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Inverted bulk-heterojunction organic solar cell using chemical bath deposited
titanium oxide as electron collection layer

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Abstract

Chemical bath deposited titanium oxide (TiO_x) as an electron collection layer is introduced between the organic layer and the indium tin oxide (ITO) electrode for improving the performance of inverted bulk-heterojunction organic thin film solar cells with 1 cm^2 active area, where regioregular poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl C_{61} butyric acid methyl ester (PCBM) were mainly used as the photo-active layer. The uniform and thin TiO_x film was easily prepared onto the ITO electrode in air by simple chemical bath deposition method. The performance of the TiO_x film inserted cell was almost maintained in an ambient atmosphere under continuous light irradiation of 100 h despite non-sealing. The cell with bulk-heterojunction organic thin film consisted of [6,6] diphenyl C_{62} bis(butyric acid methyl ester) (bis-PCBM) and P3HT prepared under best condition showed the power conversion efficiency (PCE) of 3.8 % under the AM1.5G simulated sunlight.

Key words: chemical bath deposition, organic thin film solar cells, titanium oxide

1. Introduction

Recent social-problems on energies and environments request a new system for providing an environment-friendly and safe energy-source instead of fossil fuel. For several years, organic solar cells have attracted global attention as its candidate[1, 2] and the power conversion efficiency (PCE) has been achieved 6-7% by development of new π -conjugated polymers [3, 4] as a donor. The device structures almost consisted of glass/indium tin oxide (ITO)/ poly(3,4-ethylenedioxythiophene) (PEDOT):poly(styrene-sulfonate) (PSS)/ π -conjugated polymer: fullerene derivative/lower work functional electrode (Al) as shown in Fig.1 (a), which are termed *normal type solar cells*. *Inverted type solar cells* have a reversed device structure against normal type solar cells as shown in Fig.1 (b), that is, their photo-generated electrons flow through external circuit from the ITO electrode to higher work functional electrode (Au or Ag).[5-9] In addition, as the inverted-type solar cells can be easily fabricated by all-solution processing and low-temperature processing in ambient atmosphere, the structured device with plastic substrate is expected as providing many advantages such as low-cost, light-weight, large-area and flexibility. Recently, an ITO/ZnO/PCBM:P3HT/PEDOT:PSS/Ag type flexible solar cell by the application of a roll-to-roll process has been reported and its module has showed over 2% of PCE.[10, 11]

(Fig. 1)

In our research, we have developed organic solar cells using a noncorrosive Au metal as a hole collection electrode, and a transparent conducting oxide (TCO)/ n-type semiconductor electrode such as anatase titanium oxide (TiO_2), amorphous-titanium oxide (TiO_x), zinc oxide (ZnO) or zinc sulfide (ZnS) as an electron collection electrode.[12-15] We reported that performance of the inverted-type organic solar cell using ITO/ TiO_x with sealing

was maintained under continuous light irradiating for 120 h in an ambient atmosphere.[16] Krebs has reported that ITO/ZnO/ZnO nanoparticles:poly-(3-carboxydithiophene) (P3CT)/PEDOT:PSS/Ag inverted-type solar cells without protection maintained 80% of the initial performance for continuous illumination for 100 h in pure air.[17] Therefore, its structure is expected as a promising approach from the viewpoints of durability improvement.

Chemical bath deposition (CBD) is one of the simplest methods for preparing semiconductor films as well as electrochemical deposition and sol-gel method, having an advantage such as low cost and easy technique to realize large area devices. TiO_2 or TiO_x may function as both of electron collection layer and hole blocking layer for organic solar cells.[18, 19] However, to our knowledge, the CBD method for preparing titanium oxide layer has not yet been used to fabricate the PV device. In this paper, we report a readily-prepared CBD- TiO_x film working as electron collection layer of organic solar cells which exhibited PCE of 3.8% under the AM1.5G simulated sunlight.

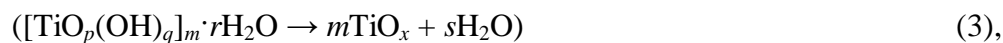
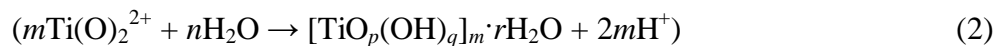
2. Experimental

The ITO electrode was ultrasonicated in 2-propanol, and then cleaned in boiling 2-propanol, and subsequently dried in air. The CBD- TiO_x film was prepared according to the following procedure. A titanium(IV) oxysulfate (TiOSO_4) solution was added in a diluted hydrogen peroxide (H_2O_2) aqueous solution, and then the mixed solution was diluted just to 50 ml with ultrapure water. The concentrations of H_2O_2 and TiOSO_4 were adjusted to 0.03 M, respectively. This solution was transferred to a screw vial to use as the reaction bath for film deposition. The glass side of the ITO substrate was covered with an imide tape to prevent an extra deposition of TiO_x , and then the ITO substrate was immersed in the bath at 80 °C. The solution became cloudy by the application of heat, and after appropriate dipping time starting from this cloudy point, the immersed ITO substrate was pulled out from the bath. The as-deposited TiO_x film on the ITO was ultrasonicated for 10 min in water and heated on a hot

plate at 150 °C for 1 h in air. Then, the chlorobenzene (CB) solution or the 2,6-dichlorotoluene: chloroform (1:1 by volume ratio, DCT:CHL) cosolvent solution containing poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl C61 butyric acid methyl ester (PCBM) of 5:4 by weight ratio was spin-coated onto the ITO/TiO_x substrate in a glove box less than 1 ppm of moisture, being subsequently heated at 120 °C for 20 min on the hot plate. Then, a PEDOT:PSS dispersion solution was spin-coated onto the P3HT:PCBM layer in an simple glove box of the relative humidity less than 35%. An Au metal as the back electrode was vacuum-deposited on the PEDOT:PSS layer. Finally, the device was heated at 150 °C for 5 min on the hot plate in air and then at 70 °C for 30 min. The effective area of the solar cell was restricted to 1.0 cm² by depositing the Au electrode using a shadow mask. The photocurrent-voltage (I-V) curves of the solar cells were measured by linear sweep voltammetry (LSV) at a scan rate of 5 V min⁻¹ under an AM 1.5G simulated sunlight with 100 mW cm⁻² intensity. The light source was from a SAN-EI Electric XES-502S solar simulator calibrated by an EKO MS-601 pyranometer equipped with a silicon diode. All the dc electric measurements were implemented using a Hokuto Denko HZ-5000 electrochemical analyzer. All measurements were carried out for non-sealed devices in an ambient atmosphere, that is, at room temperature of 15-30 °C and under relative humidity of 40-60 %.

3. Results and discussion

We assumed the deposition mechanism of a TiO_x film on the ITO electrode as follows:



where the italicized characters m , n , p , q , r , s , and x in the above equations are unknown numbers, although the x value in TiO_x is less than 2. Titanyl ions are oxidized to titanium(IV) peroxide ($\text{Ti}(\text{O})_2^{2+}$) ions by H_2O_2 (Eq. 1) at room temperature, then a titanium(IV) oxyhydroxide ($[\text{TiO}_p(\text{OH})_q]_m \cdot r\text{H}_2\text{O}$) is deposited on the ITO plate by hydrolysis (Eq. 2) around 80°C . Finally, the as-deposited $[\text{TiO}_p(\text{OH})_q]_m \cdot r\text{H}_2\text{O}$ is converted to the amorphous titanium(IV) oxide (TiO_x) by heat treatment at 150°C for 1 h in air (Eq. 3). Fig. 2 shows the photographs before and after the hydrolysis in the chemical bath containing TiOSO_4 and H_2O_2 . As-prepared CBD solution displays red color based on the generation of $\text{Ti}(\text{O})_2^{2+}$ ions as shown in Fig. 2(a). When heated at 80°C for about 10 min, the solution got clouded defining as 0 sec of deposition initiation, see Fig. 2(b). Then, an increase in white turbidity was observed by keeping at 80°C as shown in Fig. 2(c) ~ (e).

(Fig. 2)

Surface AFM images of the TiO_x films are shown against the dipping time in the chemical bath at 80°C , see Fig. 3. The AFM images showed that the ITO substrates are gradually covered with TiO_x precursor particles. The film thickness of TiO_x film increased about linearly with the dipping time as shown in Fig. 4, but its film was considerably flat in the nano-scale, see the height scale of surface AFM images in Fig. 3.

(Fig. 3)

(Fig. 4)

The photo I-V curves of the ITO/CBD- TiO_x /PCBM:P3HT/PEDOT:PSS/Au solar cells with various thicknesses of the CBD- TiO_x layer is shown in Fig. 5, where the PCBM:P3HT (5:4 by weight ratio) blend film was prepared by spin-coating the CB solution. The cell

without TiO_x layer showed the PCE of 0.82%, see dash curve in Fig. 5. Whereas the cell with TiO_x layer of 20 nm thickness exhibited a large increase in the short-circuit current (J_{sc}) and the fill factor (FF) due to rectification improvement, after all, we obtained the maximum J_{sc} of 7.22 mAcm⁻², the open-circuit voltage (V_{oc}) of 0.57 V, the FF of 0.57, and the PCE of 2.35%, see green solid curve in Fig. 5. This result shows that the CBD-TiO_x film acts effectively as an electron collection layer for the organic solar cell.

(Fig. 5)

Fig. 6 shows the PCE change against irradiation time in air for the TiO_x cell without sealing. The PCE maintained 94% of the maximum value even after continuous light irradiation for 100 h. Further, even when the non-sealing TiO_x cell was put in relative humidity of 85% and at environmental temperature of 85 °C in the dark for 50 h, the PCE surprisingly maintained 54% of the maximum value. Very high stability was demonstrated for the non-sealing CBD-TiO_x inserted cell.

(Fig. 6)

In order to improve the energy conversion efficiency of the solar cells, we have attempted to prepare an organic active layer with better morphology by thermal-annealing and controlling solvent evaporation speed after spin-coating. In a similar manner of previous report for the sol-gel TiO_x inserted solar cells,[16] the PCBM:P3HT film prepared by DCT:CHL cosolvent solution showed slightly high PCE compared with that prepared by the CB solution in the CBD-TiO_x inserted solar cells, see Fig. S1. The cosolvent cell showed the J_{sc} of 8.49 mA cm⁻², the V_{oc} of 0.61 V, the FF of 0.62, and the PCE of 3.21%, reasonably increasing compared to the CB cell (PCE = 2.35%). The improvement of the device performance may be caused by

a morphology change in the blend film suppressing the solvent evaporation rate by the DCT of higher boiling temperature. The PCE of the CBD-TiO_x inserted solar cell is by 30% higher than the PCE (2.47%) of the sol-gel TiO_x inserted solar cells under equal conditions.[16] This may be because the stabilizing agent such as acetylacetone remained in the sol-gel TiO_x film and resulted in higher film resistance. The morphology of the PCBM:P3HT film prepared by DCT:CHL exhibited much smaller nano-scale phase separation than that by CB, see Fig. S2. Therefore, the enhanced J_{sc} and FF as shown in Fig. S1 suggest that more well-connected networks were formed for each micro-separated phase of donor and acceptor in the PCBM:P3HT film prepared by DCT:CHL.

(Fig. S1)

(Fig. S2)

It is known that blending [6.6] diphenyl C62 bis(butyric acid methyl ester) (bis-PCBM) as an acceptor into P3HT as a donor enhances the Voc of normal type solar cells compared to blending PCBM as the acceptor, because bis-PCBM has higher LUMO by ca. 100 meV than PCBM.[20] The performance of the CBD-TiO_x cell with the PCBM:P3HT or the bis-PCBM:P3HT prepared by DCT:CHL cosolvent is summarized in Table 1. The bis-PCBM cell showed the J_{sc} of 7.84 mA cm⁻², the Voc of 0.76 V, the FF of 0.63, and the PCE of 3.81%. The photocurrent slightly decreased compared to the PCBM cell and the FF was the same. On the other hand, the Voc increased by ca. 0.15V, leading higher PCE of the bis-PCBM cell. We confirmed that the Voc increment by using bis-PCBM was obtained even for the inverted type solar cell. The slightly decreased J_{sc} of the bis-PCBM:P3HT cell may be explained by the fact that the electron transfer from donor P3HT to acceptor bis-PCBM became inconsiderably difficult due to the increase of the acceptor LUMO level.

(Table 1)

4. Conclusion

In conclusion, we have proposed very convenient and useful CBD-TiO_x thin film as the electron collection layer of the inverted type organic solar cell. In the ITO/CBD-TiO_x/bis-PCBM:P3HT/PEDOT:PSS/Au device, we obtained relatively large PCE value of 3.8%. We believe that the chemically stable CBD-TiO_x film works as a promising electron collection layer for developing polymer solar cells with high efficiency and high durability. Since the uniformed and air-stable CBD-TiO_x film can be easily prepared onto large-area ITO substrates in air, the fabrication of large-area inverted type organic solar cell will be possible, being important to develop low-cost solar cells.

Acknowledgements

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Figures and Table

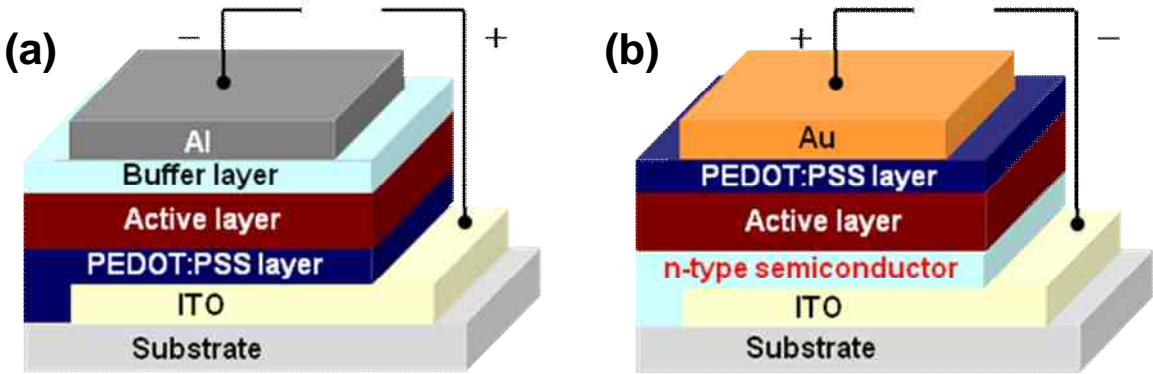


Figure 1. Schematic structures of normal (a) and inverted-type organic solar cells (b).

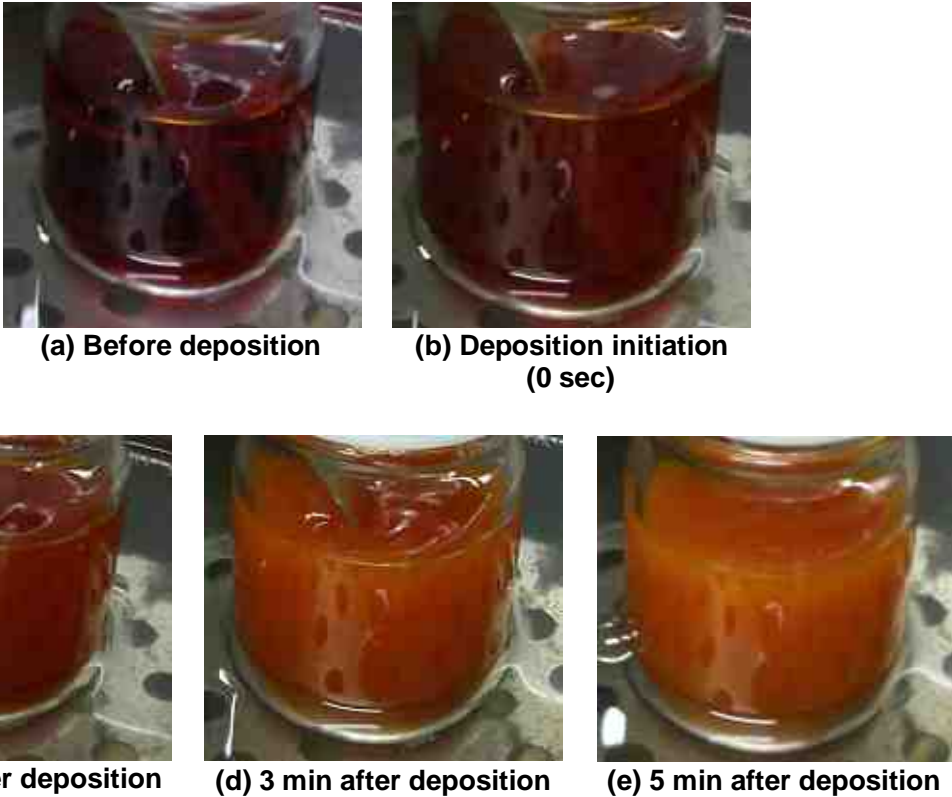


Figure 2. Photographs before and after the hydrolysis in the chemical bath for depositing TiO_x .

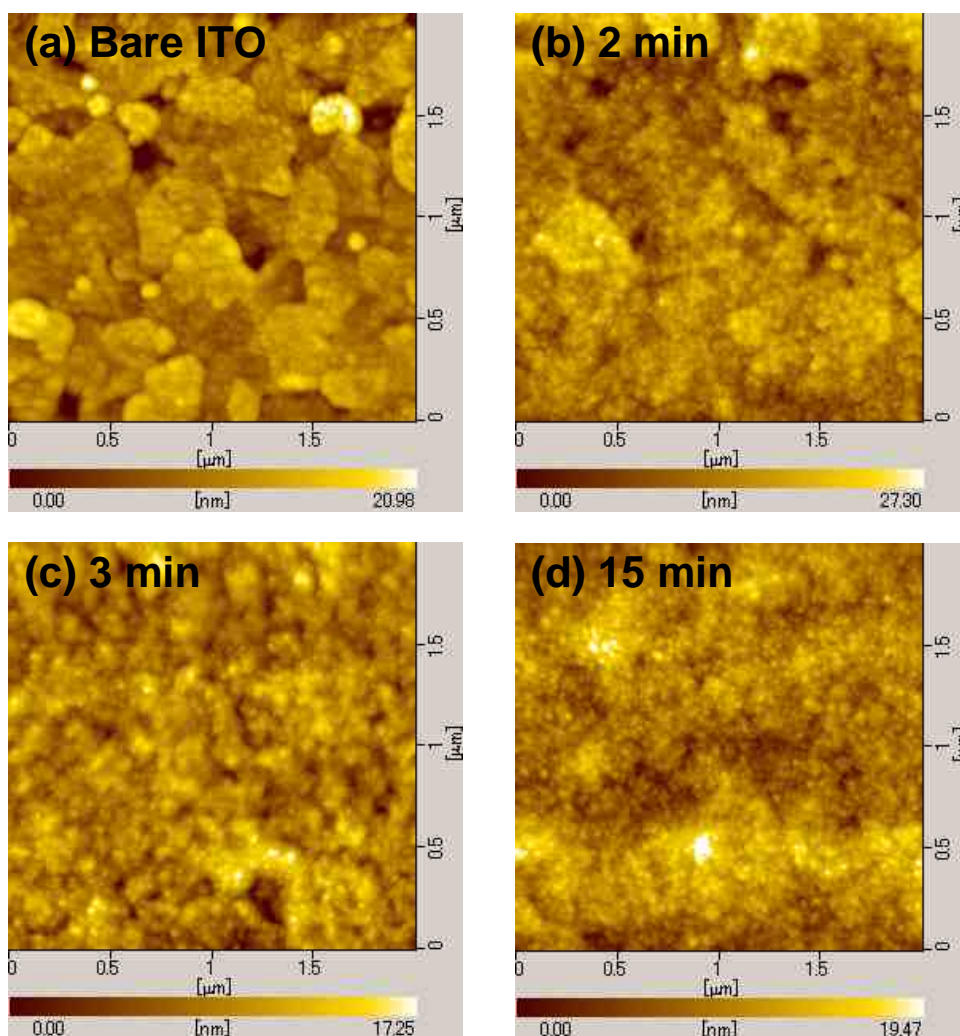


Figure 3. Dipping time dependence of the surface AFM images of the TiO_x films prepared by CBD method. Dipping time; (a) 0 min (bare ITO), (b) 2 min, (c) 3 min, and (d) 15 min.

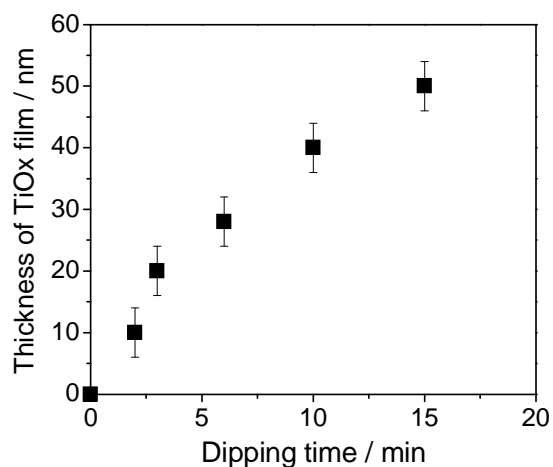


Figure 4. Plots of the thickness of TiO_x film versus the dipping time.

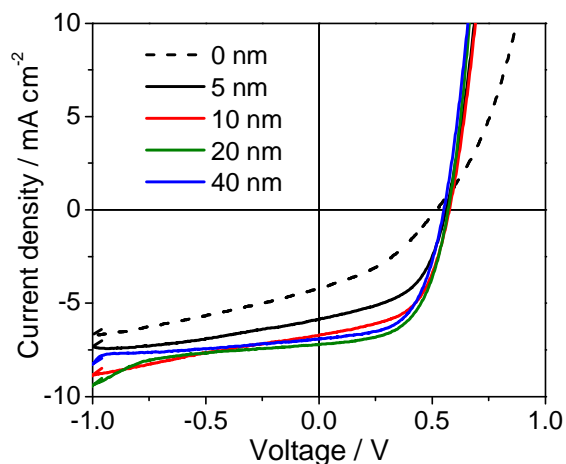


Figure 5. Photo I-V curves of the organic solar cells with various thicknesses of the CBD-TiO_x layer. The PCBM:P3HT blend film was prepared using the CB solution.

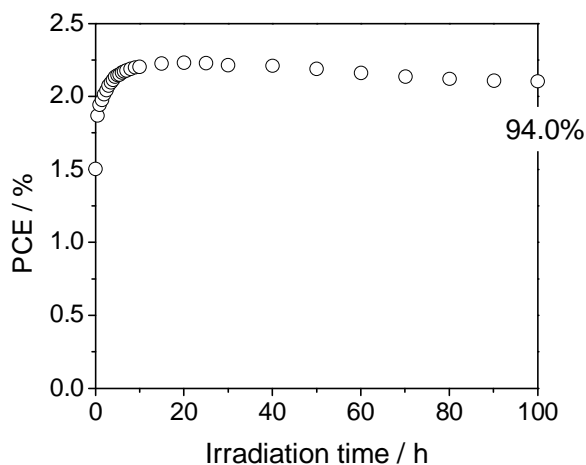


Figure 6. Irradiation time dependence of the PCE for the non-sealed CBD-TiO_x inserted cell in air. The PCBM:P3HT blend film was prepared using the CB solution. The PCE maintained 94.0% of the maximum value (2.23%) even after continuous light irradiation for 100 h,

Table 1 Photovoltaic parameters of the PCBM:P3HT and bis-PCBM:P3HT solar cells under AM 1.5G light irradiation at 100 mW cm⁻².

Active layer	Solvent	J _{sc} / mA cm ⁻²	V _{oc} / V	FF	PCE / %
PCBM:P3HT	CB	7.22	0.57	0.57	2.35
PCBM:P3HT	DCT:CHL	8.49	0.61	0.62	3.21
bis-PCBM:P3HT	DCT:CHL	7.84	0.76	0.63	3.81

Supplementary Materials for
Inverted bulk-heterojunction organic solar cell using chemical bath deposited titanium oxide as electron collection layer

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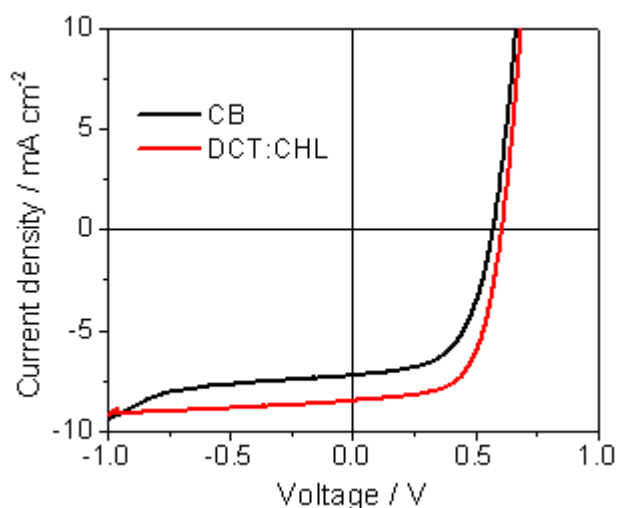


Figure S1. Photo I-V curves of inverted solar cells with PCBM:P3HT blend films prepared by chlorobenzene (CB) solvent and 2,6-dichlorotoluene:chloroform (DCT:CHL) cosolvent under light irradiation of AM 1.5G-100mWcm⁻².

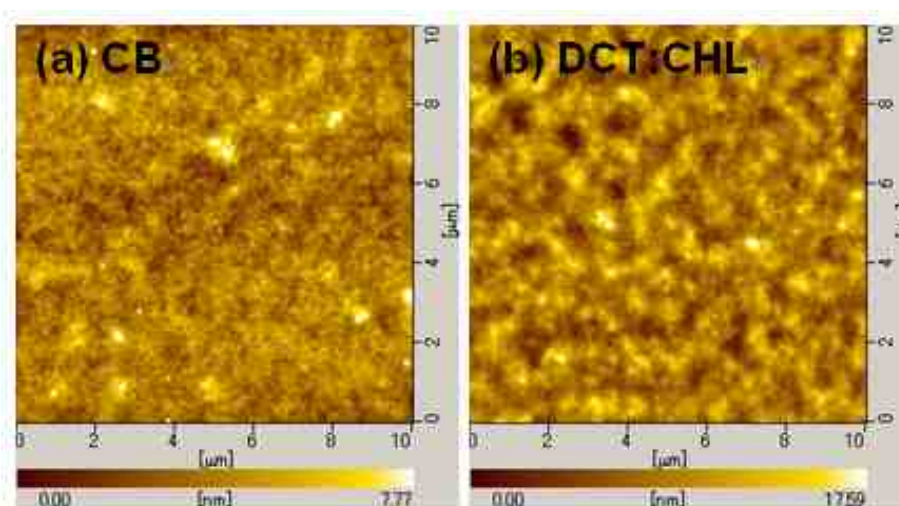


Figure S2. AFM images of PCBM:P3HT-blend films prepared from CB solvent (a) and DCT:CHL cosolvent (b).