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Scanning Transmission X-ray Microscopy of Individual Multi-Walled Carbon Nanotubes: Linear Dichroism and Functionalization Chemistry

A.P. Hitchcock,* E. Najafi,* M. Obst,* J.-J. Pireaux,** B. Douhard,** and A. Felten**

* Brockhouse Inst. Materials Research, McMaster University, Hamilton, ON, L8S 4M1, Canada.
** LISE, University of Namur, 61 rue de Bruxelles, 5000, Namur, Belgium

Carbon nanotubes (CNTs) are key components of nanotechnology due to their exceptional mechanical, electrical and thermal properties. However these properties are highly dependent on the quality of the nanotube, with defects and surface chemical modifications often degrading their properties, although sometimes being desirable to add specific functionality to the CNT. Transmission electron microscopy provides unparalleled imaging at high spatial resolution but, even with electron energy loss (EELS) techniques, it can be difficult to determine aspects of the structure critical to their functionality. We are developing spectral and dichroic imaging in scanning transmission X-ray microscope (STXM) as a means to probe the properties of CNTs, specifically their defect densities, chemical impurities and functionalization. Our ultimate goal is to apply the techniques described here to characterize electronic and chemical sensing devices based on single carbon nanotube structures.

C 1s near-edge x-ray absorption fine structure (NEXAFS) spectroscopy in STXMs at the Advanced Light Source (ALS) and the Canadian Light Source (CLS) has been used to probe the electronic structure of individual multi-wall carbon nanotubes (MWCNT) at a spatial resolution of better than 40 nm [1,2]. The C 1s $\rightarrow \pi^*$ transition (285.1 eV) is found to have a strong polarization dependence [3], with the greatest intensity when the E-vector is perpendicular to the tube axis, and least intensity when the E-vector is parallel to the tube axis (Fig. 1). This is the first direct experimental verification of the strong linear dichroism of carbon nanotubes predicted by Banerjee et al. [4]. We have compared the dichroic response of high quality arc discharge (AD) MWCNTs and lower quality, highly defective, chemical vapour deposition (CVD) MWCNTs. The π^* dichroic effect is much stronger in the AD relative to the CVD MWCNT (Fig. 2), consistent with this signal reflecting the density of sp^2 defects in the two types of tubes. Fig. 3 plots the difference in the π^* intensities for $\underline{E}_{\perp}$ and $\underline{E}_{//}$ extracted from continuum normalized spectra of individual tubes, against an estimated degree of sp^2 'perfection', which was derived by defining a defect free tube as have the intensity difference derived by extrapolation to $I_{//} = 0$, and assuming a linear relationship between dichroic response and defect density. This is a crude calibration curve relating normalized π^* intensity difference to the fraction of defect sites. Studies of MWCNT samples with controlled variation in defect densities are underway to further define this relationship. Measuring the linear dichroism with a high sampling density on individual MWCNTs can be used to map spatial variations of sp^2 defects, as has been presented elsewhere [3].

The effects of modifications of MWCNT by plasma discharge, treatments with strong acid, high temperature annealing, UV-ozonation, and functionalization with fluoropolymers were investigated by STXM. Selected results from this work will be presented. Localization of chemical modifications at specific sites (side wall, end caps, etc) were found (Fig. 4). Such studies are being carried out to optimize carbon nanotube functionalization targeted for polymer reinforcement applications [5].

References
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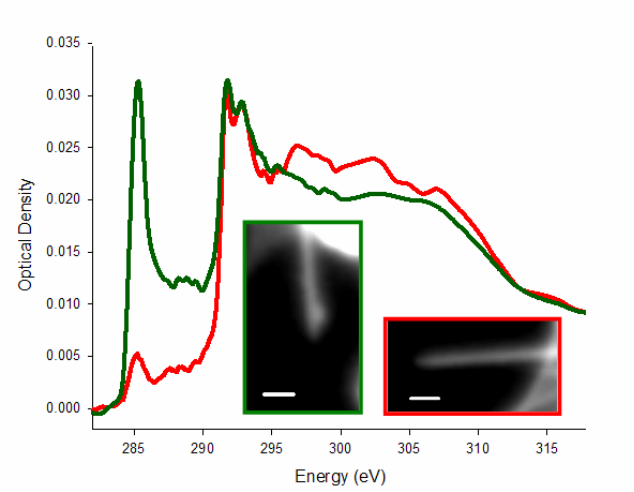

Fig. 1 C 1s NEXAFS recorded from two different arc-discharge (AD) carbon nanotubes, oriented perpendicular and parallel to the E-vector (ALS) (scale bar = 100 nm)

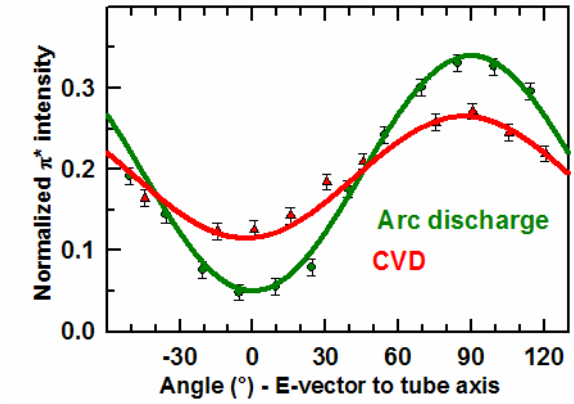

Fig. 2 Linear dichroism of C1s → π* transitions of selected regions of AD and CVD MWCNTs (CLS)

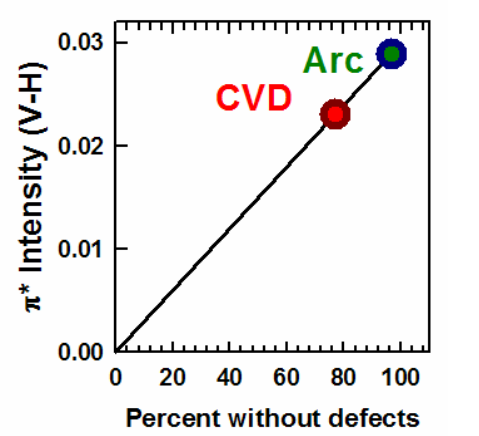

Fig.3 Estimated fractional defects in selected regions of the AD and CVD MWCNTS. See text for details.

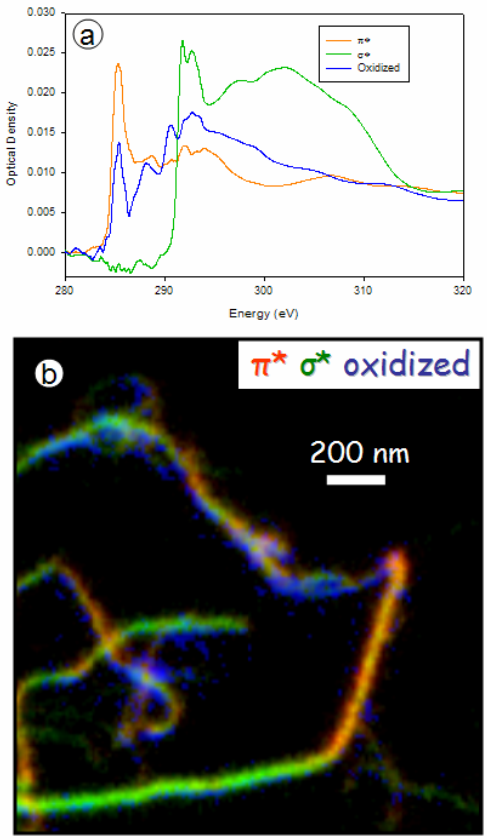

Fig. 4 (a) C 1s spectra used to fit a C 1s image sequence of a CVD MWCNT recorded using linear horizontal polarized X-rays (ALS). (b) Color coded component maps of the orientation and oxidation distributions derived from the C 1s image sequence.