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Flexible inverted polymer solar cells containing an amorphous titanium oxide
electron collection electrode

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Abstract

An inverted polymer solar cell was fabricated on a polyethylene terephthalate (PET) substrate. The cell structure was ITO/ amorphous titanium oxide (TiO_x)/[6,6]-phenyl C_{61} butyric acid methyl ester (PCBM): regioregular poly(3-hexylthiophene) (P3HT) /poly (3,4-ethylenedioxylenethiophene):poly(4-styrene sulfonic acid) (PEDOT:PSS)/Au (TiO_x cell). It was achieved using low boiling point diethyl amine (DEA) as a Ti^{4+} complexing agent, and high boiling point 1,2,3,4-tetrahydronaphthalene (Tetralin) containing 2 vol. % 1,8-octanedithiol (ODT) as the solvent for PCBM:P3HT film preparation. With heat treatment at 100 °C, the use of DEA and Tetralin:ODT made it possible to prepare a TiO_x electron collection layer and PCBM:P3HT photoactive layer, respectively. Fabricating the TiO_x cell on the thin PET film was possible, as PET did not warp at 100 °C. The power conversion efficiency (PCE) of the TiO_x cell fabricated on PET was 2.43 %, under AM1.5G conditions. When fabricated on glass, the PCE was 2.76 %. When [6,6] diphenyl C_{62} bis(butyric acid methyl ester) (bis-PCBM) was instead used as the electron acceptor in the photoactive blend layer, the flexible air-stable cell provided a PCE of 2.81 %.

Key words: air-stable, amorphous titanium oxide, flexible solar cell, polymer solar cell

1. Introduction

Much attention has recently been given to polymer solar cells, as candidates for the next generation of solar cells. They are expected to provide a low-cost, environmentally friendly, flexible, easily scaled up and lightweight alternative to the silicon solar cells currently in widespread use.[1-3] The organic active layer of polymer solar cells typically consists of a *p*-conjugated polymer donor and fullerene derivative acceptor, and is prepared by wet-processes such as spin-coating or roller-printing. The power conversion efficiency (PCE) of polymer solar cells has recently achieved 6-7%, which has arisen from the development of new *p*-conjugated polymers [4-7] and fullerene derivatives.[8, 9] The *p*-conjugated polymers such as copolymers of benzodithiophene and thienothiophene absorb at long wavelengths and may also possess a low energy HOMO level. Studies investigating their commercial viability (e.g. durability improvement, cost effective production of large-scale flexible cells) are also of great interest and importance, in addition to those investigating their efficiency enhancement. We have been developing air-stable inverted polymer solar cells. Such inverted cells are comprised of a multilayered structure and have a reverse geometry compared with that of a normal cell. Both cell geometries are depicted schematically in Figure 1. In a normal solar cell, the back Al electrode effectively collects electrons because of its low work function. However, its performance is quickly degraded when Al surface deposition is not carried out under ultrahigh vacuum.[10] High durability can be obtained for the inverted solar cell geometry because the transparent metal oxide (e.g. amorphous titanium oxide (TiO_x) or zinc oxide (ZnO)) provides a non-corrosive electron collection electrode. We previously reported that the performance of an unsealed inverted polymer solar cell with the structure $\text{ITO}/\text{TiO}_x/\text{PCBM}:\text{P3HT}/\text{PEDOT}:\text{PSS}/\text{Au}$ (denoted as TiO_x cell) was maintained under continuous light irradiation for 100 h in an ambient atmosphere.[11] This structure is a promising candidate for further studying polymer solar cell durability improvement.[12-14]

Preparing robust, light weight, flexible polymer solar cells is important for encouraging their widespread use. Several papers have reported the fabrication of polymer solar cells on flexible substrates.[15-21] Krebs et al. fabricated modules from PET-ITO/ZnO nanoparticles/PCBM:P3HT/PEDOT:PSS/Ag cells using a roll-to-roll process,[22] and showed that the PCE reached 2.33% from a working area of 4.8 cm². Flexible inverted polymer solar cells containing ZnO nanoparticles as an electron collection layer,[22, 23] or Cs₂CO₃ as a buffer layer,[24] have been reported by other research groups. However, such solar cells containing TiO_x films have not been reported, because the PET substrate easily warps during heat treatment. In the current study, we report a flexible TiO_x cell fabricated on a PET substrate, with a photoactive area of 1 cm². This cell exhibited a maximum PCE of 2.8 % under AM1.5G conditions.

2. Experimental Section

2.1. Materials.

Titanium (IV) isopropoxide (Ti(OCH(CH₃)₂)₄), acetylacetone (AA) (CH₃C(O)CH₂C(O)CH₃), diethylamine (DEA) (CH₃CH₂NHCH₂CH₃), regioregular P3HT (Mw 87,000), PEDOT:PSS 1.3 wt % dispersion in water, polyoxyethylene tridecyl ether (PTE), chlorobenzene (CB), o-dichlorobenzene (DCB), 1,2,3,4-tetrahydronaphthalene (Tetralin) and 1,8-octanedithiol (ODT) were purchased from Sigma-Aldrich Chemical Co., Inc. PCBM was purchased from Frontier Carbon Corporation. Bis-PCBM was purchased from ATR Company. All chemicals were used as received. Glass-ITO substrates (sheet resistance = 10 Ω/sq.) and Au wires were purchased from the Furuuchi Chemical Corporation. PET-ITO substrates (sheet resistance = 30 Ω/sq., thickness of PET sheet = 125 μm) were obtained from Nakai Industrial Co., Ltd.

2.2. Preparation of TiO_x layers

TiO_x precursor solutions were prepared under a N₂ atmosphere as described in our previous paper.[12] Precursor solutions were stored under a N₂ atmosphere following filtration, and were then diluted with 2-propanol, to prepare TiO_x layers by spin-coating onto the ITO electrode at 2000 rpm. The films were then hydrolyzed for 30 min in a controlled atmosphere with a relative humidity about 45%. The films were heated at various temperatures for 1 h on a hot plate, to remove the solvent and complexing agent. Two kinds of TiO_x films prepared from the precursor solutions containing complexing agents AA and DEA were denoted as AA-TiO_x and DEA-TiO_x, respectively. Figure S1 shows the plots of the thickness of TiO_x film versus the concentration of the DEA-TiO_x precursor solution. The thickness was estimated by cross-sectional AFM imaging. The TiO_x films of 30 and 100 nm in thickness were used for the TiO_x cells containing Glass-ITO and PET-ITO substrates, respectively.

2.3. Fabrication of organic solar cells.

ITO-Glass electrodes were cleaned by sonication in 2-propanol, washed in boiling 2-propanol, and then dried in air. PET-ITO electrodes were cleaned only by sonication in 2-propanol to prevent substrate warping. For spin-coating, PET-ITO electrodes were fixed on glass plates using adhesive tape. Cell fabrication was carried out in a N₂ filled glove box with less than 1 ppm moisture and 1 ppm oxygen as follows. The AA-TiO_x or DEA-TiO_x films were prepared by the method described above. A mixed solution of P3HT and PCBM (weight ratio = 5:4) was spin-coated onto the ITO/TiO_x substrate. A PEDOT:PSS dispersion in water containing 0.01 wt.% PTE was heated to 85 °C, and then spin-coated onto the PCBM:P3HT layer. The Au back electrode was vacuum-deposited at 2×10^{-5} torr onto the PEDOT:PSS layer. Finally, the device was heated at various temperatures for 5 min to crystallize the P3HT, and

then at 70 °C for 30 min. The effective area of the solar cell was restricted to 1 cm², by depositing the Au electrode with a shadow mask.

2.4. Measurements.

I-V curves of solar cells were measured by linear sweep voltammetry at a scan rate of 5 V min⁻¹, under AM 1.5G simulated sunlight conditions of 100 mW cm⁻² intensity. The light source was a SAN-EI Electric XES-502S solar simulator calibrated by an EKO MS-601 pyranometer. All electric measurements were performed using a Hokuto Denko HZ-5000 electrochemical analyzer. UV-vis absorption spectra were measured using a Hitachi U-3310 spectrophotometer. Atomic force microscopy (AFM) was carried out using a SII SPI3800N AFM apparatus. All measurements were carried out under an ambient atmosphere (15-30 °C, 40-60% relative humidity).

3. Results and Discussion

3.1. TiO_x layer prepared by drying at 100 °C

The boiling points of DEA (55 °C) and AA (140 °C) are sufficiently low to allow their use as complexing agents for TiO_x precursor solutions, and to fabricate TiO_x cells at low-temperature. TiO_x films on ITO-glass substrates prepared from the AA-TiO_x and DEA-TiO_x precursor solutions were dried at 100 or 150 °C. Figure 2 shows *I-V* curves of the polymer solar cells containing TiO_x films, and cell performance is summarized in Table 1. When the TiO_x layer was dried at 150 °C, and TiO_x cells containing PCBM:P3HT were annealed at 150 °C, both AA-TiO_x and DEA-TiO_x cells exhibited PCE values of ~2.2 %. These two cells are denoted as AA-150/CB-150/glass and DEA-150/CB-150/glass, respectively. Throughout this manuscript, the first label represents the complexing agent and TiO_x film heating temperature. The second label represents the solvent and PCBM:P3HT film

heating temperature. The third label represents the substrate, as glass or PET. For a controlled experiment, a TiO_x cell was fabricated using a TiO_x layer prepared from a precursor solution containing no complexing agent (denoted as Non-150/CB-150/glass). TiO_x layers prepared from precursor solutions containing complexing agents acted as electron collection layers, and were superior to that prepared from a precursor solution without complexing agent. When TiO_x layers were dried at 100 °C, PCE values of the AA- TiO_x and DEA- TiO_x cells decreased to 0.66 and 1.10 %, respectively. TiO_x cells containing PCBM:P3HT blend film prepared from the CB solution, were heated at 80 °C for 5 min (denoted as AA-100/CB-80/glass and DEA-100/CB-80/glass). Their PCE values were small compared with those of the cells prepared by treatment at 150 °C, and the performance of DEA-100/CB-80/glass was better than that of AA-100/CB-80/glass. DEA could more easily be removed from the TiO_x film by heat treatment at 100 °C than AA, as the DEA boiling point was lower than the drying-temperature. This may have resulted in a small electrical resistance of the DEA- TiO_x film, and a higher PCE was obtained for DEA-100/CB-80/glass prepared at lower temperatures.

3.2. PCBM:P3HT films prepared by heating at 100 °C

When the DEA- TiO_x layer was dried at 150 °C, DEA-150/CB-80/glass exhibited a low PCE of ~1.1 % (Table 1). This was probably because P3HT in the blend film had not crystallized at 80 °C, and suggested that PCBM:P3HT did not act as a sufficient photoactive layer. Solvent annealing is one of the major methods used so far to improve the performance of P3HT:PCBM bulk-heterojunction solar cells.[25-27] The blend film was slowly prepared by using high boiling point solvents such as o-DCB (180.5 °C), and the crystallization of P3HT was achieved without thermal annealing. Thus, DCB was used instead of CB to obtain a more effective photoactive layer. Figure 3 shows *I-V* curves of cells containing CB and

DCB, and their performance is summarized in Table 2. For DEA-100/DCB-80/glass, a PCE of ~2.4 % was obtained, because P3HT crystallization had proceeded considerably. This was confirmed from absorption spectra of the PCBM:P3HT film, where crystalline P3HT showed an enhanced shoulder at around 600 nm (Figure S2).

3.3. Fabrication of flexible TiO_x cells

DEA- TiO_x cells containing PCBM:P3HT prepared using DCB, were fabricated on ITO-glass and PET-ITO substrates at a relatively low temperature of 100 °C. DEA-100/DCB-100/glass showed the short-circuit photocurrent (J_{sc}) of 6.91 mA cm^{-2} , an open-circuit voltage (V_{oc}) of 0.59 V, a fill factor (FF) of 0.60, and a resulting PCE of 2.45 % (Table 3). DEA-100/DCB-100/PET exhibited $J_{sc} = 6.54 \text{ mA cm}^{-2}$, $V_{oc} = 0.58 \text{ V}$, $FF = 0.60$, and a PCE of 2.27 %. The PCE was ~10% lower than that for DEA-100/DCB-100/glass. This originated from a lower transmittance at wavelengths below 600 nm, especially in the UV region (see transmission spectra of ITO-glass and PET-ITO, Figure S3). None the less, a fabrication method for TiO_x -containing inverted polymer solar cells on thin PET films was successful.

To improve the performance of the flexible cell, we tested Tetralin as a high boiling point solvent,[28] and Tetralin containing a small amount of ODT (denoted as Tetralin:ODT). Tetralin was chosen in attempt to more efficiently generate and separate photo-charge. Figure S2 shows absorption spectra of PCBM:P3HT films prepared using these solvents. When the blend film was prepared using Tetralin and heated at 100 °C, an enhanced shoulder was observed at ~600 nm, indicating a greater degree of P3HT crystallinity. The addition of ODT into the PCBM:P3HT solution enhanced the PCE because of improvements in nanoscale phase separation.[29, 30] Thus, a 2 % ODT vol. ratio was added to DCB and Tetralin (denoted as DCB:ODT and Tetralin:ODT, respectively). The

performance of DEA-100 solar cells prepared using DCB, Tetralin, DCB:ODT and Tetralin:ODT is summarized in Table 3. For DEA-100/DCB:ODT-100/glass, the PCE was 2.4 %. This was the same as for DEA-100/DCB-100/glass, regardless of addition of ODT. DEA-100/Tetralin-100/glass showed a relatively small PCE of 1.48 %, although greater crystallinity was observed for P3HT in the blend film (Figure S2). For PCBM:P3HT prepared using Tetralin:ODT, the absorbance at ~600 nm was lower than that of the blend film prepared without ODT (Figure S2). The performance of DEA-100/Tetralin:ODT-100/glass exhibited $J_{sc} = 7.09 \text{ mA cm}^{-2}$, $V_{oc} = 0.59 \text{ V}$, $FF = 0.66$, and a PCE of 2.76 %. The PCE was much larger than that for DEA-100/Tetralin-100/glass. Figure 4 shows surface AFM images of PCBM:P3HT films prepared using Tetralin containing varying ODT vol. %. Lee et al. reported AFM images of exposed *p*-conjugated polymer PCPDTBT networks after selective removal of C₇₁-PCBM from PCPDTBT:C₇₁-PCBM blend film using alkanedithiol.[30] They distinguished interconnected regions consisting of polymer and porous domains consisting of PCBM by such a method. On the analogy from such an investigation, we presumed that interconnected regions of lower height were P3HT-rich domains and dotted regions of higher height were PCBM-rich domains from the surface AFM images of PCBM:P3HT films in Figure 4. For PCBM:P3HT prepared by adding ODT of 2 vol. % or greater, the phase particle size of P3HT-rich and PCBM-rich domains greatly diminished, compared with those in films prepared using Tetralin containing 0 or 1 vol. % ODT. Figure S4 shows plots of PCE and J_{sc} against vol. % of ODT for DEA-100/Tetralin:ODT-100/glass. When the blend film was prepared using Tetralin containing 2 vol. % ODT, a better performance with $J_{sc} = 7.14 \text{ mA cm}^{-2}$ and a PCE of 2.77 % was observed. When the blend film was prepared using Tetralin containing ODT of 6 vol. %, J_{sc} and PCE values decreased. This was despite AFM images showing little particle size change (compare Figure 4(c) and 4(f)). This may have been

caused by residual ODT in the PCBM:P3HT film. These results suggest that controlling the morphology of the blend film, in addition to enhancing P3HT crystallinity, is important for overall cell performance. Figure 5 shows *I-V* curves of DEA-100/Tetralin:ODT-100/glass and DEA-100/Tetralin:ODT-100/PET, where PCBM:P3HT films were prepared using Tetralin containing 2 vol. % ODT, and heated at 100 °C. The flexible DEA-100/Tetralin:ODT-100/PET exhibited better performance, with $J_{sc} = 6.89 \text{ mA cm}^{-2}$, $V_{oc} = 0.57 \text{ V}$, $FF = 0.61$, and a PCE of $= 2.43 \%$. Its PCE was smaller than that of DEA-100/Tetralin:ODT-100/glass at 2.77 %.

It is known that blending bis-PCBM as an acceptor into P3HT as a donor enhances the V_{oc} of polymer solar cells compared to blending PCBM as the acceptor, because bis-PCBM has ca. 100 meV higher LUMO than PCBM.[11, 31] Hence, we tried to use the bis-PCBM as the acceptor. A Tetralin:ODT solution containing 21.8 mg mL⁻¹ P3HT and 17.4 mg mL⁻¹ bis-PCBM (weight ratio = 5:4) was spin-coated as the organic active layer. The film thickness was ca. 250 nm. As we would expect, the flexible DEA-100/Tetralin:ODT-100/PET containing bis-PCBM acceptor showed higher performance of $J_{sc} = 6.22 \text{ mA cm}^{-2}$, $V_{oc} = 0.72 \text{ V}$, $FF = 0.62$, and a PCE of 2.81 %.

4. Conclusions

When DEA was used as the complexing agent in the TiO_x precursor solution, the resulting DEA-TiO_x film functioned sufficiently well as an electron collection layer, even when drying at 100 °C was carried out. When using a solvent of high boiling point such as Tetralin containing 2 vol. % ODT, the morphology of the resulting PCBM:P3HT blend film gave higher cell performance. Combining these two techniques, we have fabricated a PET-ITO/TiO_x/PCBM:P3HT/PEDOT:PSS/Au cell without warping of the thin PET film. The resulting PCE was 2.43 %, for the unsealed device with a 1 cm² working area in air. A PCE

value of 2.81 % was obtained for the PET-ITO/TiO_x/bis-PCBM:P3HT/PEDOT:PSS/Au cell, when bis-PCBM was instead used as the electron acceptor. We employed a spin-coating method for preparing the TiO_x electron collection and PCBM:P3HT photoactive layers. However, this device could have easily been fabricated by other coating methods such as doctor blading and roller printing.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found online at doi:xx.xxxx/j.orgel.xxxx. xx.xxx.

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Table 1 Performance of TiO_x cells on ITO-glass containing Non-TiO_x, AA-TiO_x and DEA-TiO_x layers. The PCBM:P3HT film was prepared from the CB solution.

Name	T _(TiO_x) ^b / °C	T _(PCBM:P3HT) ^c / °C	J _{sc} / mA cm ⁻²	V _{oc} / V	FF	PCE / %
Non-150/CB-150/glass	150	150	7.25	0.57	0.46	1.93
AA-150/CB-150/glass	150	150	6.92	0.58	0.57	2.26
DEA-150/CB-150/glass	150	150	7.40	0.56	0.54	2.22
AA-100/CB-80/glass	100	80	4.08	0.57	0.28	0.66
DEA-100/CB-80/glass	100	80	5.70	0.57	0.34	1.11
DEA-150/CB-80/glass	150	80	6.26	0.54	0.32	1.10

b: Drying-temperature of TiO_x. c: Heating-temperature of PCBM:P3HT.

Table 2 Performance of TiO_x cells on ITO-glass containing a DEA-TiO_x layer dried at 100 °C, and a PCBM:P3HT film prepared from CB or DCB solution.

Name	Solvent	T _(PCBM:P3HT) ^a / °C	J _{sc} / mA cm ⁻²	V _{oc} / V	FF	PCE
DEA-100/CB-80/glass	CB	80	6.26	0.54	0.32	1.10
DEA-100/CB-100/glass	CB	100	6.87	0.54	0.36	1.33
DEA-100/DCB-RT/glass	DCB	room temp.	5.18	0.59	0.56	1.72
DEA-100/DCB-80/glass	DCB	80	6.83	0.59	0.59	2.38
DEA-100/DCB-100/glass	DCB	100	6.91	0.59	0.60	2.45

a: Heating-temperature of PCBM:P3HT

Table 3 Performance of TiO_x cells on ITO-glass and PET-ITO, containing DEA-TiO_x layers dried at 100 °C and PCBM:P3HT layers prepared from various solvents and heating at 100 °C.

Sample		J _{sc} / mA cm ⁻²	V _{oc} / V	FF	PCE / %
Substrate	Solvent (volume ratio)				
DEA-100/DCB-100/glass		6.91	0.59	0.60	2.45
Glass-ITO	DCB				
DEA-100/DCB:ODT-100/glass		6.32	0.59	0.64	2.38
Glass-ITO	DCB:ODT (98:2)				
DEA-100/Tetralin-100/glass		4.60	0.59	0.54	1.48
Glass-ITO	Tetralin				
DEA-100/Tetralin:ODT-100/glass		7.09	0.59	0.66	2.76
Glass-ITO	Tetralin:ODT (98:2)				
DEA-100/DCB-100/PET		6.54	0.58	0.60	2.27
PET-ITO	DCB				
DEA-100/Tetralin:ODT-100/PET		6.89	0.57	0.61	2.43
PET-ITO	Tetralin:ODT (98:2)				

Figure captions

Figure 1 Schematic illustrations showing the structures of normal (a) and inverted (b) polymer solar cells.

Figure 2 *I-V* curves of polymer solar cells containing TiO_x on glass substrates, prepared from AA- TiO_x and DEA- TiO_x precursor solutions.

Figure 3 *I-V* curves of polymer solar cells on glass substrates containing DEA- TiO_x layers dried at 100 and 150 °C.

Figure 4 Surface AFM images of PCBM:P3HT blend films prepared using Tetralin containing varying ODT vol. %. (a) 0, (b) 1, (c) 2, (d) 2.5, (e) 3 and (f) 6 vol.%

Figure 5 *I-V* curves of DEA- TiO_x cells prepared on glass and PET substrates, by treatment at 100 °C. PCBM:P3HT films were prepared using Tetralin containing 2 vol. % ODT.

Figures

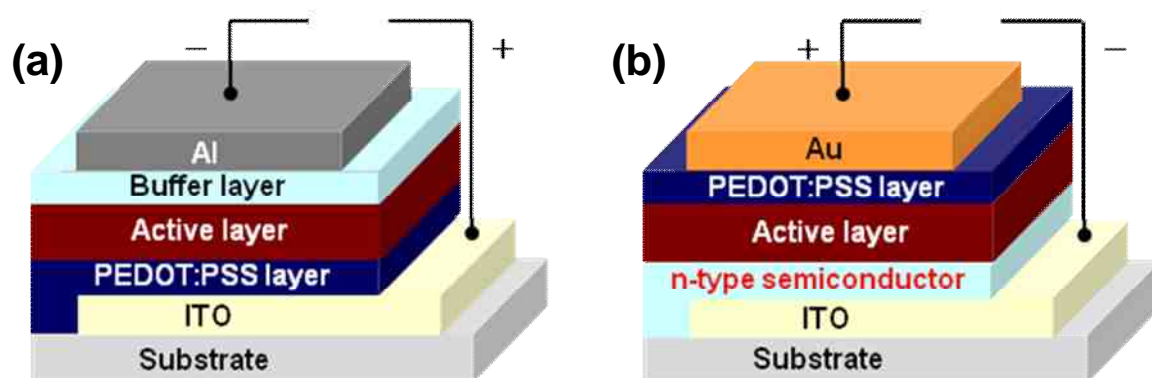


Figure 1

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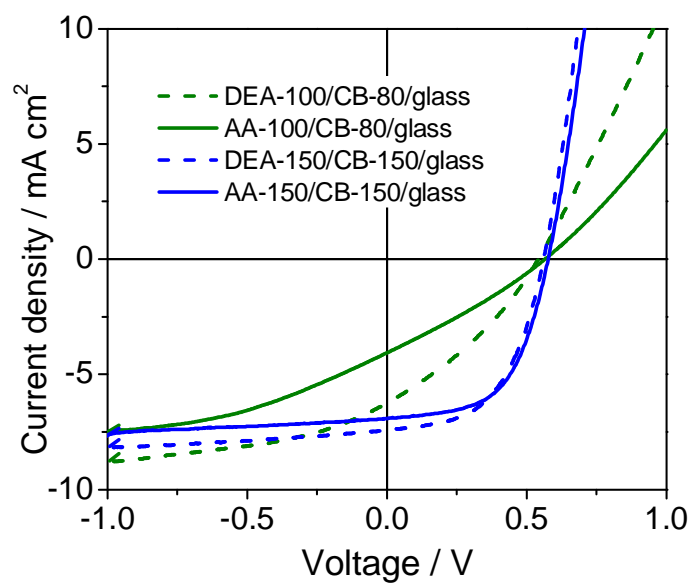


Figure 2

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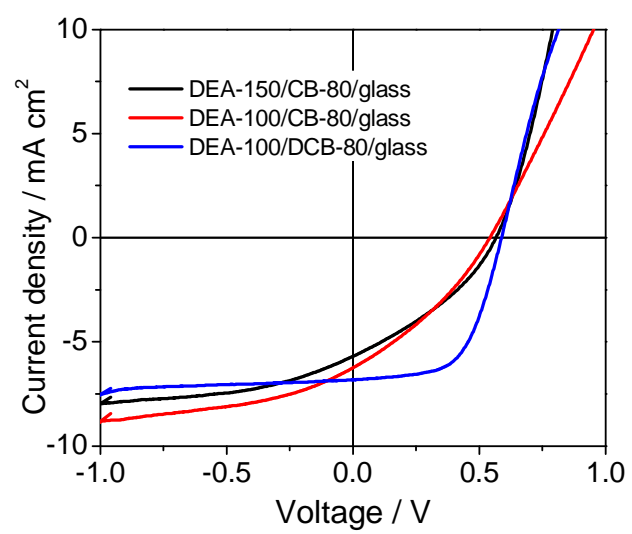


Figure 3

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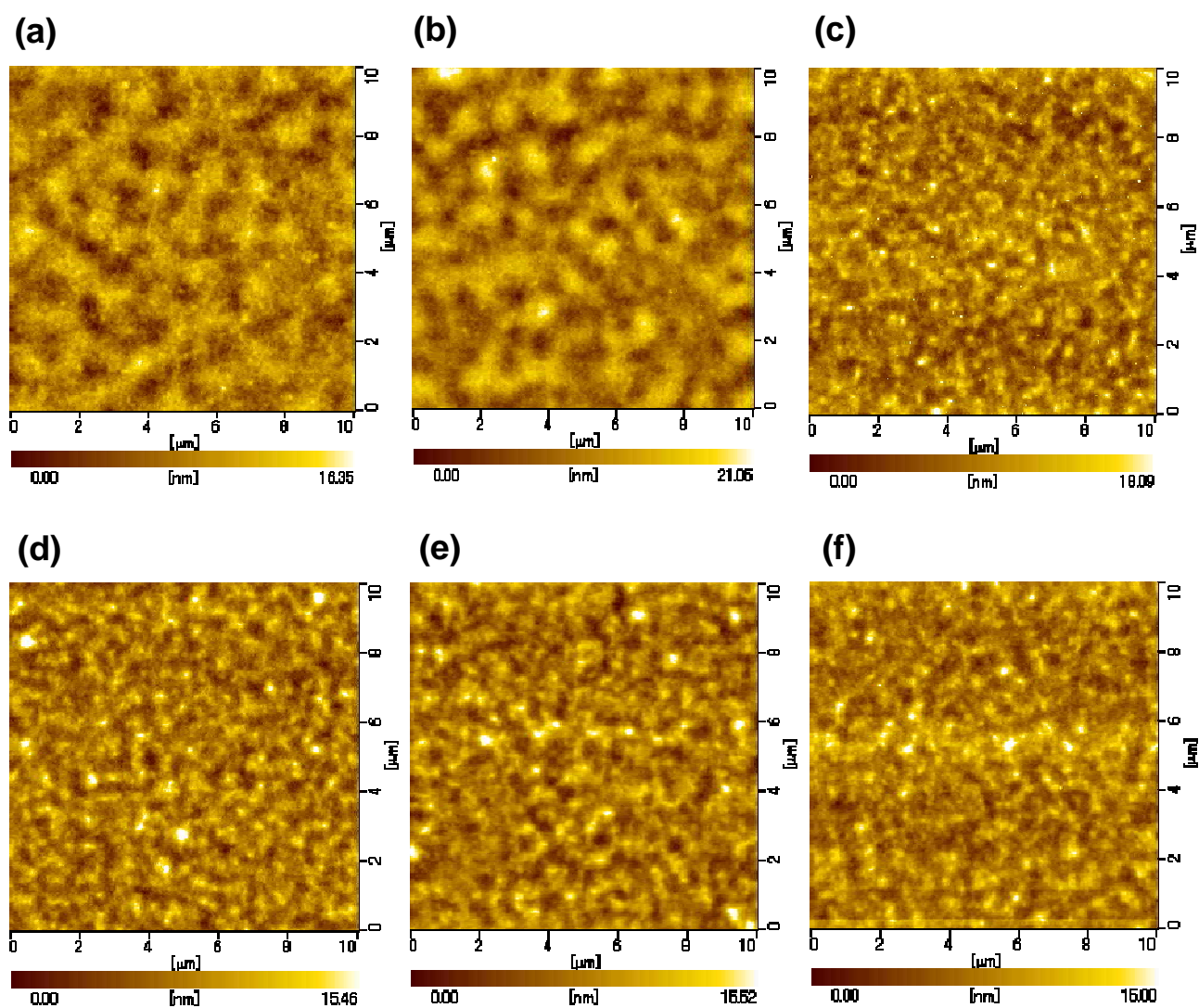


Figure 4

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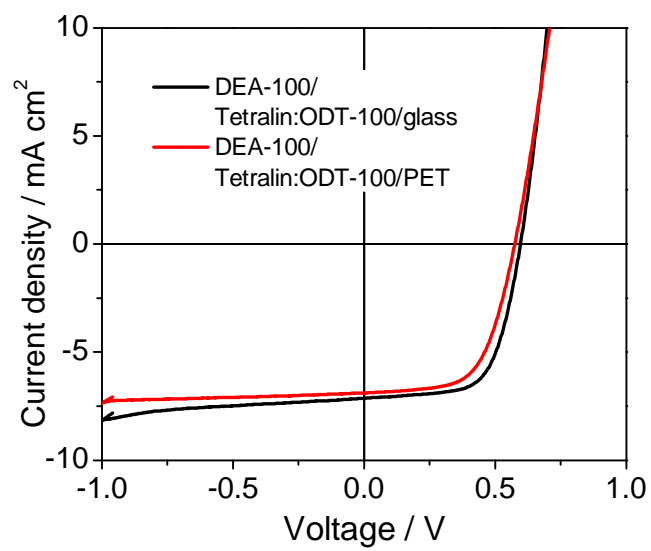


Figure 5

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Supporting Information

Figure S1 Plot of TiO_x film thickness versus the concentration of DEA- TiO_x precursor solution.

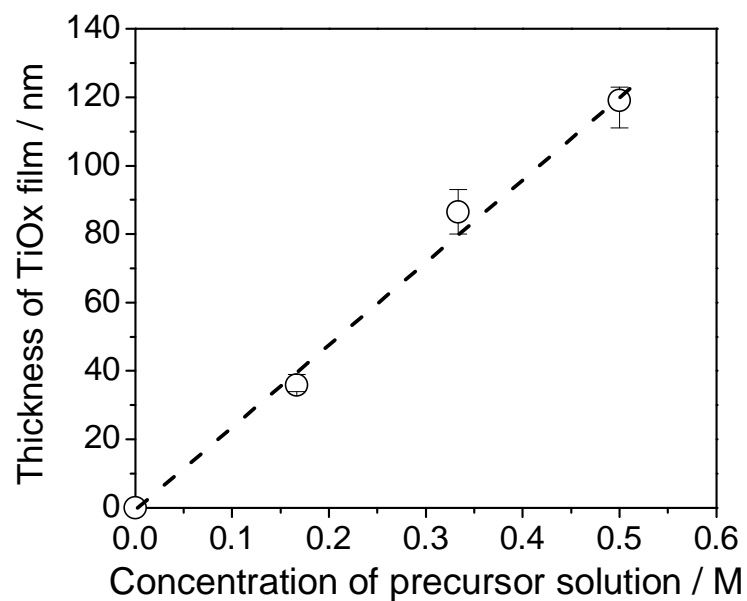


Figure S2 Absorption spectra of PCBM:P3HT blend films prepared on glass substrates from various solvents. The PCBM:P3HT blend film prepared using CB was heated at 150 °C for 5 min, and those prepared using DCB, Tetralin and Tetralin: 2 vol. % ODT mix were heated at 100 °C for 5 min and then 70 °C for 30 min.

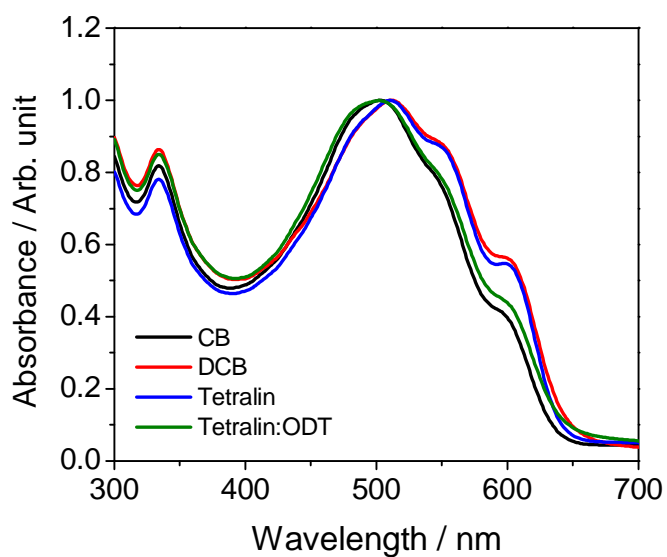


Figure S3 Transmission spectra of glass-ITO and PET-ITO electrodes.

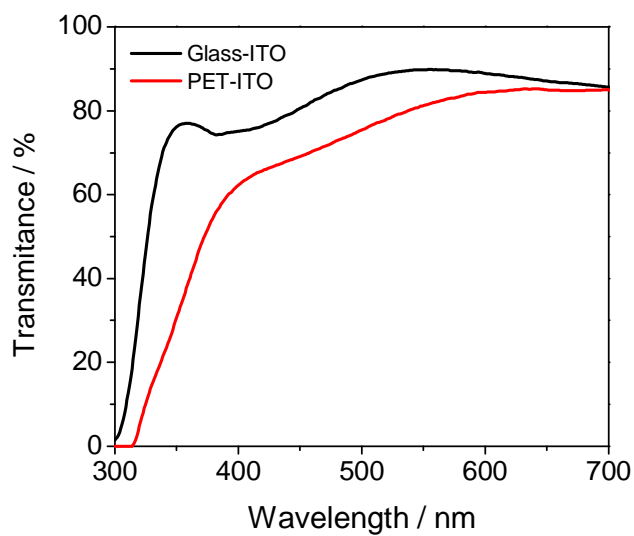


Figure S4 Plots of PCE (filled circles) and J_{sc} (open circles) of DEA-100/Tetralin:ODT-100/glass containing PCBM:P3HT blend film prepared using Tetralin:ODT, against vol. % of ODT added.

