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Pentacene nanostructural interlayer for the efficiency improvement of polymer solar cells

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Abstract

In poly(3-hexylthiophene) mixed with phenyl C61-butyric acid methyl ester heterojunction polymer solar cells, organic small molecular pentacene was introduced as the interfacial layer between PEDOT:PSS coated ITO substrates and polymer layer. It is found that the short circuit current density and power conversion efficiency were distinctly improved due to the introduction of nanostructural pentacene interlayer. The nearly 100% power conversion efficiency improvement was obtained on the cells with 4 nm pentacene interlayer, which benefit from the increased short circuit current from 2.34 mA/cm² to 5.76 mA/cm². The morphology of different thickness of pentacene thin films was observed by atomic force microscopy. The effect of pentacene interlayer's thickness on the distribution of light in the active layer was simulated by using a transfer matrix mode.

Keywords: polymer solar cells, interlayer, morphology

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Introduction

The effective conversion of solar energy into electricity has attracted intense scientific interest for solving the rising energy crisis. Organic solar cells, a kind of green energy source, show great potential application due to low production costs, mechanical flexibility and the versatility in organic materials design [1, 2]. In the past years, the key parameter, power conversion efficiencies (PCE), is up to 6% under the standard solar spectrum, AM1.5G [3, 4]. The PCE of solar cells are co-determined by the open circuit voltage (V_{oc}), the fill factor (FF) and the short circuit density (J_{sc}) [5]. Researchers have made great efforts in both developing new organic materials with low optical band gap and designing different structural cells for harvesting exciton in the visible light range [3, 6-8]. Liu et al. reported the favorable improvement harvesting exciton in organic-inorganic hybrids solar cells by using resonance energy transfer [9]. It is important to note, however, that the harvesting exciton improvement could not result in the good performance of OSCs due to subsequently occurring with other complex process, such as exciton diffusion and dissociation, charge carrier transporting and collection. The balance of these dynamic processes plays a very important role for improving the power conversion efficiency.

The interface engineering on organic active layer/electrodes has been comprehensively carried out for the improvement of charge injection or collection, especially due to mismatched energy levels between organic materials and metal electrodes [10-12]. Recently, molybdenum trioxide (MoO_3) is introduced in OSCs, functioning multiple role, such as hole transport and collection layer in conventional devices [10, 13], intermediate layer in tandem devices [14-16], protection layer in inverted device [17]. We reported the effect of ultra thin MoO_3 layer and illumination intensity on the performance of OSCs, it was found that the MoO_3 layer could effectively prevent the exciton quenching at the ITO anode side, resulting in the small variation of the FF for the devices with the MoO_3 layer compared to the devices without the MoO_3 layer under different illumination intensity [10]. However, the detailed understanding of these dynamic processes is not completely articulated,

especially the balance between light absorption and charge carrier collection dependence on the thickness of organic active layer.

Zhang et al. also demonstrated that the copper phthalocyanine (CuPc) interlayer between anode and the blended active layer forming poly(3-hexylthiophene-2,5-diyl) (P3HT) and [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) for efficient light harvesting, resulting in the improvement of J_{sc} and PCE [18]. Hayashi et al. reported that the V_{oc} was improved by incorporating poly(2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene) (MEH-PPV) into P3HT:PCBM bulk heterjunction (BHJ) solar cells [19]. Lee et al. reported that the OSCs performance could be effectively improved by introducing a thin pentacene interlayer between aluminum cathode and active layer, which was mainly attributed to an additional path for electron transfer provided by the thin pentacene layer [20]. In our pervious paper, we reported that pentacene thin films acting as hole transporting layer can improve the electroluminescence intensity and efficiency of organic light emitting diodes based on Alq₃ as the emission layer [21]. The improvement was attributed to the large hole mobility of pentacene and the increased interfacial surface area induced by its pyramid-like morphology, which result in the increase of the recombination region at the interfaces between pentacene and Alq₃ layers. [22]. Organic semiconductor pentacene has attracted much attention in organic thin film transistor for its higher mobility and strong tendency to form molecular crystals even for low substrate temperature [23, 24]. In this paper, the different thickness pentacene thin films were introduced into OSCs with P3HT: PCBM as the active layer, the distinguished effect of pentacene interlayer on the parameters of OSCs was observed and the underlying mechanism is discussed.

Experimental details

Indium tin oxide (ITO) coated glass substrates with a sheet resistance of 60 Ω /square were cleaned consecutively in ultrasonic baths containing acetone, ethanol and de-ionized water and then dried by nitrogen. UV–ozone treatment on the pre-cleaned ITO substrates was carried out for 5 minutes to enhance the work

function of ITO substrate. The poly (3,4-ethylenedioxythiophene) –poly (styrenesulfonate) (PEDOT:PSS) (Aldrich) was spin-coated onto ITO substrates under 3000 rpm (round per minute) with 45 seconds. Then PEDOT:PSS-coated ITO (PITO) substrates were heat-treated for 10 minutes at 180°C in atmosphere. Subsequent, organic thin films, pentacene and P3HT:PCBM, were fabricated on the PITO by thermal evaporation and spin coating methods, respectively. The thickness of pentacene film and the deposition rate were monitored by a quartz-crystal microbalance during the thermal evaporation process. Polymers P3HT and PCBM were separately dissolved in chloroform (10 mg/ml) and mixed each other with 1:1 volume ratio. Finally, the aluminum (Al) cathode, consisting of 100 nm thickness and active areas about 0.9 cm², was deposited by thermal evaporation through foursquare shadow mask under 5×10^{-3} Pa vacuum levels. The schematic diagrams of the present OSCs and the energy level alignment of used materials are shown in the Fig.1.

Figure 1

The current-voltage (I–V) characteristics of the OSCs were measured both in dark and under illumination at 100mW/cm² by using a 150 W Xenon lamp. The absorption spectra of the active layer were measured with Shimadzu UV-3101 PC spectrometer. The morphology of thin films was investigated by atomic force microscopy (AFM) (D5000, Veeco) operated in tapping Mode. All measurements were carried out at the atmosphere and room temperature.

Result and discussion

It is known that the operation of OSCs mainly involves the five following steps: (i) the light absorption by the active layer; (ii) the formation of exciton and subsequent diffusion to the interface of donor and acceptor; (iii) the exciton dissociation into the electrons and holes; (iv) free charge carriers transport in their individual pathway or layer; (v) charge extraction by their corresponding electrodes. So the first key issue for the improvement of OSCs performance is the harvesting photon in the active layer. The absorption spectra of five kinds of organic thin films were measured and are shown in the Fig.2. It is apparent that pentacene interlayer could effectively enhance

light absorption in the active layer, especial in the longer wavelength range. From the variation of absorption spectra of P3HT:PCBM and pentacene/P3HT:PCBM thin films, it could be deduced that pentacene thin films were not damaged by spin coating P3HT:PCBM solvent onto it. In the Ref [24], we have also reported that only minor changes of the pentacene thin film morphology occurred when organic solvent chloroform spins onto it.

Figure 2

Another important reason for the introduction of pentacene interlayer, pentacene thin films could act as the buffer layer due to its higher hole mobility and forming good crystalline or ordered pyramid-liked surface morphology, as shown in the Fig.3. The morphology image of PITO substrates and different thickness of pentacene thin films on PITO substrates are shown in the Fig. 3. The morphology image of 4 nm pentacene thin films shows distinguished layered structural surface, this surface may affect the alignment of polymer's chains on it. There is apparent pyramid-liked surface morphology for the 8 nm thickness pentacene thin films, similar to morphology of pentacene on SiO₂ substrate [25]. According to the AFM images shown in the Fig.3, the root mean square (RMS) surface roughness is about 8.0 nm, 9.5 nm, 18.3 nm and 24.7 nm, which strongly depends on the thickness of pentacene thin films. The bigger surface roughness of pentacene thin films, the larger donor/acceptor interfaces is. The increased interfaces would facilitate the exciton dissociation.

Figure 3

The third reason for the introduction of pentacene interlayer is the effect of pentacene thin film thickness on the electromagnetic field in P3HT:PCBM. Figure 4 shows the electromagnetic field distribution in P3HT:PCBM layer modulated by different thickness of pentacene layer, which was simulated by a transfer matrix model [26-28] (where, solar energy data from ASTM Standard G173, 2003e, ASTM International [29]). The absorption near 620nm in the P3HT:PCBM layer has been enhanced along with the pentacene thickness increasing, which could prove its optical

performance by inserting a pentacene layer. It likes an optical spacer between active layer and cathode to reduce the harmful interference.

Figure 4

Figure 5

Figure 5 shows the illuminated current density-voltage (J-V) characteristics of ITO/PEDOT:PSS/pentacene(x nm)/P3HT:PCBM/Al under the intensity of 100 mW/cm². These key parameters of fabricated OSCs are summarized in the Table 1. The devices with 4 nm pentacene interlayer shows substantially improved short circuit density from 2.34 mA/cm² to 5.76 mA/cm² and power conversion efficiency from 0.53% to 1.03% compared to the devices without pentacene interlayer. In this study, we focus our attention on the enhanced the short circuit current, which makes key contribution to the power conversion efficiency improvement.

TABLE 1

The enhanced photocurrent should be attributed to more exciton generated by the introduction of pentacene interlayer under illumination. This explanation should be effectively supported from the absorption spectra of the active layer, as shown in the Fig.2. On the other hand, pentacene interlayer could effectively prevent the exciton quenching induced by PITO anode and avoid the direct contact between PITO and PCBM. Recently, Orimo studied the surface segregation at the aluminum interface of P3HT:PCBM heterojunction OSCs induced by thermal annealing before and after Al deposition [30]. The weight fraction of PCBM at the post-annealed surface was as high as 72% at the Al interface and the contact P3HT with Al cathode was decreased, which resulted in the enhanced performance of OSCs. In the present work, organic semiconductor pentacene, high charge carrier mobility and strong absorption at the longer wavelength, was used at the interlayer between anode and active layer to decrease exciton quenching nearby the anode.

From the device structure seen, the devices with pentacene interlayer could be considered as two parallel connection solar cells consisting of pentacene/PCBM and P3HT:PCBM parts. The J-V characteristics of ITO/PEDOT:PSS/pentacene/PCBM/Al

cells under dark and illumination conditions are shown in th Fig.6. By contrast, the cells using pentacene/PCBM as the active layer show the smaller V_{oc} (0.33 V) and J_{sc} (1.4 mA/cm^2) compared with the cells using P3HT:PCBM as the active layer (the data shown in the Fig.5).

Figure 6

The low performance of ITO/PEDOT:PSS/pentacene/PCBM/Al could be explained from the number of photon absorbed in the active layer and the length of exciton diffusion for this kind of bi-layer structured OSCs. From absorption spectra shown in the Fig.2, it is apparent that the active layer pentacene/PCBM shows a narrow absorption range from 550nm to 700 nm. The absorption intensity of pentacene/PCBM layer should strongly depend on the pentacene layer thickness, because PCBM has no apparent absorption in the visible light range. Despite the number of photon absorbed in the pentacene layer could be enhanced with the increase of pentacene layer thickness, unfortunately, the exciton dissociation rate would be decreased due to the prolonged length of exciton diffusion from the inside pentacene layer to the interface with PCBM layer. The typical exciton diffusion length in organic semiconducting thin films is less than 20 nm [31]. If the exciton could not transport to the donor/acceptor interface and be dissociated in time, it will be de-excited via thermalization or vibration.

The V_{oc} of cells based on pentacene/P3HT:PCBM as the active layer was decreased from 0.64 V to 0.46 V with the increase of pentacene thickness, however the J_{sc} increases from 2.34 mA/cm^2 to 6.18 mA/cm^2 . The change trend of V_{oc} and J_{sc} also demonstrates that the cells with pentacene/ P3HT:PCBM as the active layer should be considered as two sub-cells with parallel connection mode. The power conversion efficiency was determined by the V_{oc} and J_{sc} , the maximum power conversion efficiency reaches to 1.03% when the pentacene interlayer thickness is 4nm.

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Table and table's caption

Table 1 the summarized parameters of OSCs with different thickness of pentacene

thickness (nm)	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	PEC (%)
0	0.64	2.34	35.5	0.53
2	0.57	3.24	33.2	0.61
4	0.54	5.76	33.1	1.03
8	0.46	6.18	31.4	0.91

Figures' captions

Fig.1 The organic solar cell schematic diagrams and the energy level alignment of used materials

Fig.2 The absorption spectra of five kinds of organic thin films

Fig.3 The AFM images of different thickness of pentacene on PITO substrates, a) 0nm pentacene, b) 1nm pentacene; c) 4nm pentacene; d) 8nm pentacene. The high scale for all images is 30 nm.

Fig.4 Electromagnetic field distribution in P3HT:PCBM layer modulated by different thickness of pentacene layer

Fig.5 The typical J - V characteristics of different thickness pentacene interlayer for P3HT:PCBM solar cells under illumination

Fig.6 The J - V characteristics of ITO/PEDOT:PSS/pentacene/PCBM/Al device under dark and irradiation conditions

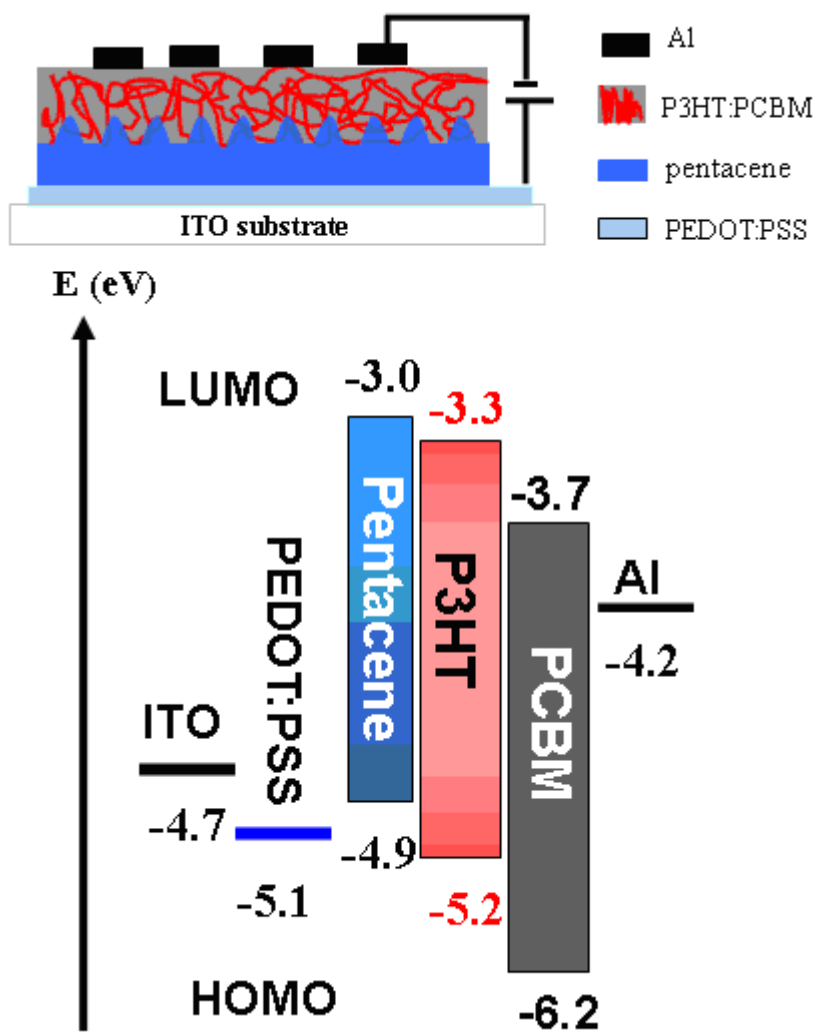


Fig. 1

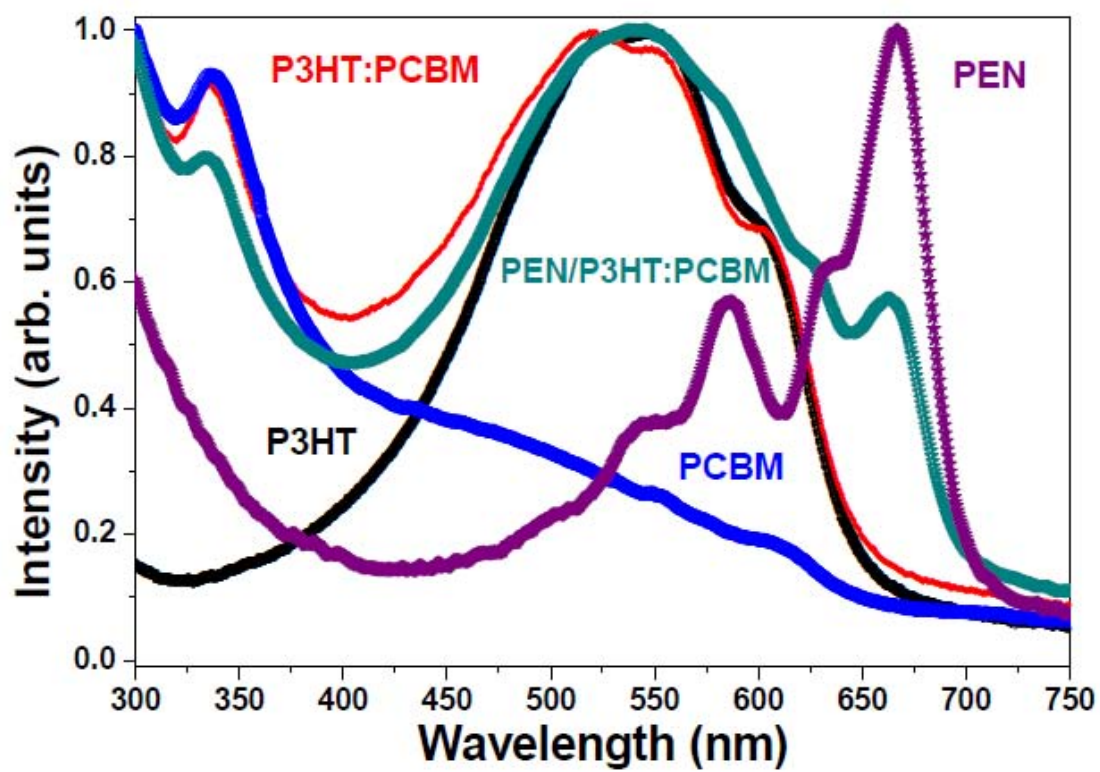


Fig. 2

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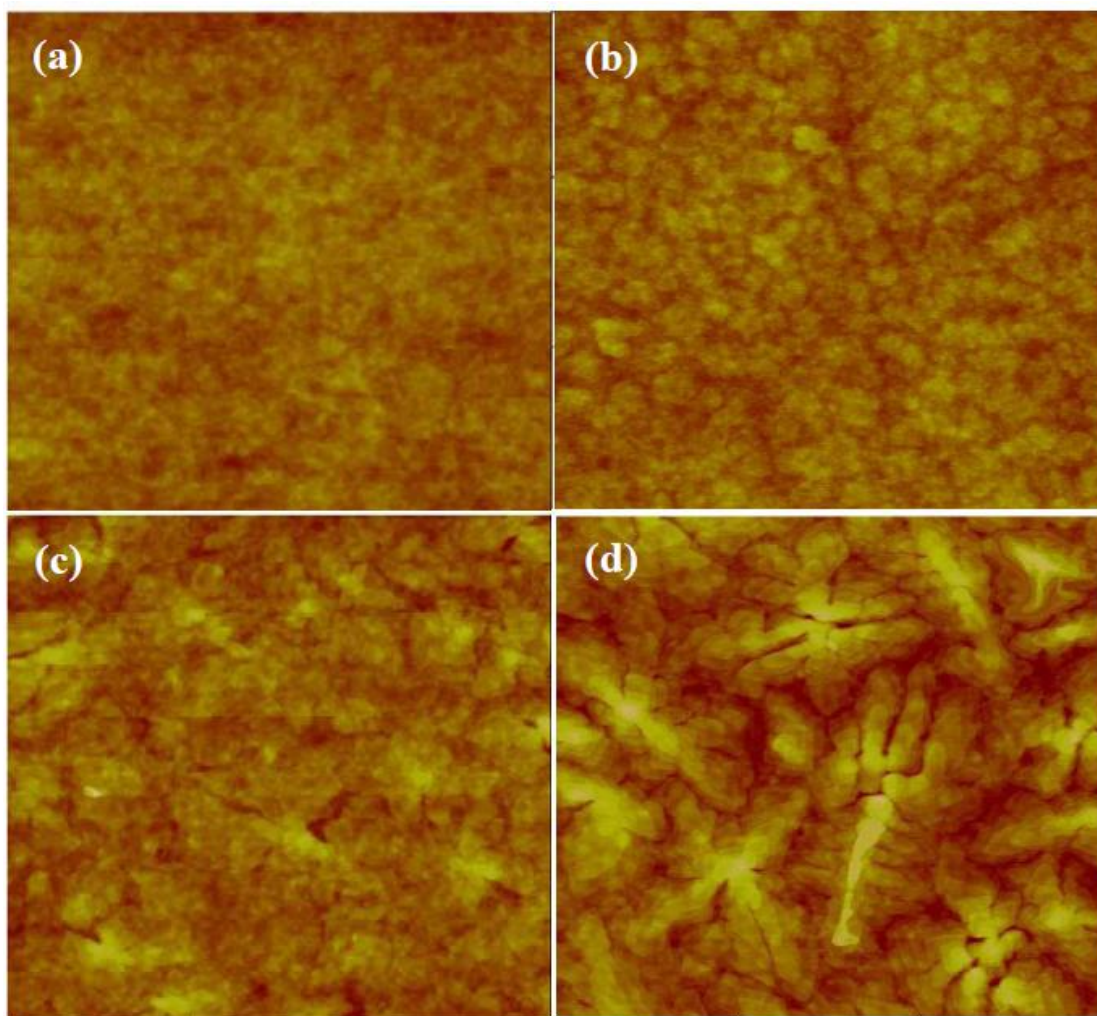


Fig. 3

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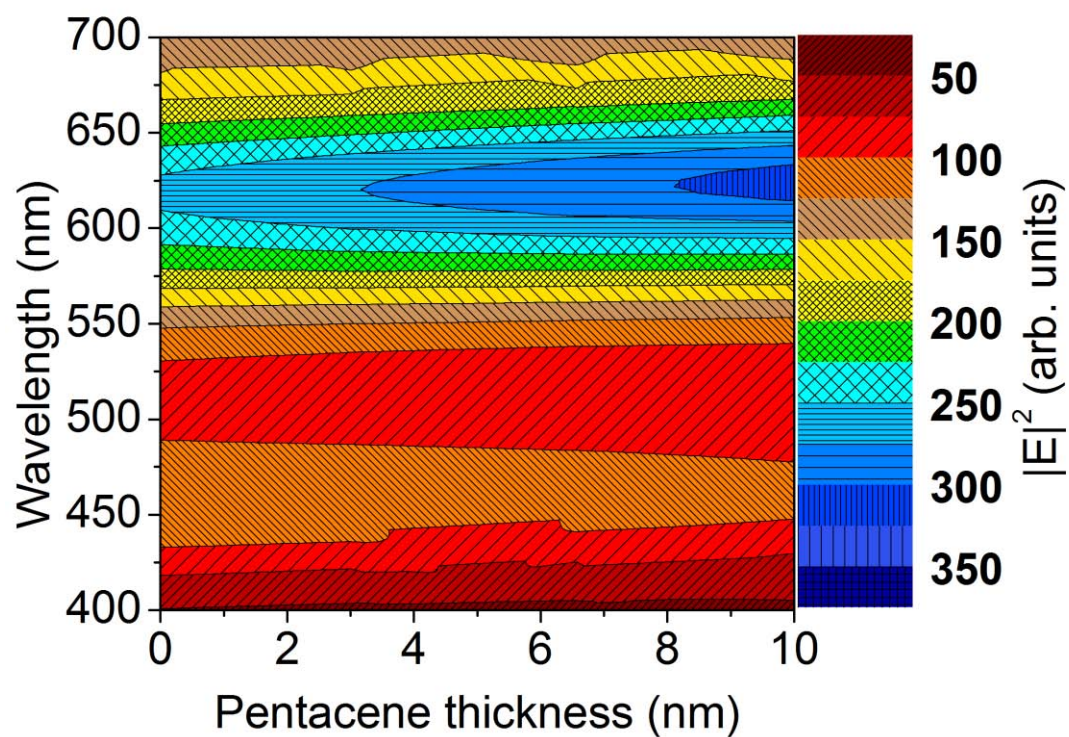


Fig. 4

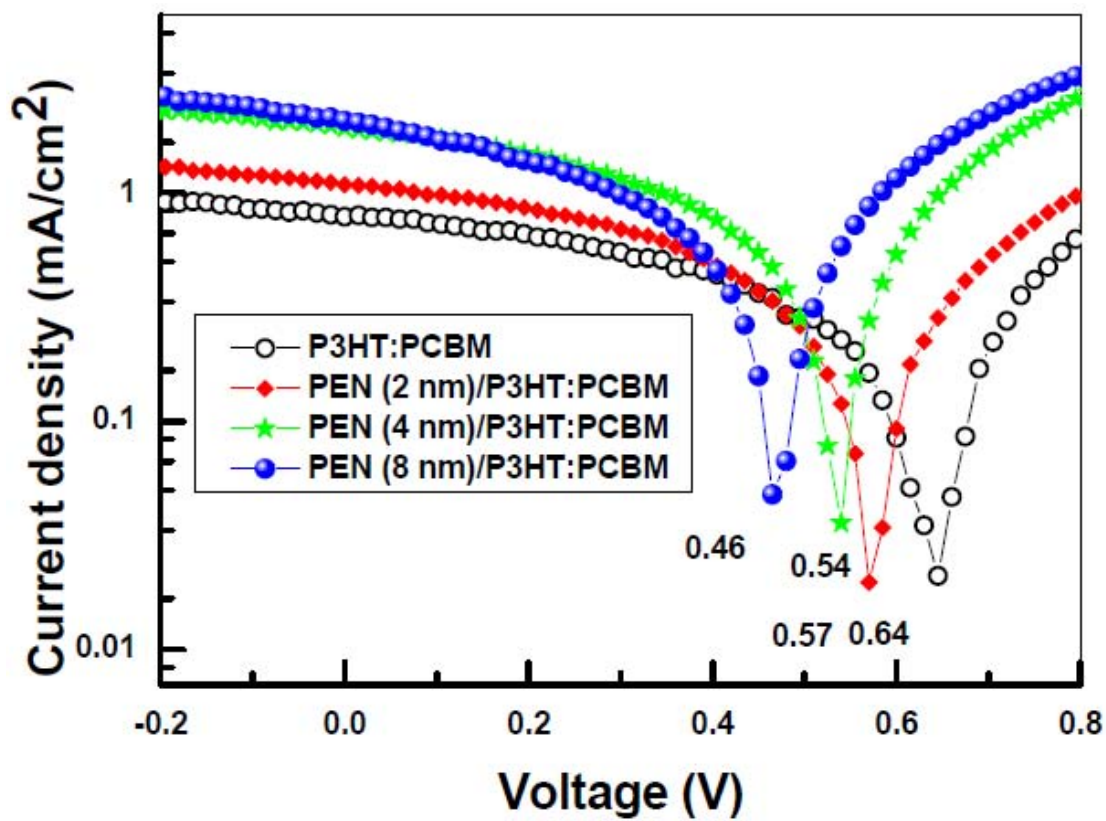


Fig. 5

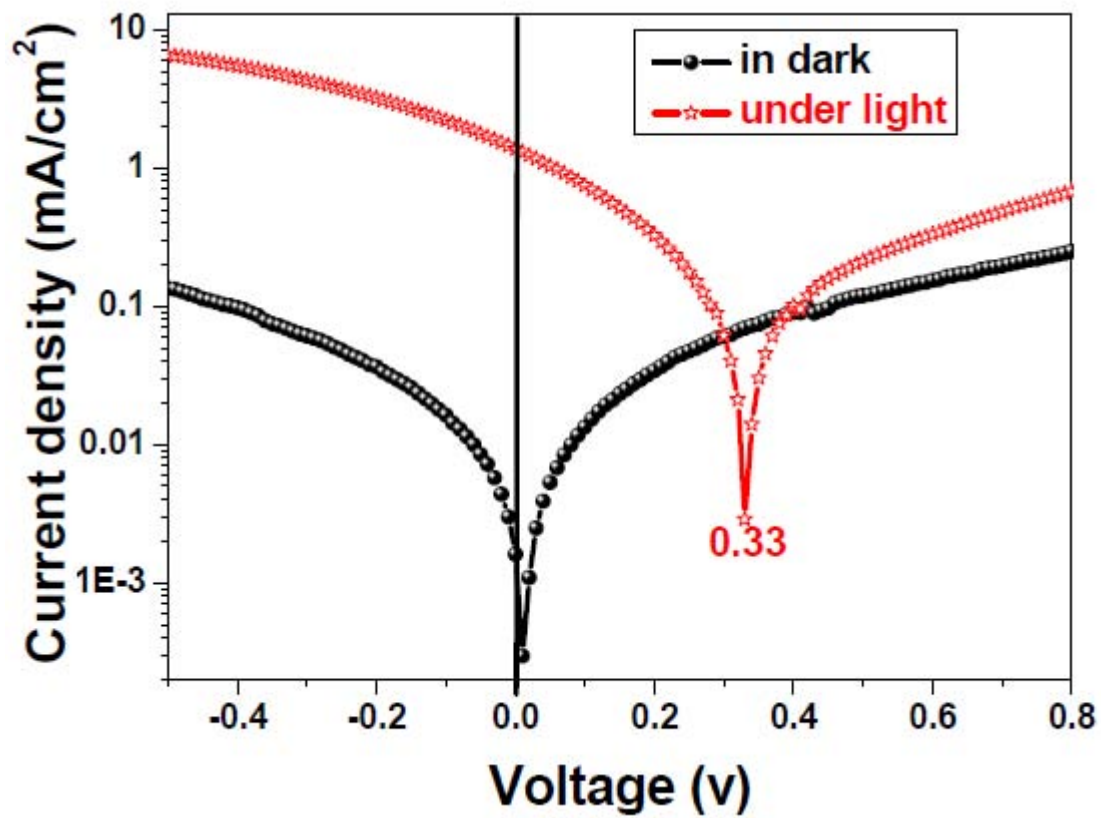


Fig. 6

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