# Correlation between charge carriers mobility and nanomorphology in a blend of P3HT/PCBM bulk heterojunction solar cell: Impact on recombination mechanisms

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## ARTICLE INFO

## ABSTRACT

Sandwich configurations consisting of hole-only and electron-only devices are employed to study the transport properties of polymer/fullerene blended material. Upon thermal annealing at 150 °C and subsequent device characterisations a direct correlation between solar cell device power conversion efficiency and charge carrier mobilities is identified. The highest power conversion efficiency reported herein resulted from the electron to hole mobility ratio of 4.78. This ratio further reduces to 0.357 at 175 °C as a result of the deterioration of electron mobility at the same time as enhancement in hole carrier mobility with no further improvement in PCE. Effects of thermal annealing on trap density reveal that the trap assisted recombination is more dominant as compared to the bimolecular recombination. Furthermore such a mechanism enhances as a result of increasing trap density at higher annealing temperatures. The effect of light intensity on the open circuit voltage $V_{OC}$ further verifies that the dominant recombination process is through trap assisted recombination.

## 1. Introduction

Recent progress in material selections and fabrication processes has led to the development of organic solar cells with efficiencies approaching 10% [1–4]. Whilst there have been extensive research based on the blend of P3HT/PCBM solar cell [5–8], no breakthrough in power conversion efficiencies (PCEs) above 10% has been realised as yet. The internal quantum efficiency is given by $\eta = \eta_A \eta_D \eta_{CT} \eta_{CC}$ [9], where $\eta_A$ is the efficiency associated with photon absorption, $\eta_D$ is the efficiency associated with exciton dissociation, $\eta_{CT}$ is the efficiency associated with charge transfer and $\eta_{CC}$ is the efficiency associated with charge collections at respective electrodes. Enhancing $\eta_A$ is very much dependent on the material selected. Amongst blended materials, poly(3-hexylthiophene) (P3HT) and phenyl-$C_{61}$-butyric acid methyl ester (PCBM) are currently the most investigated [10–12]. This is attributed to the high degree of crystallinity of P3HT and its absorption spectrum extending in the region of 650 nm, and suitable electronic bandgap favouring efficient charge transfer [13]. When considering $\eta_D$ and $\eta_{CC}$, again material selection is a significant factor concerning efficient charge separations resulting from differences in the lowest unoccupied molecular orbitals (LUMO) of the blended materials and charge transport properties.

Furthermore donor/acceptor interfaces, nanodomain, transport pathways to the respective electrodes, charge carrier mobilities, loss mechanisms via recombination, etc. all have an impact on the device power conversion efficiencies [14–18]. Owing to the processing conditions of these blends, PCEs can remarkably improve upon subjecting the device to various physical and chemical processes [19–22]. Previously [23] we reported on the PCBM cluster formation resulting from different thermal annealing strategies and its impact on photocurrent generation. Nanostructuring of the photo-active layer significantly influences charge carrier mobilities, charge separation and recombination processes, all of which have a direct impact on power conversion efficiencies. It is known that the charge carrier mobilities enhances exciton dissociations and charge carrier recombination which are believed to be a competing process [24]. This parameter can improve or deteriorate upon thermal annealing. To address the influence of trap density on charge carrier mobility, we suggest a range of thermal annealing temperatures above the glass transition temperature of P3HT, for this phenomenon to be studied. It is well established that the best device efficiency reported for P3HT/PCBM blend is at the annealing temperature of ∼140 °C [25]. However, thermal annealing at this temperature results in restructuring of nanodomains which consequently has a direct impact on exciton dissociation as well as recombination processes, as a byproduct of changes in the polymer/fullerene interface. This manuscript is therefore focused on the effects of thermal annealing

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on transport properties of solar cell devices based on blended materials (P3HT/PCBM) as well as establishing the processes supporting recombination mechanisms.

## 2. Experimental

P3HT (regioregularity of 96.6%, Ossila Ltd.) and PCBM (Solenne BV, The Netherlands) were first dissolved in 1,2-dichlorobenzene (DCB) separately and stirred for 1 h at ~45 °C. The two pristine solutions were then blended to make a solution of total concentration of 25 mg/mL, a 1:1 weight-ratio of P3HT:PCBM. This was left to stir for another 1 h before filtering through a 0.45 μm PTFE filter. The filtered P3HT/PCBM blend solution was then left to stir for a period of 16–18 h at room temperature in a nitrogen-filled glove box ( < 1 ppm $O_2$ and $H_2O$). Before device fabrication, ITO coated substrates ( ~10 Ω/cm²) were first cleaned with deionised water, acetone, and isopropyl, sequentially in an ultrasonic bath for 10 min each. Cleaned substrates were then transferred to a nitrogen-filled glove box. This was followed by spin casting at 5000 rpm, a layer ( ~40 nm) of poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) (Sigma Aldrich), onto the ITO coated substrate. PEDOT:PSS was filtered through a 0.45 μm filter prior to spin casting. The PEDOT:PSS film was subjected to 10 min of baking at ~150 °C. Following the cooling down of the substrate, P3HT/PCBM blend films were spun casted onto the PEDOT:PSS layer and left to dry in the desiccator. To complete the device fabrication, an aluminium (Al) layer ( ~100 nm) was thermally deposited onto the active layer through a shadow mask, under a vacuum pressure of ~$10^{-6}$ mbar. The device's active area, defined by a shadow mask is 0.14 cm². To measure charge carrier mobilities, hole- and electron-only devices were fabricated. The hole-only device was fabricated following the same procedure as for the solar cell device above, but replacing the aluminium top electrode with gold (Au). And as for electron-only device, PEDOT:PSS was replaced with a thin layer of Caesium carbonate ($Cs_2CO_3$), spun casted from solution in 2-ethoxyethanol.

The current–voltage (I–V) curves were measured with a Keithley 2400 source meter in dark and under Air Mass 1.5 (AM 1.5), 100 mW/cm² illumination provided by an LOT Oriel 150-W solar simulator fitted with a Xenon lamp. For voltage dependence on light intensity measurements, the illumination intensity of the solar simulator was varied by varying the power output of the lamp's power supply. The intensity of the illumination was checked every time before measurements with a calibrated Si reference solar cell and meter (Newport and Oriel Instruments). The thicknesses of the thin films were determined using a DektakXT stylus profiler. All thermal annealing of devices were done inside a nitrogen filled glove box. For hole- and electron-only devices, I–V characterisations (for hole- and electron-only devices) were performed in dark, whereas for solar cell device, this was done under illumination. All devices were tested inside a nitrogen filled glove box.

## 3. Results and discussions

### 3.1. Implications of thermal annealing on bulk network transport properties

Fig. 1(a) represents current density/voltage characteristics for hole-only device fabricated using the sandwich structure of ITO/ PEDOT:PSS/P3HT:PCBM/Au. Upon the positive application of voltage to Au contact with respect to PEDOT:PSS, there is no potential barrier and holes are injected from Au into the highest occupied molecular orbital (HOMO) of P3HT (reverse bias). This is illustrated
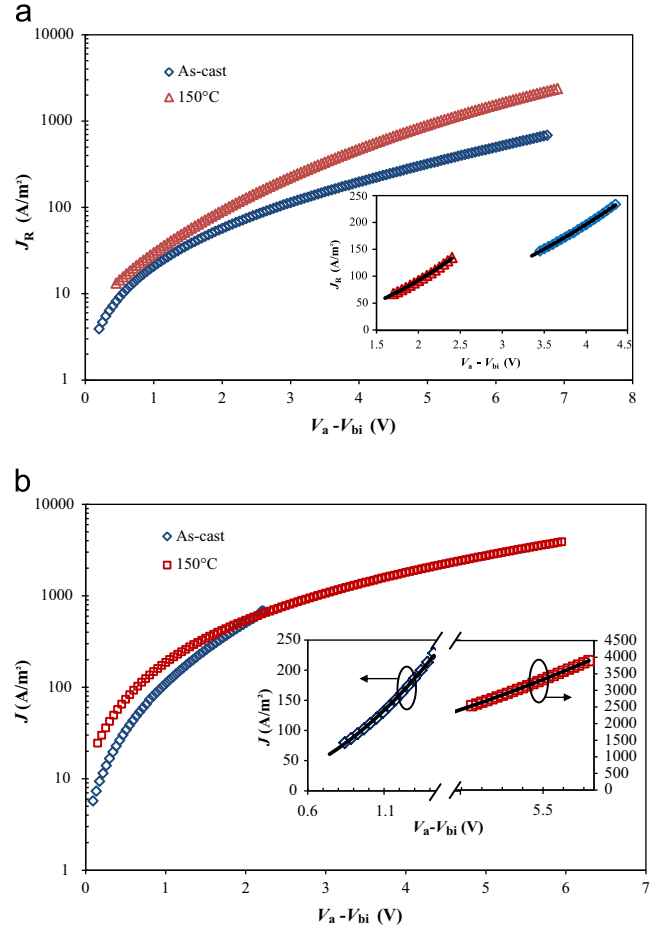


**Fig. 1.** Dark J–V characteristics of P3HT:PCBM blend: (a) hole-only device (reversed biased) and (b) electron-only device (forward biased). The inserts show the fits of experimental data to the SCLC model in Eq. 2.

in Fig. 2(a). At effective applied voltage 0.2 V < $V_{eff}$ < 0.7 V ($V_{eff}$ being the applied bias corrected for the built-in potential arising from the difference between the work-function of contacts) the current density voltage obeys Ohm's law and the relationship may be written as

$$J = qn_{e(h)}\mu_{e(h)}\frac{V}{d} \qquad (1)$$

where $q$ is the electron charge, $\mu_{e(h)}$ is the electron (hole) carrier mobility, $n_{e(h)}$ is the electron (hole) concentration, and $d$ is the device active layer thickness. At higher effective applied field 3.5 V < $V_{eff}$ < 4.4 V the current density voltage relationship defers from the Ohmic behaviour and follows space charge limited current (SCLC). The current density dependence on voltage for trap filled limited SCLC is given by the square law

$$J = \frac{9}{8}\varepsilon_0\varepsilon_r\mu_{e(h)}\frac{V^2}{d^3} \qquad (2)$$

where $\varepsilon_0$ represents the permittivity of free space, $\varepsilon_r$ is the dielectric constant of the blended material ~3.4, $\mu_{e(h)}$ is the electron (hole) carrier mobility and $d$ is the device active layer thickness ~150 nm. Using the slope corresponding to the square law in Fig. 1(a) and appropriate parameters, Eq. (2) yields a value of the hole mobility for as cast device as $\mu_h = 1.15 \times 10^{-9}$ m² V$^{-1}$ s$^{-1}$. This is in close agreement with published data for this parameter [26,27]. Similarly the Ohmic region of Fig. 1(a) together with appropriate parameters in Eq. (1) leads to a hole carrier concentration of $1.49 \times 10^{22}$ m$^{-3}$ which is of the same order of magnitude reported in the literature [27].