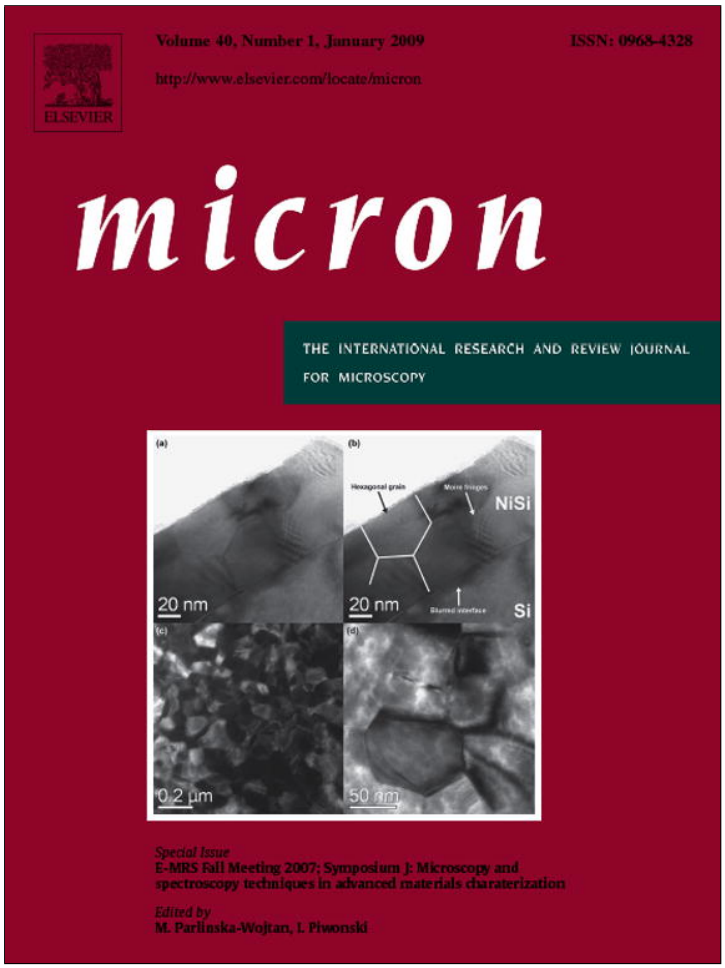

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Functionalization of MWCNTs with atomic nitrogen

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Abstract

In this study of the changes induced by exposing MWCNTs to a nitrogen plasma, it was found by HRTEM that the atomic nitrogen exposure does not significantly etch the surface of the carbon nanotube (CNT). Nevertheless, the atomic nitrogen generated by a microwave plasma effectively grafts amine, nitrile, amide, and oxime groups onto the CNT surface, as observed by XPS, altering the density of valence electronic states, as seen in UPS.

Keywords: CNTs; Chemical functionalization; Photoelectron spectroscopy; Plasma; Surface treatment; High-resolution microscopy; Synchrotron radiation

1. Introduction

Carbon nanotubes (CNTs) are being considered for several applications such as transistors or gas sensors (Ciraci et al., 2004), for which their surface reactivity and electrical and/or mechanical properties must be tailored by adding atoms or molecules to the side walls (Collins et al., 2000). Functionalization is often accomplished by immersing the nanotubes in appropriate chemical solutions or exposing them to vapors at high temperatures (Ciraci et al., 2004). By contrast, a cold plasma treatment has the advantage of being clean and providing a wide range of different functional groups depending on the parameters used to generate the plasma (Ruelle et al., 2007; Khare et al., 2004; Felten et al., 2005).

To study the influence of grafting nitrogen atoms onto CNT surfaces, multi-walled carbon nanotubes (MWCNTs) were exposed to atomic nitrogen generated by dissociating molecular nitrogen in an $Ar + N_2$ microwave (MW) plasma (Ruelle et al., 2007). High-resolution transmission (HRTEM) and scanning (SEM) electron microscopy were used to investigate the surface morphology. The resulting modification of the electronic structure of the CNT was investigated by X-ray and ultra-violet photoelectron spectroscopy.

2. Experiments

Samples were prepared using commercial MWCNT (NC7000) supplied by Nanocyl S.A. Functionalization was performed in the post-discharge chamber of an $Ar + N_2$ microwave plasma (2.45 GHz), the details of which were published by Ruelle et al. (2007). The average discharge power was set to 400 W with a flow ratio of Ar to N_2 equal to 14:1. The samples were prepared by exposing the CNTs to the plasma for three different treatment times: 5, 15, and 45 min and were kept in the air until they were introduced in the electron microscope or the photoelectron spectrometer.

Depending on the subsequent analysis method, the MWCNT powder was mounted on different supports before plasma

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treatment. For photoemission analysis, it was supported on a conductive adhesive tape compatible with ultra-high vacuum. The samples for the TEM analysis were first dissolved in ethanol and dropped on a honeycomb film supported by a copper grid.

Photoemission measurements were performed in Hasylab. X-ray photoemission measurements (XPS at a photon energy of 3300 eV) were performed on the BW2 beamline, described in details by Drube et al. (1995, 1998). Ultra-violet photoelectron spectroscopy (UPS) experiments were performed at the FLIPPER II beamline (Johnson and Reichardt, 1983), using a photon energy of 110 eV, the overall resolution of the system (source + analyser) was 0.2 eV. Binding energies were calibrated with respect to the 4f level (in the case of XPS) or to the Fermi edge (in the case of UPS) of a continuous thick evaporated gold film.

HRTEM was carried out using a Philips CM30 FEG instrument operated at 300 kV. In addition, scanning electron microscopy was performed using a JEM-5510 instrument.

3. Results and discussion

The samples were analyzed by HRTEM and SEM to evaluate the possible etching of CNT walls due to exposure to atomic nitrogen. Figs. 1 and 2 show respectively typical SEM and HRTEM images recorded from a treated sample after 45 min in the $Ar + N_2$ microwave plasma. The excellent condition of the walls of the CNTs indicates that, for the chosen parameters, the plasma treatment does not damage the CNT surface.

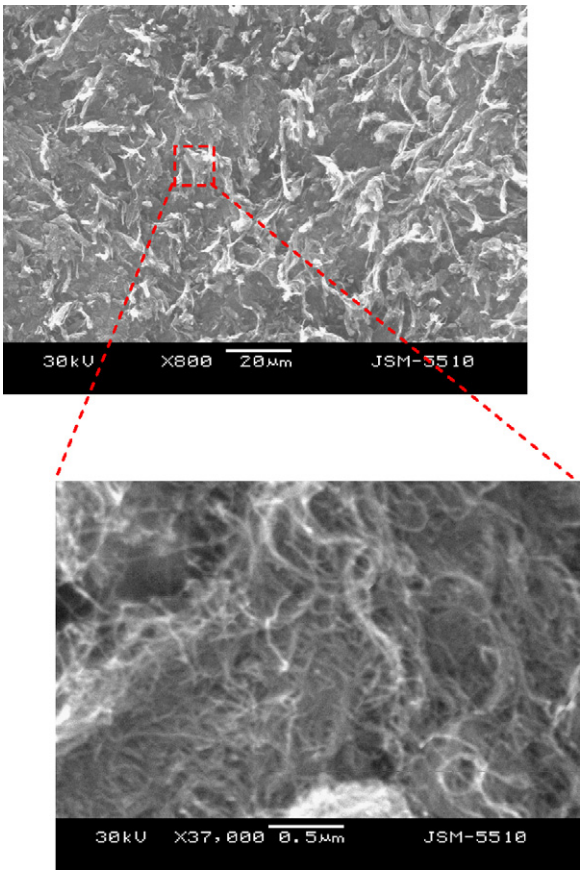

Fig. 1. SEM image of MWCNTs treated in the post-discharge region of an Ar–N_2 microwave plasma.

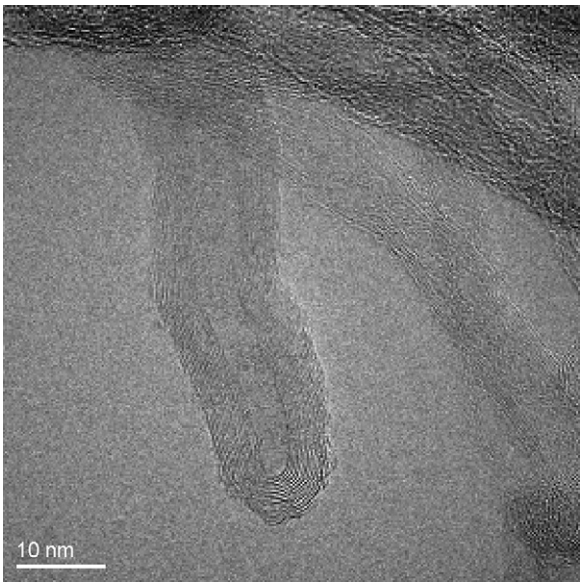

Fig. 2. HRTEM image of MWCNTs treated in the post-discharge region of an Ar–N_2 microwave plasma.

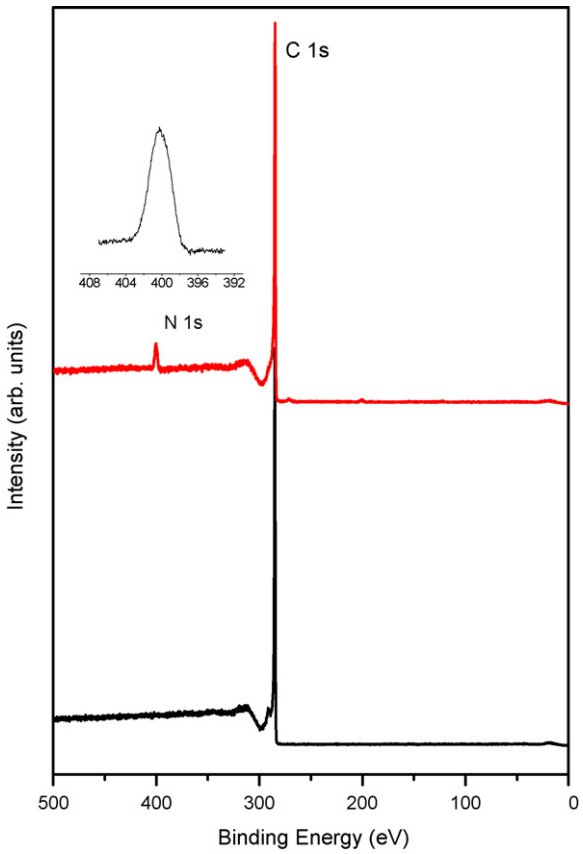

Fig. 3. Overview XPS spectra (a) pristine MWCNTs and (b) MWCNTs exposed to atomic nitrogen flow in the post-discharge region for 15 min. The inset shows the XPS N 1s spectrum.

X-ray photoelectron spectroscopy was used to evaluate the chemical nature of the CNT surface after exposure to atomic nitrogen. Fig. 3 shows the comparison of XPS spectra recorded on pristine CNTs and on N-functionalized CNTs. The peak at 284.3 eV binding energy, observed in both spectra, arises from photoelectrons emitted from the C 1s core level. The presence of the peak near 399 eV, in the spectrum recorded on the nitrogen-plasma treated sample, proves the effective grafting of nitrogen (Beamson and Briggs, 1992). Fig. 4 shows a comparison between the C 1s peaks recorded from pristine and treated MWCNTs. The chemical modification produced by the plasma treatment is revealed by the new broad structure near 287.5 eV that is attributed to photoelectrons emitted from carbon atoms belonging to amine, nitrile, amide, and oxime groups (Ruelle et al., 2007; Khare et al., 2004; Felten et al., 2005).

The changes in the valence electronic states are revealed in Fig. 5, which summarizes the ultraviolet photoelectron spectroscopy valence band spectra obtained from four different samples: pristine MWCNTs and MWCNTs exposed to atomic nitrogen for 5, 15, and 45 min. The valence band spectra were recorded at a photon energy of 110 eV. The characteristic features arising from the threefold coordination of the C atoms are the 2p–π band near 3.5 eV, the 2p–σ states near 5.5 and 8.0 eV, and the mixed 2s–2p hybridized states at 13.6 eV. The feature near 14 eV was reported by Lim et al. (2002) to be related to oxygen molecules physisorbed on the wall and at the edges of the MWCNTs. In addition to the features observed in the UPS valence band spectrum recorded on the pristine CNTs reference sample, spectra recorded after the N-treatment have a band peaking near 4.2 eV that was attributed to photoelectrons emitted from nitrogen lone pair states (sp^2 hybridized nitrogen) (Björkqvist et al., 1998; Lim et al., 2002). The dominant feature centered at 8.5 eV contains contributions from C and N 2p electrons associated with π bonds overlapping the σ-bond feature of the C 2p electrons located at about 7.5 eV (see Fig. 5, pristine sample). The band located at 9.8 eV is generated by photoelectrons emitted from C 2p–N 2p σ-states (Chen et al., 1999; Hammer et al., 2000). A small quantity of oxygen was observed to be grafted onto the CNT surface (the oxygen relative atomic concentration derived from XPS was 2.8%). It may originate either from the residual gas in the plasma chamber or during the *ex situ* sample preparation.

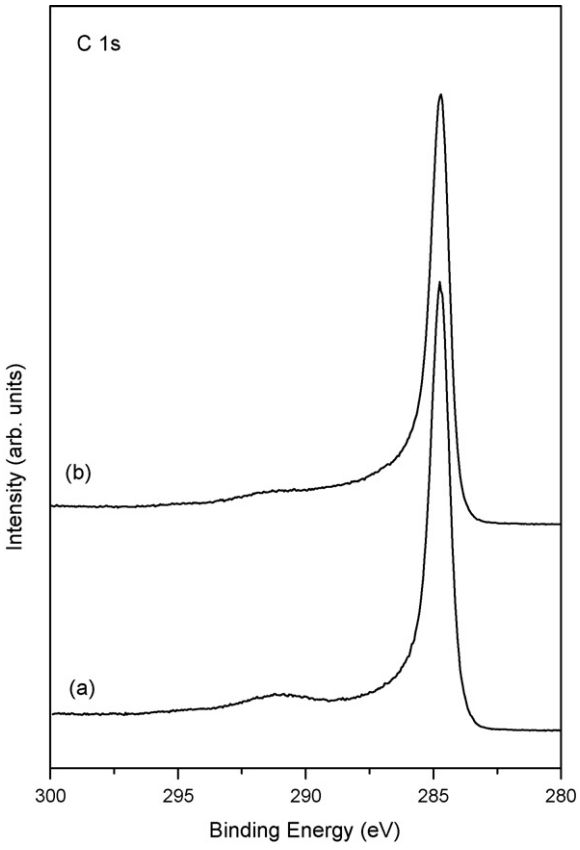

Fig. 4. XPS C 1s spectra recorded on (a) pristine CNTs and (b) atomic-nitrogen treated CNTs.

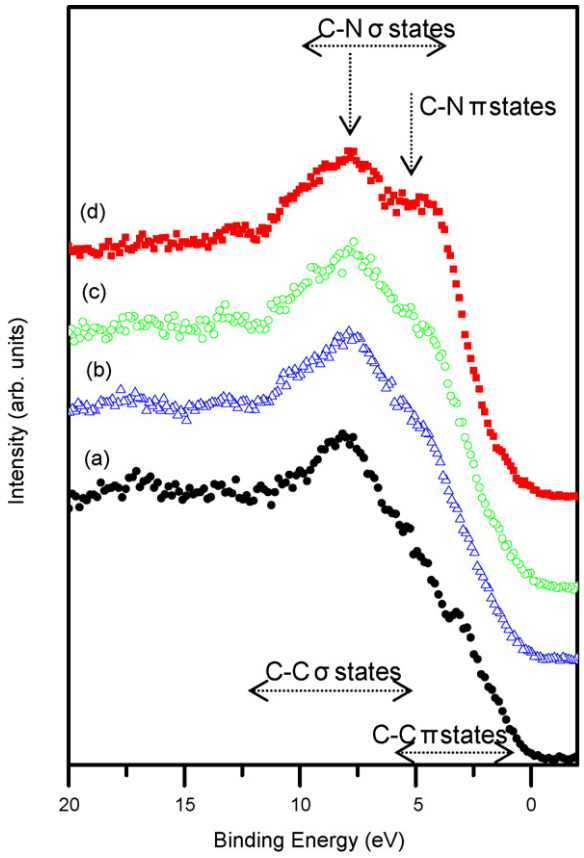

Fig. 5. Valence band spectra recorded on pristine MWCNTs (a) and MWCNTs exposed to atomic nitrogen produced by MW Ar–N_2 plasma for 5 min (b), 15 min (c), and 30 min (d). Horizontal arrows indicate the extension of the valence band states whereas vertical arrows indicate the reported calculated value (Hammer et al., 2000).

4. Conclusion

Photoelectron spectroscopy analysis showed that by exposing MWCNTs to atomic nitrogen generated in a microwave plasma, nitrogen chemical groups can be grafted onto the CNT surface altering the density of electronic states. After the plasma treatment, the 2p–π states can no longer be observed and the contribution of 2p–σ states is enhanced. This suggests

that the chemical groups introduced by treating CNTs in the post-discharge zone of a microwave Ar + N_2 plasma contribute to the 2p–σ states. The HRTEM and SEM images reveal that the atomic nitrogen plasma does not damage the surface of the CNTs.

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