

CONTROLLING THE 3D NANOSCALE ORGANIZATION OF BULK HETEROJUNCTION POLYMER SOLAR CELLS*

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Abstract In this study, the three dimensional nanoscale organization in the photoactive layers of poly(3-hexylthiophene) (P3HT) and a methanofullerene derivative (PCBM) is revealed by transmission electron tomography. After annealing treatment, either at elevated temperature or during slow solvent evaporation, nanoscale interpenetrating networks are formed with high crystalline order and favorable concentration gradients of both components through the thickness of the photoactive layer. Such a tailored morphology accounts for the considerable increase of the power conversion efficiency in corresponding solar cell devices.

Keywords: Polymer solar cells; Morphology; Electron tomography; Device performance.

INTRODUCTION

Nanostructured polymer solar cells (PSC) have evolved as a potential alternative to conventional silicon-based photovoltaics for the upcoming sustainable energy economy^[1]. Since PSC can be fabricated by processing polymers, eventually together with other organic materials, from solution and printing them onto different types of substrates by roll-to-roll production processes like newspapers, they offer important advantages over their inorganic counterparts due to low cost of fabrication and easy processing^[2–4]. Besides, such PSC are lightweight, mechanically flexible and the properties of the photoactive layer can be straightforwardly tuned by adjusting the chemical architecture of its components.

In a typical polymer solar cell, light absorption creates strongly bound excitons, which can dissociate into free charges only at donor/acceptor interfaces by rapid electron transfer from the donor to acceptor^[5, 6]. Besides the chemical architecture of the components applied, the local nanoscale organization of the photoactive layer in all three dimensions is largely responsible for the efficiency of the PSC. The challenge is to generate a maximized interface between donor and acceptor materials within the whole volume of the photoactive layer for maximum exciton dissociation, and to ensure the creation of continuous, preferably short, pathways for charge transport to both of the electrodes (a so-called bulk heterojunction structure)^[2, 3, 7–11]. In semi-conductive organic and polymeric materials, charge carrier transport can be enhanced by increasing mesoscopic order and crystallinity, which results in maximized intramolecular π -stacking^[12]. In addition, one may expect that

* This work forms part of the research program of the Dutch Polymer Institute (DPI), project # 524. Additional financial support was provided by the Dutch Science Organization (NWO).

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Invited lecture presented at the International Symposium on Polymer Physics, 2008, Xiamen, China

Received August 29, 2008; Accepted September 8, 2008

collection of charge carriers should be facilitated in the case where there is enrichment of the electron acceptor material at the side of a photoactive layer close to a negative (metal) electrode and enrichment of the donor material close to the positive electrode (like indium doped tin oxide, ITO, used in this study)^[13].

It has been shown that both the processing conditions of donor/acceptor mixtures from solution and the post-production treatment like annealing have a large influence on the performance of PSC, because they strongly affect the morphology, eventual crystalline order and phase separation of the photoactive layer^[14–19]. An appropriate length-scale of phase separation in the photoactive layer is the key point for the high performing polymer solar cells. To realize such nanoscale organization, one has to make a compromise between the interface area and efficient pathways for the transportation of free charge carriers towards correct electrodes so as reduce charge carriers recombination within the photoactive layer. Although some useful insights into the interplay between photoactive layer organization and PSC performance have been obtained, a comprehensive understanding of the underlying processing-structure-property relationships is still lacking (Table 1).

Table 1. Molecular and morphology requirements for the photoactive layer of a high-performance polymer solar cell

Requirement	Influenced by	
	Molecular architecture	Morphology
Utilization of incident light	Molecule design to tune band gap (s)	Layer thickness, roughness of interfaces
Exciton dissociation	Match of band properties between donor and acceptor	Max. interface Small acceptor/donor phases within exciton diffusion range
Charge transport	Molecule design with high charge carriers mobility	Short and continuous pathways to the electrodes Ordered (crystalline) transportation pathways
Processability	Optimized molecular architecture (stereoregularity, molecular weight, and branching)	Thermodynamics and kinetics of film formation and phase separation

Currently, one of the most promising PSC, both in terms of efficiency and long term stability, is the system based on regioregular poly(3-hexylthiophene) (P3HT) as the electron donor and the fullerene derivative [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) as the electron acceptor material. The best reported power conversion efficiencies of such system reach up to 5%^[16, 20, 21]. In this study we report on the creation of the 3D nanoscale organization of P3HT/PCBM bulk heterojunctions upon thermal and solvent assisted annealing of the photoactive layers, which were spin-coated from solution with partly aggregated P3HT, and its impact on the performance of corresponding PSC. For the first time, we have performed a comprehensive analysis of the 3D volume organization of the photoactive layer with nanometer resolution in all three dimensions by applying transmission electron microscopy tomography (TEM tomography), with aim to identify the nature of the interpenetrating network formed by the two functional materials within the volume of the photoactive layer; and to determine the critical morphology parameters contributing to the improved performance of annealed P3HT/PCBM devices.

EXPERIMENTAL

Device Fabrication

P3HT ($M_n = 19400$ and PDI = 1.4 as determined by GPC, and regioregularity of 98% as determined by NMR, from Plextronics, Inc.) and PCBM (with purity of > 99%, Solenne B.V.) were used as received. Mixed solutions were prepared by dissolving both components simultaneously in 1,2-dichlorobenzene (ODCB) (10 mg P3HT and 10 mg PCBM per 1 mL ODCB) and stirring at room temperature in the dark for 2 h. Few P3HT aggregates were formed in solution, and solutions were not filtered. The solar cell devices were fabricated by spin-coating a

solution of P3HT and PCBM, sandwiched between a transparent anode and a cathode. The anode consisted of cleaned indium tin oxide (ITO) patterned glass substrates (Philips Research) covered by spin-coating a poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) (PEDOT:PSS) dispersion (Baytron® P VP AI 4083; H.C. Starck) after filtration using a 0.45 μm filter. The thickness of the PEDOT:PSS layer was around 70 nm as determined with a Tencor P-10 surface profiler. The cathode consisted of LiF (1 nm) capped with Al (100 nm).

The ITO-coated glass substrates were cleaned by ultrasonic treatment in acetone, followed by rubbing with soap, rinsing in demineralised water, refluxing in isopropyl alcohol to remove water and finally they were treated in a UV-ozone oven for *ca.* 30 min.

Spin-coating of a P3HT/PCBM solution in ODCB on top of a PEDOT:PSS layer with a spin speed of 500 r/min for 4 min resulted in formation of homogeneous layers with thickness of about 100 nm. After spin-coating, the samples were transferred into a glove-box with a nitrogen atmosphere to evaporate LiF and Al at pressure of 9×10^{-6} mbar. The active device area was 16.2 mm². Thermal annealing was performed on complete devices at 130°C for 20 min on top of a hot plate inside a glove-box. For solvent assisted annealing, a P3HT/PCBM solution was spin-coated inside a glove-box at 500 r/min for 1 min only, so that the resulting layer remained wet, and putting the sample inside a closed Petri dish immediately after spin-coating, where it stayed for the duration of annealing. The thickness of photoactive layers thus obtained was also about 100 nm. Thicknesses of the photoactive layers were determined with a Tencor P-10 surface profiler.

Several devices of each type (obtained by spin-coating only, by spin-coating followed by thermal annealing and by solvent assisted annealing) were prepared for characterization of their performance. Current-voltage characteristics were measured with a Keithley 2400 source measurement unit. Illumination was carried out with UV (GG 385) and infrared (KG1) filtered light from an uncalibrated tungsten halogen lamp (75 mW/cm²). The light intensity of this light source provides for P3HT:PCBM blends a power output that is within 20% of the AM1.5 (100 mW/cm²) performance.

Absorption data were acquired using a Perkin Elmer UV-Vis spectrometer Lambda 40.

Transmission Electron Microscopy Measurements

The P3HT/PCBM layers were floated from the water soluble PEDOT:PSS substrate onto the surface of demineralised water and picked up with 400-mesh or 200-mesh copper TEM grids for TEM investigation.

Bright field TEM morphology observation, acquisition of tilt series for TEM tomography and acquisition of electron diffraction patterns were performed on a Technai G² 20 and on a TITAN-Krios TEM (both FEI Co.) operated at 200 kV and at 300 kV, respectively. All tilt series were obtained in an automatic fashion by using EXPLORE 3D software, the alignment and reconstruction of the data series was performed by using INSPEC 3D (both FEI Co.), and visualization of the 3D reconstructed volume was done with Amira 3.1 (Mercury Computer Systems, Inc.).

RESULTS AND DISCUSSION

Characteristic bright-field (BF) TEM images of P3HT/PCBM photoactive layers obtained by spin-coating only, by spin-coating followed by thermal annealing (TA), and by solvent assisted annealing (SAA) are presented in Figs. 1(a)–(c). Because of the lower density of P3HT crystals (1.1 g/cm³) as compared with PCBM (1.5 g/cm³), bright P3HT nanowires are seen in the images surrounded by the darker PCBM phase. The P3HT fibrillar crystals have average widths of around 15 nm, which is in the order of the exciton diffusion length^[6] thus ensuring dissociation of a great number of excitons at their interfaces with PCBM. In spin-coated films the P3HT fibrillar crystals seem to be short and show low contrast with PCBM. Several trends can be observed in the morphology development upon both thermal and solvent assisted annealing: first, contrast between P3HT and PCBM gets much more pronounced, with P3HT nanowires having a micrometer length after annealing; second, redistribution of PCBM takes place such that more of PCBM-rich regions are formed along the P3HT fibrils; and third, the P3HT nanowires seem to form a pronounced network all over the film area.

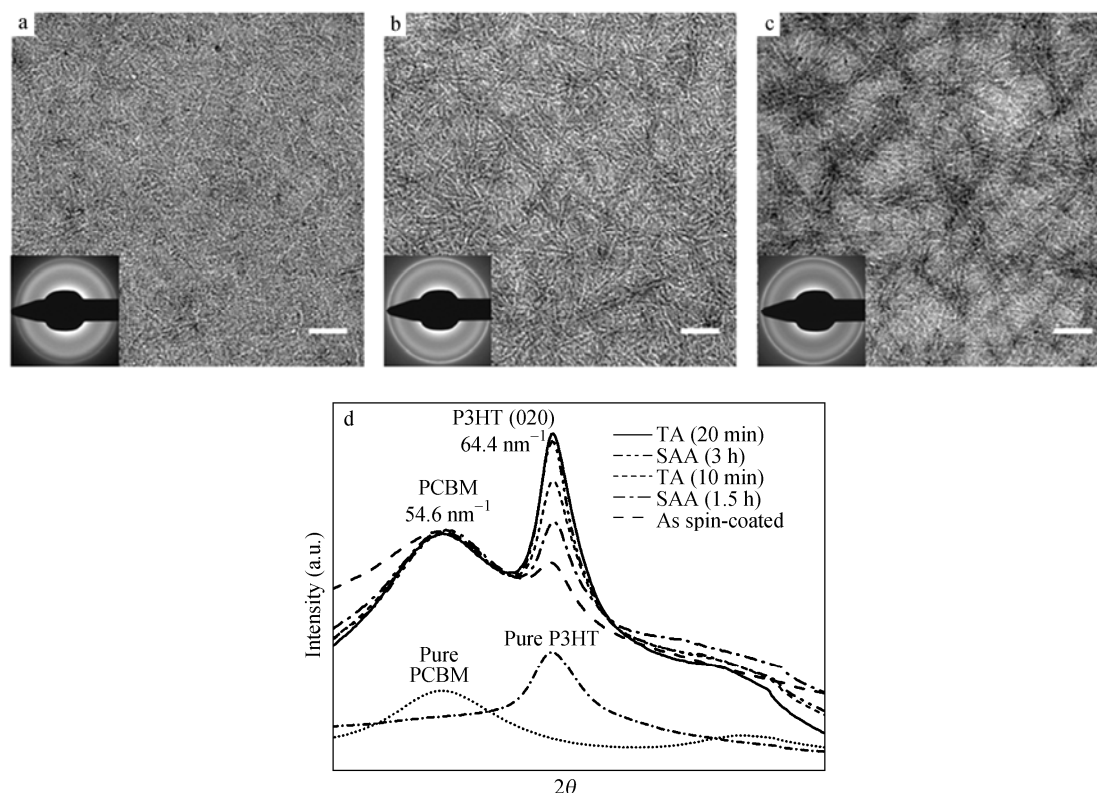


Fig. 1 (a–c) Bright-field TEM images of P3HT/PCBM photoactive layers: (a) as spin-coated, (b) thermally annealed (TA) and (c) solvent assisted annealed (SAA) for 3 h (The scale bar is 200 nm. The insets are corresponding electron diffraction patterns acquired at the same spot as the TEM images.) and (d) 1D plots of the intensities of electron diffraction patterns of P3HT/PCBM photoactive layers (normalized to the PCBM-peak maximum) for different annealing conditions

The desired presence of P3HT nanowire crystals in spin-coated P3HT/PCBM layers is confirmed by electron diffraction shown as insets in Figs. 1(a)–(c) and in more detail as a semi-quantitative 1D plot in Fig. 1(d). A bright outer Debye-Scherrer ring corresponds to (020) reflections of the P3HT fibrillar crystals randomly oriented within the film sample area^[22], and a broader inner Debye-Scherrer ring is attributed to nano-crystalline PCBM structures^[23]. Because of a large number of stacking defects in the P3HT crystals its overall crystallinity in spin-coated P3HT/PCBM layers is low. Semi-quantitative analysis of the electron diffraction patterns, performed using the assumption that crystallinity of PCBM does not change substantially upon annealing, reveals that the crystallinity of P3HT increases upon thermal or solvent assisted annealing and that the highest level of P3HT crystallinity is reached in P3HT/PCBM layers obtained by thermal annealing at 130°C for 20 min and by solvent assisted annealing for 3 h. (Neither thermal nor solvent assisted annealing for a longer time lead to a further increase in polythiophene crystallinity.) Enhanced crystallinity of P3HT leads to higher hole mobility^[12, 24] and results in a red shift of the polythiophene absorption matching better with the solar spectrum^[24, 25].

When studying morphological organization by means of TEM, it should be borne in mind that conventional bright-field TEM images represent 2D projections of the actual 3D organization of the specimen under investigation, and interpretation of such images in terms of volume organization is not always straightforward. The technique that overcomes this limitation is TEM tomography: it enables one to reconstruct the three-dimensional structure of a specimen with nanometer resolution from a series of two-dimensional projections obtained by tilting the specimen^[26]. An additional advantage of this technique is that it results in an improved signal-to-noise ratio. TEM tomography is thus the tool of choice to gain insights into the three-dimensional

nanoscale organization of photoactive layers of bulk heterojunction PSC.

Results of the volume reconstruction applied to as spin-coated and annealed P3HT/PCBM photoactive layers are shown as snapshots in Figs. 2(a)–(c). The volume data demonstrate evidently the presence of 3D nanoscale networks of both the P3HT nanowires and PCBM. In the volume data some indication for inclination of the crystalline P3HT nanowires can be found, which is required for the creation of genuine 3D rather than 2D networks and is beneficial for hole charge transportation from any place within the photoactive layer to the hole collecting electrode (Fig. 2d).

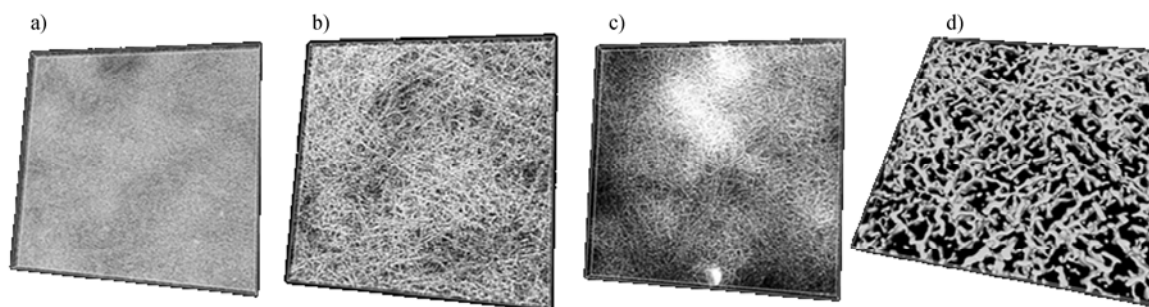


Fig. 2 Results of TEM tomography

a–c) Snapshots of a reconstructed 3D volume of P3HT/PCBM photoactive layers: a) as spin-coated, b) thermally annealed and c) solvent assisted annealed for 3 h (The volume dimensions are about $1700\text{ nm} \times 1700\text{ nm} \times 100\text{ nm}$.), d) representation of the three-dimensional network of P3HT nanowires formed in a thermally annealed P3HT/PCBM layer

By going slice by slice through the reconstructed volume of the annealed P3HT/PCBM films, the amount of crystalline P3HT nanowires can be quantified in relation to the actual z-position within the photoactive layer (Figs. 3a–c, exemplarily performed on the thermally annealed P3HT/PCBM layer). As evident from Fig. 3(c), there is enrichment of crystalline P3HT nanowires in the lower part of the film close to the hole collecting electrode and, correspondingly, enrichment of PCBM close to the top (electron collecting) electrode: a situation that is beneficial for collection of free charges. The same trend is observed in case of P3HT/PCBM obtained by solvent assisted annealing for 3 h. We conclude that enrichment of crystalline P3HT close to the bottom electrode is either due to the difference in surface tension at the bottom and top surfaces promoting the P3HT crystal growth close to the bottom and/or due to the fact that P3HT aggregates, present already in solution, sediment under impact of gravity during the spin-coating process and act as nuclei for formation of P3HT nanowires. For the preparation conditions chosen, the presence of P3HT aggregates in the solution is demonstrated evidently by corresponding UV-Vis spectroscopy and TEM studies. No indication is found for aggregation of PCBM in the same solution.

It should be noted that only crystalline P3HT nanowires are accounted for in this 3D morphology analysis since they have the required contrast with PCBM and get readily visualized in bright-field TEM. Based on density values of P3HT and PCBM and a 1/1 weight ratio of these components in the photoactive layer, P3HT should occupy *ca.* 58% of the total volume of the layer. From the plot presented in Fig. 3(c), we can estimate that approximately 35% of the layer volume is actually made up of crystalline P3HT nanowires, which indicates a high crystallinity of P3HT of about 60%.

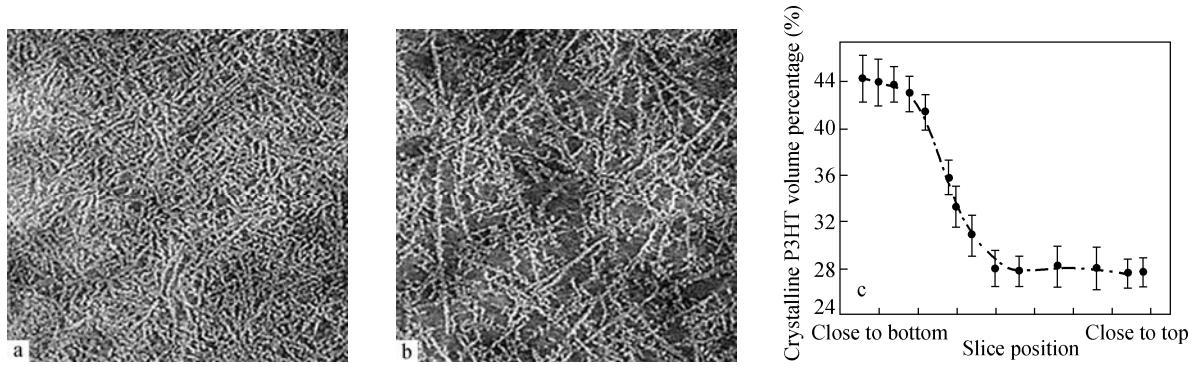


Fig. 3 (a–b) Slices taken out of a reconstructed 3D volume of thermally annealed P3HT/PCBM: (a) close to the hole collecting PEDOT:PSS/ITO electrode and (b) close to the electron collecting LiF/Al electrode (The dimensions of a slice are around 1700 nm × 1700 nm.) and (c) volume percentage of crystalline P3HT nanowires through the thickness of the thermally annealed P3HT/PCBM photoactive layers

All the changes in a 3D volume organization of the P3HT/PCBM photoactive layer after annealing, resulting in the formation of nanoscale interpenetrating networks of P3HT nanowires and PCBM nanocrystals with favorable gradients within the thickness of the layer, are paramount for obtaining high efficiency PSC. Indeed, characterization of corresponding PSC shows that values of the short-circuit current density (J_{sc}), the open circuit voltage (V_{oc}) and fill factor all increase substantially after thermal or solvent assisted annealing (see Table 2). The overall efficiencies (not corrected for spectral mismatch and without performing device optimization) almost doubled from 2.0% for as spin-coated P3HT/PCBM devices up to 3.8% for annealed devices.

Table 2. Parameters of P3HT/PCBM solar cells: short circuit current density J_{sc} , open circuit voltage V_{oc} , fill factor FF, and power conversion efficiency η (not corrected for spectral mismatch)

Sample	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	η (%)
As spin-coated	7.3	0.50	0.55	2.0
Solvent assisted annealing (1.5 h)	8.9	0.58	0.64	3.3
Solvent assisted annealing (3 h)	10.7	0.55	0.64	3.8
Thermal annealed	10.9	0.58	0.61	3.8

The higher values of J_{sc} obtained after annealing imply that more charges are being extracted from the PSC. In general, this is attributed to improved light absorption and/or better dissociation of excitons at the interface between the P3HT and PCBM phases and/or better transport of free charges to the corresponding electrodes^[25]. Indeed, we have demonstrated that, after annealing, light absorption of the P3HT/PCBM layers increases as confirmed by UV-Vis spectroscopy analysis (data not shown), that additional interface is formed in the volume of the photoactive layer and that hole transport is improved owing to the formation of micrometer long P3HT fibrillar crystals, whereas nanocrystalline PCBM ensures efficient electron transport.

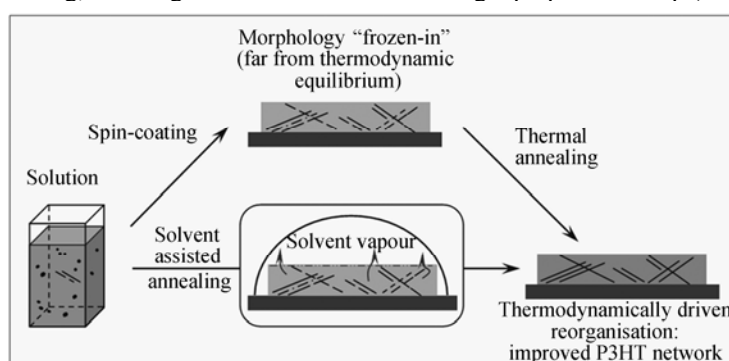
Further, the open circuit voltage (V_{oc}) is determined by a difference between the HOMO level of the donor and the LUMO level of the acceptor molecule and should be around 1 V for the P3HT/PCBM photoactive layer. Lower values of V_{oc} are attributed to contact losses: experimentally these losses are often found to be around 0.2 V per electrode^[27, 28]. Upon annealing, the roughness of P3HT/PCBM films increases slightly, still remaining in the nanometer range, as AFM studies confirm (data not shown), and we suppose this increased roughness is responsible for improved contact with the top electrode and thus higher values in experimentally determined V_{oc} after thermal and solvent assisted annealing.

Finally, a higher fill factor (FF) after annealing implies an improved balance of electron and hole transport, low traps and negligible space-charge effects. Electron mobility in PCBM is (intrinsically) higher than the

mobility of holes in P3HT, so higher FF values suggest improved hole mobility of the P3HT/PCBM layer caused by the increased crystallinity and length of P3HT nanowires after annealing^[24]; both arguments result ultimately in a lower number of hopping events required for hole transportation to the hole collecting PEDOT:PSS/ITO electrode.

CONCLUSIONS

We have analyzed a 3D nanoscale organization of P3HT/PCBM photoactive layers and identified the critical morphology parameters contributing to the improved performance of P3HT/PCBM solar cell devices after thermal or solvent assisted annealing. After spin-coating from solution in which few P3HT aggregates are already present, the film morphology formed is far from thermodynamic equilibrium. Both P3HT and PCBM are present in their nanocrystalline form only, as electron diffraction results show. In particular, the P3HT crystals are full of stacking defects, which accounts for low contrast in the resulting TEM images and for low fill factor and J_{sc} values of devices obtained by spin-coating. However, after controlled annealing (thermal or solvent assisted), thermodynamically driven reorganization of the P3HT/PCBM morphology takes place: highly crystalline and up to micrometers long P3HT nanowires form a 3D network and, serving as physical barriers to PCBM diffusion, suppress large scale phase separation of PCBM at any time of the preparation process. In case of solvent assisted annealing, such organization is created in a single preparation step (see Scheme 1).



Scheme 1 Controlled morphology development in P3HT/PCBM photoactive layers depending on the film preparation method

In solution, some aggregates of P3HT are already present; After spin-coating, the film morphology formed is far from thermodynamic equilibrium: in particular, the P3HT crystals are full of stacking defects; Annealing treatment creates and stabilizes a 3D nanoscale interpenetrating network with high crystalline order and favorable concentration gradients of both components through the thickness of the photoactive layer.

As a consequence of such tailored organization of the P3HT/PCBM photoactive layer, the obtained red shift of the polythiophene absorption results in a better overlap with the solar spectrum so that more photons can be harvested and more excitons created. The excitons are easily dissociated into free charge carriers at the interface between the P3HT nanowires having typical width of about 15 nm (in the order of the exciton diffusion length) and PCBM. Further, the high crystallinity of the P3HT nanowires and their micrometer length allow optimum hole transport with high mobility along the nanowires and the percolating network to the hole collecting electrode. Finally, favorable concentration gradients of both components through the thickness of the photoactive layer — enrichment of P3HT close to the hole collecting electrode and enrichment of PCBM close to the electron collecting electrode — and inclination of the P3HT nanowires ensure effective transfer from any place within the volume of the photoactive layer and collection of free charges at the respective electrodes. By controlling the morphology formation of the bulk heterojunction photoactive layer as described, a substantial increase of the performance of devices is achieved. This approach towards controlled morphology creation can be easily applied to other functional polymer systems in the research field of organic electronics.

ACKNOWLEDGEMENTS The authors thank René Janssen, Martijn Wienk, Sjoerd Veenstra and Xiaoni Yang for their incredible help and inspiring discussions.

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