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Imbalanced charge mobility in oxygen treated polythiophene/fullerene based bulk heterojunction solar cells

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Abstract:

The effect of oxygen induced traps on charge mobility in bulk heterojunction solar cells using poly (3-hexylthiophene) (P3HT):1-(3-methoxycarbonyl)-propyl-1-phenyl-(6, 6) methanofullerene (PCBM) blend have been studied using photoinduced charge extraction by linearly increasing voltage (PhotoCELIV) technique. The solar cells exposed to oxygen exhibit dual PhotoCELIV peaks, whereas the solar cell without oxygen treatment show single PhotoCELIV peak with the charge mobility of the order of $10^{-4} cm^2/Vs$. It is demonstrated that the oxygen treatment imbalance the charge mobility in the P3HT/PCBM photoactive layer, which affects the power conversion efficiency and lifetime of the solar cell. The single PhotoCELIV peak for the device without oxygen treatment indicates that the charge mobility is balanced, that causes the overlapping of electron and hole transients.

Keywords: Charge mobility, PhotoCELIV, organic photovoltaic, conjugated polymer

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The development of efficient and stable photovoltaic cells is the major challenge with the current polymeric solar cell (PSC) technology. Significant improvements on the power conversion efficiency (PCE) have been achieved for the bulk heterojunction (BHJ) based PSC's.[1-3] The poly (3-hexylthiophene) (P3HT) and 1-(3-methoxycarbonyl)-propyl-1-phenyl-(6, 6) methanofullerene (PCBM) based solar cells is the most established system with the reported values of PCE's around 4-6 %.[4, 5] The efficiency and stability of polymer solar cells are strongly dependent on the charge transport properties, which varies with the nano-morphology of the electron donor-acceptor composite film.[6, 7] Therefore the systematic investigation on the charge transport properties is important to improve PCE as well as to investigate the lifetime issues. The charge transport in solar cells can be investigated using the photoinduced charge extraction by linearly increasing voltage technique (PhotoCELIV).[8-11] Mozer et al have studied the charge transport and recombination properties in PSC's using the PhotoCELIV technique.[12-13] The PhotoCELIV studies on various polymer/fullerene based photoactive layers exhibited only one peak[8, 9] although it is experimentally possible to study the electron and hole mobility simultaneously. The sign of the charge carriers extracted using PhotoCELIV was also under debate and most of the time it was related to the slowest carriers such as holes. Recently, Anderson et al [14] have observed dual CELIV peaks on PSC's based on a low band gap polymer (APFO-Green)/PCBM (>75%) composite film. However, there is no known literature reporting the dual photoCELIV peaks on the highly optimized P3HT:PCBM solar cells. In this study, we showed that it is possible to observe dual PhotoCELIV transients in P3HT:PCBM layer exposed to oxygen (O_2)/air, which makes the electron and hole mobility differs significantly from each other.

Devices were prepared by first spin coating a 40nm thick PEDOT:PSS layer onto a pre-cleaned ITO pre-patterned glass substrates. Subsequently, P3HT and PCBM (1:0.8) layer was spin coated from a 1,2-dichlorobenzene solution. The O_2 treatments were carried out in a vacuum chamber with a constant O_2 partial pressure of 0.01 mbar for 0.5 and 1.0 hours. Then the top layer of Al (100nm) electrode was deposited in a vacuum chamber with a base pressure less than 10^{-5} mbar. After that, the device was thermally annealed at 120°C for 10 minutes in an inert glove-box environment. An exposure of the solar cells in air for up to 20 hours was also tested for comparison studies. The current density-voltage (J-V) curves were measured under simulated AM 1.5G illumination at 100 mW/cm^2. The PhotoCELIV set-up was composed of a pulsed Nd:YAG laser (532nm), a function generator and a digital oscilloscope and the measurement details are described elesewhere.[8-13,15]

The PhotoCELIV transients measured for the control device is shown in Fig. 1 (a). The PhotoCELIV transients exhibit single peak and the time taken to reach the extraction current maxima was decreasing with the increase of A, which indicates the electric field dependence of charge mobility. The calculated charge mobility is in the range of 2-3.5 x 10^{-4}cm^2/Vs at an applied field from 7.1x10^3 V/cm to 1.4 x10^4 V/cm respectively. This result is consistent with the literature values on P3HT/PCBM composite film with similar devices.[16] The PhotoCELIV transients for the 0.5h O_2 exposed device are broader than the transients observed for the control device and the charge mobility was in the range of 1.9x10^{-4}cm^2/Vs. The broadening of PhotoCELIV transients for 0.5h O_2 exposed device may indicate that the O_2 induced traps are starting to influence on the charge transport properties. The PhotoCELIV transients for the 1h O_2 exposed device shows a distinct

shoulder (Peak 2) at long time scale in addition to the main PhotoCELIV peak (peak1) (shown in Fig. 1(b)). The peak positions (peak 1 & peak 2) were shifted towards shorter time scale when the rate A is increased, which indicates the field dependence of charge extraction time. The PhotoCELIV transients for the air exposed device also exhibited dual peak behavior and the time taken to reach the steady state was longer (100 µs) than the time required for the devices without O_2 treatment and for the device exposed to 0.5h. The charge mobility was approximately estimated from the second PhotoCELIV peak and it was found to be in the order of 10^{-5}cm^2/Vs. The variation of charge mobility with applied electric field for the all the devices are shown in Fig. 2. The obtained charge mobility results from the four devices with and without O_2/air treatment indicate that there is no significant changes in the charge mobility corresponding to the first PhotoCELIV peak position, however it is clearly seen that the second PhotoCELIV maximum starts appearing when the device is exposed to O_2/air for long time. These results indicate that the oxygen interacts with the photoactive layer and slows down the mobility of one of the charge carrier. It is well known that the charge transport in P3HT is very sensitive to O_2 and moisture. The charge mobility in pure P3HT decreases by one order of magnitude from 10^{-4}cm^2/Vs to 10^{-5}cm^2/Vs after 3 hours exposure to O_2 as the total trap density was increased after air exposure.[17] The oxidation and the subsequent degradation of thiophene rings breaks the macromolecular backbone configuration which affects the hole mobility in the system. The charge mobility estimated from the first PhotoCELIV peak observed in the present study is assigned to the extraction of electrons and the second PhotoCELIV peak is assigned to holes based on the literature reports.[10,17] The observed results also indicates that the single PhotoCELIV transient reported for

P3HT/PCBM composites in the literature were the superposition of electron and hole transients as the electron and hole mobility is in the same order of magnitude.

The effects of O_2/air induced traps on the photovoltaic performance were also evaluated. The J-V characteristics of devices with and without O_2 are shown in Fig. 3 (a) and the extracted device parameters are summarized in table I. The average PCE of the control devices was around 3.5 %, and it decreased to 2.66% after the cells were exposed to air for 20 hours. The lifetime characteristics of the devices were also studied by continuously illuminating the cells and the results are shown in Fig.3 (b). The rate of change in PCE as a function of operation time is much faster in the O_2/air exposed devices compared to the control device. The PCE of the control cells decreased to 80 % of its initial value after 20 hours of continuous illumination, whereas the PCE of the cells that had pre-exposed to air for 20 hours reduced to ~ 40% of the its initial value after 20 hours aging test. The obtained results indicate that the diffusion of O_2 into the photoactive layer may be one of the major causes for device degradation.[17-19] This discussion also agrees with our findings indicating that the O_2 induced charge traps in active layer are one of the primary factors that are responsible for the imperfection in the charge transport properties and hence the performance of the polymer solar cells.

The effect of oxygen/air induced traps on charge mobility and device performance in P3HT/PCBM based solar cells is studied. The dual photoCELIV transients obtained for the O_2/air treated devices indicate the imbalance of electron and hole mobility. The obtained results demonstrate that O_2 induced traps in the photoactive layer are one of major degradation pathways, which deteriorate the performance of solar cells.

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Table I. The photovoltaic parameters measured for the solar cells that were treated with different oxygen/air exposures.

Oxygen exposure prior to cathode deposition	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE (%)
Control cell	0.60	11.78	48.95	3.46
30 mins	0.59	11.88	47.79	3.35
1.0 hr	0.59	11.50	46.13	3.13
Air 20 hrs	0.59	10.44	43.18	2.66
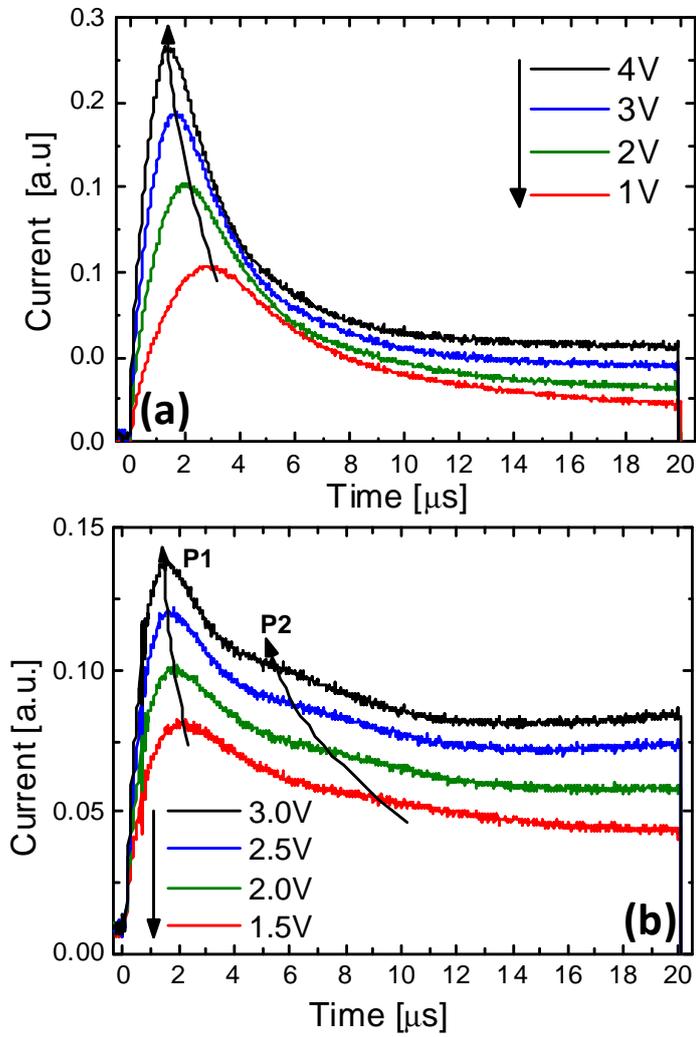
Fig 1. PhotoCELIV transients for the **(a)** control device without oxygen treatment and **(b)** 1 hour exposure to oxygen
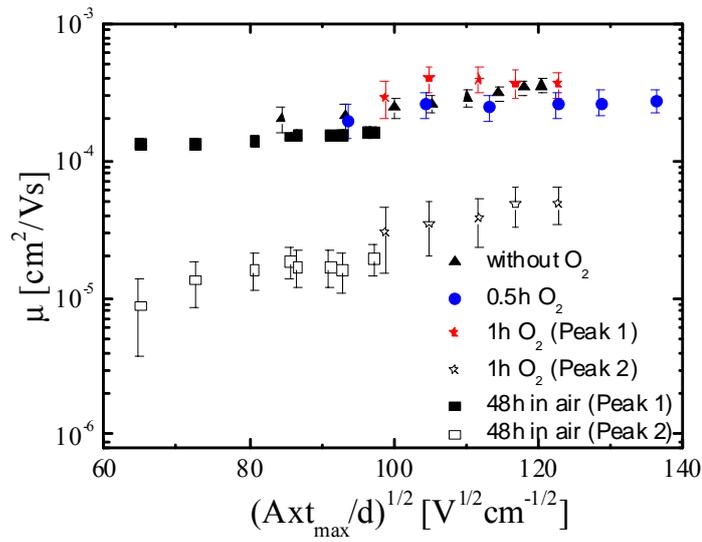
Fig 2. Variation of charge mobility with applied electric field for the devices with and without oxygen/air exposure
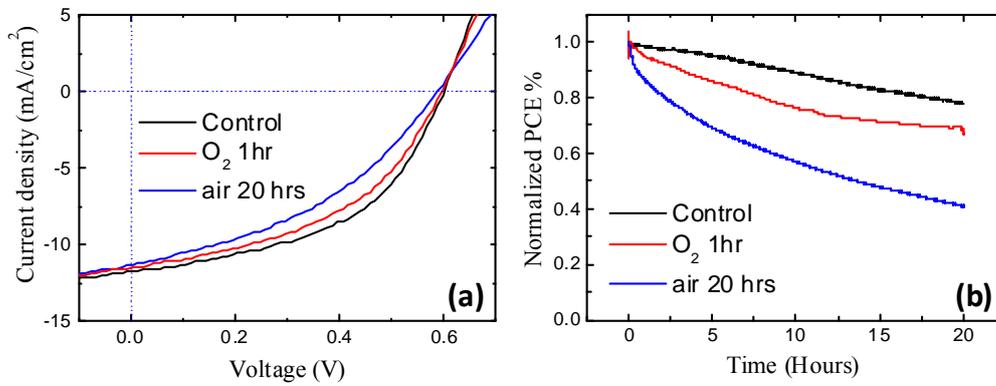

Fig 3 (a). J-V characteristics of the solar cells treated with different oxygen/air exposures; (b) the behavior of normalized PCE as a function of operation time for a set of identical solar cells that were exposed to different oxygen/air exposure conditions.