Low-dose cryogenic O_2 and H_2O mapping in organic photovoltaics

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Organic photovoltaics (OPV) are promising materials for energy generation. However, they degrade much quicker than silicon photovoltaics, in the presence of oxygen and water. The effects of oxygen and water uptake on the bulk performance is relatively well understood, but there is a lack of nanoscale understanding. More specifically, the uptake of oxygen and water in the donor phase, the acceptor phase and at the donor-acceptor interface is not understood. By using model systems, containing a donor matrix with acceptor columns, transmission electron microscopy (TEM) can be employed to solve this problem, since the interface of the acceptor columns and the donor matrix is perpendicular to the sample plane.

The most important consideration for reliable TEM experiments of our beam-sensitive samples is their preservation, with applicable techniques being Energy Filtered TEM, STEM-EELS and STEM-EDX. This requires the effects of beam-sample interaction and exposure of volatile species to the high-vacuum of the electron column to be minimized. To this end we employ low-dose cryogenic TEM coupled with a quantitative analysis of electron beam damage. The presence of oxygen and water during sample preparations increases the rate of beam damage in cryogenic conditions, suggesting volatile species are present in the sample at cryogenic conditions[1]. This was confirmed with Energy Electron Loss Spectroscopy, since a sharp oxygen edge was present exclusively in the sample in cryogenic conditions. Furthermore, the decrease of this signal was measured as a function of accumulated electron dose, resulting in a critical dose for measuring oxygen content, i.e., the electron dose at which the added signal is equal to the added shot-noise. This critical dose was used to acquire oxygen maps with maximum information content. Image analysis protocols (Figure 1a) were used to quantify the average oxygen uptake in the three different regions of the OPV model system, resulting in relative intensity profiles across the donor-acceptor interface (Figure 1b). Different regions were localized using sulfur maps, since sulfur is only present in the donor phase, consisting of poly(3-hexylthiophene) (P3HT), and not in the acceptor phase, containing phenyl-C_{61}-butyric acid methyl ester (PCBM).

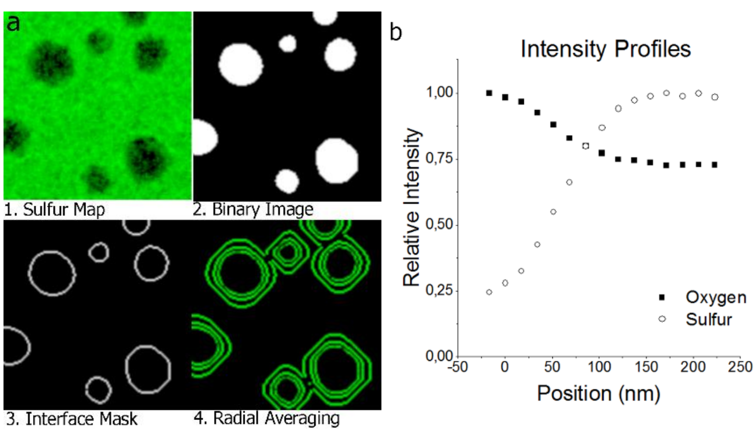

Figure 1

Results from STEM-EDX, STEM-EELS and Energy Filtered TEM are compared to determine the best technique for low-dose application. STEM-EDX was able to distinguish between phases, based on the Sulfur K-edge, but failed to measure changes in oxygen content. For STEM-EELS and EFTEM, a compromise between energy resolution and spatial resolution is required. At the same electron dose, STEM-EELS achieves a higher energy resolution, while with EFTEM a higher spatial resolution is achieved at similar signal to noise ratios. Both techniques were able to distinguish between the donor and acceptor phase, and to measure oxygen content at the nanoscale. In conclusion, by using EFTEM and STEM-EELS we show that oxygen is mainly taken up in the acceptor phase of the model system, containing PCBM, and no preferential uptake at the interface is observed.

1. Leijten, Z.J.W.A., Keizer, A.D.A., de With, G., Friedrich, H. J. Phys. Chem C **2017**, *121*, 10552-10561