

Electrical characterization with high spatial resolution of P3HT:PCBM blends used in organic photovoltaics by means of conductive atomic force microscopy

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ABSTRACT

In the present work, conductive atomic force microscopy is used to obtain high spatial resolution electrical characterization of a donor conjugated polymer, poly(3-hexylthiophene-2,5-diyl) blended with an acceptor fullerene derivative, 95% PC70BM ([6,6]-Phenyl-C71-butyric acid methyl ester) and 5% PC60BM ([6,6]-Phenyl-C61-butyric acid methyl ester), as used in the fabrication of the active layer of bulk heterojunction organic photovoltaic devices. Local spectroscopy scans are performed in dark and light conditions with the objective of analyzing charge carrier transport properties and photocurrent generation. Differences in the electrical properties of semiconducting polymers are evidenced when blending with the acceptor fullerene derivative. Finally, conductive atomic force microscopy is used to provide morphological characterization at the nanoscale using contact scans of biased samples allowing to obtain electrical maps depicting compositional differences.

Keywords: bulk heterojunction, organic photovoltaics, conductive atomic force microscopy.

1 INTRODUCTION

Bulk heterojunction (BHJ) organic photovoltaics (OPV) represent a low cost alternative to traditional inorganic solar technologies [1] primarily due to reduced manufacturing costs [2] that result from solution processing at low temperatures [3]. Furthermore, OPV can be easily produced in flexible thin films opening market opportunities and allowing the integration of organic solar cells to other products [4]. However, OPV are not as widespread as inorganic, mostly silicon, solar cells due to the low power conversion efficiency [5] that they attain and their shorter lifetime. Electrical characterization of the bulk heterojunction active layer is of outmost importance in order to develop more efficient solar cells capable of competing in the growing solar technologies market.

Conductive atomic force microscopy (CAFM) is a high spatial resolution technique used to characterize the electrical properties of BHJ active layers at the nanoscale.

The mobility of the main charge carriers [6] [7] [8] [9], the photocurrent produced upon exposure to sun simulated light [6] [10] and morphological characterization [11] have been widely reported in literature. In the present work, this technique is utilized to obtain local spectroscopy scans, i.e. I-V curves, and determine charge carrier mobility and photo-generated current upon exposure to UV-light on BHJ active layers of P3HT and PCBM for different concentration ratios. Furthermore, contact scans of biased samples allow for differentiation of phases within the active layer.

2 METHODS

Conductive AFM measurements are performed on glass/ITO/P3HT:PCBM thin film samples. Glass/ITO (indium tin oxide) unpattern substrates purchased from Ossila Ltd (UK) are thoroughly cleaned by sonication in separate baths of acetone, isopropanol and DI water. Solutions of P3HT/chlorobenzene and PCBM/chlorobenzene are prepared at concentrations of 10 mg/mL, using poly(3-hexylthiophene-2,5-diyl) (RR 93.6%, M_w 31 300, M_n 15 600) and a mixture of 95% PC70BM ([6,6]-Phenyl-C71-butyric acid methyl ester) and 5% PC60BM ([6,6]-Phenyl-C61-butyric acid methyl ester) (M113) (UK) (M_w : 1031 g/mol. Purity: 95/5% (C70/C60)), purchased from Ossila Ltd. The solutions are stirred at 55°C overnight. Later they are mixed in the proper amounts to obtain P3HT:PCBM concentration ratios of 0, 44, 50 and 54wt% of PCBM. P3HT and the P3HT:PCBM solutions are spin coated onto the glass/ITO substrates in order to obtain layers \approx 100 nm thick. All the samples are annealed at 150°C for 10 minutes. Solution preparation, mixing, spin coating and annealing are all performed inside an MBraun glovebox (MB200) under nitrogen atmosphere ($H_2O < 1$ ppm, $O_2 < 1$ ppm), equipped with an MBraun MB-SC-200 spin-coater to prevent polymer degradation by reaction with oxygen and moisture [12]. CAFM spectroscopy scans are conducted in ambient conditions within 6 hours of spin coating to prevent polymer conjugation loss upon aging, using an Asylum Research Cypher atomic force microscope. Diamond-coated silicon probes from NanoSensors with a spring constant $k=1$ N/m and a tip radius of $R=150$ nm are used to conduct the measurements under dark and light conditions. For the latter,

a UV generator from Oriel Instruments is used at 330 W of power.

3 RESULTS

Spectroscopy scans under dark and light conditions are shown in Fig. 1 for different concentration ratios of P3HT and PCBM. These I-V curves are the average of 800 curves obtained in 10 different locations for each sample. A decrease in the current flowing through the sample at a certain voltage can be observed upon blending the donor polymer with the fullerene derivative. This has been attributed to a more disordered microstructure and a decrease in P3HT crystallite size upon blending [13]. However, performance peaks for a concentration of 50wt% of PCBM [14]. Testing under “light ON” conditions shows a higher current flowing through the sample for all voltages as a result of photo-generated charge carriers.

Charge carrier mobility was determined by fitting the I-V curves obtained in dark conditions using Mott-Gurney equation [15]

$$J = \frac{9}{8} \epsilon \epsilon_0 \mu \frac{V^2}{L^3} \quad (1)$$

where ϵ is the relative dielectric constant of the material (≈ 3 for organic photovoltaic blends), ϵ_0 is the vacuum permittivity, μ is the charge carrier mobility and L is the thickness of the active layer. Charge carrier mobility values obtained by fitting the experimental I-V curves in dark with Mott-Gurney law are plotted in Fig. 2 along with the normalized photocurrent at 0 bias. These values, however, do not represent a quantitative characterization of these two properties. On the contrary, they have to be analyzed with caution.

The mobility calculated using Mott-Gurney law to fit I-V curves obtained by CAFM has been reported to be up to three orders of magnitude higher than that obtained by means of macroscopic measurements [6] [8]. The difference between the geometry of a plane parallel capacitor test and the tip-sample layout of CAFM has been identified as the main reason for this discrepancy [8]. In addition, high electric fields develop throughout the sample that give rise to Frenkel effect [16] further differentiating the real experiment from the assumptions of Mott-Gurney law. In other work of the authors [17], Hartke’s equation which accounts for high electric fields, Frenkel effect and geometry is considered.

$$J = \frac{2\mu\theta_0\epsilon\epsilon_0 V}{\beta^2 L} \exp\left[\beta\left(\frac{V}{L}\right)^{\frac{1}{2}}\right] \quad (2)$$

where θ_0 is defined as $\theta_0 = (N_c/N_t) \exp(-A/kT)$, N_c is the effective density of conduction-band states, N_t is the effective density of trapping effects and A is the energy of trapping level close to the band edge. β is defined as $\beta = (q^3/\pi\epsilon\epsilon_0)^{1/2}/kT$ for the plane parallel electrode case. When this model is used, quantitative results of charge

carrier mobility can be obtained by means of CAFM tests (see Table 1).

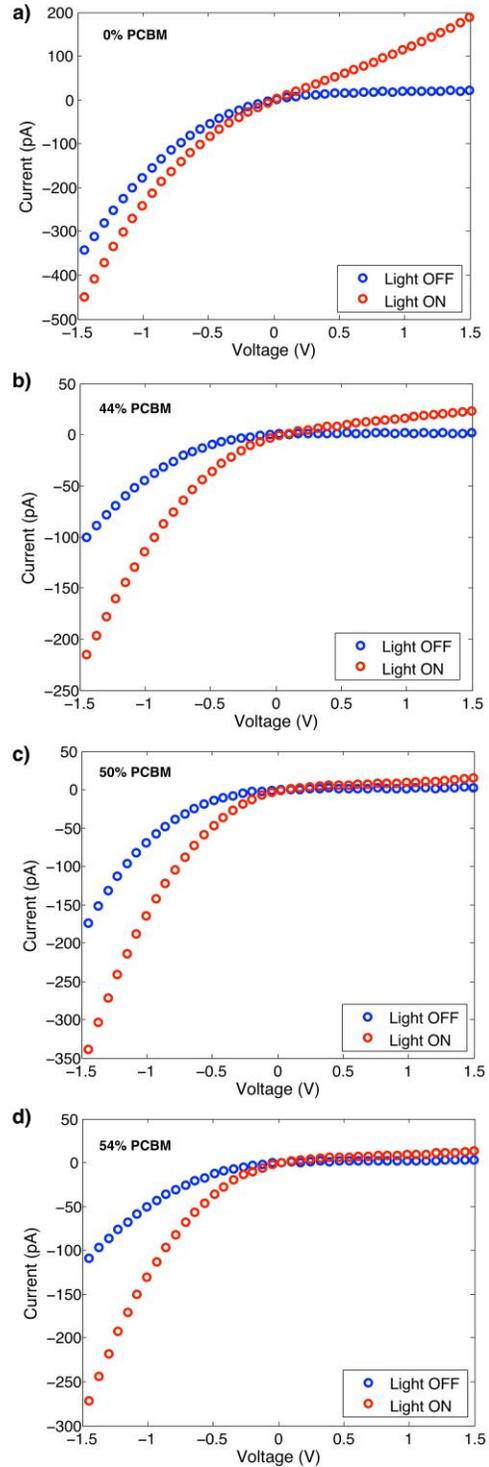


Figure 1: Current-voltage curves under dark and light conditions for (a) P3HT, (b) P3HT-44wt%PCBM, (c) P3HT-50%PCBM and (d) P3HT-54wt%PCBM.

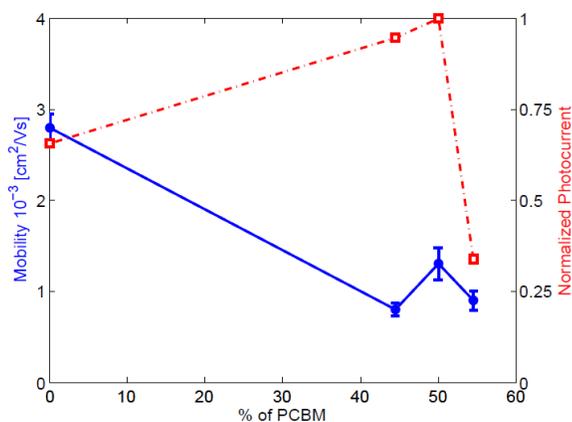


Figure 2: (blue solid circles) Mobility values obtained by fitting the I-V curves obtained under dark conditions for different concentration ratios of P3HT and PCBM with Mott-Gurney law. (Red hollow squares) Normalized photocurrent at 0 bias between tip and sample upon exposure to UV light.

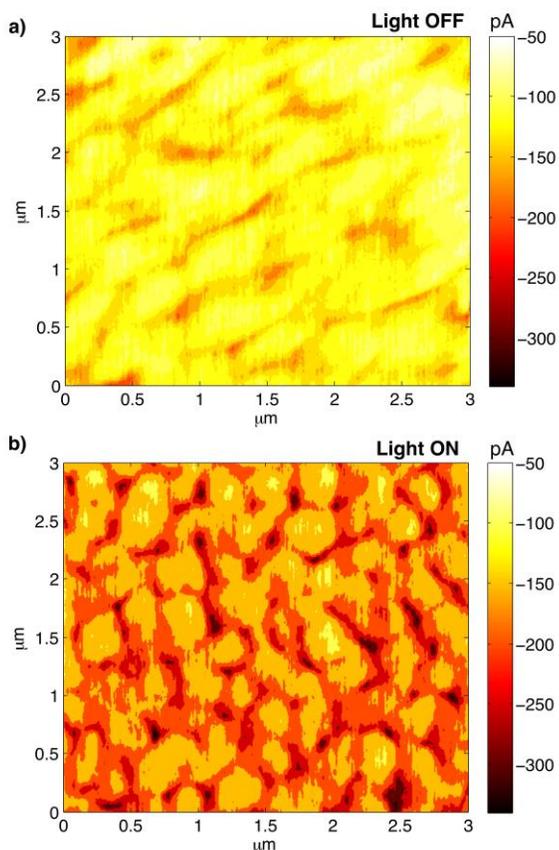


Figure 3: Morphological characterization obtained by a scan performed on P3HT-54wt% PCBM sample at a bias of -1.5V applied to the ITO substrate. (a) Under dark; (b) under UV light. Areas rich in P3HT (dark red/black) can be observed surrounding PCBM rich round grains (light orange/yellow).

% of PCBM	Mott-Gurney μ [10^{-3} cm ² /Vs]	Hartke μ [10^{-5} cm ² /Vs]
0	2.8±0.4	3.4±0.5
44	0.8±0.2	0.9±0.2
50	1.3±0.5	1.3±0.4
54	0.9±0.3	1.0±0.4

Table 1: Mobility values obtained by Mott-Gurney and Hartke's equations. A difference of two orders of magnitude between them can be observed. The mobility values obtained with Hartke's equation are in good agreement with macroscopic measurements.

The photocurrent values obtained from the I-V curves at 0V (Fig. 2) can only be used in a relative context, i.e., to compare one sample with respect to another, since contact effects do not allow for quantitative comparisons between results provided by CAFM tests and device measurements [10].

In Fig. 3, an example of morphological characterization using CAFM is shown. Scans were performed on the P3HT-54wt% PCBM sample at a bias of -1.5V applied to the ITO under dark (Fig. 3a) and under light (Fig. 3b) conditions. The later allows for differentiation between highly conductive areas, attributed to high concentration of ordered P3HT, surrounding less conductive round grains attributed to areas with high concentration of PCBM. This result demonstrates the robustness of the technique for nanoscale characterization of features of the same size or bigger than the tip radius of the CAFM probe.

4 CONCLUSIONS

In summary, the potential of CAFM to characterize organic bulk heterojunction blends has been depicted. Qualitative values of charge carrier mobility and photo-generated current were reported and allowed for the determination of the best concentration ratio, 50wt% PCBM, when it comes to maximize these two parameters. Finally, morphological characterization of the active layer blend was performed by scanning the sample while applying a bias. Areas with different electrical properties were identified.

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