

Femtosecond Electron Delocalization in Polymer:Fullerene Blend Films

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Synopsis Ultrafast electron dynamics in the low-femtosecond regime was evaluated for a low band-gap polymer and its blend with fullerene by resonant Auger spectroscopy. Remarkable changes developed by tuning the photon energy along the sulfur and silicon 1s absorption edges. The effect of thermal annealing and molecular orientation on the charge transfer delocalization times were probed and correlated with solar cells performance.

Ultrafast electron dynamics is a relevant topic for fundamental and applied areas like femtochemistry, surface photochemistry, molecular electronics, solar energy, and so on. It is possible to apply two different spectroscopic approaches to pursue it. Ultrashort pulse laser pump-probe spectroscopies have been used widely, where delocalization of excited electrons in the presence of delocalized valence hole states are probed. Besides laser-based pump-probe methods, resonant Auger spectroscopy following core excitation emerges as an alternative with major advantages. First, the core hole lifetime probed by core level spectroscopy can be used as a fast internal clock and insofar very low time scales in the range of femtoseconds down to hundred attoseconds can be achieved, the so-called core-hole clock (CHC) method. Second, the inherent atomic specificity of core levels, which deals with localized hole states, can be explored.

A fundamental aspect regarding charge transfer dynamics is related to the organizational level of the polymeric films and its morphology. In this regard, X-ray absorption spectroscopy is a powerful technique which gives information about the orientation of molecular films with respect to the surface while probing unoccupied density of states. One way in pursuing this organization is by means of thermal annealing treatments, which changes the polymer morphology and possibly enhances its charge transport properties.

In the present work, we have selected the internal donor/acceptor copolymer poly[2,7-(9,9-bis(2-ethylhexyl)-dibenzosilole)-alt-4,7-bis(thiophen-2-yl)benzo-2,1,3-thiadiazole] (PSiF-DBT) and its blend with fullerene (PSiF-DBT:PCBM) to investigate how the thermal annealing treatment affects molecular orientation and consequently the charge delocalization time (τ_{CT}) [1,2].

Near edge X-ray absorption fine structure (NEXAFS) and Resonant Auger spectra were measured at the soft X-ray spectroscopy (SXS) beamline at the Brazilian Synchrotron Light Source (LNLS), in Campinas, São Paulo. It was demonstrated a decrease of the τ_{CT} after thermal annealing which may be associated with more ordered polymeric films, as probed by NEXAFS, with the increase of orbital overlapping, and consequently electron delocalization. Further reduction of the τ_{CT} was observed for the polymer:fullerene blends and the subsequent annealing. These results will be presented and discussed in the context of solar cells performance.

Work supported by LNLS, CNPq, FAPERJ and CAPES.

References

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