X-ray assisted investigation on degradation of P3HT:PCBM bulk heterojunction solar cells

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Solution-processable organic photovoltaics have shown great promise for providing an entirely new generation of ultralow-cost, lightweight, and flexible electronic devices, which would be an ideal alternative to replace the traditional expensive silicon-based cells. Here, the most prominent material system 1,2-dichlorobenzene solution processed P3HT (region-regular poly(3-hexythiophene)):PCBM (phenyl-C61-butyric acid methyl ester) bulk heterojunction (BHJ) non-optimized solar devices were characterized under constant 1 AM0 (134.79 mW/cm²) with varied illumination time at room temperature. GISAXS (grazing incidence small angle x-ray scattering) was applied to reveal the inner structural changes of the active layers of the solar cells, and to better understand the degradation mechanism of polymer-based solar cells.

Figure 1: Solar cell characteristics a) open circuit voltage \( U_{oc} \), b) short circuit current \( I_{sc} \), c) fill factor \( FF \) and d) power conversion efficiency \( \eta \) are plotted as a function of time under permanent illumination of 1 AM0 at constant 28 °C. Error bar is added arising from the possible deviation from the measurement of the pixel size.

In general, degradation of polymer-based solar cell could be caused by an increasing amount of defects with the consequence of a reduced lifetime of charge carriers. Degradation in OPVs...
primarily occur in three places: (1) polymer active layer; (2) interface between active layer and electrodes and (3) electrode. From our experimental data of the constant 1 AM0 illumination series, $U_{oc}$ almost remains the same without influence from the accumulated radiation doses under constant temperature, owing to the fact that open circuit voltage is determined by the materials properties, that is, the energy difference between the HOMO level of the donor and the LUMO level of the acceptor material. $I_{sc}$, FF, Power conversion efficiency $\eta$, however, decreases rather dramatically. To explain the degradation phenomenon by changes of the morphology, GISAXS measurements are performed.

From the GISAXS measurement, molecular resolution of the buried interfaces of the thin films or multilayer systems is obtained without damaging the sample. As seen from the two-dimensional GISAXS images shown in Figure 2 as well as the cuts in vertical (see figure 2b) and horizontal (see figure 2c) direction, the films undergo changes in the morphology due to the illumination. Fitting of the data is performed within the model of the effective surface approximation. The resulting lateral P3HT domain size is rather constant (50±5 nm) during the illumination process which shows that the main degradation is not caused by lateral structural changes in the active layer.

![Figure 2](image)

**Figure 2:** a) 2d GISAXS data of BHJ solar cell as a function of illumination time b) vertical cuts of the 2d intensity as a function of the detector angle $\alpha_i + \alpha_f$, c) horizontal cuts at the critical angle of P3HT. Solid lines are the fits with the effective surface approximation to determine the prominent in-plane length scale. The curves are shifted along the intensity axis for clarity.

The does not changes as well as reported by Gang, who also proves that the degradation phenomenon is not caused by polymer crystallinity and/or reduced light absorption [1]. Therefore, the charge accumulation at the interfaces and the external oxygen diffusion into the device through the aluminium electrode [2], would be the primary reasons for the degradation of the polymer-fullerene BHJ solar cells. The former hypothesis is supported by the dramatic changing trend of the short-circuit current, while the latter one is proved by isotopic labelling $^{18}$O$_2$ of C$_{12}$-PSV-based organic photovoltaics.

**References**