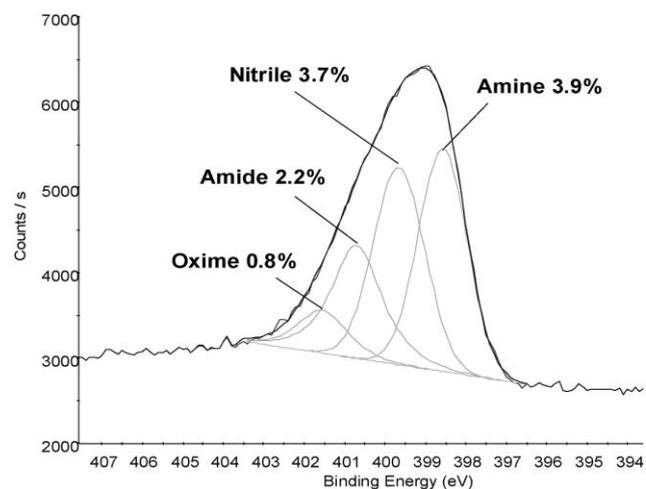
Fig. 3 XPS N1s spectrum fitting.
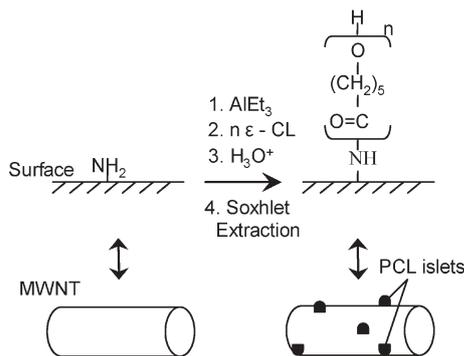
Fig. 4 Scheme of ROP of ε-CL initiated by amines grafted on MWNTs.
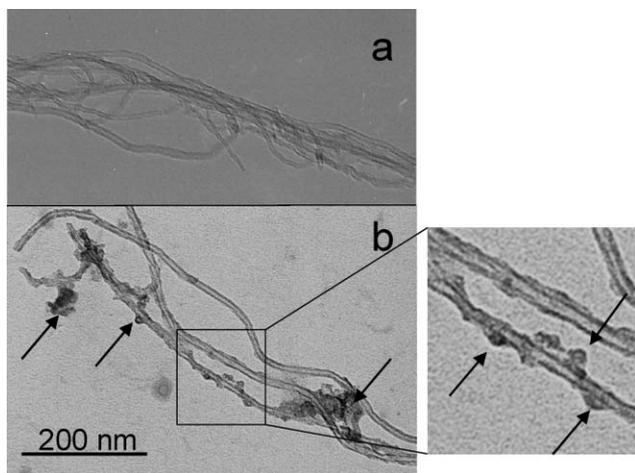
Fig. 5 TEM micrographs: a) pristine MWNTs; b) MWNTs with grafted polyester islets formed by ROP of ε-CL initiated by amines grafted by Ar + N_2 microwave plasma functionalization.

suspension was mixed with 2.2 ml of $AlEt_3$–toluene (0.095 M), the ROP reaction occurred for 25 min at 40 °C. The polymerization was stopped by adding some drops of HCl (3 mol l^{-1}). The polymer was precipitated in a large excess of cold heptane and the so-precipitated polymer was recovered with MWNTs by filtration. In order to eliminate the poly(ε-caprolactone) (PCL) chains that could be formed directly in toluene solution and therefore not surface-grafted onto the MWNTs, the crude precipitate was treated by Soxhlet extraction in toluene (good solvent of free PCL chains) for 24 h. The remaining carbon nanotubes surface-grafted by PCL chains were finally dried under vacuum at 55 °C for one day.

PCL-grafted MWNTs were analysed by TEM. Fig. 5a presents the pristine MWNTs while in Fig 5b the PCL-grafted MWNTs can be observed as long carbon nanotubes separated from starting bundles with numerous PCL islets distributed along the MWNT surfaces. This observation gives credit for the effective presence of reactive amine functions spread all along the MWNT surfaces. In other words, the treatment of CNTs in post-discharge of the Ar + N_2 microwave plasma allows for a very efficient covalent functionalization reaction taking place on the external surface of the nanotubes. At this stage, the functionalization is not homogeneous. All the MWNTs of the sample exposed have not

been functionalized similarly. The nanotubes of the upper side of the sample have the highest amount of amine functions on their surface. First experiments with permanent mechanical stirring of MWNTs placed under the atomic nitrogen flow have been carried out. Accordingly, homogeneous surface functionalization on all the treated nanotubes has been detected by XPS (as recorded on various parts of the sample, with an amine content of *ca.* 1.5%)

In conclusion, this preliminary study has highlighted the very simple, rapid and straight amino-functionalization of carbon nanotubes *via* Ar + N_2 microwave plasma in the post-discharge chamber avoiding any structural alteration and polluting substances. Parameters such as plasma power, gas flow, pressure, mechanical stirring and treatment time need to be tuned to improve the selectivity of this surface treatment. First results are promising and will be topic of a forthcoming paper.

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