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Combined HRTEM and STXM-NEXAFS study of a patterned CNT

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Abstract – HRTEM and scanning transmission x-ray spectromicroscopy (STXM-NEXAFS) were used to evaluate the electronic, structural and chemical changes induced by irradiating a CNT at different ion/electron doses. The NEXAFS spectra recorded on the pristine CNT show strong $\vec{E}$-polarization dependence (linear dichroism) due to the anisotropy of the electronic structure. For increased irradiation time the $\vec{E}$-polarization dependence decreases due to creation of sp^2 defects. Local defect densities can be evaluated by the spatial distribution of the π^* intensity.

The relatively low reactivity of the CNT surface presents a challenge for their integration in actual devices. To tackle this drawback the interface reactivity can be tailored through the activation of the CNT-surface via grafting functional groups. Recently, site-selective functionalization of CNTs with nanoscale spatial resolution was shown to be possible. Using focused-ion-beam (FIB) irradiation high-chemical-reactivity segments can be created along the CNT axis via spatially resolved defect generation, followed by mild chemical treatments [1].

Irradiating CNTs with ions or electrons generates defects (vacancy clusters and unsaturated bonds) altering the CNT structure and influencing the local electronic properties. In this work, we combine HRTEM and scanning transmission x-ray microscopy (STXM) to evaluate the electronic, structural and chemical changes induced by irradiating a CNT at different doses. Different segments of the very same carbon nanotube, supported on a labelled grid commonly used for TEM analysis, were irradiated in a FEI Nova 200 FIB/SEM Dual Beam system equipped with a FIB of 5-30 kV Ga^+, and a SEM. HRTEM was carried out in a JOEL 3000F at EMAT, University of Antwerp, while STXM-NEXAFS was carried out at beamline 5.3.2 at the Advanced Light Source, Berkeley.

STXM-NEXAFS combines near-edge absorption fine structure spectroscopy with energy resolution of 0.15 eV and microscopy with a spatial resolution better than 25 nm allowing studies of isolated nanotubes. Figure 1 compares NEXAFS spectra recorded on different segments of the same CNT. The spectrum recorded on the pristine segment (I) shows strong $\vec{E}$ polarization dependence; the intensity of the C1s → π* transition is found to be the highest when the E-vector is perpendicular to the tube axis, while it almost completely vanishes when the E-vector is parallel to the tube axis [2]. The polarization dependence decreases for increasing irradiation time (II, III) due to an increase in the density of sp^2 defects.

In addition to a gradual loss of the dichroic intensity of the C1s → π* peak for increasing irradiation time, the NEXAFS spectra show a gradual increase in the intensity of oxygen-related resonance peaks ranging from 287 to 289 eV indicating that ion-bombardment induced defects increase the chemical reactivity of the ion-irradiated CNT segment and enable selective functionalization.

CNT structural modification and the creation of defects due to the irradiation will be discussed in the view of HRTEM analysis.

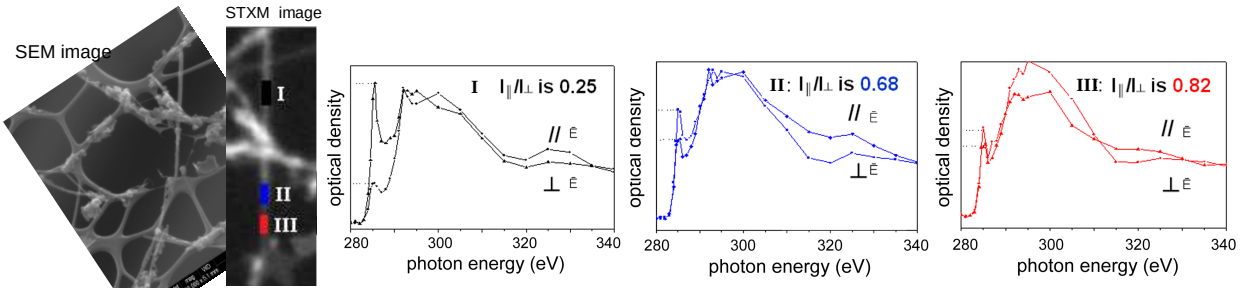

Figure 1: STXM images (left) in the region around the irradiated CNT (see SEM image). NEXAFS spectra recorded with the nanotube paralell and perpendicular to the E-vector (right). Region I: pristine segment, region II: outer region of the irradiation zone, region III: center of the irradiated zone

References

1. M. S. Raghuveer, A. Kumar, M. J. Frederick, G. P. Louie, P. G. Ganesan and G. Ramanath, Adv. Mater. 18 (2006) 547.
2. E. Najafi, D. Hernández Cruz, M. Obst, A.P. Hitchcock, B. Douhard, J.-J. Pireaux and A. Felten, Small 4 (2008) 2279.