Probing the Origin of Photocurrent in Nanoparticulate Organic Photovoltaics

Natalie P. Holmes^{a}, Nicolas Nicolaidis^a, Krishna Feron^{a,b}, Matthew Barr^a, Kerry B. Burke^a,
Mohammed Al-Mudhaffer^a, Prakash Sista^c, A.L.David Kilcoyne^d, Mihaela C. Stefan^c,
Xiaojing Zhou^a, Paul C. Dastoor^a, Warwick J. Belcher^a*

^a Centre for Organic Electronics, University of Newcastle, University Drive, Callaghan NSW
2308, Australia

^b CSIRO Energy Technology, Newcastle, NSW 2300, Australia

^c Department of Chemistry, University of Texas at Dallas, 800W Campbell Road BE26,
Richardson, TX 75080, USA

^d Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, CA 94720,
USA

CORRESPONDING AUTHOR:

*Natalie P. Holmes, Natalie.Holmes@uon.edu.au, +61 4 1926 6393

KEYWORDS: Morphology, nanoparticle, organic photovoltaic, photocurrent contribution,
scanning transmission X-ray microscopy

ABSTRACT

Varying the donor-acceptor ratio is a common technique in optimising organic photovoltaic (OPV) device performance. Here we fabricate poly(3-hexylthiophene) (P3HT): phenyl C₆₁ butyric acid methyl ester (PCBM) nanoparticle OPVs with varied donor-acceptor ratios from 1:0.5 to 1:2. Device performance increases with PCBM loading from 1:0.5 to 1:1, then surprisingly from 1:1 to 1:2 the performance plateaus, unlike reported trends in bulk heterojunction (BHJ) OPVs where device performance drops significantly as the donor:acceptor ratio increases beyond 1:1. Scanning transmission X-ray microscopy (STXM) measurements reveal core-shell nanoparticles for all donor:acceptor ratios with a systematic increase in the PCBM nanoparticle core volume observed as the PCBM loading is increased. This increases the functional PCBM domain size available for exciton harvesting, contrary to the result observed in BHJ OPV devices where increasing the PCBM loading does not lead to an increase in functional PCBM domains. In addition, STXM measurements reveal that the core-shell nanoparticles have core and shell compositions that change with PCBM loading. In particular, we observe that the PCBM component in the nanoparticle shell phase increases from a concentration that is below the percolation limit to one that is close to the optimal weight fraction for charge transport. This increase in the functional PCBM volume is reflected in an increase in PCBM photocurrent calculated from external quantum efficiency (EQE) measurements.

1. INTRODUCTION

The holy grail of OPV device fabrication is the control of domain morphology to ensure complete exciton separation and efficient charge transport and hence optimum device performance [1-5]. Indeed, different optimal morphologies have been proposed but never

successfully implemented due to the complexity of structuring active layers on the nanoscale [5]. As a result the bulk heterojunction structure is now considered as optimal and this architecture by far dominates OPV device studies [6]. Consequently, a judicious choice of additives, solvents and/or fabrication conditions is typically required to engineer indirectly the BHJ active layer morphology [7-11].

Varying the donor-acceptor ratio within the active layer is one of the many methods used to optimise BHJ OPV performance [5,9,11-13]. The optimal ratio of P3HT to PCBM in BHJ devices is generally reported to be between 1:1 and 1:0.8 [11], beyond this ratio in either direction performance rapidly drops [13,23,32]. This drop is due to both P3HT being the major contributor to photocurrent and a deterioration in bulk film morphology [13]. Three morphological quantities have been identified as being critically related to the solar cell efficiency of P3HT:PCBM blends: (i) the donor/acceptor domain size, which must be compatible with the exciton diffusion length, (ii) the specific interfacial area, which influences the exciton dissociation rate, and (iii) the percolation pathways, which influence charge carrier transport to the electrodes [12]. Indeed, the prevalence of the BHJ architecture in the literature is driven by the fact that they appear to address all three of these requirements.

In general, P3HT:PCBM OPV devices are fabricated and optimised from the viewpoint that P3HT is the primary exciton generation material with the fullerene acting mainly as an acceptor and electron transport material [14]. As such, optimisation of device performance has focussed upon improvement of the P3HT photoresponse often at the expense of PCBM performance, with the interplay between P3HT crystallisation and fullerene aggregation playing a crucial role [2,15]. In particular, the annealing step that results in P3HT

crystallisation, which is essential for efficient hole transport, simultaneously causes PCBM aggregation in the amorphous P3HT interlamellar regions on the $>10 - 20$ nm length scale, with excess PCBM expelled to either the domain boundaries or the surface of the active layer [15]. Consequently, the PCBM in the BHJ architecture contributes very little to total charge generation despite having strong complementary absorption [14].

In the last decade a new materials system for OPVs has been developed, whereby the active layer is fabricated from nanoparticles composed of polymer:fullerene blends [16-20]. Studies of P3HT:PCBM nanoparticles show that a core-shell morphology is adopted; consisting of semicrystalline P3HT-rich shells and PCBM-rich cores [18,21]. Annealing the nanoparticle active layer modifies this initial morphology resulting in retention of the PCBM-rich cores within a matrix of the P3HT-rich shell material [21]. Modelling in these systems has demonstrated that charge transport is not inhibited by this core-shell morphology [22].

In this paper, we constrain the NP core-shell morphology to produce PCBM-rich core and P3HT-rich shell domain dimensions that are comparable to reported exciton diffusion lengths. We observe an increase in PCBM-rich nanoparticle core volume with an increase in PCBM loading; but the entire core volume is still within the exciton diffusion length of the core-shell interface, hence all excitons generated in the PCBM-rich cores can diffuse randomly and undergo dissociation at a core-shell interface. For the 1:2 P3HT:PCBM material feed ratio we do not observe a deterioration in bulk film morphology as reported for BHJ devices [23]. By varying the initial P3HT:PCBM donor:acceptor ratio we are also able to alter the core and shell compositions of the nanoparticles. Consequently, we observe highly efficient harvesting of PCBM generated excitons far in excess of that observed previously for optimised BHJ devices. As such, this work demonstrates that the NP approach

delivers a level of control of the mesoscale morphology not possible with conventional BHJ architectures and provides a mechanism via which NP active layer morphologies can be used to outperform conventional BHJ counterparts.

2. MATERIAL AND METHODS

2.1 Materials

Poly(3-hexylthiophene) (P3HT) was synthesised via the Grignard metathesis (GRIM) method using the procedure reported previously [21]. Molecular weight was measured by Size Exclusion Chromatography (SEC) analysis on a Viscotek VE 3580 system equipped with ViscoGEL™ columns (GMHHR-M), connected to a refractive index (RI) detector. GPC solvent/sample module (GPCmax) was used with HPLC grade tetrahydrofuran (THF) as the eluent and calibration was based on polystyrene standards. Running conditions for SEC analysis were: flow rate = 1.0 mL/min, injector volume = 100 µL, detector temperature = 30 °C, column temperature = 35 °C. The polymer sample was dissolved in THF and the solution was filtered through a PTFE filter (0.45 µm) prior to injection. The regioregularity (RR) and the degree of polymerisation (DP_n) of the synthesised polymer was determined from the ¹H NMR analysis as described previously [24]. The P3HT material characterisation is detailed in Table 1.

Phenyl C₆₁ butyric acid methyl ester (PCBM) was purchased from Lumtec. Anhydrous chloroform and sodium dodecyl sulphate (SDS) surfactant used for nanoparticle fabrication were purchased from Sigma Aldrich.

2.2 Nanoparticle fabrication

Solutions of P3HT and PCBM in chloroform were prepared in the following ratios 1:0.5 (33 wt. % PCBM loading), 1:0.8 (44 wt. % PCBM loading), 1:1 (50 wt. % PCBM loading), 1:1.2 (55 wt. % PCBM loading), 1:1.5 (60 wt. % PCBM loading) and 1:2 (67% PCBM loading). These organic phases each had a total solids content of 53.6 mg/ml. Sodium dodecyl sulphate (SDS) was used as the surfactant in the aqueous phase at a concentration of 10.7 mg/ml. The two phases were combined to form miniemulsions and then nanoparticle dispersions according to the method described previously [18]. Nanoparticles fabricated for STXM morphological investigations had a reduced concentration of surfactant in the aqueous phase (0.36 mg/ml) in order to achieve larger particles and a broader distribution in particle sizes for imaging.

2.3 Nanoparticle and nanoparticle film characterisation

Particle size measurements were made by dynamic light scattering (DLS) on a Zetasizer Nano ZS (Malvern Instruments) with a 633 nm laser and a backscatter detector angle of 173°. NP inks were diluted from their original 6 wt% solids content to 0.006 wt% solids using Milli-Q purified water before measurement. Samples were measured at room temperature using disposable plastic cuvettes. A value of 1.33 was used for the refractive index of water and 1.93 for the refractive index of P3HT:PCBM. The refractive index of P3HT:PCBM was determined prior to DLS measurements via optical modelling. The reflectance and transmittance of a solid film along with its thickness were measured, with this experimental information the material was modelled using a set of optical oscillators to accurately model the observed behaviour in the measured film. A total of ten DLS measurements were performed for each sample, one of these ten measurements that represents the average has been included in Supplementary Information as a plot of the intensity size distribution for

each sample. The Z-average particle diameter was also determined for each sample and is provided in Section 2.3.

For the UV-vis characterisation, the nanoparticle inks were spin coated onto quartz glass slides at the original ink concentration for film measurements. An ultraviolet-visible absorption spectrometer (UV-vis, Varian Cary 6000i) was used to study the absorption of films.

Films were spun at 1750 rpm on quartz for analysis with spectral ellipsometry to match device preparation conditions. A M2000X JA Woollam Spectroscopic Ellipsometer was used to measure the reflection ratio Ψ and phase difference Δ over the wavelength range of 210 - 1000 nm. The samples were measured using incident angles of 55° to 75° using 20 revolutions of the analyser per measurement. Optical models were developed by fitting ellipsometry measurements together with transmittance and near normal reflectance measurements using a Varian Cary 6000i UV-vis spectrometer.

Samples were prepared for scanning transmission X-ray microscopy (STXM) by spin coating 2.5 μl nanoparticle suspension onto low stress silicon nitride windows with silicon dioxide coating for hydrophilicity (window dimensions $0.25 \times 0.25 \text{ mm}^2$, window thickness 15 nm, frame $5 \times 5 \text{ mm}^2$) at 3000 rpm, 1 min, low acceleration of 112 rpm/s. Spin coated samples were air dried, thermally dried and annealed samples matched device conditions stated below. STXM measurements were performed on beamline 5.3.2.2 at the Advanced Light Source [25]. The samples deposited on silicon nitride are mounted in the sample chamber which is backfilled with helium (0.33 atm) and are raster scanned with respect to the monochromatic x-ray beam. The transmitted x-ray beam is detected by a scintillator and a photomultiplier tube. The energy of the x-ray beam was varied between 270 and 340 eV, covering the C K-

edge region at a resolution of 0.1 eV. Singular value decomposition was used to fit a sum of the pristine spectra to the measured blend spectrum, at each pixel in the STXM images. Image analysis was performed with the aXis2000 package (<http://unicorn.mcmaster.ca/aXis2000.html>). Nanoparticle core and shell P3HT compositions were determined by first taking a radial composition profile of each particle from STXM percent composition maps, then rotating this to average the composition over the particle. Shell thicknesses were estimated from the percentage composition maps.

The silicon nitride substrates with deposited nanoparticles were transported back to Newcastle (Australia) where transmission electron microscopy (TEM) was used to reimage the same particles where possible for further spatial correlation with the STXM images. TEM was performed on a Jeol 1200 EXII at an accelerating voltage of 80 kV.

Samples were prepared for SEM by spin coating 2.5 μL of nanoparticle ink (3000 rpm, 1 min, low acceleration of 112 rpm/s) onto a conductive silicon substrate. SEM was performed on a Ziess Sigma ZP FESEM at accelerating voltage of 1 to 3 kV, and magnification ranges of 10,000 to 100,000 times.

2.4 OPV device fabrication and testing

PEDOT:PSS (Baytron P) films were spin-coated (5000 rpm) on pre-cleaned patterned ITO glass slides and annealed at 140 °C for 30 min to eliminate water in the films. P3HT:PCBM nanoparticle layers were deposited by spin coating 35 μL of the dispersion (1750 rpm for 1 minute) in air. Following deposition the film was dried at 110 °C for 4 min and then transferred into a vacuum chamber for cathode evaporation. Calcium/aluminium (Ca/Al) electrodes were evaporated on the active layers in vacuum (2×10^{-6} Torr), with masking such

that the device area was 5 mm². The thickness of the Ca and Al layers were measured to be approximately 30 nm and 100 nm respectively using a quartz crystal monitor. After Ca/Al electrode deposition, devices were annealed at 140°C for 4 min. Photocurrent density-voltage (J-V) measurements were conducted using a Newport Class A solar simulator with an AM 1.5 spectrum filter. The light intensity was measured to be 100 mW cm⁻² by a silicon reference solar cell (FHG-ISE) and the J-V data were recorded with a Keithley 2400 source meter. External quantum efficiency (EQE) measurements utilised an Oriel Cornerstone 130 monochromator and tungsten halogen lamp, a Stanford Research Systems SR830 DSP digitising lock-in amplifier measured device current.

The current contributions were calculated by first fitting the spectral ellipsometry data obtained (see Supplementary Information). The imaginary part of the dielectric function was then decomposed into two contributions to allow the absorption to be calculated for the two components in this device structure, as described previously [14]. The EQE was partitioned into two components according to the weight of the calculated absorption and scaled to an AM1.5 spectrum to calculate the component currents.

For BHJ OPV devices fabricated for comparison, active layer solutions were prepared in the six P3HT:PC₆₁BM ratios at a concentration of 19 mg/ml in chloroform and sonicated for 60 min. followed by stirring at 40°C for 30 min. to dissolve. PEDOT:PSS films were prepared as described above, the active layer was then spun at speeds of 600 - 700 RPM (to target a 100 nm film thickness) in a N₂ atmosphere, followed by drying at 60 °C for 5 min. After Ca/Al electrode deposition, devices were annealed at 140 °C for 4 min.

3. RESULTS AND DISCUSSION

Poly (3-hexylthiophene) (P3HT) was synthesised with targeted low PDI and high regioregularity (RR). The number average molecular weight (M_n), weight average molecular weight (M_w) and polydispersity (PDI) determined from GPC measurements, and degree of polymerisation (DPn) and RR determined from ^1H NMR measurements are listed in Table 1, with the GPC measured molecular weight somewhat higher than that resulting from the multiplication of DPn and monomer molecular weight, consistent with previous studies for this polymer [26].

Table 1. P3HT polymer characterisation parameters.

M_n (Da)	M_w (Da)	PDI	DPn	RR
13,290	15,590	1.17	44	98.5

P3HT:PCBM blend nanoparticles with a varied ratio of donor to acceptor were fabricated using the method described previously [18]. The nanoparticle size was measured with dynamic light scattering (DLS) yielding a mean diameter of approximately 26 nm for all donor acceptor ratios ($\sigma = \pm 1$) (see Supplementary Information for plotted size distributions).

UV-visible spectroscopy measurements were performed on as spun nanoparticle films, and then additionally following drying and annealing treatments. Spectra for spin coated films are presented in Figure 1a for each of the P3HT:PCBM ratios. However, there was minimal change in the spectra of dried and annealed films and hence this data is not presented here. The P3HT:PCBM ratio of the nanoparticles is reflected in the relative intensity of the PCBM (below 400 nm) and the P3HT (above 400 nm) components [27,28]. A vibronic peak, at approximately 610 nm, is present in all nanoparticle films indicating crystalline ordering of

the P3HT [29,30]. The presence of this structure is consistent with previous studies of P3HT:PCBM nanoparticles reported by our research group [21,31].

Nanoparticle OPV devices were fabricated from each batch of nanoparticles and tested both before and after thermal annealing. Those tested before thermal annealing are referred to as ‘dried’ (due to the thermal treatment applied to the nanoparticle active layer before cathode deposition), whilst those annealed at 140°C for 4 min post-cathode deposition are referred to as ‘annealed’. A film thickness of 120 nm was targeted [1], with the film thickness data presented in Supplementary Information. BHJ OPV devices with a varied donor-acceptor ratio were also fabricated for comparison, the data is presented in Supplementary Information.

The J-V characteristics of the devices are presented in Table 2 and the average PCE (with standard deviation) is plotted as a function of fractional PCBM loading by mass in Figure 1b (J-V curves are provided in Supplementary Information). PCE is observed to increase with increased PCBM loading for both dried and annealed devices until a ratio of 1:1 is reached and then plateaus. Indeed for the 1:1 through to 1:2 device ratios (both dried and annealed) the device characteristics are almost identical within experimental error. The increase in PCE from 1:0.5 to 1:1 P3HT:PCBM ratios is primarily due to an increase in J_{SC} and FF. Given that P3HT is the main contributor to photocurrent, it is surprising that the performance of the devices remains invariant as the P3HT:PCBM ratio changes from 1:1 to 1:2, especially since a decrease in performance is observed for BHJ devices both in the literature [13,23,32] and in the reference BHJ OPV devices fabricated for this study (see Supplementary Information). Furthermore, these previous reports of BHJ OPV performance with varied P3HT:PCBM ratio have all used a different batch of P3HT as well as different processing parameters, yet the

trend in device performance is still the same, a drop in performance occurs when the donor-acceptor ratio goes beyond 1:1. EQE measurements of annealed NP OPV devices (Figure 1c) reveal that for ratios beyond 1:1, the PCBM photocurrent contribution increases, such that the overall J_{SC} is maintained, preventing a drop in device performance.

Table 2. Nanoparticle OPV device characteristics for best devices, with the averages ($\pm$ standard deviation) of 12 devices in brackets.

Donor acceptor ratio	Dried				Annealed			
	V_{OC} (mV)	J_{SC} (mA/cm ²)	FF	PCE (%)	V_{OC} (mV)	J_{SC} (mA/cm ²)	FF	PCE (%)
1:0.5	465.5 (447.9 ± 16.8)	2.41 (1.85 ± 0.42)	0.32 (0.29 ± 0.02)	0.36 (0.25 ± 0.08)	515.8 (496.0 ± 12.5)	2.48 (1.97 ± 0.86)	0.32 (0.32 ± 0.04)	0.40 (0.36 ± 0.04)
1:0.8	318.0 (310.8 ± 10.4)	3.74 (3.43 ± 0.18)	0.44 (0.43 ± 0.01)	0.52 (0.45 ± 0.04)	502.6 (496.8 ± 14.0)	3.72 (3.45 ± 0.16)	0.42 (0.41 ± 0.01)	0.78 (0.70 ± 0.05)
1:1	346.3 (310.5 ± 18.1)	3.56 (3.40 ± 0.22)	0.44 (0.43 ± 0.02)	0.54 (0.45 ± 0.06)	524.8 (531.4 ± 5.0)	4.23 (3.90 ± 0.18)	0.42 (0.40 ± 0.01)	0.93 (0.84 ± 0.05)
1:1.2	347.0 (318.4 ± 11.2)	3.77 (3.57 ± 0.30)	0.45 (0.44 ± 0.01)	0.59 (0.50 ± 0.06)	530.0 (526.9 ± 2.6)	4.51 (4.09 ± 0.32)	0.41 (0.41 ± 0.00)	0.99 (0.89 ± 0.07)
1:1.5	334.3 (326.9 ± 8.8)	3.77 (3.57 ± 0.20)	0.44 (0.42 ± 0.03)	0.56 (0.50 ± 0.06)	522.8 (519.8 ± 2.5)	4.45 (4.24 ± 0.20)	0.42 (0.41 ± 0.01)	0.98 (0.89 ± 0.05)
1:2	397.3 (376.3 ± 18.1)	3.68 (3.50 ± 0.23)	0.44 (0.43 ± 0.01)	0.64 (0.56 ± 0.06)	524.3 (529.0 ± 4.7)	4.60 (4.18 ± 0.27)	0.42 (0.41 ± 0.01)	1.00 (0.91 ± 0.07)

Figure 1. (a) UV-visible absorption spectra of spin coated P3HT:PCBM nanoparticulate films and (c) plot of external quantum efficiency (EQE) for the best performing annealed P3HT:PCBM nanoparticulate OPV devices with donor-acceptor ratio 1:0.5 light dotted line, 1:0.8 heavy dotted line, 1:1 light dashed line, 1:1.2 heavy dashed line, 1:1.5 light line, 1:2 heavy line. (b) Trend in power conversion efficiencies (PCE) of dried (open circles) and annealed (closed circles) P3HT:PCBM nanoparticle OPV devices and (d) calculated PCBM photocurrent contribution (closed circles) for annealed devices according to fractional PCBM loading by mass including calculation based on PCBM mass (red dashed line). Error bars represent standard deviation between replicate devices for (b) and absolute error for (d).

The EQE has been deconvoluted to yield the PCBM photocurrent contribution for each P3HT:PCBM ratio (Figure 1d and tabulated in Table 4). As PCBM loading increases, the calculated contribution of photocurrent attributed to PCBM increases from 7.9% for 1:0.5 to 14.3% for 1:1 to 30.0% for the 1:2 ratio. While the PCBM photocurrent contribution for the 1:1 ratio device is in good agreement with that previously calculated for 1:1 P3HT:PCBM BHJ devices [14], the PCBM photocurrent contribution for higher PCBM loadings deviates significantly from that observed for BHJ devices. Pandit *et al* [13] reported that a P3HT:PCBM ratio of 1:0.8 is optimal in BHJ devices and observed significant decreases in PCE at higher or lower PCBM loadings, which are attributable to the creation of film morphologies outside of the optimal regime. Indeed, these observations are in broad agreement with early work by Kim *et al* [32], who reported EQE measurements for P3HT:PCBM ratios between 1:0 and 1:4. From Table 2, we see that the J_{sc} is the same, within error, for the annealed devices with a donor:acceptor ratio of 1:1 through to 1:2, whereas Kim *et al* [32] report that J_{sc} decreases at higher PCBM loadings, in contrast to our observations for the NP system.

For a thin absorbing layer, the exciton generation rate from PCBM is proportional to the amount of PCBM present and thus we might expect a linear relationship between the PCBM contribution to photocurrent and the PCBM weight fraction. However, as shown in Figure 1d, the PCBM contribution to photocurrent deviates significantly from a linear relationship for PCBM weight fractions greater than 1:1. It is clear, therefore, that increased PCBM exciton harvesting due to the increased PCBM concentration cannot completely explain the observed increase in PCBM photocurrent. As such, we hypothesise that there must be a decrease in the recombination rate with increasing PCBM weight fraction, which most likely arises from change in compositional morphology of the nanoparticle film.

In order to probe the NP structure and morphology, STXM measurements were conducted on as spun, dried and annealed nanoparticles of a broad size range (as described in Section 2.2 and 2.3) for three key P3HT:PCBM ratios: 1:0.5, 1:1 and 1:2. Matching TEM for the same nanoparticles was obtained post-STXM to provide high resolution detail to complement the chemical contrast maps.

Figure 2. STXM percentage composition maps showing P3HT concentration (first row) and PCBM concentration (second row) and matching TEM (third row) for spin coated P3HT:PCBM nanoparticles prepared from a P3HT:PCBM donor acceptor ratio of 1:0.5 (a to c), 1:1 (d to f) and 1:2 (g to i). All scale bars are 600 nm. The colour contrast is scaled such that light colours correspond to higher component concentrations. Minima and maxima for the colour scale are black = 0 and white = 100%, with the exception of (e) and (h) where white is set to 85% for a clearer visualisation of morphology.

The STXM measurements revealed that for all donor acceptor ratios the structure of the as-spun nanoparticles was core-shell over a range of particle sizes down to the resolution limit of the STXM instrument [18]. The particles possessed a P3HT-rich shell and PCBM-rich core (Figure 2), consistent with previous reports for 1:1 nanoparticles of this material system [21]. Based on quantitative analysis of multiple particles, we observe an increase in PCBM core radius with increasing PCBM loading from 1:0.5 (43 ± 6 % of total radius) to 1:1 (51 ± 4 % of total radius) to 1:2 (56 ± 3 % of total radius). The matching TEM (images of the same areas as the STXM) also reveals that the nanoparticle shape becomes increasingly spherical with increasing PCBM concentration (Figure 2c $\rightarrow$ f $\rightarrow$ i).

Figure 3. STXM percentage composition maps showing P3HT concentration (first row) and PCBM concentration (second row) and matching TEM (third row) for dried P3HT:PCBM nanoparticles prepared from a P3HT:PCBM donor acceptor ratio of 1:0.5 (a to c), 1:1 (d to f) and 1:2 (g to i). All scale bars are 600 nm. The colour contrast is scaled such that light colours correspond to higher component concentrations. Minima and maxima for the colour scale are black = 0 and white = 100%, with the exception of (e) where white is set to 85% for a clearer visualisation of morphology.

Drying the disperse nanoparticle films above the polymer glass transition temperature (T_g) [33], at 110°C for 4 min, results in joining of the P3HT-rich shell domains whereas the PCBM cores remain isolated and discrete in nature (Figure 3). This change in morphology is also evident in the TEM images, where the nanoparticles have become less well-defined in comparison to the nanoparticles prior to thermal treatment (Figure 2).

Figure 4. STXM percentage composition maps showing P3HT concentration (first row) and PCBM concentration (second row) and matching TEM (third row) for annealed P3HT:PCBM nanoparticles prepared from a P3HT:PCBM donor acceptor ratio of 1:0.5 (a to c), 1:1 (d to f) and 1:2 (g to i). For each of the nine image panes, the left half illustrates the majority phase, the right half illustrates the minority phase. All scale bars are 600 nm. The colour contrast is scaled such that light colours correspond to higher component concentrations. Minima and maxima for the colour scale are black = 0 and white = 100%, with the exception of (e) where white is set to 85% for a clearer visualisation of morphology.

Annealing the P3HT:PCBM NP films at 140°C for 4 min results in the formation of two film morphology types, (i) a majority phase comprising a network of joined P3HT-rich shells with distributed and discrete PCBM-rich cores (similar to that in the dried sample), and (ii) a minority phase where gross phase segregation has occurred (Figure 4). The regions of gross phase segregation are characterised by PCBM aggregates surrounded by residual P3HT-rich shell material. Electron microscopy of the 1:1 P3HT:PCBM nanoparticle films provides further confirmation that the dominant annealed film morphology is characterised by a joined polymer-rich shell network and distributed, discrete PCBM-rich cores (Figure 5).

Figure 5. SEM of 1:1 P3HT:PCBM NP film spin coated (a) and annealed (b); (c) TEM of the annealed NP film showing that in the majority of the film the PCBM cores remain discrete and intact, with magnified region (d). Scale bars are 1 μm.

A compositional analysis of the STXM images was performed according to the procedure reported previously [21]. The composition of the dominant component is reported for each domain morphological type (shell, core or joined shell) in Table 3. The data reveals that as PCBM loading is increased from 1:0.5 to 1:2, a constant core composition of approximately 75 % PCBM is reached and that the core composition at each P3HT:PCBM ratio is effectively invariant with heat treatment. By contrast the shell composition changes systematically both with PCBM loading and heat treatment. In particular, the spread of shell composition values for the different P3HT:PCBM ratios increases slightly with increased heat treatment (Figure 6).

Table 3. P3HT compositions of the P3HT-rich domains and PCBM compositions of the PCBM-rich domains as calculated from the STXM maps for the spin coated, dried and annealed samples. The standard deviation of the composition is given in parenthesis. The domain morphologies are categorised and noted accordingly as: shell (S), core (C) and joined shell (JS). Note for the 1:2 nanoparticles the shell thickness is now approaching the STXM beam spot size [34] and hence the shell compositions represent a lower limit for P3HT composition.

		P3HT:PCBM ratio		
		1:0.5	1:1	1:2
Spin coated	P3HT composition of P3HT-rich region (%) (σ)	82 (3) S	70 (1) S	67 (9) S
	PCBM composition of PCBM-rich region (%) (σ)	66 (17) C	74 (12) C	73 (6) C
Dried	P3HT composition of P3HT-rich region (%) (σ)	81 (6) JS	69 (6) JS	57 (6) JS
	PCBM composition of PCBM-rich region (%) (σ)	60 (11) C	75 (6) C	75 (8) C
Annealed	P3HT composition of P3HT-rich region (%) (σ)	85 (5) JS	67 (6) JS	54 (3) JS
	PCBM composition of PCBM-rich region (%) (σ)	62 (1) C	73 (7) C	73 (4) C

Based upon the STXM study, we observe that neither the core size nor composition changes significantly for P3HT:PCBM ratios of 1:1 and 1:2. For both of these ratios, the core composition is 73 % PCBM and thus photocurrent from the core is dominated by excitons generated from PCBM. Since the core radius is ~ 5.6 to 7.3 nm for the nanoparticles used in OPV device fabrication, which is well within reported exciton diffusion lengths for PCBM [35], we expect that all of the excitons generated within the core will reach the core-shell interface where they can be efficiently separated into free charge carriers.

Figure 6. P3HT percentage composition of P3HT-rich shell domains for spin coated nanoparticles and P3HT-rich joined shell network for dried and annealed nanoparticle films for 1:0.5 (diamonds), 1:1 (open circles) and 1:2 (closed circles) P3HT:PCBM ratios.

The PCBM fraction of the shell composition is observed to systematically increase with increased PCBM loading (Figure 6). For the annealed 1:0.5 ratio nanoparticle films, the joined shell phase contains less than 20% PCBM, which is below the minimum concentration

of PCBM required to form continuous PCBM percolation pathways (percolation threshold) in the bulk film [36-38]. However, for the 1:1 and 1:2 ratio NP films, the PCBM shell fraction increases to $\sim 1/3$ and $1/2$ respectively; approaching the optimum blend ratio required for balanced charge mobility [39]. As such, the photogenerated charges that originate from excitons generated by the dominant PCBM in the core are more effectively extracted with increasing PCBM loading in the shell phase; resulting in the observed increasing PCBM photocurrent contribution (Figure 1d). Moreover, in the case of PCBM in the shell, the shell thickness is again less than the exciton diffusion length. As such, the proportion of photocharge that originates from excitons generated by PCBM in the shell also increases with increasing PCBM loading.

Consequently, it seems reasonable to speculate that with the NP architecture (unlike BHJ films) it should be possible to harvest all charges from excitons generated in the PCBM. This hypothesis is supported by considering the *specific photocurrent* (J_{sp}) generated by each component of the blend. Here, we define the *specific photocurrent* as the J_{sc} produced by the blend component divided by its weight fraction (Table 4).

Table 4. Calculated PCBM (J_{sc}^{PCBM}) and P3HT (J_{sc}^{P3HT}) photocurrent contribution and specific PCBM (J_{sp}^{PCBM}) and P3HT (J_{sp}^{P3HT}) photocurrent contribution for annealed devices as a function of PCBM and P3HT weight fraction.

PCBM				P3HT			
wt fraction	J_{sc} fraction	J_{sc}^{PCBM} (mA/cm ²)	J_{sp}^{PCBM} (mA/cm ²)	wt fraction	J_{sc} fraction	J_{sc}^{P3HT} (mA/cm ²)	J_{sp}^{P3HT} (mA/cm ²)
0.33	0.08	0.16	0.48	0.67	0.92	1.81	2.70
0.44	0.12	0.4	0.91	0.56	0.88	3.05	5.45
0.50	0.14	0.56	1.12	0.5	0.86	3.34	6.68
0.55	0.18	0.72	1.31	0.45	0.82	3.37	7.49
0.60	0.22	0.94	1.57	0.4	0.78	3.3	8.25
0.67	0.30	1.25	1.87	0.33	0.70	2.93	8.88

Figure 7 shows that for both the P3HT and the PCBM the amount of current generated per weight fraction (and hence per mass in these devices) increases with increased PCBM content in the blend. By contrast, if exciton generation and transport were limiting the charge extraction then the *specific photocurrent* would be constant since the photocurrent generated by each component would depend simply upon the weight fraction of each.

Figure 7. Variation of PCBM and P3HT *specific photocurrent* as a function of PCBM and P3HT weight fraction.

As the shell phase approaches a more balanced charge transport matrix so recombination reduces in the NP devices. In particular, we speculate that it is *bimolecular* recombination that is most influenced by the changing shell composition [13]. Critically, it is unlikely that the increase in the PCBM component in the shell domain of annealed nanoparticles is on a molecularly distributed scale, or else bimolecular recombination would be an issue in these devices [40]. We propose that the 54 % P3HT 46% PCBM composition of the 1:2 nanoparticle shells constitutes continuous percolation pathways, resulting in the observed improvement in charge collection in these devices.

This work highlights the differences between the nanoparticulate and BHJ OPV structures. Here we have shown that, unlike in the BHJ case, device performance is maintained for PCBM weight fractions greater than 0.5. This behaviour arises from the fact that there are two distinct domains (core and shell) in the NP case, the compositions of which differ from the donor:acceptor ratio of the blend. OPV performance in these devices is a balance between charge generation and transport. For small cores, all of the charge can be efficiently extracted when the shell composition reaches the required level for effective charge transport percolation pathways through the shell phase. Furthermore, the presence of the cores does not disrupt the performance of the shell material. As such, the NP structure offers a pathway to overcoming current issues with ternary blend devices, wherein the ternary component has a detrimental effect on the BHJ morphology and hence performance [41]. In the NP case, the ternary component can be located in the core and still contribute fully to charge generation.

4. CONCLUSIONS

Morphology is a key contributor to effective OPV device performance and the parameters affecting OPV structure are continually being optimised. Nanoparticle OPVs offer a more nuanced approach to controlling device morphology by allowing preforming of the active film structure. The initial core-shell structure of these nanoparticles means we can increase the PCBM loading and directly harvest more PCBM photocurrent, in comparison to BHJ devices where an increase in PCBM loading often leads to a degradation of bulk film morphology such that exciton dissociation and charge transport are no longer efficient. This work shows that a judicious choice of particle size combined with a nanoparticle shell blend composition that is more balanced allows efficient exciton dissociation and efficient extraction of the resultant charges.

ACKNOWLEDGMENTS

Special thanks to at the University of Newcastle Electron Microscopy and X-ray Unit. The University of Newcastle and the Australian Renewable Energy Agency (ARENA) are gratefully acknowledged for PhD scholarships (N.P.H.). ARENA is also acknowledged for supporting a postdoctoral fellowship (K.F.). We acknowledge financial support from the Commonwealth of Australia through the Access to Major Research Facilities Program. The ALS is supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. This work was performed in part at the Materials and NSW node of the Australian National Fabrication Facility, which is a company established under the National Collaborative Research Infrastructure Strategy to provide nano and microfabrication facilities for Australia's researchers. Special thanks to Adam Fahy and to Mohammed Fadhil for experimental

assistance. M.C.S. gratefully acknowledges financial support from the Welch Foundation (AT1740), and National Science Foundation (DMR-0956116 & CHE-1126177).

SUPPORTING INFORMATION

Supporting Information for this publication includes spectral ellipsometry data, dynamic light scattering (DLS) particle size distributions for the nanoparticles used to fabricate NP OPVs, nanoparticle film thickness measurement data, J-V curves for the best dried and annealed NP OPV devices with varied donor-acceptor ratios; and BHJ OPV device data for varied donor-acceptor ratio for comparison to the NP OPV data.

ABBREVIATIONS

OPV, organic photovoltaic; RR, regioregularity; M_n , number average molecular weight; M_w , weight average molecular weight; PDI, polydispersity index; NP, nanoparticle; P3HT, poly(3-hexylthiophene); PCBM, phenyl C₆₁ butyric acid methyl ester; STXM, scanning transmission x-ray microscopy; DLS, dynamic light scattering; BHJ, bulk heterojunction; NEXAFS, near edge X-ray absorption fine structure.

REFERENCES

1. S. van Bavel, E. Sourty, G. de With, K. Frolic, J. Loos, Relation Between Photoactive Layer Thickness, 3D Morphology, and Device Performance in P3HT/PCBM Bulk-Heterojunction Solar Cells, *Macromolecules* 42 (2009) 7396–7403.

2. D.R. Kozub, K. Vakhshouri, L.M. Orme, C. Wang, A. Hexemer, E.D. Gomez, Polymer Crystallization of Partially Miscible Polythiophene/Fullerene Mixtures Controls Morphology, *Macromolecules* 44 (2011) 5722–5726.
3. A.J. Moulé, K. Meerholz, Controlling Morphology in Polymer–Fullerene Mixtures, *Adv. Mater.* 20 (2008) 240–245.
4. W. Ma, C. Yang, X. Gong, K. Lee, A.J. Heeger, Thermally Stable, Efficient Polymer Solar Cells with Nanoscale Control of the Interpenetrating Network Morphology, *Adv. Funct. Mater.* 15 (2005) 1617–1622.
5. F. Liu, Y. Gu, J.W. Jung, W.H. Jo, T.P. Russell, On the Morphology of Polymer-Based Photovoltaics, *J. Polym. Sci., Part B: Polym. Phys.* 50 (2012) 1018–1044.
6. C.J. Brabec, S. Gowrisanker, J.J.M. Halls, D. Laird, S. Jia, S.P. Williams, Polymer-Fullerene Bulk-Heterojunction Solar Cells, *Adv. Mater.* 22 (2010) 3839–56.
7. L. Ye, S. Zhang, W. Ma, B. Fan, X. Guo, Y. Huang, H. Ade, J. Hou, From Binary to Ternary Solvent: Morphology Fine-Tuning of D/A Blends in PDPP3T-Based Polymer Solar Cells, *Adv. Mater.* 24 (2012) 6335–41.
8. W.-H. Baek, H. Yang, T.-S. Yoon, C.J. Kang, H.H. Lee, Y.-S. Kim, Effect of P3HT:PCBM Concentration in Solvent on Performances of Organic Solar cells, *Sol. Energy Mater. Sol. Cells* 93 (2009) 1263–1267.

9. G. Li, Y. Yao, H. Yang, V. Shrotriya, G. Yang, Y. Yang, “Solvent Annealing” Effect in Polymer Solar Cells Based on Poly(3-hexylthiophene) and Methanofullerenes, *Adv. Funct. Mater.* 17 (2007) 1636–1644.
10. G. Nagarjuna, D. Venkataraman, Strategies for Controlling the Active Layer Morphologies in OPVs, *J. Polym. Sci., Part B: Polym. Phys.* 50 (2012) 1045–1056.
11. M.T. Dang, L. Hirsch, G. Wantz, P3HT:PCBM, Best Seller in Polymer Photovoltaic Research, *Adv. Mater.* 23 (2011) 3597–3602
12. C.-K. Lee, C.-W. Pao, Solubility of [6,6]-Phenyl-C₆₁-butyric Acid Methyl Ester and Optimal Blending Ratio of Bulk Heterojunction Polymer Solar Cells, *J. Phys. Chem. C.* 116 (2012) 12455-12461.
13. B. Pandit, B.R. Gautam, T.P. Basel, Z.V. Vardeny, Correlation Between Ultrafast Transient Photomodulation Spectroscopy and Organic Photovoltaic Solar Cell Efficiency Based on RR-P3HT/PCBM Blends, *Org. Electron.* 15 (2014) 1149–1154.
14. N.C. Nicolaidis, B.S. Routley, J.L. Holdsworth, W.J. Belcher, X. Zhou, P.C. Dastoor, Fullerene Contribution to Photocurrent Generation in Organic Photovoltaic Cells, *J. Phys. Chem.* 115 (2011) 7801–7805.
15. P. Kohn, Z. Rong, K.H. Scherer, A. Sepe, M. Sommer, P. Müller-Buschbaum, R.H. Friend, U. Steiner, S. Hüttner, Crystallization-Induced 10-nm Structure Formation in P3HT/PCBM Blends, *Macromolecules* 46 (2013) 4002–4013.

16. T.R. Andersen, T.T. Larsen-Olsen, B. Andreasen, A.P.L. Böttiger, J.E. Carlé, M. Helgesen, E. Bundgaard, K. Norrman, J.W. Andreasen, M. Jørgensen, F.C. Krebs, Aqueous Processing of Low-Band-Gap Polymer Solar Cells using Roll-to-Roll Methods, *ACS Nano* 5 (2011) 4188–4196.
17. A. Stapleton, B. Vaughan, B. Xue, E. Sesa, K. Burke, X. Zhou, G. Bryant, O. Werzer, A. Nelson, A.L.D. Kilcoyne, L. Thomsen, E. Wanless, W. Belcher, P.C. Dastoor, Multilayered Approach to Polyfluorene Water-Based Organic Photovoltaics, *Sol. Energy Mater. Sol. Cells* 102 (2012) 114–124.
18. S. Ulum, N. Holmes, D. Darwis, K. Burke, A.L.D. Kilcoyne, X. Zhou, W. Belcher, P. Dastoor, Determining the Structural Motif of P3HT:PCBM Nanoparticulate Organic Photovoltaic Devices, *Sol. Energy Mater. Sol. Cells* 110 (2013) 43–48.
19. S. Gärtner, M. Christmann, S. Sankaran, H. Röhm, E.-M. Prinz, F. Pentth, A. Pütz, A.E. Türeli, B. Pentth, B. Baumstümmeler, A. Colsmann, Eco-Friendly Fabrication of 4% Efficient Organic Solar Cells from Surfactant-Free P3HT:ICBA Nanoparticle Dispersions, *Adv. Mater.* 26 (2014) 6653–6657.
20. T.S. Gehan, M. Bag, L.A. Renna, X. Shen, D.D. Algaier, P.M. Lahti, T.P. Russell, D. Venkataraman, Multiscale Active Layer Morphologies for Organic Photovoltaics Through Self-Assembly of Nanospheres, *Nano Lett.* 14 (2014) 5238–5243.
21. N.P. Holmes, K.B. Burke, P. Sista, M. Barr, H.D. Magurudeniya, M.C. Stefan, A.L.D. Kilcoyne, X. Zhou, P.C. Dastoor, W.J. Belcher, Nano-domain Behaviour in P3HT:PCBM Nanoparticles, Relating Material Properties to Morphological Changes, *Sol. Energy Mater. Sol. Cells* 117 (2013) 437–445.

22. K. Feron, S. Ulum, N.P. Holmes, A.L.D. Kilcoyne, W.J. Belcher, X. Zhou, C.J. Fell, P.C. Dastoor, Modelling Transport in Nanoparticle Organic Solar Cells using Monte Carlo Methods, *Appl. Phys. Lett.* 103 (2013) 193306.
23. C. Müller, T.A.M. Ferenczi, M. Campoy-Quiles, J.M. Frost, D.D.C. Bradley, P. Smith, N. Stingelin-Stutzmann, J. Nelson, Binary Organic Photovoltaic Blends: A Simple Rationale for Optimum Compositions, *Adv. Mater.* 20 (2008) 3510–3515.
24. M.C. Iovu, E.E. Sheina, R.R. Gil, R.D. McCullough, Experimental Evidence for the Quasi-“Living” Nature of the Grignard Metathesis Method for the Synthesis of Regioregular Poly(3-alkylthiophenes), *Macromolecules* 38 (2005) 8649–8656.
25. A.L.D. Kilcoyne, T. Tyliczszak, W.F. Steele, S. Fakra, P. Hitchcock, K. Franck, E. Anderson, B. Harteneck, E.G. Rightor, G.E. Mitchell, A.P. Hitchcock, L. Yang, T. Warwick, H. Ade, Interferometer-Controlled Scanning Transmission X-ray Microscopes at the Advanced Light Source, *J. Synchrotron Radiat.* 10 (2003) 125–136.
26. J. Liu, R.S. Loewe, R.D. McCullough, Employing MALDI-MS on Poly(alkylthiophenes): Analysis of Molecular Weights, Molecular Weight Distributions, End-Group Structures, and End-Group Modifications, *Macromolecules* 32 (1999) 5777–5785.
27. S.T. Turner, P. Pingel, R. Steyrleuthner, E.J.W. Crossland, S. Ludwigs, D. Neher, Quantitative Analysis of Bulk Heterojunction Films Using Linear Absorption Spectroscopy and Solar Cell Performance, *Adv. Funct. Mater.* 21 (2011) 4640–4652.
28. R.C. Hiorns, R. de Bettignies, J. Leroy, S. Bailly, M. Firon, C. Sentein, A. Khoukh, H. Preud'homme, C. Dagron-Lartigau, High Molecular Weights, Polydispersities, and

- Annealing Temperatures in the Optimization of Bulk-Heterojunction Photovoltaic Cells Based on Poly(3-hexylthiophene) or Poly(3-butylthiophene), *Adv. Funct. Mater.* 16 (2006) 2263–2273.
29. F. Ouhib, M. Tomassetti, J. Manca, F. Piersimoni, D. Spoltore, S. Bertho, H. Moons, R. Lazzaroni, S. Desbief, C. Jerome, C. Detrembleur, Thermally Stable Bulk Heterojunction Solar Cells Based on Cross-Linkable Acrylate-Functionalized Polythiophene Diblock Copolymers, *Macromolecules* 46 (2013) 785–795.
30. M.D. Barnes, M. Baghar, Optical Probes of Chain Packing Structure and Exciton Dynamics in Polythiophene Films, Composites, and Nanostructures, *J. Polym. Sci., Part B: Polym. Phys.* 50 (2012) 1121–1129.
31. N.P. Holmes, S. Ulum, P. Sista, K.B. Burke, M.G. Wilson, M.C. Stefan, X. Zhou, P.C. Dastoor, W.J. Belcher, The Effect of Polymer Molecular Weight on P3HT:PCBM Nanoparticulate Organic Photovoltaic Device Performance, *Sol. Energy Mater. Sol. Cells* 128 (2014) 369–377.
32. Y. Kim, S.A. Choulis, J. Nelson, D.D.C. Bradley, S. Cook, J.R. Durrant, Composition and Annealing Effects in Polythiophene/Fullerene Solar Cells, *J. Mater. Sci.* 40 (2005) 1371–1376.
33. P.E. Hopkinson, P.A. Staniec, A.J. Pearson, A.D.F. Dunbar, T. Wang, A.J. Ryan, R.A.L. Jones, D.G. Lidzey, A.M.A. Donald, Phase Diagram of the P3HT:PCBM Organic Photovoltaic System: Implications for Device Processing and Performance, *Macromolecules* 44 (2011) 2908–2917.

34. K.B. Burke, E.J. Lubber, N.P. Holmes, A.J. Murray, W.J. Belcher, X. Zhou, D. Mitlin, P.C. Dastoor, A Knife-Edge Measurement of the Beam Profile of STXM 5.3.2.2 Using a Focussed Ion Beam Milled Metallic Glass, *J. Electron Spectrosc. Relat. Phenom.* 185 (2012) 453-457.
35. S. Cook, A. Furube, R. Katoh, L. Han, Estimate of Singlet Diffusion Lengths in PCBM Films by Time-Resolved Emission Studies, *Chem. Phys. Lett.* 478 (2009) 33-36.
36. A.J. Mozer, N.S. Sariciftci, Conjugated Polymer Photovoltaic Devices and Materials, *C. R. Chim.* 9 (2006) 568-577.
37. K. Vakhshouri, D.R. Kozub, C. Wang, A. Salleo, E.D. Gomez, Effect of Miscibility and Percolation on Electron Transport in Amorphous Poly(3-hexylthiophene)/Phenyl-C₆₁-Butyric Acid Methyl Ester Blends, *Phys. Rev. Lett.* 108 (2012) 026601.
38. J.A. Bartelt, Z.M. Beiley, E.T. Hoke, W.R. Mateker, J.D. Douglas, B.A. Collins, J.R. Tumbleston, K.R. Graham, A. Amassian, H. Ade, J.M.J. Fréchet, M.F. Toney, M.D. McGehee, The Importance of Fullerene Percolation in the Mixed Regions of Polymer-Fullerene Bulk Heterojunction Solar Cells, *Adv. Energy Mater.* 3 (2013) 364-374.
39. J. Huang, G. Li, Y. Yang, Influence of Composition and Heat-Treatment on the Charge Transport Properties of Poly(3-hexylthiophene) and [6,6]-Phenyl C₆₁-butyric Acid Methyl Ester Blends, *Appl. Phys. Lett.* 87 (2005) 112105.
40. P.K. Watkins, A.B. Walker, G.L.B. Verschoor, Dynamical Monte Carlo Modelling of Organic Solar Cells: the Dependence of Internal Quantum Efficiency on Morphology, *Nano Lett.* 5 (2005) 1814-8.

41. S. Honda, T. Nogami, H. Ohkita, H. Benten, S. Ito, Improvement of the Light-Harvesting Efficiency in Polymer/Fullerene Bulk Heterojunction Solar Cells by Interfacial Dye Modification, *ACS Appl. Mater. Interfaces* 1 (2009) 804–10.

Graphical abstract