Enhancing the photocurrent in poly(3-hexylthiophene)/[6,6]-phenyl C_{61} butyric acid methyl ester bulk heterojunction solar cells by using poly(3-hexylthiophene) as a buffer layer

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This work presents an approach for improving the unfavorable vertical composition gradients of poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl C_{61} butyric acid methyl ester (PCBM) in the photoactive layer of bulk heterojunction solar cells. The proposed method involves simply depositing a thin layer of P3HT on top of poly(3,4-ethylenedioxythiophene):poly(styrene-sulfonate) (PEDOT:PSS) prior to the P3HT:PCBM blend is spin coated. The results from photoluminescence and photovoltaic measurements indicate that incorporating this P3HT layer significantly enhances the electron blocking ability of PEDOT:PSS, the efficiency of photoinduced electron transfer and the photocurrent of the device, resulting in an improvement of the power conversion efficiency from 3.98% to 5.05%. © 2009 American Institute of Physics. [doi:10.1063/1.3242006]

Polymer solar cells have attracted considerable attention in recent years owing to the advantages of low cost, mechanical flexibility, light weight, and simplicity of fabrication.[1–3] Among numerous photoactive donor/acceptor composites, the blend of poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl C_{61} butyric acid methyl ester (PCBM) has been intensively investigated in recent years because the cell based on such composite has been shown to have a power conversion efficiency of as high as 3%–5%.[4–8] Many studies have demonstrated that appropriate annealing treatment[5,6] or the use of a high-boiling-point liquid as processing additive in the coating solution[9,10] during device fabrication is essential to obtain a high-efficiency cell. These processes focus mainly on increasing the number and size of the crystalline domains of P3HT and form simultaneously bi-continuous interpenetrating networks of two materials to transport carriers to electrodes. However, recent works have shown that these procedures frequently lead to a vertical composition gradient of PCBM and P3HT with a profile of PCBM-rich blend near the poly(3,4-ethylenedioxythiophene):poly(styrene-sulfonate) (PEDOT:PSS) layer and P3HT-rich blend adjacent to the top surface of the composite film[11] due to the difference between the surface energies of the two components and the induced dipole-dipole interactions between PCBM and the surface of the base layer.[12] This vertical composition profile is the opposite to that of the ideal donor-rich structure close to the anode and acceptor-rich structure next to the cathode, possibly lowering the area of the donor/acceptor interface and charge extraction efficiency. Accordingly, several approaches have been proposed for overcoming this drawback, including the use of an inverted cell structure,[12,13] the surface modification of the bottom layer with self-assembled layers,[11] and the sandwiching of a C_{60} derivative thin film between the donor/acceptor blend and the cathode.[14,15] Herein, we demonstrated that the insertion of a thin P3HT layer between P3HT/PCBM composite and

PEDOT:PSS films considerably increases the exciton dissociation efficiency and effectively blocks the free electron to the anode, increasing the photocurrent and cell efficiency.

P3HT/PCBM-based solar cells were fabricated by spin-coating a layer of PEDOT:PSS (Baytron P VP AI4083) on a pre-cleaned ITO glass (15 Ω sq^{-1}) and drying at 140 °C for 10 min in air to yield a dried film with a thickness of approximately 40 nm. After the thus-prepared substrates had been transferred into a nitrogen-filled glove box, a 1.0 wt % P3HT solution in chlorobenzene was spin-coated on top of the PEDOT:PSS at 1500 rpm for 30 s to form a 60-nm-thick film. Subsequently, a mixed solution of P3HT and PCBM (P3HT:PCBM=1:0.8 in weight) in chlorobenzene with a P3HT concentration of 15 mg/ml was spun on top of the P3HT layer. When the blend solution was dropped onto the substrate, the pre-coated P3HT film was partially dissolved to form a polymer-dominated mixture in the lower regions of the coating solution. To prevent the entire dissolution of the pristine polymer layer during coating, a high-molecular-weight P3HT with a weight-average molecular weight (M_w) of 47 000 g mol^{-1} and a polydispersity index of 1.33 was adopted in this step. The total thickness of the P3HT and P3HT:PCBM layers was determined using a Veeco Dektak 6M surface profiler and was about 175 nm. For comparison, a control device was also prepared by directly coating the P3HT/PCBM solution on top of PEDOT:PSS. The thickness of this composite film was measured to be around 160 nm. These films were then thermally annealed on a digitally controlled hot plate at 160 °C for 10 min. After they had been transferred into a vacuum chamber, and the chamber had been pumped down to a vacuum of 10^{-6} torr, the films were coated with Ca and then Al by thermal evaporation through a shadow mask (6 mm^2) to complete the devices. Figure 1(a) schematically depicts the configuration of the device.

Figure 1 displays the electronic energy level diagram of the device components, as well as the device structure of the P3HT/PCBM-based solar cell in which the blend film of P3HT:PCBM was the photoactive layer of the device. The energy levels of P3HT were determined by electrochemical

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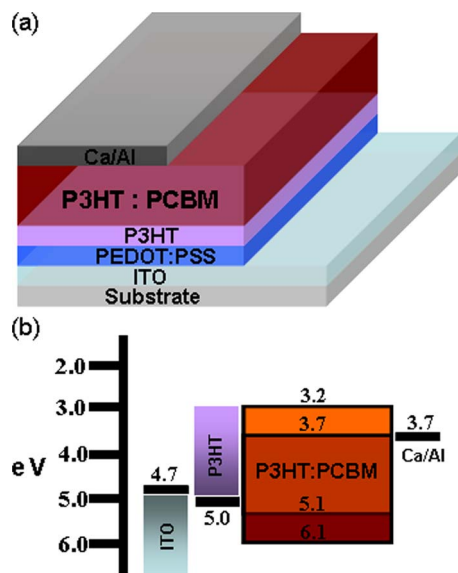
(a)

(b)

FIG. 1. (Color online) Layout of P3HT/PCBM-based solar cell. (a) Device structure, comprising PEDOT:PSS and P3HT as interfacial layers and a P3HT/PCBM active layer, sandwiched between ITO anode and calcium/aluminum cathode. (b) Schematic energy level diagram of device components.
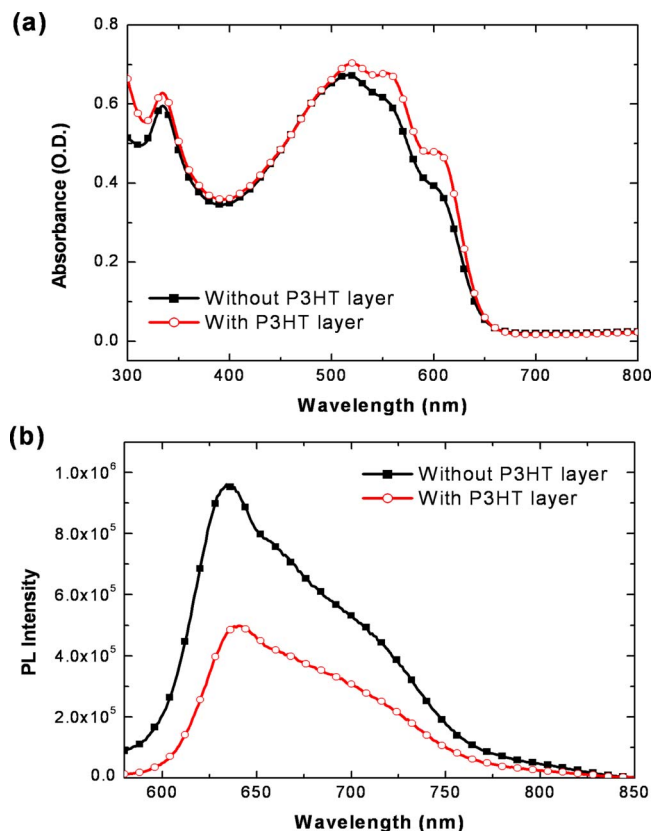
(a)

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FIG. 2. (Color online) (a) Dark J-V characteristic of P3HT/PCBM-based solar cell with and without a P3HT layer after thermal treatment and (b) corresponding J-V curve measured under AM1.5G filtered spectral illumination at an incident intensity of 100 mW/cm^2.

cyclic voltammetry. The lowest unoccupied molecular orbital energy level of P3HT is higher than that of PCBM, promoting the blocking of the transport of electrons to the anode from the active layer. An additional p-n junction is formed with those PCBM molecules that reside at the bottom of the active layer, increasing the donor-acceptor interfacial area and then the photoinduced electron transfer efficiency.

Figure 2(a) plots the dark J-V curves of P3HT/PCBM-based solar cells with and without a P3HT layer. The rectification ratio of the control device was 5.3×10^4 at ± 2 V, while the inclusion of a thin P3HT layer between PEDOT:PSS and P3HT/PCBM effectively increased the rectification ratio by a factor of around four to 2.2×10^5, revealing that the P3HT-inserted cell had a higher injection current at positive voltage and a lower leakage current at negative voltage. Previous investigations have shown that PEDOT:PSS is not an effective electron blocking layer.[16] This observation implies that the P3HT layer greatly increases the blocking of the transport of electrons to the anode in the cell.

Figure 2(b) plots the J-V characteristics of P3HT/PCBM-based solar cells with and without a P3HT layer under AM1.5G illumination at an incident intensity of 100 mW/cm^2, which was calibrated using a mono-Si reference with a KG5 filter (PV Measurements, Inc.). The control device exhibited an open-circuit voltage (V_{oc}) of 0.60 V, a short-circuit current density (J_{sc}) of 9.78 mA/cm^2, a fill factor (FF) of 67.8%, and a power conversion efficiency (PCE) of 3.98%. As expected, the presence of an extra P3HT layer had a minor effect on the V_{oc} but, interestingly, greatly increased the photocurrent of the device by approximately 20% to 12.00 mA/cm^2 and slightly improved the FF to 69.0%, yielding the highest power conversion efficiency of 5.05 %. Statistical data from 20 devices showed that the P3HT-inserted cells have a V_{oc}, J_{sc}, FF, and PCE of 0.60 ± 0.01 V, 11.83 ± 0.36 mA/cm^2, $68.1\% \pm 0.72\%$ and $4.89\% \pm 0.16\%$, respectively. This observation suggests that

this P3HT layer creates new contacts with those PCBM molecules that are distributed near the bottom of the P3HT:PCBM film, thus increasing the rate of generation of free carriers and the photocurrent density. Moreover, a separate set of experiments revealed that the cell using a low-molecular-weight P3HT ($M_w = 16\,200$) as the underlayer had a V_{oc} of 0.60 ± 0.01 V, a J_{sc} of 10.11 ± 0.28 mA/cm^2, a FF of $65.3\% \pm 2.14\%$, and a PCE of $3.93\% \pm 0.11\%$, which were comparable to the performance of the control device. This finding clearly demonstrates a high-molecular-weight P3HT is essential as an effective buffer layer to increase the short-current density and power conversion efficiency of a cell.

Figure 3(a) presents the UV-visible spectra of the devices with and without a P3HT layer. The P3HT/P3HT:PCBM film has a slightly higher optical density than the P3HT:PCBM film, suggesting that the incorporation of P3HT layer does not contribute significantly to light harvesting because the thickness (15 nm) of P3HT is much less than that (160 nm) of P3HT:PCBM. The spectrum of P3HT/P3HT:PCBM included more noticeable peaks at 550 and 620 nm with higher absorbance in the range of 550–660 nm than that of P3HT:PCBM, mainly because of the high crystallinity of pristine P3HT. Furthermore, the photoluminescence spectra of both films were measured at an excitation wavelength of 550 nm and presented in Fig. 3(b). The emission intensity of P3HT:PCBM clearly exceeds that of P3HT/P3HT:PCBM although the latter has higher absorbance at the excitation wavelength. This finding further supports the hypothesis that the presence of the P3HT layer greatly increased the interfa-
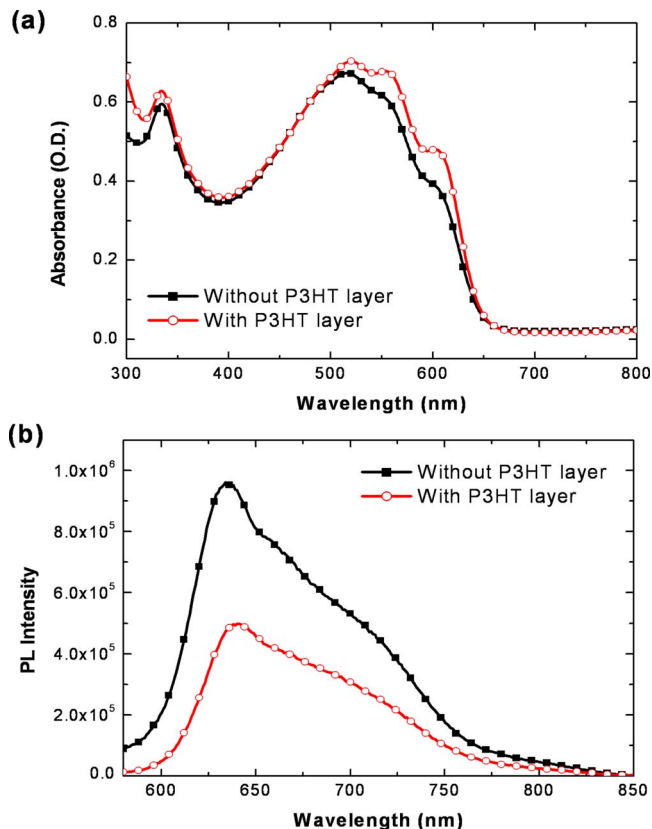
(a)

(b)

FIG. 3. (Color online) (a) UV-visible absorption spectra and (b) photolumi-nescence spectra of P3HT/PCBM film without a P3HT layer (filled square) and P3HT/P3HT:PCBM film (open circle) on ITO glass.
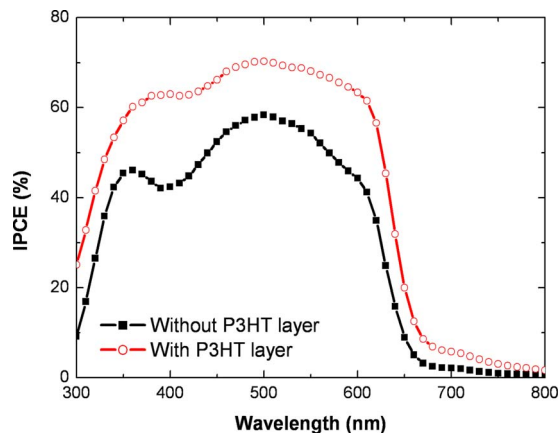

FIG. 4. (Color online) Incident photo-to-electron conversion efficiency spectra of P3HT/PCBM-based solar cells with (open circle) and without (filled square) a P3HT layer.

cial area between the donor and the acceptor materials and the efficiency of photoinduced electron transfer.

The IPCE spectra of P3HT-inserted and control cells after thermal treatment were displayed in Fig. 4. Both spectra have similar shapes but the device with a P3HT layer exhibited an IPCE of between 60% and 70% at incident wavelengths of between 350 and 600 nm, which are about 20% higher than those of the control cell, and consistent with the improvement in photocurrent in Fig. 2(b).

In conclusion, simply sandwiching a thin layer of high-molecular-weight P3HT between PEDOT:PSS and photoactive P3HT:PCBM layers greatly enhanced the short-circuit current density of the solar device through the creation of an extra donor/acceptor interface close to the bottom of the composite. Additionally, this layer substantially increased the electron blocking capability of PEDOT:PSS, leading to a large increment of the rectification ratio of the cell. As a result, an overall power conversion efficiency of 5.05% was obtained under AM1.5 illumination.

[1]C. J. Brabec, N. S. Sariciftci, and J. C. Hummelen, Adv. Funct. Mater. **11**, 15 (2001).
[2]M. W. Rowell, M. A. Topinka, M. D. McGehee, H. Prall, G. Dennler, N. S. Sariciftci, L. Hu, and G. Gruner, Appl. Phys. Lett. **88**, 233506 (2006).
[3]B. C. Thompson and J. M. J. Fréchet, Angew. Chem., Int. Ed. **47**, 58 (2008).
[4]F. Padinger, R. S. Rittberger, and N. S. Sariciftci, Adv. Funct. Mater. **13**, 85 (2003).
[5]W. Ma, C. Yang, X. Gong, K. Lee, and A. J. Heeger, Adv. Funct. Mater. **15**, 1617 (2005).
[6]G. Li, V. Shrotriya, J. Huang, Y. Yao, T. Moriarty, K. Emery, and Y. Yang, Nature Mater. **4**, 864 (2005).
[7]Y. Kim, S. Cook, S. M. Tuladhar, S. A. Choulis, J. Nelson, J. R. Durrant, D. D. C. Bradley, M. Giles, I. McCulloch, C. S. Ha, and M. Ree, Nature Mater. **5**, 197 (2006).
[8]A. J. Moulé and K. Meerholz, Adv. Mater. **20**, 240 (2008).
[9]J. Peet, J. Y. Kim, N. E. Coates, W. L. Ma, D. Moses, A. J. Heeger, and G. C. Bazan, Nature Mater. **6**, 497 (2007).
[10]Y. Chang and L. Wang, J. Phys. Chem. C **112**, 17716 (2008).
[11]M. Canpoy-Quiles, T. Ferenczi, T. Agostinelli, P. G. Etchegoin, Y. Kim, T. D. Anthopoulos, P. N. Stavrinou, D. D. C. Bradley, and J. Nelson, Nature Mater. **7**, 158 (2008).
[12]Z. Xu, L.-M. Chen, G. Yang, C.-H. Huang, J. Hou, Y. Wu, G. Li, C.-S. Hsu, and Y. Yang, Adv. Funct. Mater. **19**, 1 (2009).
[13]H. H. Liao, L. M. Chen, Z. Xu, G. Li, and Y. Yang, Appl. Phys. Lett. **92**, 173303 (2008).
[14]Q. Wei, T. Nishizawa, K. Tajiima, and K. Hashimoto, Adv. Mater. **20**, 2211 (2008).
[15]A. Kumar, G. Li, Z. Hong, and Y. Yang, Nanotechnology **20**, 165202 (2009).
[16]A. L. Ayzner, D. D. Wanger, C. J. Tassone, S. H. Tolbert, and B. J. Schwartz, J. Phys. Chem. C **112**, 18711 (2008).