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Efficient and stable, structurally inverted poly(3-hexylthiopen): [6,6]-phenyl-C61-butyric acid methyl ester heterojunction solar cells with fibrous like poly(3-hexylthiopen)

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ABSTRACT

We investigated an inverted organic photovoltaic device structure in which a densely packed ~100 nm thin TiO₂ layer on fluorine doped conducting glass serves as anode and poly(3,4-ethylenedioxythiophene): poly (styrenesulfonate)/Au layer on top of the active layer serves as cathode. The active layer is comprised of a blend of poly(3-hexylthiopene) (P3HT) and [6,6]-phenyl-C61-butyric acid methyl ester (PCBM). The rectification behavior of such a device is improved significantly and injection losses are minimized compared to devices without any compact TiO₂ layer. Moreover, nanostructured P3HT active layer was achieved in-situ by spin coating concentrated pure P3HT and P3HT:PCBM blend and solar cell performances on thickness of the active layer were also investigated. For the inverted solar cells constructed with different concentrations of P3HT and PCBM keeping the P3HT:PCBM ratio 1:0.8 (wt.%), the highest short circuit current and efficiency was observed when the P3HT and PCBM concentration was equal to 1.5 (wt.%) and 1.2 (wt.%) respectively. This leads to highly stable and reproducible power conversion efficiency above 3.7% at 100 mW/cm² light intensity under AM 1.5 conditions.

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1. Introduction

Polymer solar cells based on conjugated polymer and fullerene composite are a promising way towards large-area and low-price photovoltaic systems [1–5]. The main advantages are the easy preparation methods, low processing temperatures and in general low-cost materials and processing technology. However, compared with traditional inorganic photovoltaics [6-8], the polymer-based devices are still limited in their performance because of the drawbacks such as the weak absorption in the long-wavelength region, poor charge transport, and low stability [9,10]. Significant efforts are underway to improve their efficiency to the level of some practical applications. Research in organic solar cells is rapidly progressing with improvements of stability and wide-range light absorption. These issues must be solved before widespread application of the organic solar cell technology can be envisaged. Recently, methods to further improve performance of the polymer-based solar cells have been actively explored by means of optimization of materials and device structures [5,11-15]. Organic solar cells, have

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demonstrated increasing efficiencies over the last few years. The efficiency has reached 6.5% in a tandem cell very recently and the efficiency that can be reached in a single junction cells is ~4–5% [16].

In most organic optoelectronic devices, the front electrode is based on a transparent conducting oxide, such as indium tin oxide (ITO), that serves as the high-work-function, positive electrode. To achieve the built-in electric field needed for most devices to operate without loss in current collection, the back electrode must be made from a low-workfunction metal such as Al that serves as the negative electrode. In a normal solar cell geometry described above, electrons generated in the active layer are collected by the back Al electrode, and holes are collected by the front ITO electrode. In addition to possible material instability, the facile oxidation of the low-work-function metal deteriorate the stability of such devices and needs better encapsulation techniques to prevent air oxidation [9]. Such a drawback is inherent in organic photovoltaic (OPV) and must be overcome considering the low stability of OPV. By constructing an inverted type of geometry, the use of low work function metal electrode could be avoided and highly stable high work function electrode such as Au can be used. This can be done by inserting a holeblocking layer between the ITO and the active layer so that only electrons can reach the ITO, and the back electrode must become the holecollecting positive electrode. By inserting another common electron blocking layer such as poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) between the top metal and the active layer, only

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holes can reach the metal electrode allowing wider charge separation needed for an efficient solar cell performance. The schematic diagram and the flow of charge carriers in an inverted polymer cell are shown in Fig. 1. Such an inverted layer sequence has already been applied for organic light emitting diodes and organic photodiodes [17-19] and attempts have been undertaken to introduce the same concept to organic solar cell very recently with limited success [20-25]. I.e. a solar cell constructed with a 150 nm thick active layer of P3HT (poly(3hexylthiopene)):PCBM([6,6]-phenyl-C61-butyric acid methyl ester) (1:1:5 wt.%) on ITO substrate and a 250 nm thick PEDOT:PSS hole blocking layer on the active layer resulted in 1.4% power conversion efficiency and short circuit current density of (I_{sc}) 4.6 mA/cm² were much lower than that of normal P3HT:PCBM solar cell prepared under similar conditions ($J_{sc} = 9.4 \text{ mA/cm}^2$) [21,26]. In another report, the improved stability of the inverted solar cell constructed with ITO/BCP/ MEH-PPV:PCBM/CuPc/Au compared to non-inverted solar cell has been observed [20]. Recent reports on inverted organic photovoltaics using solution based ZnO [22-24] and TiO_x[27,28] underlayers as electron selective contact show good power conversion efficiencies. Stability of inverted P3HT:PCBM has been reported recently by Zimmermann et al. [29] and Hsieh et al. [30]. The same authors reported high open-voltage solar cells adding indene-C60 as the acceptor [31]. To improve the solar cell performance of the inverted polymer solar cells further, vertically segregated polymer blend with enhanced charge transport within the interpenetrating networks is indispensable which could be achieved by increasing the mesoscopic order and crystallinity of polymers [27,32]. Herein we report the preparation of inverted solar cells having a compact TiO₂ under layer prepared by spray pyrolysis and a PEDOT:PSS overlayer on polymer blend having an interpenetrating network of P3HT and PCBM (Fig. 1). The advantage of this method is that, by using higher P3HT:PCBM concentrations, efficient and highly stable solar cells with thicker active layers could be prepared compared to conventional thinner film used in OPV. We also obtained higher Jsc by varying P3HT: PCBM concentrations. The effect of active layer concentration and resulting thickness on solar cell parameters are also studied and compared. Further, the morphology of active layer is extensively studied and the role of respective blend layer is explained.



Fig. 1. The device structure of the inverted polymer solar cell.

2. Experimental methods

Titanium(IV)bis(acetoacetonato)-di(isopropanoxylate) (TAA) (Aldrich), P3HT (Rieke), PCBM (Shenon) and PEDOT:PSS (Aldrich) were purchased and used as received. Glass substrates (Tec) covered with 3 mm fluorine-doped tin oxide (FTO) layer having sheet resistances of 8 Ω per square were purchased from Hartford Glass Co. Inc., Indiana, USA. Chlorobenzene was purchased from Aldrich. The TiO₂ blocking layer (hereafter referred as TiO₂-bl) was prepared by spray pyrolysis deposition technique and the method has been discussed in detail by Peng et al. and hence only a brief account is mentioned here [33]. The TiO₂ precursor, TAA, diluted with ethanol to a concentration of 0.2 M was used as the spraying solution and the pyrolysis was carried out at 400 °C. After the required number of spraying cycles under optimized conditions were done, the substrates were annealed at 400 °C for another hour before cooling down to room temperature. The substrates were kept in an inert atmosphere for further layer preparation.

The polymer photovoltaic devices were fabricated by spin-coating blends of regio regular-P3HT:PCBM in various concentrations. P3HT (5, 10, 20, 30 and or 40 mg) and PCBM (4, 8, 16, 24 and 32 mg) were dissolved in 1 ml of chlorobenzene separately. After complete dissolution of the powders, P3HT and PCBM solutions were mixed to obtain P3HT:PCBM blend of 1:0.8 by weight. Films were prepared by spin coating this solution onto TiO₂-blocking layer coated Fluorine doped tin oxide (FTO) glass substrates followed by spin coating a PEDOT:PSS layer on the P3HT:PCBM active layer. For the annealing process, samples were placed on the hot plate under an inert atmosphere and heated at 150 °C for 5 min and removed immediately from the hot plate. To finish, the Au electrode was deposited by electron beam deposition in a vacuum chamber of BA 510 type from Balzers (Liechtenstein) and the active surface is 0.12 cm^2 . The Photovoltaic current-voltage measurements have been carried out by a Keithley 6517 Source-Measure unit under AM 1.5G conditions (Xenon arc lamp, Air Mass Filters from Oriel). The intensity of light was calibrated with a standard Si-reference cell from the Fraunhofer Institut für Solarenergie (ISE), Freiburg as 100 mW/cm². All efficiency values reported in this work were not corrected by the spectral mismatch factor. The incident photon to current conversion efficiency (IPCE) values were measured using a lock-in amplifier (SR830, Stanford Research Systems) with a current preamplifier (SR570, Stanford Research Systems) under shortcircuit conditions after illuminating the devices with monochromatic light from a xenon lamp passing through a monochromator (Spectra-model). UV-vis spectra were recorded with a Perkin Elmer Lambda 900 spectrometer, and emission spectra with a Hitachi F-4500 spectrophotometer. Surface and cross-sectional features of blocking TiO₂ layers, P3HT, PCBM and P3HT:PCBM blend films were examined using LEO 1530 Gemini field emission scanning electron microscope (FE-SEM) at 1-2 kV.

3. Results and discussion

3.1. Absorption properties of P3HT, PCBM and blend of P3HT:PCBM films

Since we wanted to study the influence of concentration of each component on optical and electric properties, the absorption spectra of pure P3HT, PCBM and polymer blend (P3HT:PCBM) were first investigated at different concentrations with and without annealing. These films were prepared by spin coating polymer on FTO conducting glass which is coated with a dense ~100 nm TiO₂ blocking layer (TiO₂-bl). The details of characterization of the TiO₂ blocking layer have been explained in an earlier publication [33]. As shown earlier, most of the small FTO particles have been covered by the TiO₂ and sharp edges of bigger FTO particles have been rounded off by the deposition of compact and crack-free ~125 nm thick TiO₂-bl. Thin

P3HT films were prepared varying the P3HT concentration from 0.25 to 2 (wt.% in chlorobenzene) providing the film thicknesses between 15 and 225 nm respectively. When studying the effect of polymer concentration on solar cell performance, thin film (~50 nm thick) obtained from 0.5 wt.% P3HT solution was taken as the reference film as it represents the concentration of average solar cell performance reported in literature and the results were compared with the thick P3HT film (film obtained from 1.5 wt.% P3HT solution, ~150 nm thick) which showed the highest efficiency in this study. Similarly films of PCBM prepared from 0.4 to 1.2 wt.% solutions were also compared with those of blends maintaining the composition always 1:0.8 (wt/wt). The absorption spectra of annealed and non-annealed P3HT films of 1.5 (wt.%) and 0.5 (wt.%) which were spin cast from chlorobenzene on TiO₂-bl are shown in Fig. 2 which were recorded by using FTO/TiO₂-bl as a reference. Obviously the thicker films exhibit higher optical densities. In the case of pure P3HT, the absorption spectra of both the annealed and non-annealed films from 0.5 wt.% and 1.5 wt.% P3HT solutions showed similar vibronic structure typical of highly ordered, regioregular P3HT except a slight increase in the optical density after annealing [1,2]. This indicates that the highly organized inter-plane stacked P3HT films could be formed by casting of concentrated (P3HT 1.5 wt.%) solutions without annealing and annealing increases the inter-chain interaction and ordering of P3HT molecules further. Also shown in Fig. 2 are the absorption spectra of non-annealed and annealed PCBM films prepared from 0.4 to 1.2 wt.% solution on TiO₂-bl. The highest occupied molecular orbital (HOMO) - lowest occupied molecular orbital (LUMO) transition of PCBM is seen in the ultraviolet region and the HOMO-LUMO transition of the annealed and non-annealed PCBM films shown in Fig. 2 are similar which indicates that the microstructural properties of PCBM are not affected upon annealing [34].

Having spectroscopic characterizations done on individual P3HT and PCBM films at different polymer concentrations, we next prepared P3HT:PCBM blend films using solutions of different concentrations keeping the P3HT:PCBM ratio at 1:0.8 (wt/wt) in each case. The following P3HT:PCBM blend concentrations were spin coated on TiO₂-bl from chlorobenzene; P3HT [0.25 wt.%] : PCBM [0.2 wt.%] = A, P3HT [0.5 wt.%] : PCBM [0.4 wt.%] = B, P3HT [1.0 wt.%] : PCBM [0.8 wt.%] = C, P3HT [1.5 wt.%] : PCBM [1.2 wt.%] = D and P3HT [2.0 wt.%] : PCBM [1.6 wt.%] = E and the corresponding thicknesses as measured by atomic force microscopy and confirmed by SEM are 25, 55, 118, 186 and 267 nm respectively. The polymer blend B exhibited comparable solar cell efficiencies to those reported



Fig. 2. The absorption spectra of pure P3HT and PCBM films on TiO_2 -bl from: from 1.5 wt.% P3HT solution (a) before and (b) after annealing, from 0.5 wt.% P3HT solution (c) before and (d) after annealing, PCBM from 1.2 wt.% solution (e) before and (f) after annealing, PCBM from 0.4 wt.% solution (g) before and (h) after annealing.

in literature and the polymer blend D showed the highest efficiency. Therefore, the absorption spectra of blend B was taken as the reference and the results were compared with that of highly concentrated polymer blend D. Fig. 3 shows non-annealed and annealed absorption spectra of blends B and D and the spectra were recorded by using FTO/TiO₂-bl as a reference. It can be clearly seen that blend D with an active layer thickness of 186 nm has very high optical density (OD > 1), whereas blend B does not absorb all the incident light (OD >0.8). The annealed and non annealed spectra of blend D have similar vibronic structure typical of highly ordered P3HT [34] and it is similar to the vibronic spectra of pure P3HT in the red region indicating that addition of PCBM does not hinder the growth of highly ordered fibrous P3HT at high P3HT concentrations. After annealing, a slight increase in optical absorption was observed which could be due to fact that the thermal annealing leads to a more thermodynamically stable internal order. More importantly, the absorption spectrum of the blend film represents a simple addition of the spectra of PCBM and P3HT film suggests the formation of phase segregated crystalline P3HT domains in the blend film. However, in the absorption spectra of low concentrated P3HT:PCBM blend (spectra b in Fig. 3), a slightly disordered absorption spectra is noticeable and thermal annealing restored the vibronic structure of P3HT [34]. As it has been shown, the formation of irregular P3HT clusters at low polymer concentrations, the addition of PCBM in these P3HT clusters may disrupt the internal order of the P3HT phase and could lead to a distorted absorption spectra [35,36]. Also, as shown in Fig. 3, with the increase in P3HT:PCBM blend concentration (blend B to D), the structure of P3HT developed into a highly ordered structure as evident by much pronounced vibronic peaks and stronger absorption in the red region [9,37]. The highly ordered P3HT structure perceived here was due to fibrous nature of P3HT and SEM analysis described in Section 3.2 confirms the formation of fibrous P3HT morphology in the highly concentrated polymer P3HT:PCBM blend.

3.2. Morphology studies of P3HT, PCBM and P3HT:PCBM blend films by SEM

SEM images of annealed and non-annealed pure P3HT (50 and 150 nm thick films) films on TiO₂-bl obtained from spin coating in chlorobenzene solution (0.5 and 1.5 wt.%) are shown in Fig. 4. In the SEM image of thick non-annealed P3HT film (Fig. 4a), formation of randomly oriented fibrous like P3HT together with few pinholes is clearly evident. We confirmed from comparative studies that P3HT exhibits bright regions in SEM. Fibrous like P3HT formation occurs as a result of self-organization of regioregular P3HT into a microcrystalline



Fig. 3. Absorption spectra of: P3HT (0.5 wt.%)/PCBM (0.4 wt.%) film (a) before and (b) after annealing, P3HT (1.5 wt.%)/PCBM (1.2 wt.%) film (c) before and (d) after annealing.



Fig. 4. SEM images of pure P3HT films on FTO-bl: P3HT 1.5 wt% (a) before and (b) after annealing, P3HT 0.5 wt% (c) before and (d) after annealing.

structure that overlap each other [28,37-40]. These fibers can aggregate by lateral stacking and aligning along their length. The average width of P3HT strands was found to be ~15 nm while the length of these strands varied from 500 to 1000 nm and even some individual longer strands were noticeable and the length and the width of the strands appeared to be unchanged after annealing (Fig. 4b). Ihn et al. studied the crystalline properties of fibrous P3HT by X-ray and electron diffraction and found the $\pi - \pi$ stacking of P3HT molecules in the direction of b-axis [41]. The high hole mobility $(0.06 \text{ cm}^2/\text{V s})$ reported for single nanofiber has been ascribed to the self-organization of P3HT molecules along the $\pi - \pi$ stacking direction and could be beneficial for better charge collection efficiency and hence for good solar cell performance in P3HT:PCBM blend. Formation of structurally similar fibrous P3HT described above has been reported in p-xylene using concentrated P3HT solution where P3HT is soluble in xylene at elevated temperature and upon cooling, it transforms into a fibrous structure [42]. However, the method described in this study has advantage over the xylene method as our method permits in-situ formation of fibrous like P3HT films at room temperature which allows in-situ preparation of well-mixed polymer blend for solar cell applications. On the other hand, in reference film obtained from P3HT concentration which is three times lower than the 1.5% P3HT solution, as shown in the SEM image of non-annealed pure P3HT (0.5 wt.%) film (Fig. 4c), fibrous like P3HT formation did not materialize indicating that high concentration of P3HT is obligatory factor for the formation of fibrous like P3HT in pure films. However, from the SEM image of low P3HT concentration, the formation of fine clusters of P3HT in the entire film is clearly evident. In low concentration active layer, the dark spots remain even after annealing, whereas in films from concentrated solutions, the dark spots disappear after annealing. The background roughness seen in both SEM images (Fig. 4c and d) is due to underlying TiO₂ blocking layer.

In both SEM images of (figures not shown) annealed and nonannealed pure PCBM (1.2 wt.%) films on TiO₂-bl which was obtained from chlorobenzene, we could not observe a clear crystalline structure even at the highest resolution. Even though, we could not observe crystalline PCBM by our SEM analysis, formation of homogeneous and densely packed fine PCBM clusters has been reported from chlorobenzene solvents through fast solvent evaporation by Transmission Electron Microscopy analysis [42]. Furthermore, these PCBM clusters appeared to form a network-like morphology connecting these clusters continuously. Thus, homogeneously and densely packed PCBM nanocrystals obtained by this method, could facilitate to form a uniform donor–acceptor distribution at the molecular level maintaining a vertical phase separation when PCBM is blended with donor polymer (i.e. P3HT) that allows for maximum charge generation as well as charge collection in donor–acceptor polymer solar cell.

We also studied the morphologies of the different blend films before and after annealing. Since there is no difference in SEM images of before and after annealing, here only SEM images after annealing are given. Fig. 5a, b, c and d show the SEM images of annealed polymer blend films obtained from spin coating P3HT:PCBM blends of A, B, C and D on TiO₂-bl in chlorobenzene solution respectively. As shown in Fig. 5a-d, when the concentration of the blend increases from A to D, formation of randomly oriented fibrous like P3HT at higher P3HT concentration is clearly evident. Earlier we have shown the growth of pure fibrous like P3HT at higher P3HT concentrations (see Fig. 4). However, in the presence of PCBM, P3HT growth into small fibrous threads of 50-150 nm long while the width increases to ~25 nm indicating that PCBM hinders the growth of thin long P3HT fibers [32]. Yang et al. reported the formation of thin and long conducting fibrous like P3HT nanowires with a width of 15 nm and a length of 500 nm in P3HT:PCBM blend that grows into longer fibrils upon annealing [28,43]. However, such a growth of P3HT nanofibers were not observed in our case indicating that the highly defined, stable nanofibers have been formed during spin coating step of P3HT film. As shown in Fig. 5d, these fibrous like P3HT appeared to be segregated more towards air interface in thicker films of blend. It is known that the sequence of the multilayer or vertical phase separation is determined by the different surface energies of the components [44]. Since P3HT has low surface energy than PCBM, P3HT could be preferentially attracted to the interface with air, while higher surface



Fig. 5. SEM images of P3HT:PCBM blends on TiO₂-bl after annealing at 150 °C for 5 min; (a) P3HT (0.25 wt.%)/PCBM (0.2 wt.%), (b) P3HT (0.5 wt.%)/PCBM (0.4 wt.%), (c) P3HT (1.0 wt.%)/PCBM (0.2 wt.%), (d) P3HT (1.5 wt.%)/PCBM (1.2 wt.%). Inset in images (c) and (d) show the magnified section of the bl ends (c) and (d).

energy of PCBM is more compatible with the high surface energy surface like TiO₂ substrate [44]. This could result in a preferential vertical segregation of P3HT and PCBM to cathode and anode electrodes respectively. This type of segregation of P3HT and PCBM provides an ideal structure where donor and accepter are distributed throughout the film with a large concentration of the accepter near the electron-collecting bottom electrode and donor near the hole collecting top electrode [45,46]. Such a phase segregation allows controlled growth of well-defined donor and acceptor interpenetrating networks leading to electron and hole transport paths that is important for optimizing the device performance. The above assignment is based on the idea that during spin coating of concentrated P3HT:PCBM blend, formation of fibrous like P3HT occurs at an early stage of drying process as it has low solubility in chlorobenzene while crystallization of PCBM occurs at a later stage of drying process allowing PCBM to percolate well with P3HT fibers leading to P3HT-rich and PCBM-rich domains [46]. The fact that the absorption spectra of the blend film represents a simple addition of the spectra of PCBM and P3HT, together with SEM image analysis of these blends strongly suggest the desired segregation of P3HT and PCBM. The advantages of such a diffusion of P3HT:PCBM blend for an efficient generation and transport of charges in OPV has been discussed by Campoy-Quiles [47].

On the other hand, when the P3HT:PCBM blend concentration is decreased to P3HT [1.0 wt.%] : PCBM [0.8 wt.%], fibrous like P3HT formation does not occur in the blend as well as in the case of pure P3HT. However from SEM image (Fig. 5c), it is clearly seen the segregation of P3HT-rich clusters and PCBM-rich domains. In the inset of SEM image of blend C, the bright spots are regularly arranged P3HT clusters while dark PCBM rich veins are concentrated in between those regularly arranged P3HT clusters leading to well segregated donor and acceptor phases. Further decrease in blend concentration P3HT [0.5 wt.%] : PCBM [0.4 wt.%] and P3HT [0.25 wt.%] : PCBM [0.2 wt.%] and resulted in uneven distribution of donor and acceptor phases. As shown in SEM images of blends A and B at low

concentrations, spherical white patches are due to large PCBM aggregates while irregular fine P3HT clusters are unevenly distributed in the entire film (the roughness in the background is due to TiO_2 blocking layer). As PCBM has high affinity to hydrophilic surfaces such as TiO_2 [49], it is reasonable to expect that PCBM get accumulated on the TiO_2 surface forming PCBM rich areas.

3.3. Photovoltaic properties

The solar cells fabricated in this study consisted of an active device area of 0.12 cm² of P3HT:PCBM blend (1.0:0.8 wt.%) which was sandwiched between TiO₂ blocking layer coated FTO anode and PEDOT: PSS layer coated Au cathode. The energy levels of various components of the inverted solar cell device are schematically shown in Fig. 6a. As shown in Fig. 6a, the conduction band (CB) of TiO₂ which is -4.4 eV can accept electrons from PCBM as LUMO of PCBM is positioned at ~-4.0 eV and acts as electrons transport layer [48]. Similarly, PEDOT: PSS accepts holes from P3HT as its HOMO energy level is situated above the energy level of P3HT and acts as holeinjection layer [48]. As the device described above was so made-up that, TiO₂ and PEDOT:PSS layers act as electron and hole transport layers respectively, an enhanced charge rectification is expected in the device performance. Fig. 6b compares the I–V characteristics of TiO₂bl, PEDOT: PSS and TiO₂-bl/PEDOT: PSS in the dark at RT. From currentvoltage (I-V) measurements shown in Fig. 6b, it becomes obvious that the presence of only electron transport layer (TiO₂-bl) or only hole transport layer (PEDOT:PSS) results in ohmic behavior due to low shunt resistance (R_{SH}) while diode characteristics improved dramatically in the presence of both electron and hole transport layers due to enhanced rectification nature.

The current density versus voltage (I–V) characteristics of P3HT: PCBM with varied active layer thickness under Air Mass 1.5 Global (AM1.5G) with irradiation intensity of 100 mW/cm² are shown in Fig. 7a. Here no mismatch factor correction could be applied for any possible deviation of our light source from the solar spectrum, but the



Fig. 6. a. Schematic illustration of the energy levels diagram of the inverted solar cell device and the arrows indicate the direction of charge flow. b. Dark rectification of (a) FTO/PEDOT:PSS/Au, (b) FTO/TiO₂-bl/Au and (c) FTO/TiO₂-bl/PEDOT:PSS/Au.

light source is calibrated with a certified Si solar cell supplied by ISE. As shown in Fig. 7a, the device performance is extremely sensitive to the thickness of the active laver. Increase in active laver thickness from 25 to 185 nm resulted in increase in n from 0.34 to 3.71%. Similarly, with the increase in active layer thickness, increase in open circuit voltage (V_{oc}) , J_{sc} and fill factor (FF) were noticeable. Further increase in active layer thickness to 260 nm leads to dramatic decrease in Voc. Jsc and FF as well as efficiency (η) and Table 1 summarizes the device performance as a function of active layer thickness. The best device performance was observed for 185 nm active layer and the observed Voc, J_{sc} , FF and η are 605 mV, 12.7 mA/cm², 49% and 3.7% respectively. Fig. 7b shows the results on IPCE measurements for devices constructed with different active layer thicknesses. Each spectrum shows the known spectral response to its bulk heterojunction components which is excellent agreement with the absorption spectra of each compound. The enhancement in IPCE for thicker P3HT:PCBM layer originates from two important contributions; an increase in charge carrier mobility due to P3HT fibrous nature and increase in absorption due to thicker layer without any pinholes and cracks.

In general, efficient polymer blend solar cells with a configuration of ITO/PEDOT:PSS/active layer/Al, operate with an active layer thickness of 50–100 nm range and exhibit an efficiency of 3% at 1 sun [49,50]. Li et al. investigated the effect of active layer thickness on the solar cell performance and the highest efficiency was reported for a 65 nm thick P3HT:PCBM active layer [40,51]. I e. for the devices fabricated with various thicknesses of P3HT:PCBM (1:1 wt.%) in dichlorobenzene by varying the spin speed, when the active layer thickness increased from 35 nm to 63 nm, the η increased from 1.87% to 4.0% while for a 155 nm active layer thickness has been assigned to optical effect and charge carrier generation rate in the active layer at



Fig. 7. a. I–V characteristics for devices as a function of P3HT:PCBM concentration. (A) P3HT (0.25 wt%)/PCBM (0.2 wt%), (B) P3HT (0.5 wt%)/PCBM (0.4 wt%), (C) P3HT (1.0 wt%)/PCBM (0.4 wt%), (D) P3HT (1.5 wt%)/PCBM (1.2 wt%), (E) P3HT (2.0 wt%)/PCBM (1.6 wt%), The measurements have been performed at 100 mW/cm² AM1.5G conditions. b. IPCE spectra of P3HT:PCBM film as a function of blend concentration. (A) P3HT (0.25 wt%)/PCBM (0.2 wt%), (B) P3HT (0.5 wt%)/PCBM (0.4 wt%), (C) P3HT (1.0 wt%)/PCBM (0.8 wt%), (D) P3HT (1.5 wt%)/PCBM (1.2 wt%), (E) P3HT (2.0 wt%)/PCBM (0.4 wt%), (C) P3HT (1.0 wt%)/PCBM (0.8 wt%), (D) P3HT (1.5 wt%)/PCBM film as a function of blend concentration. Substrate (A) is without TiO₂-bl and substrates (B)–(F) are with TiO₂-bl. (A) P3HT (1.5 wt%)/PCBM (0.4 wt%), (C) P3HT (0.5 wt%)/PCBM (0.4 wt%), (D) P3HT (1.0 wt%)/PCBM (0.2 wt%), (E) P3HT (1.5 wt%)/PCBM (0.4 wt%), (C) P3HT (0.5 wt%)/PCBM (0.4 wt%), (C) P3HT (1.0 wt%)/PCBM (0.4 wt%), (C) P3HT (1.5 wt%)/PCBM (0.4 wt%), (C) P3HT (1.5 wt%)/PCBM (0.4 wt%), (C) P3HT (1.5 wt%)/PCBM (0.4 wt%), (D) P3HT (1.0 wt%)/PCBM (0.8 wt%), (E) P3HT (1.5 wt%)/PCBM (1.2 wt%), (E) P3HT (1.5 wt%)/PCBM (1.2 wt%), (E) P3HT (1.5 wt%)/PCBM (1.2 wt%).

 Table 1

 Summary of the device performance for active layer thickness.

Device	Thickness (nm)	V _{oc} (mV)	J _{sc} (mA/cm ²)	FF (%)	Efficiency (%)
A P3HT (0.25 wt.%)/PCBM (0.2 wt.%)	25	330	2.43	42	0.34
B P3HT (0.5 wt.%)/PCBM (0.4 wt.%)	55	463	6.09	44	1.22
C P3HT (1.0 wt.%)/PCBM (0.8 wt.%)	118	575	10.27	52	3.07
D P3HT (1.5 wt.%)/PCBM (1.2 wt.%)	186	605	12.71	49	3.73
E P3HT (2.0 wt.%)/PCBM (1.6 wt.%)	267	560	10.05	37	2.18

anode and cathode. In recent articles, 3.64% and 4.4% power conversion efficiencies have been reported for 165 and 175 nm active layers respectively by increasing the regionegularity of P3HT polymer [5,40]. These films contained domains of tightly packed fibril P3HT crystallites and pure or mixed PCBM clusters, which were segregated in the region between these P3HT clusters. As mentioned earlier, in the inverted solar cell device which we observed 3.7% efficiency, the active layer was 186 nm thick and it was formed by mixing equal volumes of P3HT (3.0 wt.%) and PCBM (2.4 wt.%) in chlorobenzene in which the formation of fibrous P3HT started only at this high polymer concentration suggesting existence of a strong correlation between solar cell efficiency and formation of fibrous like P3HT. In view of the fact that the fibrous like P3HT polymer contained well interconnected crystal nanofibrils, enhanced solar cell performance could be expected as it would facilitate efficient charge separation as well as charge collection [43,52]. Earlier, we already described the existence of interpenetrating fibrous P3HT throughout the active layer. Therefore, the observed high solar cell efficiency could be attributed to the result of distribution of donor and acceptor throughout the film together with accumulation of accepter near the bottom electrode and donor near the top electrode allowing percolation of electrons and holes in respective charge transport pathways. Furthermore, higher hole mobility of fibrous P3HT compared to P3HT clusters, would also enhance the charge transport and hence solar cell performance [53].

As explained above, the morphological differences in P3HT:PCBM blend with the function of polymer concentration are one of the major reasons for observed higher solar cell efficiency of OPV. Further we have noticed the variations in R_{SH} and R_S as a function of active layer thickness and herein we show how these variations contribute to increase in Jsc. Fig. 7c shows the dark I-V curves of P3HT:PCBM blends as a function of active layer thickness. It is clearly seen that the R_{SH} increases with the increase of active layer thickness from 25 to 250 nm, while R_s remains the same for different layer thicknesses. Based on the equivalent circuit of a photovoltaic cell, high J_{sc} can be expected with large R_{SH} and small R_S[49]. Hence, the observed high J_{sc} for thicker active layer can be justified based on this model. On the other hand, since FF is limited by the carrier drift length ($L_d = \mu \tau E$, where μ , τ and E are carrier mobility, carrier recombination lifetime and electric field respectively), a high mobility or thin film is necessary for efficient charge carrier extraction [54–55]. As shown in Fig. 7a and Table 1, the FF increases with the increase in active layer thickness up to 186 nm and thereafter it decreases rapidly. If only charge carrier length is considered, the FF should decrease with the increase of active layer thickness. Since the charge carrier mobility through fibrous P3HT is better than that of P3HT clusters, with the formation of fibrous P3HT, the thickness of the active layer can be increased without increasing the Rs and hence without losing the FF values. Also it has been reported that to absorb greater than 95% of incident light in the visible region, a P3HT film of 240 nm thickness is needed [2]. Hence it can be concluded that the trade-off between charge carrier mobility and active layer thickness establish the optimum device performance for 186 nm thick film. Furthermore, we compared the rectification behavior of P3HT:PCBM films with and without TiO_2 -bl. Traces A and E in the Fig. 7c are dark IV curves of active layer thickness of 186 nm or the P3HT (1.5 wt.%)/PCBM (1.2 wt.%) samples without and with TiO_2 blocking layer respectively. As obvious, a better rectification in the presence of TiO_2 -bl for the same active layer thickness is clearly noticeable indicating that TiO_2 -bl actively enhances the charge collection and diode behavior which in turn contribute to higher solar cell efficiencies.

It is known that the efficiency of the devices is limited by transport properties of the absorber and as a result, the active layer thickness must be kept low at the expense of the photogeneration of charge carriers. Since we used relatively a thicker active layer, we investigated the J_{sc} and V_{oc} dependence on illumination intensity to verify that the charge carriers are not limited by space charge buildup in our system [56,57]. Fig. 8 shows the J_{sc} and V_{oc} as function of light intensity for a 180 nm thick active layer solar cell device. The V_{oc} increased monotonically with an increase in the light intensity and approached 0.6 V under at 80 mW/cm². As shown in Fig. 8, J_{sc} increases with the increase of light intensity and nearly linear dependence of the J_{sc} against light intensity indicates that there is no substantial space charge buildup in the 186 nm thick active layer device. It also points out that the efficiency of device is mainly limited by the charge-transport properties of the absorber materials.

As explained above, an inverted architecture of OPV fabricated using concentrated P3HT:PCBM blend resulted in enhanced solar cell performance. Considering the structural properties of the blend film, the higher efficiency of the inverted solar cell could be assigned to; (a) formation of fibrous like P3HT and (b) interpenetrating P3HT fibers/PCBM blend throughout the film. Since the interpenetrating network enhances the charge separation while enhanced rectification helps to direct the charge towards their respective electrodes and reduce charge recombination, the high solar cell performance obtained in this study is very obvious.

Since, the short operational stability and lifetime still remain one of the key issues of polymer photovoltaic which limits their widespread applications, we studied the storage stability of nonencapsulated polymer cells under ambient conditions and the results are shown in Fig. 9. For stability test measurements, non-capsulated polymer cells were stored under air in RT and IV measurements were done every 7 days. As shown in Fig. 9, the Voc and FF remain unchanged for 100 days while J_{sc} and efficiency remain above 83% and 81% respectively of their initial values for more than 50 days. These results are really remarkable if one considers the very low stability of



Fig. 8. Plot of J_{sc} and V_{oc} of the inverted P3HT:PCBM (186 nm thick) solar cell with different incident light intensities from 0.1 to 100 mW/cm² (AM1.5G solar spectrum).



Fig. 9. Plots of Voc, J_{sc}, FF and η as a function of days. The samples were stored in air under dark at RT and IV measurements were done on every 7 days at illumination intensity of 100 mW/cm² AM1.5G.

non-inverted conventional devices with ITO/PEDOT:PSS/active layer/ Al configuration [58]. However, after 100 days, J_{sc} and efficiency posses 42% and 40% of their initial values respectively. The FF is stable over the times, but V_{oc} decreases slightly. These stability results are remarkable for non-capsulated P3HT:PCBM solar cells and can be attributed to the following reasons; organic solar cells degrade because of their low resistance towards oxygen, light, high temperatures, etc. [59]. Both the photoactive layer and the top electrode material are affected by combined influence of oxygen, light, humidity and temperature. Most notably when aluminum is employed as the anode, it has been demonstrated that aluminum metal reacts with the organic materials moisture and gradually degrades giving rise to a poor electrical contact and rapid lowering of the short circuit current. Also, low work function aluminum gets oxidized rapidly and form oxide layer owing to oxygen diffusion. Since inverted structure is designed in this study, low work function aluminum was replaced with the high work function gold, which is very stable with respect to oxygen diffusion and therefore a lowering in Jsc would not be expected due to deterioration of cathode electrode. Also, in normal polymer solar cells, PEDOT:PSS is deposited on ITO glass which is known to corrode ITO layer specially at elevated temperature due to highly acidic nature of PEDOT:PSS which results in unstable polymer solar cells [60,61]. As this problem is avoided by using an underlying titanium oxide layer in the inverted structure, a significant improvement of stability of anode can be expected. Also another common drawback of most organic solar cells is that P3HT and PCBM are sensitive to moisture and oxygen that can be overcome by encapsulation the device. At the moment we are not sure whether the fibrous nature of P3HT additionally contributes to enhanced stability. We are in the process of investigating the long term stability with encapsulated device.

4. Conclusions

We prepared fibrous like P3HT films on conducting glass by increasing the polymer concentration in chlorobenzene. By using these fibrous like P3HT polymers, we fabricated highly stable P3HT: PCBM solar cells with an inverted structure in which both electron and hole transport layers at respective interfaces improve charge collection. In such an inverted structure, solar cell performances were highly sensitive to the film thickness of the polymer blend. Solar cell performance studied as a function of film thickness indicated that a desired thick absorption film can be prepared resulting in the formation of fibrous like P3HT without losing charge collection efficiency. The higher efficiency can be attributed to the combined effects of enhanced rectification and charge mobility of fibrous P3HT. Interpenetrating network of donor-acceptor throughout the film provides ideal structure for better charge separation as well as charge transport. Inverted OPVs are found to be more stable than normal OPVs. Thus the conflict between low charge transport in thick active layers and the necessity of thick layers for efficient light harvesting is elegantly solved in an inverted cell.

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