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Performance Improvements in Polymer Nanofiber: Fullerene Solar Cells with External Electric Field Treatment

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ABSTRACT: Organic solar cell (OSC) devices based on predominantly poly(3-hexylthiophene-2,5-diyl) (P3HT) nanofibers (NFs) exhibit inferior device performance compared to their conventional nano-domain P3HT:PCBM systems – credited to the low interfibrillar mobility between the NFs [Kurniawan, M.; et. al. *J. Phys. Chem. C* **2012**, 116, 18015]. To improve the charge transport of these devices, external electric field (E-field) treatment of the active layer is performed in a bid to align the random polymer chains between the NFs perpendicular to the electrode. Extensive device testing revealed a 22.7% improvement in power conversion efficiency and higher mobilities (37.5% improvement) for the E-field treated devices compared to the control. Transient absorption spectroscopy shows an improved initial generation of carriers and formation of polarons in the E-field treated samples over the control samples in the fs-ns timescale. However, in the absence of any sweep-out voltage in the E-field treated films, a higher recombination rate in the ns- μ s timescale is observed. Concomitant with the improved device efficiencies and higher mobilities measured in the E-field treated devices and the higher recombination rate over the ns- μ s timescale in the E-field treated films, we interpret that the E-field treatment improved charge mobility and transport of P3HT-NF:PCBM through improved orientation of the polymer chains in the amorphous P3HT phase co-existing with the NFs.

KEYWORDS: electric field, thiophene polymer, nanofibers, morphology, transient optical spectroscopy, and charge dynamics

1 Introduction

Organic solar cells hold great promise for commercialization due to their easy processing of large area thin film solar cells at low temperatures, high flexibility, lower cost production and material availability¹⁻⁴. Systems based on poly(3-hexylthiophene-2,5-diyl) (P3HT) as electron donor and methano-fullerene derivatives as electron acceptors are the most widely studied⁵⁻⁹ with efficiencies approaching 5%. Although the P3HT system is fast losing its popularity in view of the development of newer conjugated polymers with better device performances¹⁰, it remains highly preferred for basic photophysical studies because it is a very well-studied system. The high degree of molecular ordering and phase separation in donor and acceptor domains in the P3HT:PCBM system is key to its high efficiency¹¹. For the optimal solar cell device performance, the domain size of the donor polymer needs to be comparable of the exciton diffusion length to maximize the diffusion and dissociation of the excitons in conjugated polymers¹². Various methods are employed to modulate the P3HT:PCBM phase distribution in the solar cells. These methods include solvent annealing^{13,14}, ordered templates¹⁵⁻¹⁷, self-assembly with marginal solvents¹⁸, etc. In addition, numerous techniques have also been used to study the organization of the polymers and their effects on the solar cell performance¹⁹.

It was recently reported that fibrillar networks coexists with the random phase in blends of P3HT:PCBM²⁰⁻²³. With enhanced absorbance and crystallinity, these interconnected P3HT nanofiber (P3HT-NF) networks that are aligned parallel to the surface of the electrode, could perform as effective light collecting antennas in OSCs²⁴⁻²⁶. In addition, their high planar charge carrier mobility and low-temperature post fabrication processing amenable with plastic substrates are also attractive for device applications²⁰. Despite the vast potential of P3HT-NFs, devices fabricated with mainly P3HT-NFs show lower power conversion efficiencies (PCEs) than conventional nanoscale phase separated structure^{14,18}. This is

attributed to the higher rate of bimolecular recombination in NFs arising from the poor interfibrillar charge transport between the NFs²⁷. Nonetheless, the P3HT-NF fiber system is still relevant for applications with flexible polymer substrates where low temperature processing is essential. Therefore, to realize the full potential of the P3HT-NF fiber system, it is imperative that strategies be formulated to overcome the limitation of poor interfibrillar charge transport.

The P3HT-NF system contains both fibrillar and amorphous phases (randomly distributed polymer chains)²⁶. P3HT is a polar molecule possessing a dipole moment of $\sim 1.0\text{--}1.6\text{D}$ ²⁸ (arising from the negatively charged sulfur atom in the heterocyclic ring). An obvious approach would be to attempt to align the NFs perpendicular to the electrodes in order to leverage on the high intrafibrillar charge mobility. However, overcoming the stiction arising from the capillary forces due to the surface tension of the solvent between the nanofibers and the substrate is non-trivial. On the other hand, alignment of the P3HT molecules in the amorphous phase through “dipole polarization” could possibly improve the orientation of the polymer chains between the NFs to facilitate the inter-fibrillar charge transport. Presently, the exact role and impact of the amorphous phase on the device performance and its interaction with the PCBM molecules are still unclear; although one could envisage this phase as analogous to the “glue” between the NFs. We hypothesize that external electric (E) field treatment during the solvent-drying step will help orientate the P3HT chains functioning as the “bridge” or “glue” between P3HT nanofibers (NFs) for the charge transport; thereby improving the device performance of P3HT-NF:PCBM OSCs. Investigating the electrical properties/device performance of functional devices and correlating them with the charge carrier dynamics of E-field treated P3HT-NF:PCBM thin films are the main objectives of this work.

Herein, we demonstrate the viability of external E-field treatment of P3HT-NF to improve the performance of P3HT-NF:PCBM OSCs. This study is performed in a comparative study involving thin film samples and devices subjected to external E-field treatment and those without E-field treatment. In the former, solvent drying is carried out at room temperature in the presence of a 1.4 kV/cm electric field; while for the latter, solvent drying takes place at room temperature only. Detailed electrical characterization with 100 devices over different batches revealed an improvement of ~22.7% in power conversion efficiency and higher mobilities for these E-field treated devices. Transient absorption spectroscopy (TAS) reveals an improved initial charge generation and polaron formation in the E-field treated samples over the control samples in the fs-ns timescale. In the absence of any sweep-out voltage and the higher mobilities in the E-field treated films, a higher recombination rate in the ns- μ s timescale is thus observed. These findings are consistent with the interpretation of improved charge mobility and transport following the E-field treatment of the P3HT-NF:PCBM. We attribute this to the improved orientation of the polymer chains in the amorphous phase of P3HT, co-existing with the NFs. Importantly, this approach is compatible with the thermal free post fabrication processing required of the flexible plastic substrates.

2 Experimental Methods

2.1 Materials and procedures

The P3HT nanofibers were prepared based on a previously published procedure¹⁸. Briefly, regioregular-P3HT was dissolved in p-xylene (8mg/ml) and heated to 80 °C. Following complete polymer dissolution, the solution was slowly cooled back to room temperature (-10 °C/h) and allowed to settle in the dark for 20 hours to form P3HT-NFs.

2.2 Device Fabrication and Characterization

Organic solar cell (OSC) devices were fabricated on clean indium-tin oxide (ITO) coated substrates. To change the ITO surface from hydrophobic to hydrophilic and to increase the work function, plasma cleaning was performed on these substrates. A thin layer of Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) (CLEVIOSTM P VP Al 4083, HC Starck) was spin-coated onto the clean substrates followed by baking in a N₂ filled glove box at 140 °C for 10 min. Subsequently, the previously prepared suspension in p-xylene was mixed with PCBM with a weight ratio of 1:0.8 and further stirred for 2h. The nanofibers blend solution was then spin-coated onto the PEDOT:PSS layer to yield film thicknesses of 100 ± 5 nm. For one group of devices, an electric field was applied across the coated blend films as they were drying at room temperature for 30 min, *i.e.*, the “electric-field dried” devices. A static electric field of $1.4 \text{ kV}\cdot\text{cm}^{-1}$ was applied using a metallic plate (aluminium) kept just above the active layer while ITO was used as the counter electrode. This field was selected on the basis of preceding reports¹³. The static field was achieved by applying 600 V between the metallic plate and ITO at a fixed distance of 4.3 mm. Solvent drying for the second set of devices (without electric field) or control devices was carried out at room temperature for 30 min. To make the cathode contact, a 100 nm thick aluminium was thermally deposited through a shadow mask (with 0.07 cm^2 device area) on the active layer in a vacuum of 10^{-6} Torr.

A Keithley SMU 2400 was employed to measure the current density–voltage (J – V) characteristics of the OSC devices at an intensity of $100 \text{ mW}/\text{cm}^2$ under simulated AM 1.5G illumination. Incident photon to current efficiency (IPCE) measurements was done using a Merlin radiometer (Newport) and incident photon was counted by reference device of calibrated silicon photodiode. Shimadzu UV-2510PC spectrophotometer was used to record the absorption spectra of blend films.

2.3 Transient Optical Characterization. To probe the carrier dynamics, transient absorption spectroscopy (TAS) measurements covering the timescales from femtoseconds to microseconds were performed using setups described previously²⁷ – see supporting information for the details.

3. Results and Discussions

3.1.1 Linear Absorption

Linear absorption spectra were measured for the thin films of similar thickness coated on glass substrate (Fig. 1). Regardless of E-field treatment, the vibronic peaks are observed in both films, attributed to the crystallinity and ordering in the polymer system. The vibronic peaks in order of decreasing energy correspond to the 0–2, 0–1, and 0–0 absorption transitions of P3HT, respectively. The relationship between the existence of these vibronic peaks and the degree of the crystallinity of the conjugate polymer is well explained by Spano *et al.*^{29,30}. As shown in Fig. 1, the E-field dried film exhibits a slightly stronger absorbance. This higher absorption results from the increased molecular orientation induced by external E-field evident from x-ray diffraction (Fig. S1). Hence, increased exciton formation is expected due to the enhanced absorption of this film.

3.1.2 Absorption Efficiency Calculation: Beer-Lambert’s law was used to evaluate the absorption coefficients (α) of the thin films. Absorption efficiency (η_A) is determined using the following relation³¹ :

$$\eta_A = \frac{\int (1 - 10^{-\alpha d}) S(\lambda) d\lambda}{\int S(\lambda) d\lambda} \quad (1)$$

where d is the film thickness and $S(\lambda)$ represents the number of photons available at a specific wavelength in the AM1.5G solar spectra – integrated over 300-800 nm wavelength. The untreated and E-field treated P3HT-NF:PCBM films absorb 37.9%, and 39.8% of the

solar spectrum respectively. Thus, the presence of E-field during the solvent drying processes of the active layer at the room temperature marginally enhances the photon absorption and exciton generation in the active layer.

3.2 Device Performance

3.2.1 Dark Characteristics: Current density–voltage (J – V) measurements in the dark were carried out for in the E-field treated and control samples. Significant improvement in the dark linear J – V characteristics (Fig. 2) is observed in E-field treated device as compared to the control. Figure 2 inset shows a comparison of the semi-log J – V characteristics of the respective devices. A higher forward current (~ 2 times larger) at +0.5 V is observed in the E-field treated devices as compared to the control devices. This increase in dark current density is attributed to the improved charge-carrier mobility in the former. The built-in potentials are found to be similar for both devices (*i.e.*, ~ 0.7 V).

Figure 3 shows the log-log plot of the current density-voltage (J - V) characteristics of the P3HT-NF:PCBM devices measured in dark. The charge-carrier mobilities are determined from a linear fit of the data. Both the E-field treated and control devices exhibit an injection region (below 0.4 V) before switching to the trap-filling region at higher J - V values. In the E-field treated devices, the traps are filled faster than the control devices. Beyond 2.5 V, the device is operating in the space-charge-limited current (SCLC) region. The charge-carrier mobility in the trap-free SCLC regime can be calculated using Child's law. Assuming a relative permittivity $\varepsilon = 3$ (typical for polymeric materials)³², the mobility is calculated to be 6.6×10^{-5} ($\text{cm}^2\text{-V}^{-1}\text{s}^{-1}$) and 4.8×10^{-5} ($\text{cm}^2\text{-V}^{-1}\text{s}^{-1}$) for the E-field treated and control devices, respectively. The higher charge carrier mobility (37.5% improvement) in the former strongly supports our hypothesis on the effect of E-field treatment.

3.2.2 IPCE Measurements: Figure 4 shows the incident-photon-to-collected-electron efficiency (IPCE) plots for the E-field treated and control samples. The IPCE at a specific wavelength is calculated using the following equation:

$$\text{IPCE } (\lambda) [\%] = 1240(J_{sc} / I_p) \quad (2)$$

where the short-circuit current density J_{sc} (mA/cm^2) is measured at wavelength λ (nm), and I_p (W/m^2) is the incident light intensity to the corresponding wavelength. IPCE improved over the wavelength range 370-650 nm for the E-field treated devices. The IPCE of the control device shows a extreme of 54.8% at a wavelength of 470 nm. Comparatively, the E-field treated device showed a maximum of 55.5% at a wavelength 520 nm. Improvement of the IPCE is more pronounced at 610 nm than 560 nm in E-field treated devices. This is directly correlated to the higher absorption at 610 nm in Fig. 1. This enhancement in the IPCE indicates that more charges are being collected in the E-field treated samples.

3.2.3 Illuminated Characteristics: Figure 5 shows the representative J - V characteristics of the solar cells under $100 \text{ mW}/\text{cm}^2$ intensity illumination of the AM1.5G spectrum. The relevant parameters (*i.e.*, overall power conversion efficiency (PCE), short-circuit current density (J_{sc}), open-circuit voltage (V_{oc}), fill factors (FF), series resistance (R_s) and shunt resistance (R_{sh}) were determined from the plots and given in Table 1. It is clear that V_{oc} and FF are comparable in the E-field treated and control devices. However, there are improvements of $\sim 17\%$ in J_{sc} and $\sim 22.7\%$ in PCE for the E-field treated devices. These are validated with extensive testing of devices fabricated in 5 independent batches with 20 devices per batch. The higher J_{sc} in the E-field treated devices is consistent with the enhanced formation and separation of photogenerated species at the D/A interfaces and the better mobility of charge carrier in these devices. The better PCE value in the E-field treated devices is therefore endorsed to the improved photon absorbance and better ordering in the

P3HT-NF:PCBM blend, which lead to the higher charge generation and more efficient transport to the electrodes.

3.2.4 Charge Generation: To clarify whether the organization of the P3HT-NF system due to the electric field improves the carrier generation, the photocurrent must be analyzed. From the slope which is flat at short circuit in the J - V characteristics at 1 sun intensity (Fig. 5), it is clear that nearly all the photo-generated carriers are being extracted out of the devices. According to the model developed for insulators by Goodman and Rose³³, the photocurrent saturates to its limit J_{sat} at large enough reverse bias, determined by the generation rate G , is given by the equation:

$$J_{sat} = qGd \quad (4)$$

where d is the device film thickness. This model could also be applied to organic BHJ solar cells. Through comparing the J_{sat} values for both the E-field treated and control devices, we can investigate if more photo-generation occurs as a consequence of the ordering. The photocurrent of the devices is plotted in log scale against $(V_0 - V)$ in Fig. 6, where V_0 is the compensation voltage (*i.e.*, defined as the voltage where the light current equals the dark current or where the photocurrent in the device is zero³⁴). Thus, $(V_0 - V)$ represents the effective voltage available for the generation of photocurrent. The V_0 values for the E-field treated and control devices are 0.72 V and 0.67 V, respectively.

From Fig. 6, it can be observed that at low effective voltages (*i.e.*, around V_{oc} where the available drift field is small), the E-field treated devices show higher photocurrent. As the voltage is increased (*i.e.*, under large reverse bias), the photocurrents for both devices saturate at different values. This means that the total photo-generated carrier density is higher in the E-field treated devices. Hence, the excess charge generation by efficient exciton dissociation is also another reason for J_{sc} improvement³². To further validate these findings from the

electrical characterization, we performed transient absorption spectroscopy to examine the charge generation and recombination dynamics.

3.3. Charge Carrier Dynamics in the Femto–microsecond Temporal Regime

3.2.1 Charge carrier dynamics in fs-ns temporal regime: To investigate the charge generation and recombination dynamics, transient absorption measurements were performed on control and E-field treated P3HT-NF:PCBM films (of thickness 100 ± 5 nm). The representative differential transmission ($\Delta T/T$) spectra of the E-field treated sample spanning 520 nm to 750 nm at different delay times following photoexcitation is shown in Figure 7. The vibronic peaks corresponding to 0-0 (at 610 nm), 0-1 (at 560 nm) absorption transitions are apparent as ground state bleaching (GSB) peaks³¹. The photobleaching (PB) signal (*i.e.*, $\Delta T/T > 0$ or relative DT > 0) is directly related to the population of the photoexcited species *i.e.* excitons and polarons in the photoexcited films³⁵, and this signal represents filled states by photogenerated species. The negative differential signal at ~700 nm is the consequence of photogenerated delocalized polarons pairs in the photoexcited film and refers to the photo-induced absorption (PIA) in P3HT. The magnitude and evolution of the DT signals from the GSB bands yields information on the relative populations of the residual excited species and their average lifetimes after excitation by a short pulse laser.

The GSB spectral profiles of both the E-field treated P3HT-NF:PCBM films (Fig. 7) and the untreated control (Fig. S2a) are very similar. At early times, the magnitude of the DT signal for the 0–0 (Fig. 3) and 0–1 bands are more pronounced in the latter E-field treated films than the control films. (see Fig. S2b in supporting information for 0-1 GSB peak). For the 0–0 transition, this is ~20% larger at the 1 ps onset. This increased PB signal from 1 ps to 1.5 ns stems from the higher absorption in the E-field treated samples – resulting in a larger population of photogenerated excitons and polarons. This is consistent with the improved

ordering of polymer chains in the nanodomains of P3HT.^{14,36} Furthermore, the invariance of the decay profiles of the E-field treated and the control samples over the first 1.5 ns indicate that the GSB decay dynamics are not affected by the E-field treatment (see Fig. S2b in supporting information). The 0-0 and 0-1 GSB peaks in both cases decay rapidly in first 100 ps and then settle in a long-lived transient that extends beyond the time window of our fs-TAS setup (Fig. 8). This rapid GSB decay within first 100 ps is attributed to either: (i) annihilation of excitons with the charges or differences in the absorption cross-sections of the P3HT exciton and the polaron.³¹ However, the DT signals of the 0-0 and 0-1 GSB peaks in the E-field treated sample are about 44% and 50% larger respectively than the control from over the 1 ps – 1.5 ns timescale, which indicates an increased population of photoexcited excitons and long-lived polarons.

Generally in solar cells, losses occur through geminate or nongeminate recombination. The former, a monomolecular type recombination that dominates at ~100 ps to few ns timescales, occurs when electron and holes generated from the dissociation of the same exciton recombine near the donor-acceptor (D/A) interface. The latter is a bimolecular type recombination process between spatially separated electrons and holes away from the D/A interfaces. Usually in all organic systems, charge carrier traps are present and the charges undergo the recombination when these charge carriers are trapped. One possible source of these traps is the trace metal impurities from residual trace catalysts in the conjugated polymer³⁷. Such trapping process is known as the Shockley-Read-Hall trap-assisted recombination^{38,39}. To probe the charge carrier dynamics over longer time scales, nanosecond laser flash photolysis spectroscopy was also performed.

3.2.2 Charge carrier dynamics in the ns- μ s temporal regime. Figure 9 shows the ns-TAS measurements of the E-field treated P3HT-NF:PCBM film at the GSB peak of 610 nm (0-1

GSB) following pump excitation at a fluence of $\sim 60 \mu\text{J}/\text{cm}^2$. The DT signals of both peaks (0-1 and 0-0 GSB – see Fig. S3) are consistently larger than those of the untreated control samples. Both these 0-0 and 0-1 GSB peaks in the E-field treated sample exhibit a faster decay than the control after the first 300 ns which is then followed by long-lived tail. This rapid decay in DT can be attributed to the higher rate of nongeminate recombination present in the E-field treated sample compared to the control samples. The nongeminate recombination rate is directly proportional to the population density of the charges (Langevin process)⁴⁰. Possible causes include: (i) the higher concentration of photogenerated carriers stemming from the enhanced absorption that leads to the higher rate of the recombination in the absence of any sweep-out voltage^{41,42}. and (ii) the presence of increased charge trapping in the bare film – resulting in the more pronounced concentration of charges⁴³.

3.2.3 Modelling the Recombination Dynamics. To gain further physical insights into the dynamical processes in these polymer blends, an analytical model was also employed to examine the charge dynamics from the ns-TAS. To account for the possibility of increased charge trapping in these NF films and that the long-lived species (with typical lifetime $>5 \mu\text{s}$) maybe from the long lived trap states, a modified model⁴⁴ was employed instead (See supporting information for the details):

$$\frac{N}{N_0} = ((1-f)^{-\alpha} + kt)^{-1/\alpha} + f \quad (2)$$

where f corresponds to the contribution from long-lived species, k is the average recombination rate and $(\alpha+1)$ is the average recombination order related to the type of recombination and concentration dependence of carrier mobilities. The recombination rate k may come from the Langevin process and/or trap-assisted recombination. The purely kinetic

Langevin model assumes that an electron and a hole will recombine upon approach to their collective capture radius.

Using this model, the decay transients of the 0-1 GSB peak for control and E-field treated films are fitted (Fig. 9) and the fitting parameters are given in Table 2. With E-field treatment, the recombination order increases from 1.1 to 1.4, indicating that the recombination has more contributions from the Langevin process. Besides, a decrease of the ratio for the long-lived component (*i.e.*, f from 0.45 to 0.26) is also observed for the E-field treated film, which we ascribe to a decrease in the deep trap density. This increased recombination rate is also observed for 0-0 GSB peak (see Fig. S3). Superficially, the higher bimolecular recombination observed in these E-field treated films is counter-intuitive and appears contradictory to the improved efficiency in the E-field treated devices. However, one has to note the absence of any sweep-out voltage in the bare films, it is therefore reasonable that the higher mobility of the charge carriers following E-field treatment resulted in more opportunities for free charges to encounter one another and undergo recombination or be trapped in the absence of any sweep-out voltage in the bare films. Hence, concomitant with the earlier findings of improved efficiency and higher mobilities measured in the E-field treated devices and these findings of higher bimolecular recombination in the E-field treated films, we attribute that the E-field treatment improved the inter-fibrillar charge transport via the better orientation of the P3HT molecules in the amorphous phase.

4 Conclusions

In summary, E-field treatment is a viable approach to improve the device performance of P3HT-NF:PCBM OSCs where low temperature processing is essential. Based on the findings from TAS and electrical device characterizations, the performance enhancement in the E-field treated devices can be attributed to: (a) higher photoabsorption; (b) higher value of

the mobility resulting from better oriented polymer chains in the region between the polymer nanofibers; and (c) the oriented chains would facilitate inter-fibrillar charge transport and extraction. These findings are consistent with the hypothesis that the external E-field treatment during the solvent-drying step help orientate the P3HT chains functioning as the “bridge” or “glue” between P3HT nanofibers (NFs) for the charge transport; thereby improving the device performance of P3HT-NF:PCBM OSCs

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Supporting Information Available

The experimental details of the transient spectroscopy setups and charge dynamics measurements, transient absorption spectra of P3HT-NF:PCBM film without E-field treatment (control films) and decay dynamics of GSB peaks from fs- μ s are described in supporting information. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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Tables

Table 1: Summary of the performance of a typical batch of devices under illumination.

Electric Field (kV/cm)	PCE (%)	J_{sc} (mA/cm ²)	V_{oc} (V)	FF
0	1.76 ± 0.06	7.2 ± 0.1	0.54 ± 0.01	0.45 ± 0.02
1.4	2.16 ± 0.04	8.3 ± 0.2	0.56 ± 0.01	0.46 ± 0.01

Table 2: Fitting parameters for the ns-TAS data.

Device	k (ns ⁻¹)	$\alpha + 1$	f
0-1 GSB w/o EF	$(2.5 \pm 0.2) \times 10^{-3}$	1.1 ± 0.1	0.45 ± 0.01
0-1 GSB w EF	$(4.4 \pm 0.3) \times 10^{-3}$	1.4 ± 0.1	0.26 ± 0.01

TOC Image