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Contrast Generation and Three-Dimensional Characterization of Organic Photovoltaic Device Structures via Low-Loss Energy-Filtered TEM

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The current route for developing high efficiency organic photovoltaic (OPV) cells is the fabrication of bulk-heterojunction (BHJ) architectures consisting of a three-dimensional (3D), interpenetrating network of donor and acceptor phases (typically a conductive polymer and a fullerene derivative, respectively) [1]. An efficient device must exhibit a continuous integrated network of the two constituents, with an inter-phase distance on the order (≈ 10 nm) of the mean-free-path for excitonic recombination, as well as an uninterrupted vertical pathway to the surface electrodes, so as to minimize uncollected charge [2]. Such complex 3D device architectures are typically fabricated via spin-casting from a solution of the two constituents. The resulting morphology is highly sensitive to processing parameters such as the choice of solvent, heat treatment, and drying time. In order to more fully understand the complex interplay between fabrication conditions, morphology, and device performance, robust characterization techniques are required to reveal the 3D distribution of the two phases.

Electron tomography performed in the transmission electron microscope (TEM) is well suited to 3D characterization at the nanometer length-scale, and OPV films have been successfully analyzed using the TEM bright-field (BF) signal [3,4]. However, the BF contrast produced from organic phases of similar composition and density can be very low, and thus this image signal is not universally suitable to OPV films. In this talk, we will detail our efforts to utilize energy-filtered (EF) TEM to generate contrast from several device configurations. As shown in Fig. 1a, the electron energy-loss spectroscopy (EELS) low-loss responses of two commonly studied OPV constituents, poly(3-hexylthiopehene) (P3HT) and phenyl-C_{61}-butyric acid methyl ester (PCBM), exhibit subtle differences, including a shifting of the plasmon peak position due to higher electron density of PCBM relative to P3HT. By utilizing EFTEM spectrum imaging in conjunction with principal component analysis (PCA), the response of the OPV blend has been thoroughly characterized and used to identify the optimal energy loss range for maximizing contrast between the two phases.

P3HT-PCBM films that were spin-cast using two different solvents, either *ortho*-dichlorobenzene (ODCB) or chlorobenzene (CB); representative energy-filtered images are shown in Figs. 1b – 1g. In both cases, the BF image exhibits negligible contrast between the two phases in these films; rather, only low-frequency features related to thickness fluctuations are visible. Conversely, the EFTEM images collected using a 5 eV energy-selecting slit centered at 19 eV and 29 eV, highlighting the P3HT and PCBM phases, respectively, show significant contrast, and reveal that the morphology of these two devices is catastrophically different. Whereas the ODCB film was found to contain elongated P3HT fibrils (Fig. 1c) surrounded by a more equiaxed matrix of PCBM (Fig. 1d), the film that was spin-cast from CB shows a more intimately mixed morphology (Figs. 1f & 1g) where the phase separation has occurred on a much finer scale.

The incoherent EFTEM signal has been shown to more robustly obey the projection requirement of tomography than BF imaging [5], which exhibit coherent contrast mechanisms such as diffraction and phase contrast. Our group has recently reported on 3D chemical imaging of OPV devices using

this approach [6], and we will discuss the potential for these techniques to elucidate the role played by the morphology of the active-layer in producing a high-efficiency organic solar-cell.

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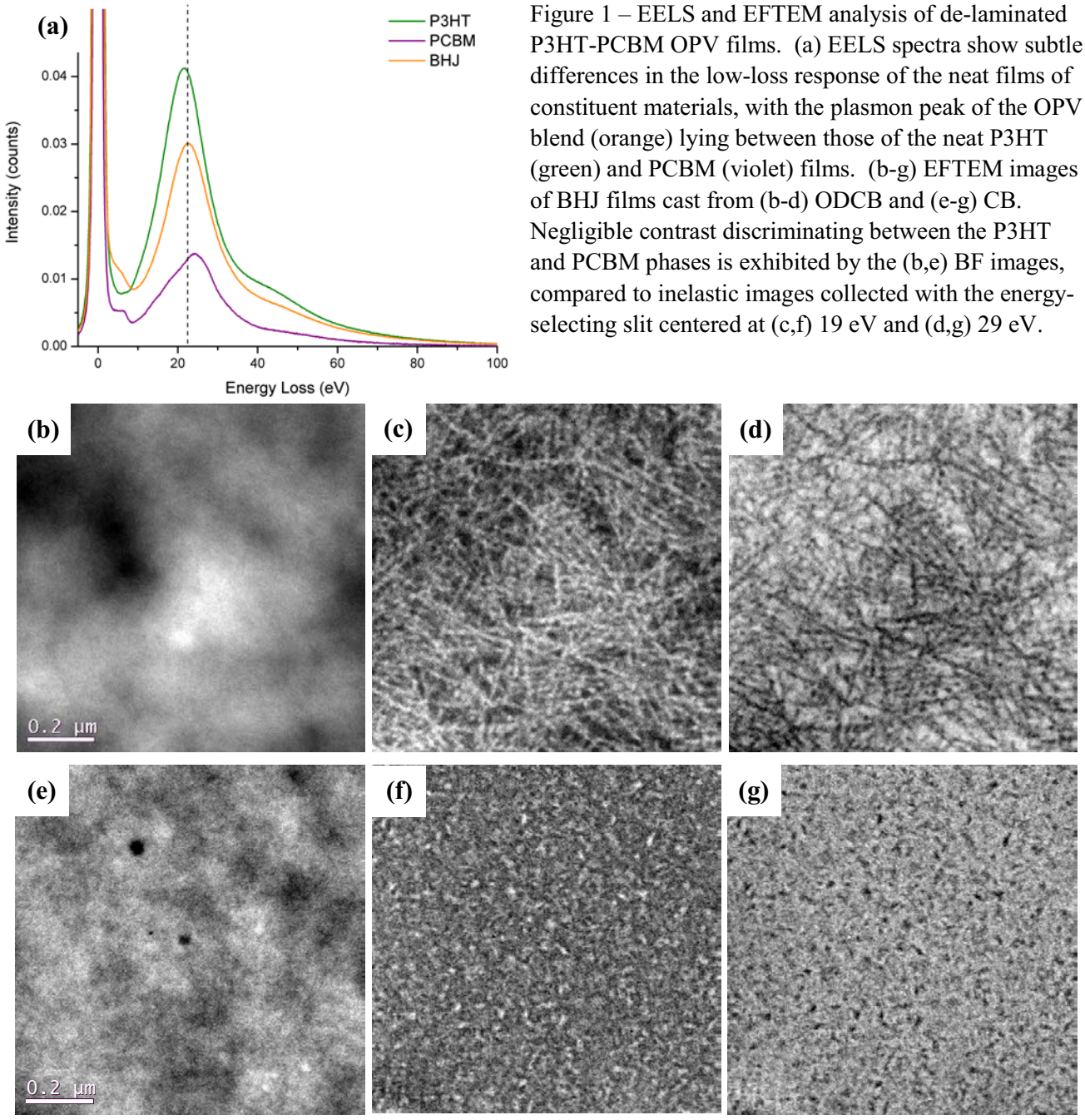

Figure 1 – EELS and EFTEM analysis of de-laminated P3HT-PCBM OPV films. (a) EELS spectra show subtle differences in the low-loss response of the neat films of constituent materials, with the plasmon peak of the OPV blend (orange) lying between those of the neat P3HT (green) and PCBM (violet) films. (b-g) EFTEM images of BHJ films cast from (b-d) ODCB and (e-g) CB. Negligible contrast discriminating between the P3HT and PCBM phases is exhibited by the (b,e) BF images, compared to inelastic images collected with the energy-selecting slit centered at (c,f) 19 eV and (d,g) 29 eV.

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