Functionalization of MWCNTs with Atomic Nitrogen: Electronic Structure

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Formation of bundles of CNTs during their synthesis is a technological problem to be overcome in order to promote their uniform dispersion in polymers matrices. Post-growth treatment such as grafting molecules to the tube sidewall has already showed its potentiality in improving dispersion and integration in polymer matrices. Thus, understanding the effect of post-treatment is essential for assessing process controllability, CNT stability and applications. The question to be addressed in this work is as follows: How does the grafting of nitrogen atoms on the tube surface modify the CNT valence band electronic structure?

In the present study the influence of grafting nitrogen atoms onto CNT surface is studied, multi-walled carbon nanotubes (MWCNTs) were exposed to atomic nitrogen generated by dissociating molecular nitrogen in an Ar + N₂ microwave (MW) plasma [1]. The resulting modification of the electronic structure of the CNT was investigated by X-ray and ultra-violet photoelectron spectroscopy (BW2 and Flipper II beamlines).

Figure 1: 1A) XPS C 1s spectra recorded on a) pristine CNTs and b) atomic-nitrogen treated CNTs. 1B) Valence Band spectra recorded on a) pristine MWCNTs and MWCNTs exposed to atomic nitrogen produced by MW Ar-N₂ plasma for b) 5 minutes and c) 15 minutes.

Figure 1a shows a comparison between the C 1s peaks recorded from pristine and treated MWCNTs. Photoelectrons emitted from carbon atoms in the “graphite-like” walls generate the main feature of these spectra at a binding energy of 284.3 eV, i.e., 0.3 eV lower than the value for photoelectrons emitted from graphite samples. This shift was associated with the weakening of the C-C bond caused by the redistribution of the electron density resulting from the curvature of the graphene sheets. 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 [1,2]. The C 1s electron energy-loss spectrum has a peak at ~ 6.6 eV loss energy (centred at a binding energy of 291.0 eV) for pristine CNTs, corresponding to a π plasmon excitation (Fig. 1). A similar loss feature is observable in the spectrum recorded from the treated CNTs. The energy position of the π plasmon loss peak is known to be related to the delocalization of 2p-π electrons; for higher plasmon energy larger electron delocalization is expected; conversely, smaller plasmon energy is related to electronic localization. The observation of the loss structure in the C 1s spectrum recorded on the treated MWCNTs suggests that the degree of electron localization was not changed by grafting nitrogen groups onto the CNT surface.

The XPS results reveal that the microwave plasma effectively grafts nitrogen groups onto the CNT surface. The changes on the valence electronic states are revealed by Fig. 1b, which summarizes the ultraviolet photoelectron spectroscopy valence band spectra obtained from three different samples: pristine MWCNTs and MWCNTs exposed to atomic nitrogen for 5 minutes or 15 minutes. The valence-band spectra were recorded at a photon energy of 55 eV. The valence-band structure of the pristine carbon nanotubes is essentially the same as that of graphite. 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. In the case of MWCNTs, the σ-π hybridization resulting from the formation of the carbon tubes is stronger and this gives rise to the intensity at 11.5 eV binding energy. The feature near 14 eV was reported to be related to oxygen molecules physisorbed on the wall and at the edges of the MWCNTs [3]. 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 (sp² hybridized nitrogen). The dominant feature centred 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. 4, pristine sample). The band located at 9.8 eV is generated by photoelectrons emitted from C 2p – N 2p σ-states.

Acknowledgements
This work was supported by the Belgian Program on Interuniversity Attraction Pole (PAI 6/1 and PAI 6/27), by the “Fonds pour la formation à la Recherche dans l’Industrie et dans l’Agriculture (FRIA)”, by DESY-HASYLAB and the EC under contract RII3-CT 2004-506008 (IASFS). JG is research associate of NFSR (Belgium).

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