Uncovering the Relationship between the Active Layer Structure and Device Performance in Organic Solar Cells

Solar power is an important component of our society's future energy portfolio.[1] In particular, photovoltaic devices composed of solution-processable organic materials may enable the wide-spread implementation of solar energy by dramatically decreasing device fabrication and manufacturing costs, albeit at lower power conversion efficiencies. Critical to the development of efficient organic photovoltaic devices is basic knowledge of how the nanometer structure of the active layer in the solar cell can affect the light-to-energy conversion efficiency.[2] Indeed, many efforts have identified processing parameters, such as the film casting conditions, to strongly affect active layer structuring, and thereby device performance.[2,3] Given that state-of-the-art organic photovoltaic devices employ mixtures of conjugated polymers with fullerene derivatives as the active layer, any crystallization of either component, which critically depends on processing details, can affect the final structuring of polymer/fullerene mixtures. Thus, it has been surmised that such changes are responsible for the variations in solar cell efficiencies. Qualitatively, increases in the conjugated polymer crystallinity have been correlated to higher output currents, since increases in polymer long-range order are expected to enhance charge transport.[4,5]

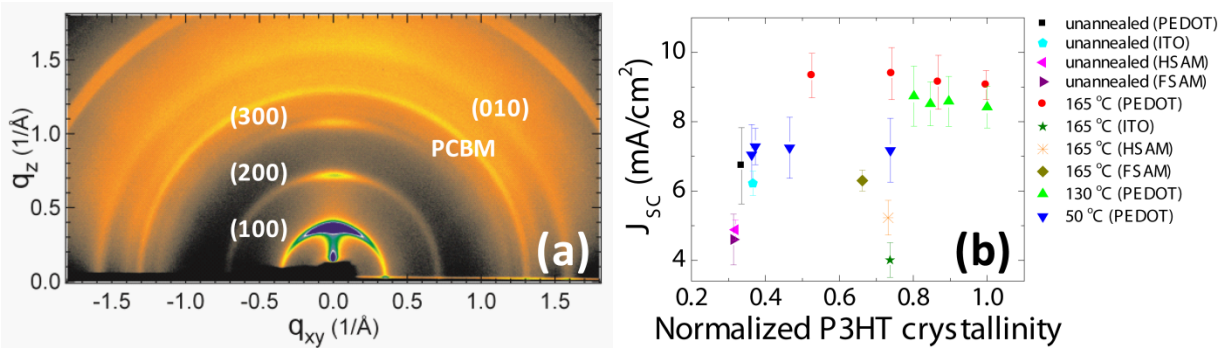

Figure 1. Characterization of the P3HT/PCBM structure through X-ray scattering. (a) 2-D GIXD data of a P3HT/PCBM mixture. The P3HT (100), (200), (300), and (010) reflections are labeled; the PCBM reflection is also labeled. (b) Device short-circuit current density (J_{SC}) vs. P3HT crystallinity for various P3HT/PCBM samples. Films were annealed for 5, 10, 30 and 60 min at 50°C, 130°C, or 165°C. Mixtures were cast on indium tin oxide (ITO), hydrocarbon molecular layers (HSAM), fluorinated molecular layers (FSAM), or poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT). Note the lack of a clear trend in the data.

Through grazing-incidence X-ray diffraction (GIXD) experiments at Beam Line 11-3 of SSRL, we have examined in detail the relationship between the active layer structure and output currents of organic solar cells. The combination of rocking scans and GIXD has allowed us to construct full pole figures to quantify the relative crystallinity of the polymer poly(3-hexylthiophene), P3HT, in active layers comprising P3HT and the fullerene derivative [6,6]-phyl-C_{61}-butyric acid methyl ester (PCBM).[6] Our results suggest a more complex interplay between crystallization of the constituents and device performance than previously surmised; the output currents are not strongly correlated

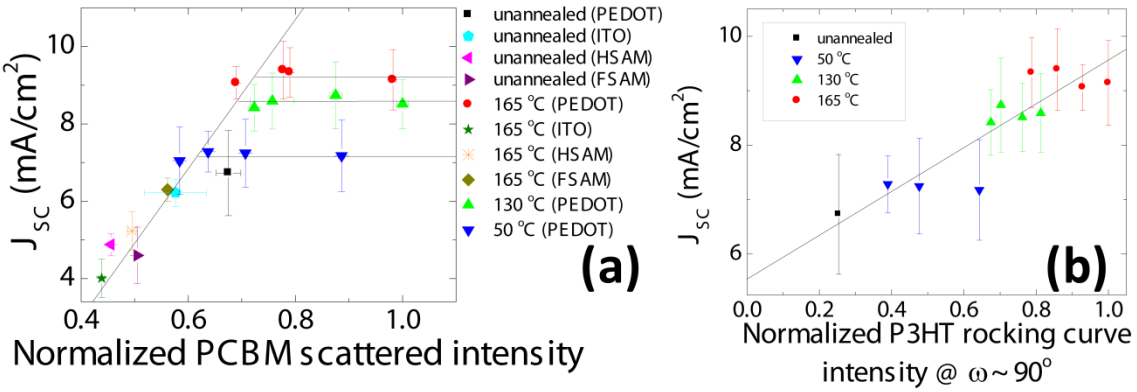

Figure 2. Structure-function relationships of bulk-heterojunction solar cells. (a) J_{SC} vs PCBM scattered intensity for P3HT/PCBM samples processed under various conditions. Note the direct correlation between device performance and the active layer structure at low PCBM scattered intensities (< 0.6). (b) J_{SC} vs. P3HT out-of-plane π-stacking for samples with PCBM scattered intensities > 0.6. There is a roughly linear relationship between the J_{SC} and out-of-plane π-stacking ((010) direction).

with P3HT crystallinity (Figure 1). However, insights into the role of structure of the active layer on device performance can be obtained by quantifying the PCBM scattering intensity. Although PCBM does not fully crystallize in the majority of our devices, the amorphous scattering intensity varies with processing conditions. We attribute increases in the PCBM scattering intensity to increases in pure PCBM aggregation. As shown in Figure 2a, the output currents of solar cells are, to first order, correlated with the scattering intensity of the PCBM. When the PCBM intensity is high, device performance is in turn dependent on the fraction of P3HT whose conjugated planes are organized along the film normal (Figure 2b).

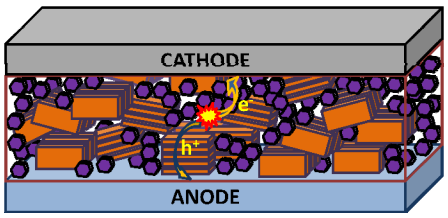

Figure 3. Schematic representation of P3HT/PCBM polymer solar cell emphasizing the structure of the active layer. The purple hexagonal boxes represent PCBM domains and the brown rectangular boxes represent P3HT crystals. Amorphous P3HT phases are not shown. After photon capture and charge separation, we hypothesize that electrons travel most effectively through PCBM domains and holes travel most effectively through P3HT crystals laying flat, with π--stacking in the out-of-plane direction.

Figures 1 and 2 highlight how the complex structuring of the constituents in the active layer can affect organic solar cell performance. Clustering of pure PCBM is important to establish efficient electron transport (Figure 3). With sufficient structuring of PCBM in place, the out-of-plane π-stacking of P3HT, which facilitates hole transport to the anode,[7] plays a role in affecting output currents. Altogether, our results implicate the complexities of structure-function relationships that govern such two-component active layers and suggest that rocking curves and GIXD as a powerful combination in the pursuit of quantitative identification of the structural characteristics driving organic solar cell performance.

Primary Citation

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