

Chemistry and Structure of Nanomaterials

Successful nanoscale materials fabrication is empowered by a detailed knowledge of the chemistry and structure of surface bound molecules; e.g., the optimization of self-assembled monolayers, molecular templates, micro-electro-mechanical system lubricants, and functionalized nanotubes. Near-Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy is ideally suited to measure non-destructively chemical bond concentration, rehybridization, and orientation with sub-monolayer molecular sensitivity in diverse nanoscale materials. Furthermore, NEXAFS can distinguish chemical bonding in the light elements, measure the orientation of interfacial molecules, and separately measure surface versus bulk chemistry simultaneously.

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Materials having low energy surfaces are used in many applications, for example, in non-wetting surfaces or fouling resistant marine coatings. We have produced a photo-responsive polymer surface by combining the reversible photo-switching nature of azobenzene with the self-assembly nature and low surface energy properties of semi-fluorinated segments, to create a fluoroazobenzene molecule surface. Upon UV exposure, this surface reorients between hydrophobic and less hydrophobic states, as shown in Figure 1 (left upper and lower panels). For such surfaces, one could imagine applications ranging from low cost surface patterning to polymer surfaces that would adsorb biological macromolecules on cue.

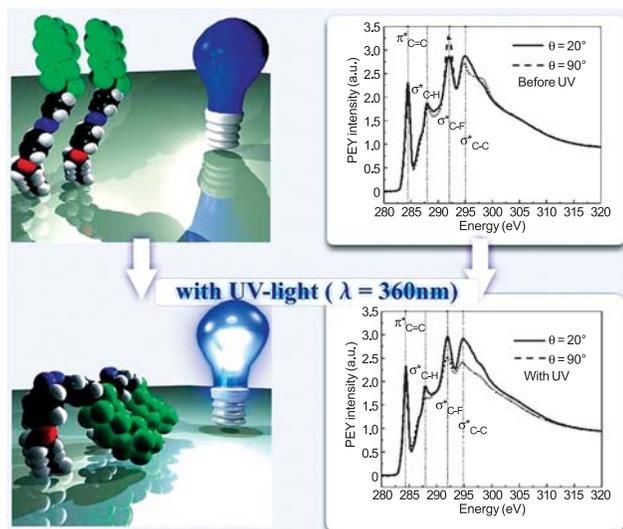


Figure 1: UV light reorients fluorobenzene semi-fluorinated segments (green) downwards, i.e., to a less hydrophobic state.

We have utilized NEXAFS to observe, verify, and quantify the reversible cis-trans molecular conformation transformation from hydrophobic to less hydrophobic states. The right panels of Figure 1 (upper and lower) show polarization dependent NEXAFS anisotropy behavior of the C–F and C–C peaks which reverse with *in situ* UV light exposure highlighting the reorientation of the semi-fluorinated segments.

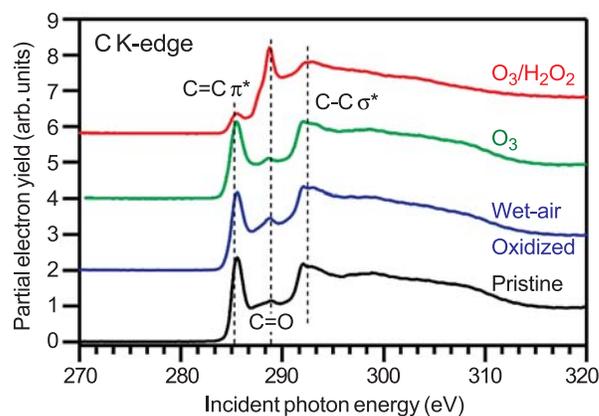


Figure 2: Carbon NEXAFS of oxidized/functionalized nanotubes.

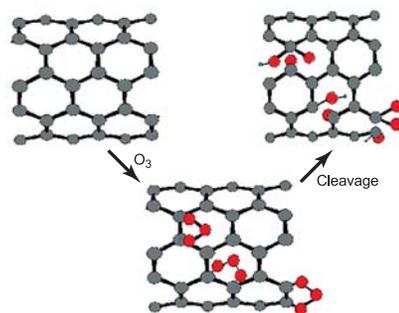


Figure 3: Model of peroxide functionalization of nanotubes.

Application of NEXAFS spectroscopy to the study of electronic structure and chemical composition is illustrated in Figure 2 for various chemically functionalized, single-walled, carbon nanotubes. Upon peroxide functionalization, the C=C ring resonance is greatly diminished on extensive sidewall functionalization indicating loss of extended conjugation and disruption of nanotube electronic structure. The C=O peak intensity is greatest for peroxide chemistry. NEXAFS spectroscopy supports a model of peroxide functionalization, shown in Figure 3.

Contributors and Collaborators

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