



The origin of performance limitations in miniemulsion nanoparticulate organic photovoltaic devices



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ABSTRACT

Nanoparticulate organic films are an attractive area of organic photovoltaic (OPV) research given their potential for controlling active layer morphology on the nanoscale. However, the power conversion efficiency of these devices remains limited in comparison to the analogous bulk heterojunction technology. Here, we report a systematic characterisation of charge carrier loss pathways in nanoparticulate OPVs prepared using poly(3-hexylthiophene) as a donor and phenyl-C₆₁-butyric acid methyl ester as an acceptor material. Optical modelling of the nanoparticle active layer morphology indicates minimal losses from scattering and negligible plasmon effects from the discrete 40 nm particles. A comparison of the modelled internal absorption for the nanoparticle films confirms negligible differences in comparison to a standard bulk heterojunction active layer structure. By contrast, the internal quantum efficiency (IQE), determined with the aid of optically modelled internal active layer and parasitic non-active layer absorption, exhibited values of 24% for the nanoparticle device whilst the bulk heterojunction showed a value of 76%. Subsequent modelling of the EQE and IQE (supported by photoluminescence quenching measurements) indicated an exciton dissociation yield of 24% for nanoparticulate devices in comparison to 81% for the corresponding bulk heterojunction, in excellent agreement with the device internal quantum efficiencies. Transient measurements of charge transport and bimolecular recombination lifetime revealed a charge carrier drift length longer than the film thickness at short circuit conditions for both device structures. Impedance spectroscopy measurements confirmed very low photoinduced chemical capacitances at short circuit and returned charge collection efficiencies in excess of 80% for both devices, suggesting only minor charge collection losses in either device at short circuit. Collectively, these results demonstrate that the dominant photocurrent loss mechanism in nanoparticulate OPVs is a poor charge generation yield rather than reduced light absorption, increased bimolecular recombination or charge extraction barriers.

1. Introduction

Organic photovoltaic cells (OPVs) are promising technology for delivering low cost electricity with acceptable efficiencies, whilst also offering the possibility of fabrication on flexible substrates, thus facilitating their use in new applications [1]. The major advantage of this technology is the ability to coat the active layers from a solution using inexpensive and high throughput printing techniques onto large flexible substrates, thus reducing the manufacturing costs substantially in comparison to other photovoltaic technologies [2]. Whilst there is substantial knowledge in the OPV community regarding the optimal physics of photoactive layer materials on the small scale [3,4], to realize their full potential, printable photoactive inks that can seamlessly

scale their efficiency from the laboratory to the larger fabrication regime remain an area that requires substantial investigation [5,6]. Towards this purpose, a sophisticated understanding of the binary phase morphology and a precise level of control over the nanostructure during fabrication is required. Nanoparticulate based devices offer an exciting route towards finely controlling the morphology by preforming the desired phase structure on the nanoscale in the particles prior to device fabrication.

Variation of active layer structure and morphology is a major factor influencing the improvement of OPV device performance. The active layer morphology consists of a network of both mixed and phase segregated regions of donor and acceptor materials [7]. The nanoscale morphology of this network has an important effect on increasing

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power conversion efficiency (PCE) of OPVs because it controls both the charge carrier generation and subsequent charge transport in the respective phases of the active layer. The popular bulk heterojunction structure minimizes the distance to a donor-acceptor interface where free charges are created from tightly bound excitons by blending the two components intimately on the nanoscale. Modifying the active layer morphology in this manner maximizes charge separation by reducing the distance an exciton must travel to reach an interface to a value below its diffusion length [8]. Alternatively, creating the active layer from preformed discrete nanoparticles (NPs) of blended donor and acceptor materials is another approach that has shown recent promise in producing efficient OPV devices [9]. The nanoparticle approach allows the organic materials to be transferred to a wider range of nontoxic solvents such as water that possess substantial benefits for cleaner and safer fabrication [10]. Furthermore, the nanoparticle morphology can also be controlled by altering their size and the internal composition to influence device performance [11]. This level of control allows the creation of an optimum active layer morphology to be decoupled from the device fabrication process; preventing the need for further post-treatments to correct the morphology [12]. This approach is receiving increasingly interest, with a range of different polymer and acceptor materials utilized to prepare nanoparticulate OPV devices with efficiencies ranging from 2% to 4% [13–17]. Critical to these efforts to improve the power conversion efficiency in nanoparticulate devices is a sophisticated understanding of the unique photophysics that dominate the conversion of sunlight into electrical energy.

Whilst the device performance of various NP-OPV fabrication procedures have been previously studied [9,12,17], the specific photophysics has only been lightly examined. This previous work confirms that the internal morphology heavily influences the device performance and is unique to the nanoparticle fabrication method, however, the specific loss mechanisms and how they may vary between fabrication routes remains an area that requires further study. In particular, the potential additional optical effects of nanoscale particles has often been overlooked. Such behaviour in organic photovoltaics has previously been studied using optical modelling techniques [18,19], which provides the opportunity to understand the design, optimum thickness of the active layer and how the various device interfaces influence the incident light [9,10]. In addition, previous work has always implied that charge collection is the dominant loss pathway in NP-OPV devices due to assumed compromised transport pathways from an increased number of traps in the core-shell nanoparticle morphology [12,20]. However, this assumption has never been directly probed, and specific measurements delineating charge generation from charge transport and collection efficiencies will allow an improved understanding of the operating physics, and allow targeted design optimisation strategies to be developed.

In this paper, we have combined optical modelling, fluorescence analysis, mobility and lifetime measurements and impedance spectroscopy to explain the shortfall in the performance of NP-OPVs prepared from the mixed emulsion technique in comparison to standard BHJ OPV devices. The internal absorbance in the photoactive layer for each device structure was calculated and found to be almost identical, indicating no detectable scattering losses and a similar overall donor-acceptor ratio in the active layer films. The internal quantum yield of devices was determined by scaling the external quantum efficiency by the measured diffuse and specular reflection and found to be significantly reduced in the NP-OPVs. Subsequent analysis of charge generation, transport and recombination pathways confirmed that a poor exciton generation yield is the dominant source of poor performance in the NP-OPVs, with the subsequent collection yields of both devices showing values above 85%. This work informs the fabrication process for mixed emulsion nanoparticles by identifying the dominant loss mechanism and providing avenues for future optimisation.

2. Experimental

2.1. Optical Model Description

The transfer matrix method (TMM) has been applied to monitor the electromagnetic wave inside each layer of the multilayer OPV device at any point [21]. The (TMM) approach assumes that the incident light (electromagnetic waves) propagates in one dimension through the device, with all layers considered to be homogeneous, isotropic, and have parallel and flat interfaces [22]. The incident light enters from an infinite medium (air), with each subsequent layer described by its complex reflective index, $\eta = n + ik$, where the real part, n , is the refractive index and the complex part, k , is the extinction coefficient of the material. From this index the reflectance and transmittance of the incident light at each successive interface layer can be computed. Due to interface reflections in this system, two electric waves will exist, one propagated in the forward direction, $E_m^+(x)$, and another, $E_m^-(x)$, propagated in the backwards direction which can interact. An interface matrix is then used to describe the complete propagation of incident light across an interface [18]. The electric field can be described using a system matrix which contains the layers and interface effects as below:

$$\begin{bmatrix} E_m^+ \\ E_m^- \end{bmatrix} = I_{12}L_1 \cdot I_{23}L_2 \cdots I_{m,m+1}L_m \begin{bmatrix} E_{m+1}^+ \\ E_{m+1}^- \end{bmatrix} \quad (1)$$

where $I_{a,b}$, is a matrix involving reflection and transmission Fresnel coefficients and accounts for interface effects between layers a and b [23]. L_m is a coherent layer matrix, which describes the change due to absorption and phase shift for incident light and is defined for each layer as below [20]:

$$L_m = \begin{bmatrix} e^{-i\delta_{1m}} & 0 \\ 0 & e^{i\delta_{1m}} \end{bmatrix} \quad (2)$$

Where d_{1m} is the layer thickness. The phase change of the electric field wave, δ , can be expressed as the following $\delta = \left(\frac{2\pi}{\lambda}\right)\eta_1 \cos\theta$, inside the layer, where θ denotes the angle of incidence. Once the electric field propagating in the device layers is known, the absorbance spectrum can be calculated from the negative derivative of the Poynting vector for one dimension [24].

$$Q(x) = \frac{1}{2}\omega\epsilon_0\epsilon_2|E(x)|^2 \quad (3)$$

where ϵ_0 and ϵ_2 are the vacuum permittivity and imaginary part of dielectric function respectively. Scout 2 software package, (M. Theiss, Aachen Germany), [25] has been used to simulate the dielectric function of all the materials that were used in this study. In addition, the internal absorption of the OPV devices was calculated using a combination of the Scout software and a custom code constructed in Matlab which adds some additional algorithms to greatly reduce the computing time required to determine the internal absorption output for individual layers.

2.2. Materials

Poly(3-hexylthiophene) (P3HT) was synthesised in-house at the University of Newcastle as previously reported [26]. The polymer properties produced under these synthesis conditions were an M_n of 22.7 kg mol⁻¹, M_w of 32.6 kg mol⁻¹ and a PDI of 1.44. PCBM was purchased from Solenne BV, Netherlands. For nanoparticle OPV devices, anhydrous chloroform and sodium dodecyl sulphate surfactant (SDS) were supplied from Sigma Aldrich.

2.3. Device fabrication

All OPV devices prepared in this study were fabricated in normal geometry. ITO-coated glass electrodes were cleaned by successive sonication in milli-Q water and isopropanol then dried under a

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