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Electron Microscopy of Organic Solar Cells Thermally Stabilized with Fullerene Nucleating Agents

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Organic Solar Cells (OSCs) have a great potential for solar energy harvesting due to their low material cost and cheap production. The most common and promising type of OSC is the bulk-heterojunction (BHJ) OSC, which have shown power-conversion efficiencies of 8-10% [1]. The absorber layer in these OSCs consists of a mix of two phases; (i) a polymer, that serves as an electron donor, and (ii) a fullerene, that serves as electron acceptor. The performance of BHJ OSCs is directly related to the three-dimensional microstructure of the absorber layer as the charge carriers generated must have access to paths of easy transport to avoid entrapment and recombination. It is thus necessary that the polymer and the fullerene phase form an intertwined continuous network on the nanoscale.

In order to upscale device fabrication and to meet requirements for solar cell standard test protocols the BHJ OSCs have to be able to withstand elevated temperatures of up to 140 °C. This will, however, result in a coarsening of the nanostructure and thereby a degradation of their properties. In this work we have used transmission electron microscopy (TEM) to study how the three-dimensional BHJ OSC microstructure can be stabilized upon annealing at 130 °C using C_{60} as a fullerene nucleating agent. The photovoltaic blends comprise a non-crystalline thiophene-quinoxaline copolymer (TQ1) and the widely used fullerene derivative [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM). The addition of C_{60} ranges from 0 up to 20 wt% with respect to PCBM. Annealing was performed at 130 °C for 10 min.

The TEM analysis was carried out using a Tecnai F20 equipped with a LaB_6 electron gun and operating at 200 kV. Tomography tilt series were recorded between ±60° with a tilt angle increment of 1°; reconstructed using the FEI software Inspect 3D and visualized using the Amira software.

Figure 1 shows the resulting microstructure for blends with 0, 5, 10 and 20 wt% C_{60}, respectively that have been annealed at 130 °C for 10 min. Without additions of C_{60} a few micron-sized PCBM crystals are formed and a depletion area is formed around these crystals. This microstructure results in a deterioration of the device properties. Upon a gradual increase of the C_{60} addition a large number of smaller PCBM clusters of crystals are formed reaching an average size of around 200 nanometers and a separation distance less than 100 nm for 10 wt% C_{60}. The crystals also form a seemingly continuous network for C_{60} additions of more than 10 wt%. Even upon annealing for more than 60 minutes the device characteristics are stable indicating that the microstructure do not coarsen further. Furthermore, from the images it is suggested that for additions of C_{60} up to 10 wt%, the blends are only composed of two phases, *i.e.* fullerene crystals and a TQ1-rich phase suggesting that fullerene crystallization is to a large extent complete. However for the sample with 20 wt% C_{60} there also seems to be an intermediate region connecting the crystals as seen in Figure 1. This may be an important contribution to the

continuous network of fullerene species as tomography reconstructions of the 20 wt% sample show that the crystals themselves don't form a continuous network.

References:

[1] Z. He *et al,* Nature Photon **6** (2012), p. 591.

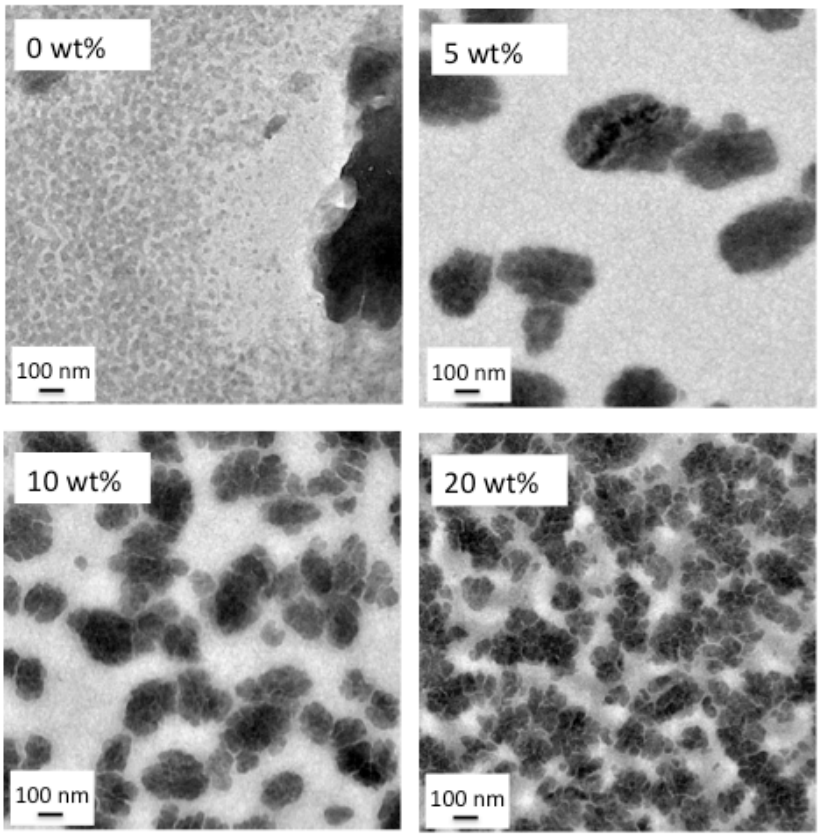

Figure 1. TEM images of TQ1:PCBM blends with additions of 0, 5, 10 and 20 wt% C_{60}, respectively after annealing at 130 °C for 10 min.

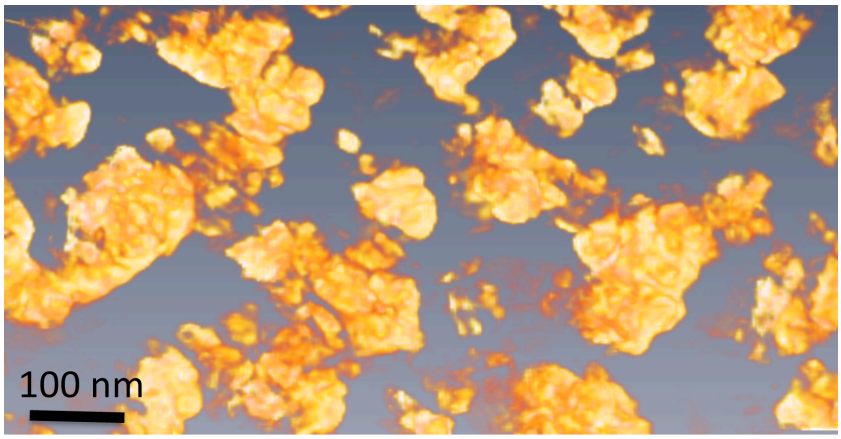

Figure 2. Reconstructed volume of the TQ1:PCBM sample with 20 wt% C_{60}. The crystals do not form a continuous network in this region.

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