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RESEARCH ARTICLE

Flexible solar cells based on PCBM/P3HT heterojunction

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Abstract [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) / poly (3-hexylthiophene) (P3HT) heterojunction has not only the absorption in ultraviolet light for PCBM, but also the absorption in visible light for P3HT, which widens the incident light harvest range, improving the photoelectrical response of hybrid solar cell effectively. Using conducting polymers blend heterojunction consisting of C_{60} derivatives PCBM and P3HT as charge carrier transferring medium to replace I_3^-/I^- redox electrolyte and dye, a novel flexible solar cell was fabricated in this study. The influence of PCBM/P3HT mass ratio on the photovoltaic performance of the solar cell was also studied. Under a simulated solar irradiation of 100 mW·cm^{-2}, the flexible solar cell achieved a light-to-electric energy conversion efficiency of 1.04%, an open circuit voltage of 0.86 V, short circuit current density of 2.6 mA·cm^{-2} and fill factor (*FF*) of 0.46.

Keywords flexible solar cell, heterojunction, [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM), poly (3-hexylthiophene) (P3HT)

1 Introduction

In the past two decades, considerable efforts have been devoted to the dye-sensitized titania nanocrystalline solar cell (DSSC) since its first prototype was reported by Grätzel [1]. The DSSC is considered to be a potential alternative to conventional silicon cells because of its low cost and simple preparation procedure [2–4]. Recently, flexible DSSCs based on polymer substrate become a new research hotspot [5,6] because of its low-cost, light-weight, flexibility and feasible shape design. In a DSSC, electrolyte plays an essential role in transferring charge carriers. There are three kinds of electrolytes [7]: 1) liquid electrolytes have higher conductivity and DSSC conversion efficiency but lower stability; 2) solid state electrolytes have lower conductivity and DSSC conversion efficiency but better stability; 3) quasi-solid-state electrolytes have moderate conductivity, DSSC efficiency and stability. The search for a new charge carrier transfer medium remains an active research.

Another important progress in solar cell is polymer solar cell in the 1990s. Polymer solar cell, as an alternative, renewable source of electrical energy has attracted considerable attention during the past decade [8,9], because of its low-cost, light-weight and flexible. An important breakthrough came with the introduction of a blend polymer heterojunction of an electron-donor and electron-acceptor as active layer by Heeger et al. [10,11]. A typical blend heterojunction comprises poly (3-hexylthiophene) (P3HT) as a donor and C_{60} derivative, [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) as an acceptor. The heterojunction can absorb incident visible and ultraviolet light, induce separation of excitons and transfer charge carriers effectively.

In this paper, PCBM/P3HT heterojunction is used to replace I_3^-/I^- redox electrolyte and dye in DSSC, a novel flexible TiO_2/PCBM/P3HT hybrid solar cell is fabricated by using low-temperature film-forming technique. The heterojunction of P3HT/PCBM cannot only transfer charge carrier, but also harvest incident light, consequently, it is expected that the photovoltaic performance of the solar cell can be improved and the device can be simplified.

2 Experiment

2.1 Materials

Poly-(3-hexylthiophene) (P3HT, purity 99.95%) and [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM, purity 99.95%) were purchased from Luoyang Microlight

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Material Technology Co., Ltd, China. TiO_2 nanoparticles (P25) were purchased from Degussa, Germany. 1,2-dichlorobenzene (CB), anhydrous ethanol, isopropanol, nitric acid, acetic acid, tetrabutyltitanate and titanium tetrachloride ($TiCl_4$) were analytic purity grade and purchased from Shanghai Chemical Agent Ltd, China. Polyethylene glycol with average molecular weight 20000 (PEG-20000) and Triton X-100 were purchased from the same company. All reagents were used without further treatment before using. Conductive flexible plate (ITO/PEN flexible, sheet resistance $12\,\Omega\cdot cm^{-2}$, purchased from Japan) was used as a substrate for precipitating TiO_2 porous film and was cut into 1 cm × 2 cm sheets, Pt-ITO/PEN (sheet resistance $5\,\Omega\cdot cm^{-2}$) was used counter electrode and purchased from Japan.

2.2 Preparation of TiO_2 film

ITO/PEN substrate was immerged in 50% ethanol solution for 24 h, and then be immerged in 95% ethanol solution to clean the substrate. The cleaned substrate was kept in absolute ethanol solution and blow dried prior to use.

Predetermined amount of TiO_2 powder (P25) was pretreated by heating at 450°C for 30 min in an electric muffle furnace, then cooling to room temperature [12]. The pretreated P25, distilled water and absolute ethanol were mixed with mole ratio of 1:1:5 and turned to an autoclave (packing volume less than 80%), followed by a hydrothermal treatment at 200°C for 24 h, thus a homogeneous and stable TiO_2 colloid was obtained.

TiO_2 colloid was coated on the ITO/PEN substrate by a doctor-scraping technique. The thickness and the area (about 0.5 cm × 0.4 cm) of TiO_2 film was controlled by the adhesive tape around the edge of the ITO/PEN substrate [13,14]. The process was repeated for three times to form a thick TiO_2 film. The film was dried in moisture-free air and was irradiated for 15 min [15,16]. The resultant TiO_2 flexible film was heated at 100°C for 30 min in air. Thus a flexible TiO_2 film electrode was obtained.

2.3 Preparation of flexible hybrid solar cell

PCBM and P3HT were mixed with a predetermined ratio and dissolved in 1,2-dichlorobenzene solvent to form a conductive polymer solution with the concentration of 15 mg/mL, under stirring at 40°C for 24 h. A flexible solar cell was assembled by injecting PCBM/P3HT solution into the aperture between the TiO_2 porous film electrode (anode electrode) and a Pt-ITO/PEN (cathode electrode). Two electrodes were clipped together and cyanoacrylate adhesive was used as a sealant to prevent polymer solution from leaking. Then the cell was placed overnight to allow PCBM/P3HT penetrating into the aperture of TiO_2 nanoporous film completely.

2.4 Measurements

UV-Vis absorption spectra of samples were measured on an Optizen (3100 UV) spectrophotometer. Photoluminescence (PL) spectra of PCBM, P3HT and hybrid PCBM/P3HT were measured by dissolving these samples in 1,2-dichlorobenzene (CB) solvent and using a FSP920 fluorescence spectrophotometer exciting with a 430 nm light.

Photovoltaic test of the flexible hybrid solar cell was carried out by measuring photocurrent-photovoltage (*J-V*) character curves under irradiation of white light with a solar simulator (XQ-500W, Shanghai Photoelectricity Device Company, China) and a computer controlled voltage current source-meter CHI660C electrochemical measurement system. The incident light intensity was $100\,mW\cdot cm^{-2}$. The fill factor (*FF*) and the overall light-to-electrical energy conversion efficiency (η) of the solar cell were calculated according to the following equations [17]:

$$\eta(\%) = \frac{V_{max} \times J_{max}}{P_{in}} \times 100\% = \frac{V_{OC} \times J_{SC} \times FF}{P_{in}} \times 100\%, \tag{1}$$

$$FF = \frac{V_{max} \times J_{max}}{V_{OC} \times J_{SC}}, \tag{2}$$

where J_{SC} is the short-circuit current density ($mA\cdot cm^{-2}$); V_{OC} is the open-circuit voltage (V), P_{in} is the incident light power and J_{max} ($mA\cdot cm^{-2}$) and V_{max} (V) are the current density and voltage at the point of maximum power output in the *J-V* curves, respectively.

Spectral response for the solar cell was determined by measuring the wavelength dependence of the incident photon-to-current efficiency (IPCE) using the light from a xenon lamp through a monochromator (PXJ43B11, Japan) and focusing onto the cell. The IPCE is calculated according to the following equation [18]:

$$\mathrm{IPCE}(\lambda) = \frac{12400 \times J_{SC}}{\lambda \times P_{in}}. \tag{3}$$

3 Results and discussion

3.1 UV-Vis absorption spectra

UV-Vis absorption spectra of PCBM, P3HT and PCBM/P3H hybrid are shown in Fig. 1. It can be seen that P3HT has a wide and strong absorption band with wavelength from 350 to 550 nm, and PCBM has a strong absorption in ultraviolet range with wavelength of 300–350 nm [19].

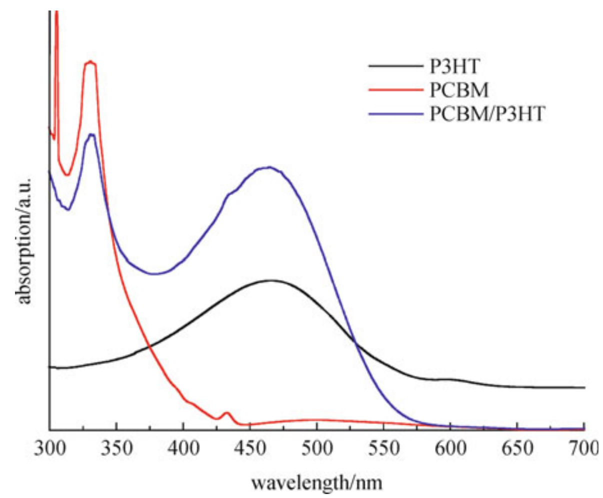

Fig. 1 UV-Vis absorption spectra of PCBM, P3HT, and PCBM/P3HT hybrid

After mixing PCBM and P3HT, visible absorption for P3HT and ultraviolet absorption for PCBM are further strengthened, which is due to the superposition absorption and heterojunction effect of PCBM and P3HT.

3.2 PL spectra

Figure 2(a) displays the PL spectra excited by a 430 nm light. It can be seen that PCBM, P3HT, PCBM/P3HT all have the maximum PL peak at 586 nm [20,21]. From the area and the half peak width covered by the curves, it is known that the PL intensity of PCBM/P3HT hybrid is larger than that of PCBM or P3HT only. When PCBM and P3HT are blended, a heterojunction PCBM/P3HT is formed, the heterojunction favors the photoluminescence, resulting in the higher PL intensity, which readies for the improvement of solar cell performance and enhancement of the photoelectric conversion efficiency. Figure 2(b) shows PL spectra of PCBM/P3HT with different mass ratios. When the mass ratio of PCBM/P3HT is 1∶2, the PCBM/P3HT has the strongest absorption.

3.3 Incident photon-to-current efficiency (IPCE)

IPCE of solar cells with PCBM, P3HT and PCBM/P3HT are shown in Fig. 3. It can be seen the solar cells have better photoelectric response in 325–375 nm (UV area), and 500–550 nm (visible area). The higher IPCE in the UV range is mainly caused by the strong absorption of PCBM on UV-induced [22]. On the other hand, it is due to TiO_2 film. TiO_2 has an absorption peak around 350 nm which is related with the direct band gap photo-electron excitation of the TiO_2 [23]. While the higher IPCE in the visible area comes from the absorption of P3HT [24], IPCE spectrum and UV-Vis absorption spectrum have a similar light

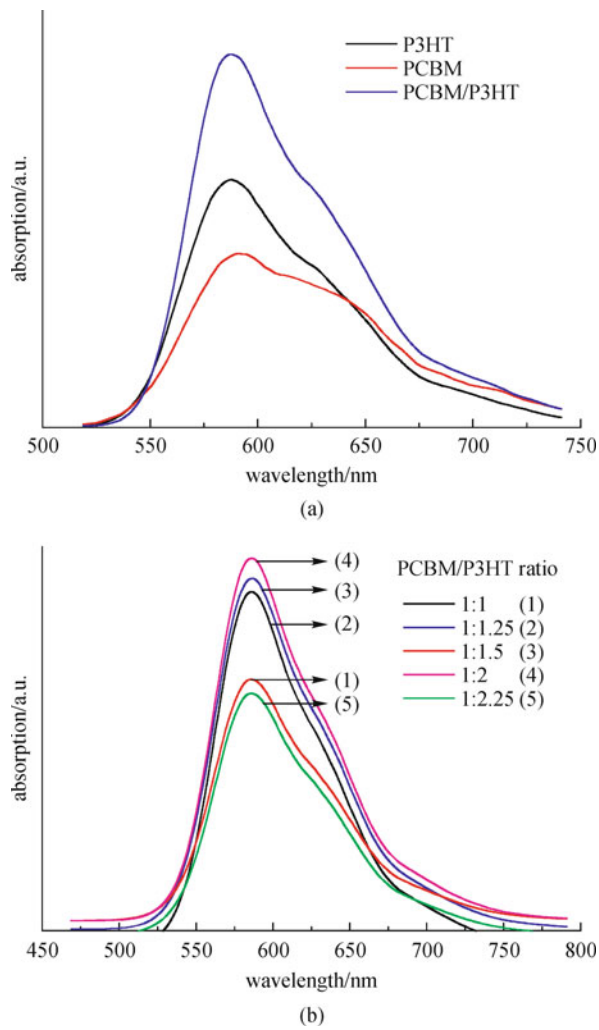

Fig. 2 PL spectra excited at 430 nm. (a) PCBM, P3HT and PCBM/P3HT; (b) PCBM/P3HT with different ratios

response range, though they do not strictly overlap in visible light, indicating that the photoelectrochemical conversion is achieved through photosensitization of PCBM/P3HT. Gebeyehu et al. [25] got the same result by using P3HT spin coated. The band gaps of PCBM and P3HT are between 1.5 and 3.0 eV, their lower unoccupied molecular orbitals (LUMOs) are much higher than TiO_2 conduction band (4.3 eV). Therefore, it is possible and practical through the polymer singlet excited state to finish charge transfer. The effective charge absorption and transfer of oxidation state of polymer readies light absorption by PCBM-TiO_2, P3HT-TiO_2 and PCBM/P3HT-TiO_2 composite films [26]. Thus, it is feasible using PCBM/P3HT heterojunction to achieve photosensitization and charge transfer, which provides an important way for developing novel solar cells.

IPCE of solar cell has an optimization result with PCBM/P3HT mass ratio at 1∶2 [21], and it has the highest performance of 3.8% at 530 nm.

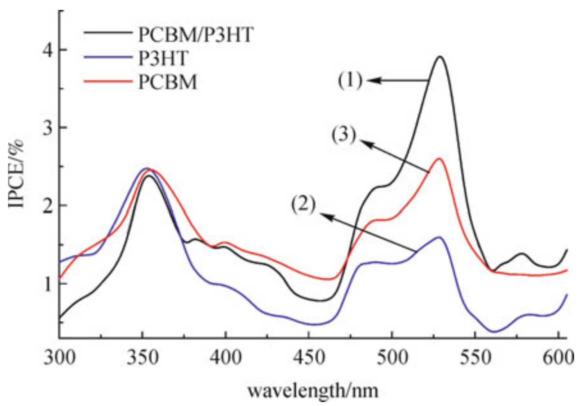

Fig. 3 IPCE of solar cells with PCBM, P3HT and PCBM/P3HT

3.4 Photovoltaic performance of solar cells with different PCBM/P3HT ratios

PCBM/P3HT mass ratio has a great influence on the photovoltaic performance of the solar cell. Under a simulated solar light irradiation of 100 mW·cm^{-2}, the *J*-*V* characteristic curves of the solar cells with different PCBM/P3HT ratios were measured, respectively. The results are shown in Fig. 4, and the open circuit voltage (V_{OC}), short circuit current density (J_{SC}), *FF*, and overall light-to-electrical energy conversion efficiency (η) of the solar cells are summarized in Table 1.

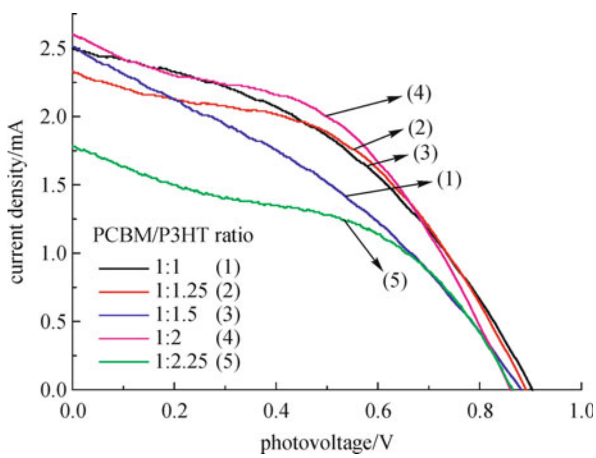

Fig. 4 *J*-*V* curves for solar cells with different PCBM/P3HT ratios

From Fig. 4 and Table 1, the solar cells with different PCBM/P3HT ratios have similar open circuit voltage (V_{OC}) of about 0.87 V, which is due to that V_{OC} is mainly determined by the energy level difference of the donor highest occupied molecular orbital (HOMO) and the acceptor LUMO, since all solar cells are composed of PCBM, P3HT and TiO_2, their V_{OC} is closed. On the other hand, the cells with different PCBM/P3HT ratios have different short-circuit current density (J_{SC}), ranging from 1.78 to 2.60 mA·cm^{-2}. J_{SC} is determined by incident visible and ultraviolet light-harvesting and charge carrier separation and transferring, PCBM/P3HT ratios for these cells are different, therefore showing different J_{SC}. It can be seen that solar cell with mass ratio of PCBM/P3HT at 1:2 possesses the best photovoltaic performance with the photoelectric conversion efficiency of 1.04%, current density of 2.60 mA·cm^{-2} and fill factor of 0.46. For the cells with the PCBM/P3HT ratios at 1:1.5 and 1:2.25, the current density (J_{SC}) are lower, which results in lower conversion efficiency of 0.68% and 0.69%, compared with other solar cells.

3.5 Influence of substrate and dye on photovoltaic parameter of solar cells

To explore the influence of substrate and dye on photovoltaic parameter of the solar cells, we prepared four kinds of solar cells with the same PCBM:P3HT mass ratio of 1:2 [21,27], their photovoltaic performances are shown in Table 2.

From Table 2, it can be seen that the substrate has a great influence on the performance of solar cells. Compared to the cells with flexible ITO/PEN substrate, the cells with FTO/glass substrate possess higher photocurrent and fill factor, which is due to that the FTO/glass substrate allow a heat treatment at 400°C, resulting in a more compact TiO_2 film electrode and better charge carrier transport; whereas ITO/PEN substrate can but endure heat treatment lower than 150°C, leading to more loose TiO_2 film and poor charge carrier transport. On the other hand, the solar cells with dye-sensitized have a better performance than those without dye-sensitized, this is because dye N719 has strong absorption ability to UV and visible light. It is notable that four solar cells have similar open circuit voltage (V_{OC}) of about 0.87 V, which is due to that V_{OC} is

Table 1 Influence of PCBM/P3HT ratios on photoelectric properties of solar cells

PCBM/P3HT ratio	V_{OC}/V	J_{SC}/(mA·cm^{-2})	*FF*/%	η/%
1:1	0.86	2.30	0.43	0.85
1:1.25	0.89	2.49	0.40	0.89
1:1.5	0.90	2.49	0.45	1.01
1:2	0.87	2.60	0.46	1.04
1:2.25	0.87	1.78	0.45	0.70

Table 2 Influence of substrate and dye on photovoltaic properties of solar cells

solar cells	V_{OC}/V	J_{SC}/(mA·cm^{-2})	*FF*/%	*η*/%
FTO/glass substrate with dye	0.87	5.52	0.64	3.09
FTO/glass substrate without dye	0.85	5.47	0.64	2.97
ITO/PEN substrate with dye	0.87	3.02	0.54	1.43
ITO/PEN substrate without dye	0.87	2.60	0.46	1.04

mainly determined by the energy level difference of the donor HOMO and the acceptor LUMO, since all solar cells are composed of PCBM, P3HT and TiO_2.

4 Conclusions

In conclusion, a novel TiO_2/PCBM/P3HT flexible solar cell was fabricated by using blend heterojunction consisting of PCBM and P3HT to replace I_3^-/I^- redox electrolyte and dye in DSSC. It is found that the P3HT/PCBM heterojunction widened the incident light-harvesting range, improved the photoelectrical response of the solar cell effectively. Under an optimized condition with PCBM/P3HT mass ratio of 1:2, the cell showed a short circuit current of 2.60 mA·cm^{-2}, open circuit voltage of 0.87 V, *FF* of 0.46, and light-to-electric energy conversion efficiency of 1.04% under a simulated solar irradiation of 100 mW·cm^{-2}. The results demonstrate the feasibility that the polymer heterojunction can be instead of redox electrolytes and dyes in DSSC, further optimizing preparation, the photoelectrical performance of solar cell will be improved.

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