

Photoabsorption and desorption studies on poly-3-hexylthiophene/multi-walled carbon nanotube composite films

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Introdução

Conjugated polymers have already demonstrated their potentiality for application in opto-electronic devices combining mechanical and semiconducting properties [1,2]. One of the main challenges in their fabrication consists in the search for materials or processes leading to higher photocurrent values. A very interesting possibility is related to composites between conjugated polymers and CNTs. In this context the poly-3-alkylthiophenes, especially the poly-3-hexylthiophene, were broadening used and different techniques were employed with the aim of improving our knowledge about the polymeric films properties. Surface photochemistry induced by x-ray synchrotron radiation still remains an exciting topic in surface science in both fundamental and applied aspects. Since core electrons are generally localized, the dominant relaxation process by means of cascading Auger will produce localized positive holes in valence orbitals, which may lead to fragmentation around the exciting atom; different elements and even inequivalent atoms in different local chemical environments within the molecule (chemical shifts) can be probed. Tunable synchrotron radiation may then allow for the controlling of chemical reactions, which can be followed by PSID (Photon Stimulated Ion Desorption) coupled to core-level excitation [3]. If ion desorption is produced indirectly, by means of outgoing energetic Auger electrons, photoelectrons and secondary electrons (XESD - X-ray induced electron stimulated desorption), due to valence excitations and ionizations, the chemical selectivity will be lost and the ion yield curves will mimic the TEY spectrum. Both processes compete and their contribution to ion desorption is still ambiguous.

Resultados e Discussão

PSID and Near-edge X-ray absorption fine structure (NEXAFS) studies have been performed on poly-3-hexylthiophene (P3HT) and nanocomposites thin films made of poly-3-hexylthiophene and multi-walled carbon nanotubes filled with iron/iron-oxide (P3HT/Fe-CNT). The experiments were performed at the Brazilian Synchrotron Light Source (LNLS) operating in a single-bunch mode following sulphur K-shell photoexcitation and using time-of-flight mass

spectrometry for ion analysis. Both PSID mass spectra show great similarity and exhibit desorption of the polymer fragments only. This result seems to be in accordance with previous morphological studies on these materials, which suggested that the nanotubes are highly dispersed and involved by the polymer. Although similar, the spectra present shifts in the direction of greater time of flights in the case of the poly-3-hexylthiophene/multi-walled carbon nanotube composite. In both cases, S⁺ desorption seems to be suppressed. Relative desorption ion yield curves have been determined as a function of the photon energy, which reproduced the photoabsorption spectrum [4].

Conclusões

Both PSID TOF spectra are similar, exhibit desorption assigned to the polymer fragments only and deviation of the whole spectra for greater time of flight values in the case of P3HT/Fe-CNT. The less pronounced appearance of sulphur species, as compared to PSID results for poly-3-methylthiophene and poly-thiophene, even at resonances peaks, may be related to the surface morphology with predominance of the hexyl side-chains. The charge transfer process with donation of electronic charge between the polymer matrix and the carbon nanotubes may account for the shifts in the time of flights of the ions. PSID results analysed through photon-energy dependencies of the partial ion yields (PIY) curves showed that the measured fragments are mainly due to the XESD process.

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