

Improving Electronic Transport in Nanostructured Organic Semiconductor Solar Cells

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Scientific Thrust Area: CFN Electronic Nanomaterials group

Research Achievement:

The highest performing organic semiconductor solar cells employ device active layers of phase-separated blends of semiconducting polymers and fullerenes. This ‘bulk heterojunction’ architecture provides a highly nanostructured internal morphology that both decouples the photogenerated exciton diffusion length (~ 10 nm) from the device active layer thickness and increases the heterojunction area available for exciton dissociation. State-of-the-art bulk heterojunction devices have demonstrated photovoltaic power conversion efficiencies between 4-5% using a single blend layer of regioregular poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM).

The performance cost associated with the bulk heterojunction solar cell architecture comes from a significantly increased probability for deleterious interfacial charge recombination, an effect that places an upper limit on the device active layer thickness for effective charge collection and thereby constrains the amount of solar photon absorption. Our experimental efforts explore methods for improving electronic transport in bulk heterojunction device active layers in order to provide more effective charge collection and ultimately better performance.

We have demonstrated improvements in photovoltaic device performance of *ambient-air processed* bulk heterojunction solar cells having an active blend layer of organic P3HT:PCBM, with power conversion efficiencies reaching as high as 4.1% - comparable to state-of-the-art similar bulk heterojunction devices fabricated in *air-free environments* (Fig. 1a). We have combined high resolution transmission electron microscopy (Figs. 1b, 1c) with detailed analysis of electronic carrier transport in both the p-type P3HT and n-type PCBM in order to quantitatively understand the effects of oxygen exposure and different thermal treatments on electronic conduction through the highly nanostructured active blend semiconductor network. Improvement in photovoltaic device performance by suitable post-fabrication thermal processing results from a reduced oxygen charge trap density in the active blend layer and is consistent with a corresponding slight thickness increase in a ~ 4 nm Al₂O₃ hole-blocking layer present at the electron-collecting contact interface (Fig. 1c).

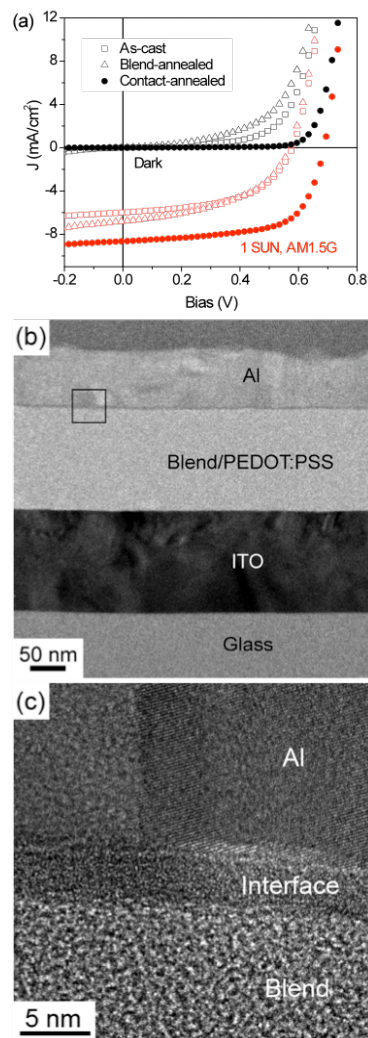


Fig. 1. (a) Dark and illuminated J - V of P3HT:PCBM blend solar cells with different anneals. (b) Bright-field TEM cross-section of a contact-annealed device. (c) High resolution image of blend-Al interface.

We can improve the transverse hole conductivity of p-type P3HT by as much as 5 times using a new experimental method for thermal crosslinking the semiconducting polymer using radical initiators (Fig. 2a). We achieve this improvement without any associated detrimental shift in the P3HT spectral light absorption to higher energies (i.e., blue shift) (Fig. 2b). Previous experimental methods to crosslink P3HT have improved mobility only at the expense of a blue shift in spectral absorption caused by a decrease in polymer chain conjugation length. Grazing incidence x-ray diffraction correlates P3HT film structural changes to measured electronic and optical properties and reveals polymer chain orientation changes responsible for increased pi-pi overlap in crosslinked P3HT. Model planar heterojunction PV devices having a crosslinked P3HT p-type active material show improved power conversion efficiency by three times as compared to otherwise identical devices having un-crosslinked P3HT active material (Fig. 2c).

We may introduce improvements in charge collection in the bulk heterojunction architecture by introducing nanostructured electrical contacts, which serve to shorten charge collection pathways in low-mobility organic semiconductor materials. We demonstrate the utility of this approach using a P3HT-fullerene blend device incorporating alkane-chain functionalized single wall carbon nanotubes into the active layer. Blend devices containing nanotubes show an 11% average increase in power conversion efficiency over control devices without nanotubes (from 3.2% to 3.5%) stemming largely from an increase in optimum device active layer thickness from ~ 90 nm to ~ 110 nm. Electrical characterization of model bi-layer devices reveals that carbon nanotube addition enhances carrier collection by effectively increasing P3HT hole mobility without an associated increase in charge recombination.

Future Work:

Future work will further explore improvements to the bulk heterojunction solar cell architecture through introduction of nanostructured electrical contacts. We will employ methods of self assembly to precisely define and tune contact dimensions (e.g., pillar height, diameter, and pitch) for understanding the interplay between length scales for solar light absorption and charge collection.

Publications:

C. -Y. Nam, D. Su, and C. T. Black, *High-Performance All Air-Processed Polymer-Fullerene Bulk Heterojunction Solar Cells*, *Advanced Functional Materials*, submitted (2009).

R. I. Gearba, C. -Y. Nam, R. Pindak, and C. T. Black, *Improved Transverse Hole Conductivity in Organic Semiconducting Polythiophene by Thermal Crosslinking*, *Applied Physics Letters*, submitted (2009).

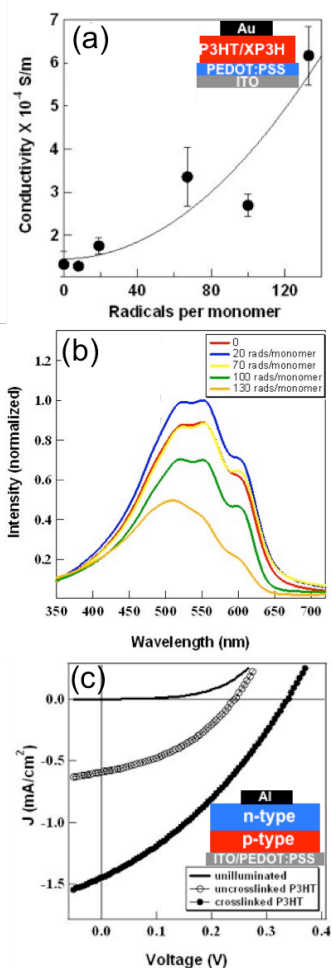


Fig. 2. (a) P3HT conductivity versus added crosslinker amount. Inset: Device schematic. (b) UV-VIS absorption spectra for P3HT films having increasing amounts of added crosslinker. (c) J - V for two planar heterojunction solar cells (1 SUN AMG). Inset: Device schematic.