

Light intensity dependence of External Quantum Efficiency of fresh and degraded organic photovoltaics



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ABSTRACT

The effect of light intensity on the External Quantum Efficiency (EQE) of encapsulated bulk heterojunction organic photovoltaics (OPV) is presented. The measurements were applied to devices based on poly(3-hexylthiophene) (P3HT) blended with the fullerene derivative phenylC61-butyric acid methyl ester (PCBM) in as-produced and various degradation states. The degradation of current collection in the OPV devices is shown to enhance the sub-linear dependence of the short-circuit current on light intensity, and the corresponding EQE decrease with increasing incident light intensity. On the other hand, fresh cells and cells exposed to a low photon dose demonstrated an increase in the fullerene-related part of the EQE with increasing light intensity, i.e. a super-linear dependence of the photocurrent in this spectral range. Generation of traps in PCBM was proposed as the underlying mechanism for this effect. Perusal of our results suggests that (1) EQE dependence on the incident light intensity should be always taken into account in measuring spectral response of fresh OPV and especially of degraded devices; (2) intensity-dependent characterization provides an insight to the degradation mechanisms of OPV and can help to separate degradation in absorption/generation from degradation of the charge collection in the cell.

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1. Introduction

Efficiency of organic photovoltaics (OPV) has recently surpassed $\sim 10\%$ [1]; however, better understanding of the physical mechanisms controlling the device performance is essential for further development. A number of protocols for accurate OPV efficiency assessment has been suggested [2–6]. It is well accepted that such assessment should include recording the irradiance spectrum and measurements of External Quantum Efficiency (EQE) of a reference cell and the tested OPV cell [7,8]. EQE is a dimensionless parameter quantifying the number of electron–hole pairs collected at the device contacts per incident photon at a given wavelength. The Short-Circuit Current Density (J_{SC}) can be calculated as the integral of the product of the measured EQE and the number of incident photons N_P at each wavelength λ , typically deduced from the AM1.5G spectrum [9], over the irradiating

wavelength range:

$$J_{SC} = \int qEQE(\lambda)N_P(\lambda)d\lambda \quad (1)$$

where q is the elementary charge. Thus, a verification of photovoltaic measurements can be assumed when the current density calculated by (1) agrees with the measured J_{SC} . In a recent commentary in Nature Photonics [7] Zimmermann et al. reviewed 1262 papers reporting current–voltage (I – V) curves of OPV, of which only 375 papers reported EQE. Comparison of integrated EQE data with the reported J_{SC} values demonstrated that 37% of the publications overestimated J_{SC} . Significant differences between these values can occur in OPV devices in which the photocurrent generation and collection depend non-linearly on the incident light intensity. Therefore, light intensity dependence of EQE is very informative for studying the operating mechanisms in OPV devices, and intensity-dependent losses should be taken into account. The published data for such behavior in OPV are very limited and restricted only to the case of linear or sub-linear dependence of J_{SC} on light intensity [10–13].

In polymer–fullerene bulk heterojunction OPV cells [14] light is absorbed by the polymer/fullerene photoactive layer resulting in the formation of a neutral excited state (binding energy ~ 0.5 eV)

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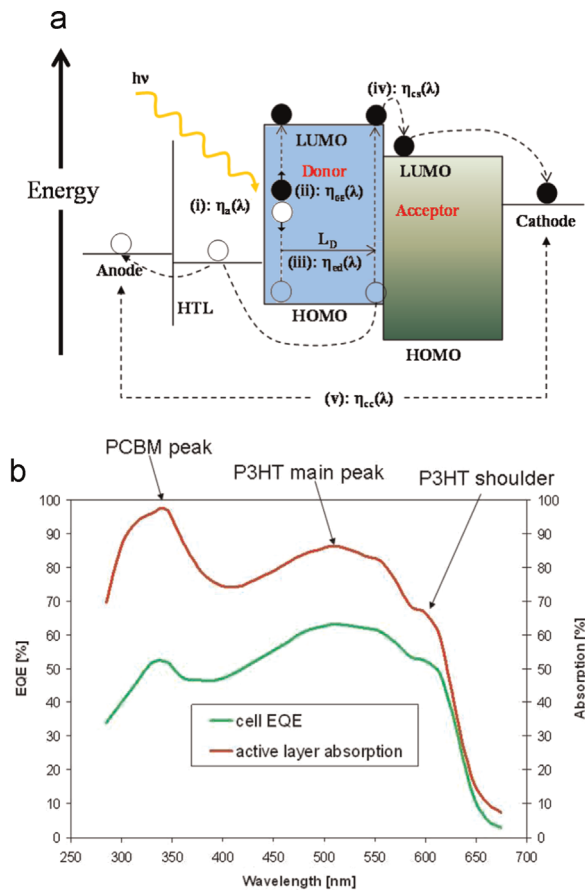


Fig. 1. (a) Schematic energy diagram of a normal architecture (including the active layer, a hole transport layer and the contacts) illustrating the five processes whose multiplied efficiencies determine the EQE: (i) absorption, (ii) exciton generation, (iii) exciton diffusion, (iv) charge separation, and (v) charge collection. (b) Absorption spectrum of a P3HT:PCBM blend and EQE spectrum for a cell with the same active layer.

[15]. Free carriers can be generated by exciton dissociation at the donor–acceptor interface, leaving the electron on the fullerene acceptor and the hole on the conjugated polymer donor. Efficient photocurrent generation requires that the donor and acceptor materials form interpenetrating and continuous networks, “phase separated” on the scale of the exciton diffusion length (~ 10 nm [16]). Following exciton dissociation into free carriers, the electrons and holes are conducted through the respective moieties toward the respective transport layers and electrodes. Accordingly, the EQE may be divided into five sub-efficiencies that correspond to the stages of the charge generation and collection in bulk-heterojunction OPV cells (Fig. 1a):

$$\text{EQE}(\lambda) = \eta_{Ab}(\lambda) \times \eta_{Ge}(\lambda) \times \eta_{ED}(\lambda) \times \eta_{CS}(\lambda) \times \eta_{CC}(\lambda) \quad (2)$$

where η_{Ab} is the photon absorption efficiency, η_{Ge} is the efficiency of exciton generation, η_{ED} is the efficiency of exciton diffusion towards the donor/acceptor interface, η_{CS} is the efficiency of the exciton separation and η_{CC} is the charge collection efficiency.

Recently EQE measurements have been suggested as an important supplementation to I – V measurements for OPV stability assessment [17,18]. Since each absorbing material in the OPV device can be identified by corresponding peaks in the light absorption and EQE spectra (Fig. 1b), analysis of EQE evolution can be a useful tool for tracking different degradation paths observed in OPV materials and devices.

In this paper we present experimental results of the effect of light intensity on the EQE of encapsulated bulk heterojunction OPV based on poly(3-hexylthiophene) (P3HT) blended with the

fullerene derivative phenylC61-butyric acid methyl ester (PCBM) in as-produced state and at the various states of accelerated degradation. To the best of our knowledge, published data on evolution of light intensity dependence of the EQE with the OPV degradation are absent. The degradation experiments were performed using concentrated sunlight [19–20]. We demonstrate that the degradation of charge collection in the OPV devices enhances the sub-linear dependence of J_{SC} on light intensity and the corresponding EQE decrease with increasing incident light intensity. On the other hand, both fresh cells and cells exposed to a low photon dose demonstrated an increase in the fullerene-related EQE signal with increasing light intensity, i.e. a super-linear behavior of the photocurrent in this spectral range. Generation of traps in PCBM was proposed as the underlying mechanism for this effect. Perusal of our results suggests that (1) EQE dependence on the incident light intensity should be always taken into account in measuring the spectral response of fresh OPV and especially of degraded devices; (2) it provides an insight to the degradation mechanisms of OPV which cannot be deduced from traditional I – V tracing and constant-intensity EQE measurements.

2. Experimental

2.1. Sample preparation

A series of ITO-free solar cells were prepared with the following layer sequence: glass substrate/Ag-grids/PEDOT:PSS/P3HT:PCBM/LiF:Al/encapsulation (Fig. S1 in Supplemental information) [21–23]. The Ag-grids had a hexagonal (honeycomb) configuration (Fig. S1b). The materials used for device preparation were highly conducting Orgacon PEDOT:PSS (Agfa-Gevaert), Poly-(3-hexylthiophene) (P3HT) (Plextronics) and [6, 6]-phenyl-C61-butyric acid methyl ester (PCBM) (Solenne BV). The active layer (220 nm thick) was spin-casted (1000 rpm) in a glove-box. All devices were encapsulated with a thin film barrier with low oxygen and water vapor transition rates (10^{-6} g m $^{-2}$ day $^{-1}$) [24]. To prevent side leakage, the organic layers were structured via laser ablation prior to encapsulation. The active area of the devices was 3.76 cm 2 .

Samples with the layer sequence glass/P3HT:PCBM/encapsulation layer were used for studying UV–vis light absorption of the P3HT:PCBM active layer. The thickness and composition of the P3HT:PCBM and encapsulation layers were similar to those in the solar cells.

2.2. Accelerated degradation experiments

Outdoor sunlight was concentrated and transferred indoors using the unique “solar furnace” developed in-house [25,26]. In this system a dual-axis tracking flat heliostat reflects sunlight into the laboratory, where a flat mirror (with a hole at its center) tilted at 45° redirects the light upward to a 526 mm-diameter paraboloidal dish with numerical aperture of 0.4, whose focal plane is just below the tilted mirror (Fig. S2). The light intensity was moderated by a louvered shutter between the heliostat and the flat indoor mirror. It should be noted that the spectrum measured at “noon time ± 2 –3 h” at Sede Boqer (Lat. 30.8°N, Lon. 34.8°E, Alt. 475 m), where the lab is located, is very close to the AM 1.5G spectrum.

Flux uniformity was achieved using kaleidoscopes placed between the paraboloid focal point and the cell (Figs. S2c and S3). Increase in the kaleidoscope exit area results in deconcentration of the sunlight delivered to the cell. The degree of concentration can be varied gradually from 0 to, for example, 100 and 10,000 sun for 1 cm 2 and 1 mm 2 cells, respectively. The incident power of concentrated sunlight was measured with a pyrometer of 5% accuracy,

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