Phase Separation, Percolation and Connectivity in Conjugated Polymer/Fullerene Based Bulk Heterojunction Solar Cells

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The nanomorphology of bulk heterojunction plastic solar cells based on conjugated polymer/fullerene blends is of high interest in current research.[1-6] We combine a variety of experimental techniques to resolve the structure of fullerene and polymer domains on the nanometer scale. In Fig. 1 the topography (obtained by atomic force microscopy) of two films spin cast from either chlorobenzene or toluene solution is depicted. Clearly, a much larger feature size as well as film roughness is found for the samples cast from toluene, indicating a coarse phase separation.

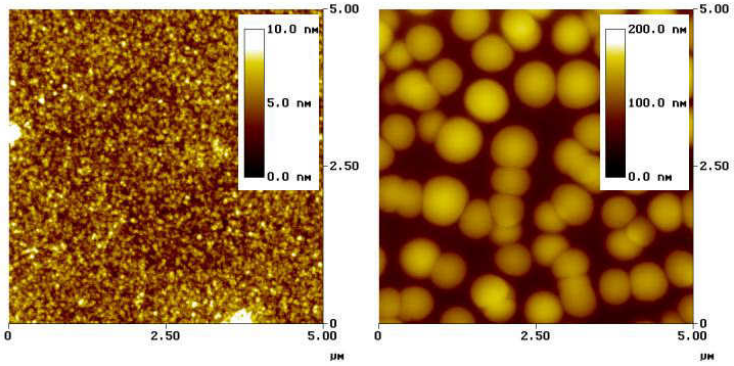

Fig. 1: Tapping mode AFM topography of MDMO-PPV:PCBM 1:4 blend films spin cast from chlorobenzene (left) and toluene (right). Scan area is 5µm × 5µm, while z-ranges are 10nm (left) and 200nm (right).

In order to image the cross-sections of these films, samples were broken and imaged from the side using a scanning electron microscope (SEM). The results are depicted in Fig. 2. Distributed nanospheres of dimensions of 15-20 nm are observed in both cases, whereas large (>500nm) and homogeneous clusters are only observed in toluene cast films.[6]

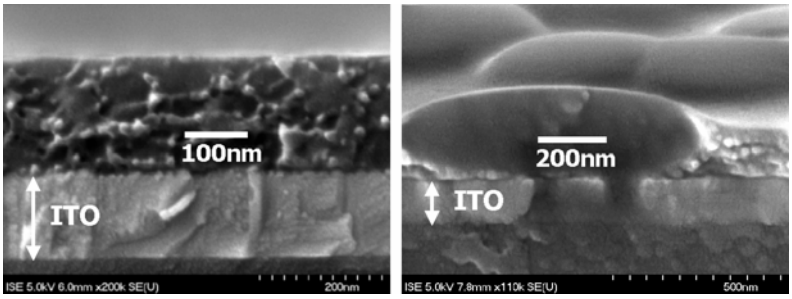

Fig. 2: Cold field emission SEM cross-section images of films spin cast from chlorobenzene (l) and toluene (r).

Fig. 3 compares the TEM image of toluene cast films before and after annealing at 150 °C for 4 hours. During annealing some microstructures evolved, and the clusters disappeared, leaving holes behind. The aggregated microstructures represent crystalline regions (compare inset, selected area electron

diffraction (SAED)), while around them no sign of any crystalline order was found. Assuming an fcc structure we calculate very comparable lattice constants for the PCBM crystals as found for bare C_{60}.[7]

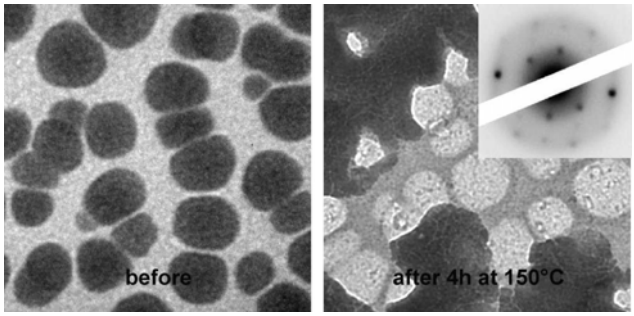

Fig. 3: TEM images obtained on toluene cast films before (left) and after a heat treatment at 150°C for 4 hours. The microstructures in the right image depict some crystalline order. Image size is about 2µm by 2µm in both cases. The inset in the right image shows the electron diffraction pattern of a PCBM crystal (inverted).

To obtain a bulk heterojunction the phase separated domain size as well as the percolation of both hole- and electron-conducting phases are crucial. Among the nanoscopic probing techniques Kelvin probe force microscopy (KPFM) was applied to study the energetics at the photoactive layer interface towards the electron-extracting cathode (compare Fig. 4).[8,9]

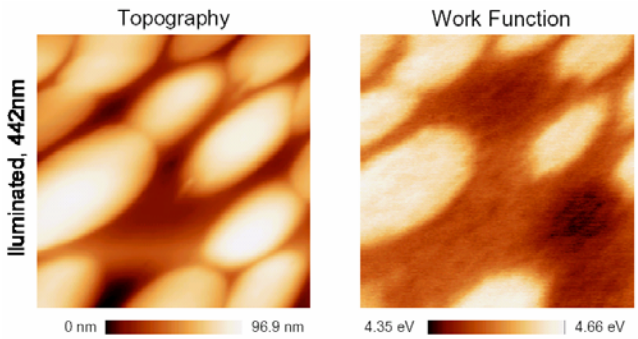

Fig. 4: Topography (left) and work function (right) of illuminated (cw-HeCd laser) toluene cast blends reveal a close correlation between morphology and energetics at the surface.

For most of the elevations in the toluene cast blends (caused by the underlying PCBM clusters) the work function is increased under illumination. However some nanostructures showing lower work functions are also observed and identified as uncovered PCBM clusters, whereas the higher work function on the other elevations points to a polymeric coverage and thus increased hole density at the surface.

In conclusion we were able to identify a morphological influence on electron extraction due to percolation and connectivity properties of the two phases. New insights are given for the conformation and distribution of the conjugated polymer (“nanospheres”) in the photoactive blends.

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