

The Inverted Double Heterojunction Organic Photovoltaic Devices using Electrospun TiO₂ Nanofibers

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Abstract— The introduction of electrospun TiO₂ nanofibers has improved the performance of inverted poly (3-hexylthiophene) (P3HT) and (6, 6)- phenyl-C₆₁- butyric acid methyl ester (PCBM) solar cells by providing efficient charge generation and collection through double heterojunction. Electrospun TiO₂ nanofibers increased the charge separation and collecting capability of the devices both from P3HT and PCBM by providing interfaces between P3HT-TiO₂ and PCBM-TiO₂ nanofibers. The resulting devices have reached to maximum power conversion efficiency (PCE) of 4.25±0.03% contributed by increased short circuit current (J_{sc}).

Keywords— Heterojunction, inverted, nanofibers, organic

I. INTRODUCTION

The simple fabrication techniques available for organic photovoltaic devices (OPV) [1-7] make them the focus of research to overcome the challenges regarding conversion of solar energy into electricity. Among the various device fabrication techniques, low temperature processed [6] solution based techniques [4,7-9] provide affordable low-cost [10] while the advantage of large-area [3,11] further enforces the concentration toward OPV devices. To achieve high-power conversion efficiency (PCE) for an OPV device is one of the challenges for the researchers.

There are various techniques [9,12-14], applied to improve the efficiency of these devices. The design of device structure [14-16] and introduction of versatile materials [17-22] are the basics techniques in this respect. The devices with the monolayer [23-25], bilayer [26,27], bulk-heterojunction [28-31] and double heterojunction [32] are the demonstrations of structure modification. The active layer in a conventional OPV device consists of a *p*-type donor (polymer) and an *n*-type acceptor (fullerene) semiconductor material. The optical properties like bandgap, the level of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are the controlling parameters for selection of the active layer materials to fabricate efficient OPV. Poly(3- hexylthiophene) (P3HT) and (6, 6)- phenyl-C₆₁- butyric acid methyl ester (PCBM) is the extensively studied active layer materials [2,33-36]. Poly[2-methoxy-5-(2'-ethylhexyloxy)-*p*-phenylene vinylene]

(MEH-PPV) [29,37] based devices are also reported to improve the PCE. There are many other reports where versatile organic materials were used as an active layer [15,17,38,39].

The poor ordering and amorphous nature of the polymer film affect the charge transport properties like carrier mobility (10⁻⁴~10⁻⁵cm²/V s) [40] and is a limiting barrier toward higher efficiency in OPV. These challenges were tried to minimize by introduction of metal oxide materials due to their excellent charge transport properties like high carrier's mobility and efficient electron transport material [41]. Though there are diverse metallic oxides [42] for this purpose but most widely used are ZnO and TiO_x/TiO₂ [43-45]. The efficiency of the devices was improved by introducing metal oxide thin layer at distinct position with respect to the active layer. The role of this layer was demonstrated in different ways, acting as interface modification [46] or an optical spacer [14,47] layer, are the highly investigated aspects. The electron and hole collecting electrode divide the device structure into normal (substrate/hole collecting contact/active layer/electron collecting contact) and inverted (substrate/electron collecting contact/active layer/hole collecting contact) one. The contact deposited on to the substrate (bottom contact) is usually indium doped tin oxide (ITO) or fluorine doped tin oxide (FTO). The deposition of metal oxide (electron acceptor) on top of active layer makes the device as normal, however, the device is inverted when electron transport/hole blocking layer is deposited on top of the bottom electrode.

The reported devices achieved maximum PCE are based on normal bulk heterojunction structure [15,48], where the blend of donor and acceptor provides the interface at an ideal distance comparable to exciton diffusion length (5-10nm) [49-52] in a donor polymer. However, the exciton dissociation alone can't increase the device efficiency until the resultant carriers are collected by the respective electrode. In order to maximize the collection of the separated carrier's loss mechanisms like, interface losses and carrier mobility has to be taken into consideration. To investigate such problems interface modification[43,53] and application of nanostructures [54] like nanotubes were introduced in inverted OPV. The efficiency of the interface modified devices increased tremendously by improving the open-circuit voltage (V_{oc}) [55] while introduction of nanostructure like nanotubes in OPV improved PCE not only by increasing V_{oc} but also a major contribution by short circuit current (J_{sc}). There are various challenges regarding porous structures like nanotubes and nanofibers network, such as; 1) the infiltration of the polymer: fullerene blend through the pores to the root of the nanotubes, and 2) the control over the thickness of the active layer.

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The incomplete infiltration introduces defects by vacant spaces/poor adhesion at the interface while the increased thickness of metal oxide (acceptor) reduces the light absorption for donor by occupying most of the device volume as an acceptor. This introduces an imbalance in the donor/acceptor ratio, which reduces device efficiency. In order to minimize such a challenge, metal oxide electrospun nanofibers are the best candidates to improve the OPV device performance. By using this technique one can control the density of nanofibers, porosity and thickness of the nanofibers. The control of the diameter of these fibers provides extra features for improvement in performance of OPV devices. We have already demonstrated the parameters controlling the infiltration of blend through the electrospun nanofibers[56].

This work demonstrates the role of electrospun TiO₂ nanofibers in P3HT: PCBM bulk heterojunction devices by providing an extra ordered heterojunction in addition with the bulk heterojunction and therefore, increased charge transfer at the interfaces and transport through the active layer to the bottom electrode and thereby, a higher resultant short circuit current.

II. MATERIALS AND METHODS

A. TiO₂ nanofiber synthesis

The TiO₂ sol for electrospinning was prepared as reported [57] by mixing poly(vinylpyrrolidone) (PVP) as a polymer. The concentration of the precursor, titanium tetraisopropoxide (Ti(OiPr)₄) (Sigma Aldrich) in the sol was optimized (0.15ml) to obtain the required parameters of nanofibers for this particular solar cell device. To obtain homogenous sol- gel for electrospinning, two separate solutions were mixed together and stirred for 10h at room temperature in order to attain optimum viscosity. The first solution contains dissolved Ti(OiPr)₄ by stirring for 35min at room temperature in a mixture of 2ml of ethanol and 0.25ml of acetic acid, which was added drop wise by using a 1ml syringe. The second solution was obtained by dissolving 0.3g PVP (Sigma Aldrich MW 40, 000) in 3ml of ethanol by stirring at room temperature for 30min.

The precursor mixture was immediately loaded into a plastic syringe equipped with a needle made of stainless steel. The internal diameter of the needle was 0.25mm. The distance between the tip of the needle and the collector plate was fixed to 10cm. The nanofibers were extracted from the needle by applying an optimum high voltage of 9.25kV between the needle and the collector plate by connecting to a positive and ground terminal of the high-voltage source respectively. The electrospinning time was optimized to 10min in order to get optimum thickness of the nanofibers mat having controlled interconnected network. The continuous nanofibers were extracted by fixing a flow rate of 0.25ml/h. The role of humidity is very important to obtain the required parameters of the nanofibers, so electrospinning was performed at room temperature, while the humidity in the air was 25~30%. Then as spun nanofibers were left in air about 12h to allow the complete hydrolysis of Ti(OiPr)₄. The TiO₂/PVP composite nanofibers were finally calcined in air at 350°C for 3h to obtain a nanofibrous network with optimum morphology.

B. Photovoltaic Devices Fabrication

The ITO coated glass substrates having sheet resistance 15Ω/sq, were cleaned by sonication of 10min each in isopropanol alcohol, acetone and de-ionized water followed by drying using nitrogen gas. A blend of poly(3-hexylthiophene) (P3HT) (Rieke Metals, Mw 48000, regioregularity 93%) and PCBM (Ossila) was prepared by mixing (1:1ratio) solution of P3HT (12mg/ml) and PCBM (10mg/ml) in chlorobenzene. The devices in this particular study were referred as D1 (ITO/blend/PEDOT: PSS/Ag), D2 (ITO/TiO₂/blend/PEDOT: PSS/Ag) and D3 (ITO/TiO₂/TiO₂ nanofibers/blend/PEDOT: PSS/Ag), having detailed structure as follows; D1) is the controlled device for studying the role of electrospun nanofibers. The blend was spin coated at 1300rpm for 30s to obtain an optimum thickness (171±15nm) of the active layer. The thickness was kept almost fixed for all the other devices by varying thickness controlling parameters in order to study the effect of electrospun nanofibers on device performance. Then a layer of PEDOT: PSS (Sigma Aldrich) was spin coated at 5000rpm for 65s on top of active layer to avoid any damage to the layer caused by top contact deposition mechanism. The device was annealed at 140°C for 10min prior to the deposition of 100nm thick Ag contact. D2) was fabricated by spin coating (2700rpm/30s) a sol of Ti(OiPr)₄ (0.10ml) dissolved in (5ml) ethanol onto ITO coated cleaned glass substrate. The substrate was placed in air for 7h to complete hydrolysis followed by annealing of the film at 350°C for 3h. This layer has a thickness of ~20nm and act as a hole blocking layer (HBL). The blend was spun coated (1250rpm/40s) to achieve active layer thickness of 184± 14nm. The device (D3) having electrospun nanofibers on top of HBL infiltrated by P3HT: PCBM blend. The remaining steps were identical for both the devices (D2, and D3) as that of the control device. The thickness of the electrospun nanofibers mat was 162±15nm, which increased to 179±13nm by blend infiltration through spin coating (1100rpm/50s) on top of it. The active area of each device was 0.84cm². The schematic of the electrospun nanofibers/P3HT: PCBM double heterojunction device is shown in Fig. 1a.

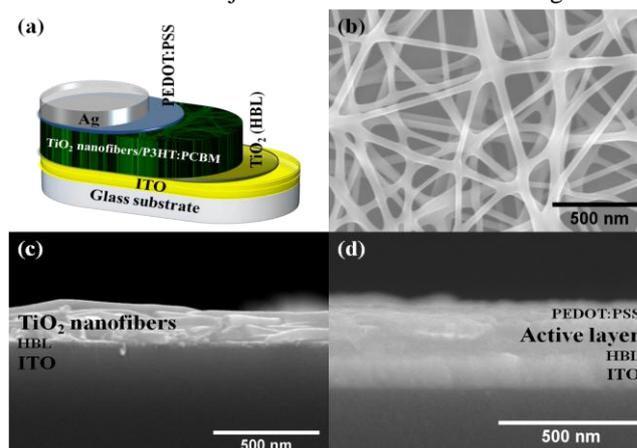


Fig. 1(a) Schematic of the inverted double heterojunction P3HT: PCBM blend infiltrated into electrospun TiO₂ photovoltaic device. FE- SEM images of; (b) electrospun TiO₂ nanofibers network used for double heterojunction devices, (c) cross-section view of the electrospun TiO₂ nanofibers network on top of a HBL coated on ITO glass substrate, and (d) cross-sectional view of the ITO/TiO₂(HBL)/electrospun TiO₂ nanofibers/P3HT: PCBM/PEDOT: PSS layers prior to contact deposition.

The morphology of the fabricated TiO₂ nanofibers was studied by Hitachi S-4700 field emission scanning electron microscope (FE-SEM), the area of the pores in the nanofibers network and diameter of nanofibers was analyzed by ImageJ software. The thickness of the layers was measured by α -step surface profiler while UV-Vis absorption spectroscopy was carried out by Perkin Elmer Lambda 750 spectrophotometer. Cell current-voltage characterization was conducted by using Keithley 236 source meter in the glove box. The photovoltaic performance of fabricated devices was studied by a solar simulator AM 1.5G, under illumination of 100mw/cm² (Newport 69911). The incident photon to current conversion efficiency (IPCE) was measured by using PV Measurements Inc.

III. RESULTS AND DISCUSSION

The surface morphology of the nanofibers and cross-sectional analysis of different device layers was analyzed by SEM images as shown in the Fig. 1b-d. The thickness and porous area of the nanofibers network control the infiltration of P3HT: PCBM blend, which is directly related to performance of the devices [56], while the diameter of the nanofibers controls the exciton dissociation. The porosity through the network among the nanofibers was calculated to be 0.016±0.01μm² while the diameter of the nanofibers was 45±17nm.

The absorption spectrum of each layer is shown in Fig. 2, which predicts the role of absorption corresponding to that particular layer in the fabricated device. The P3HT: PCBM blend has a maximum absorption around 518nm, while the absorption tail at lower wavelength is abrupt. The introduction of TiO₂ (HBL) layer not only increased the absorption efficiency of the blend but also broadened the narrow tail toward the UV-region of the wavelength. This indicates an increase of absorption in the lower wavelength region. The electrospun nanofibers on to the HBL layer, infiltrated by the blend show the maximum absorption and occupy most of the UV- Vis spectra.

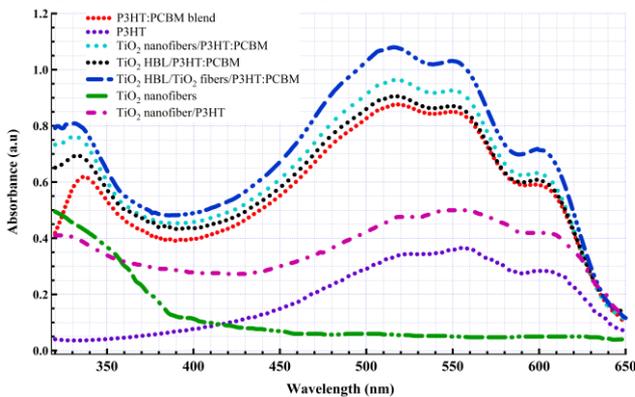


Fig.2 UV- Vis spectroscopy of P3HT film spin coated on glass substrate and the other structural layers as indicated.

The *J-V* characteristic of the fabricated inverted geometry devices illuminated by 1.5 G solar simulator is shown in Fig.3, which explains the effect of various device geometries on *V_{oc}* and *J_{sc}*. The devices fabricated only by P3HT: PCBM blend have the lowest PCE (1.53±0.03%) as compared to other devices as explained in Table 1. The low PCE of the control device is the result of disordered structure, which provides poor carriers mobility[58].

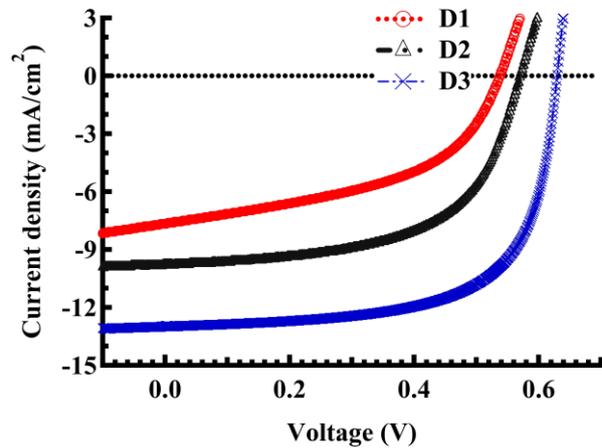


Fig.3 *J-V* characteristics under 1.5G solar illuminations, of the devices with different structures; (D1) ITO/P3HT: PCBM/PEDOT: PSS/Ag, (D2) (ITO/TiO₂ (HBL)/P3HT: PCBM/PEDOT: PSS/Ag), and (D3) (ITO/TiO₂ (HBL)/TiO₂ nanofibers/ P3HT: PCBM/PEDOT: PSS/Ag).

Table 1 The parameters of the fabricated inverted organic photovoltaic devices under 1.5 G solar illuminations

Device	Structure detail	<i>V_{oc}</i> (V)	<i>J_{sc}</i> (mA/cm ²)	FF	PCE (%)
D1	ITO/P3HT: PCBM/PEDOT: PSS/Ag	0.53	7.673	0.37	1.53±0.03
D2	ITO/TiO ₂ (HBL) /P3HT: PCBM/PEDOT: PSS/Ag	0.57	9.8	0.56	3.13±0.02
D3	ITO/TiO ₂ (HBL)/TiO ₂ nanofibers/P3HT: PCBM /PEDOT: PSS/Ag	0.63	12.98	0.52	4.25±0.03

The one-diode model [59], was used to analyze the behavior of the devices by considering the *J-V* curve. The double heterojunction provided by electrospun nanofibers improved the charge collection at the interface, which is evidenced by the increased *J_{sc}* as shown in Fig. 3 and confirmed by IPCE in Fig. 4 for the device, D3. The TiO₂ nanofibers increased the absorption of the incident photons (Fig. 2), consequently, increased exciton generation. On the other hand, nanofibers helped; 1) in exciton dissociation at the P3HT/nanofiber interface so maximum carriers are generated, 2) to extract carriers both from P3HT and PCBM and finally 3) to guide the carriers straight to the electrode by providing low mobility. The nanofibers, therefore, have fewer recombination centers and reduced losses to improve *J_{sc}*. The nanofibers/PCBM interface enhanced the electron transfer from PCBM to nanofibers and to the cathode of the device. In this way, the device fabricated by double heterojunction delivered maximum power conversion efficiency (PCE) (4.25±0.03%), which is a contribution of the increased *J_{sc}* provided by introduction of nanofibers network as discussed earlier.

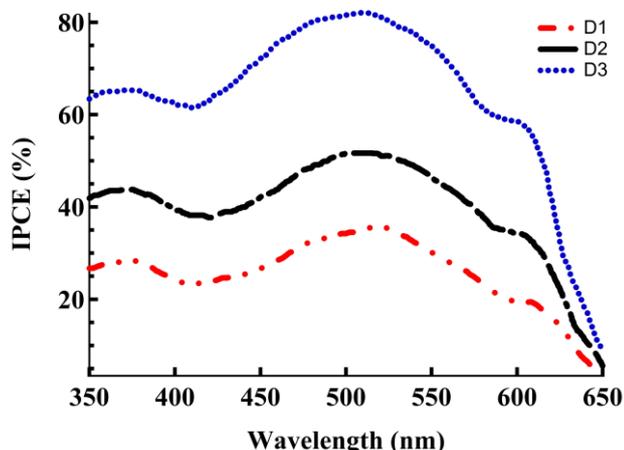


Fig.4 Incident photon to current conversion efficiency of the inverted fabricated devices (D1) ITO/P3HT: PCBM/PEDOT: PSS/Ag, (D2) (ITO/TiO₂ (HBL)/P3HT: PCBM/PEDOT: PSS/Ag), and (D3) (ITO/TiO₂ (HBL)/TiO₂ nanofibers/P3HT: PCBM/ PEDOT: PSS/Ag).

The fill factor (FF) of the control device (D1) is reduced by the high series resistance (10 Ω-cm²) and low shunt resistance (~203 Ω-cm²) compared to other devices. This is one of the possible reasons to reduce the V_{oc} of the devices. On the other hand, introduction of TiO₂ layer in the device D2 and D3 affected the performance of the devices drastically in different ways. Firstly, it acts as HBL to improve the FF (0.56) by surface modification, as well as suppressing the contact resistance [60]. This layer has also increased the V_{oc} up to 0.57V as reported earlier [41,42]. The second advantage of the layer is as a hydrophilic surface, which is always beneficial to the adhesion of polymer films (devices D2 and D3) and electrospun nanofibers (device D3), leads to increased FF. The thickness of this layer is critical for a contribution toward series resistance and therefore, FF of the device.

There was an increase in series resistance (6.5 to 8.7 Ω-cm²), of the devices fabricated with electrospun nanofibers (D3) as compared to the devices (D2) without nanofibers, which reduced the FF (0.56 to 0.52) of these devices as indicated in Table 1.

The IPCE determined the number of photogenerated charge carriers contributing to the photocurrent per incident photon and has a highest value more than twice (82% at 512nm) for the devices fabricated by electrospun TiO₂ nanofibers (D3), as compared to the control devices (D1) having maximum IPCE about 35%. This improvement is attributed to the introduction of double heterojunction provided by electrospun nanofibers and evidenced by an increase in both, the absorption (Fig. 2) and J_{sc} (Fig. 3). The HBL layer (D2), plays the role of electron selective layer, which in turn enhanced electron transport to the ITO electrode and thus enhanced IPCE [61] as depicted by Fig. 4. Though this layer is very important for the electrospun nanofibers based devices (D3) as for as adhesion of nanofibers is concerned to improve FF, but contribution toward increased IPCE is small (51.6%) compared to nanofibers, as predicted from Fig. 4.

The series resistance of the device (D3) has increased by the introduction of nanofibers as interfaces are increased due to deposition of a number of nanofiber layers but shunt resistance has also increased 1350 Ω-cm², which is much higher than the value (203 Ω-cm²) for control device (D1). Such variations in the device resistance have contributed

toward performance by reducing the FF (0.52 to 0.56) [58], increasing the V_{oc} (0.57 to 0.63V), and finally improving the PCE to a maximum value of 4.25±0.03%.

IV. CONCLUSION

The inverted P3HT: PCBM heterojunction devices were fabricated by interface modification through TiO₂ spin coated thin layer, which improved both the V_{oc} and FF up to 0.57V and 0.56 respectively. The PCE of these devices was higher as 3.13%. This work was further extended by introduction of electrospun TiO₂ nanofibers, which improved both the V_{oc} (0.63V) and J_{sc} (12.98mA/cm²) by providing a double heterojunction in the P3HT: PCBM blended active area. The nanofibers enhanced the IPCE of the devices up to 82% by increased absorption of the incident photons, which leads the devices to attain 4.25±0.03% PCE.

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