Solar Energy Materials & Solar Cells 97 (2012) 71–77

Contents lists available at SciVerse ScienceDirect

Solar Energy Materials & Solar Cells

journal homepage: www.elsevier.com/locate/solmat

Influence of $PC_{60}BM$ or $PC_{70}BM$ as electron acceptor on the performance of polymer solar cells

Fujun Zhang [a,*], Zuliang Zhuo [a], Jian Zhang [b,*], Xin Wang [a], Xiaowei Xu [a], Zixuan Wang [a], Yusheng Xin [a], Jian Wang [a], Jin Wang [a], Weihua Tang [c,*], Zheng Xu [a], Yongsheng Wang [a]

[a] Key Laboratory of Luminescence and Optical Information, Ministry of Education, Beijing Jiaotong University, Beijing 100044, People's Republic of China
[b] State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, 457 Zhongshan Road, Dalian 116023, People's Republic of China
[c] Key Laboratory for Soft Chemistry and Functional Materials, Ministry of Education, Nanjing University of Science and Technology, Nanjing 210094, People's Republic of China

ARTICLE INFO

Article history:
Received 21 July 2011
Received in revised form
1 September 2011
Accepted 5 September 2011
Available online 5 October 2011

Keywords:
P3HT
$PC_{70}BM$
$PC_{60}BM$
Photon harvesting
Power conversion efficiency

ABSTRACT

Two series of P3HT-based polymer solar cell (PSCs) only with different electron acceptors $PC_{70}BM$ or $PC_{60}BM$ were investigated under the same conditions. The PSCs with $PC_{70}BM$ as the electron acceptor exhibit a relatively strong and broad absorption in the visible range and high external quantum efficiency, which results in a relatively high open circuit voltage (V_{oc}) of 0.62 V, short circuit current density (J_{sc}) of 11.85 mA/cm^2 and power conversion efficiency (PCE) of 3.52%. The PSCs with $PC_{60}BM$ as the electron acceptor have a relatively low V_{oc} of 0.58 V, J_{sc} of 10.68 mA/cm^2 and PCE of 3.02% due to the weak absorption of $PC_{60}BM$ in the visible light range. The function of $PC_{70}BM$ instead of $PC_{60}BM$ as electron acceptor could be summarized as follows: i) the strong absorption $PC_{70}BM$ in the visible range results in much more photon harvesting; ii) the relatively low electron mobility and relatively big size of $PC_{70}BM$ molecule influences the charge transporting and phase separation. The ultimate performances of PSCs are codetermined by the photon harvesting, exciton dissociation, charge carrier transport and collection.

1. Introduction

Polymer solar cells (PSCs) have attracted more and more attention as a new energy source due to their light weight, ease of large scale manufacture, compatibility with flexible substrates and the need to develop an inexpensive clean and sustainable renewable energy source for satisfying economic development and human living [1–4]. Krebs et al. have reported a series of landmark research works in the development of large area, high stability, high efficiency and different configuration PSCs [5–8]. Recently, some imaginative scientists have already paid much more attention to the lifetime and degradation mechanism of PSCs with different cells configurations, especially to the inverted configuration with high work function metal as the top anode [9–12]. However, many challenges have to be efficiently addressed before the vision of large scale manufacture and widespread usage of low-cost PSCs can be anticipated, including high efficiency, high stability, low-cost, high speed production, large-area and environment friendly process. The fundamental issues, such as the interfacial states, the stability/degradation of devices, the effect of annealing treatment and doping concentration, the balance of charge carriers, are still not very clear [13–17]. Krebs et al. have already developed solvent-free and environmentally friendly solvent processing methodologies [18,19]. The all-water-processing solar cells with inverted structure exhibited a PCE up to 0.70% [18]. Besides the obvious processing advantage of the solubility switching, removing the side chains from the bulk active layer furthermore means removal of non-absorption material. Several studies show enhanced stability of the active layer towards general degradation [20,21]. The possibility of achieving aqueous processing and operator safety and avoiding environmentally harmful solvents has been demonstrated, which is a great step towards the commercialization of PSCs.

In the past years, much more attention was paid to develop high efficiency polymer donors with strong and broad absorption in the visible light range [9]. In fact, the electron acceptors are of the same importance as that of the electron donors for high performance PSCs. Up to date, [6,6]-phenyl-C-61-butyric acid methyl ester ($PC_{60}BM$) is the most commonly investigated electron acceptor for solution processed PSCs. Recently, some new fullerene derivatives with up-shifted lowest unoccupied molecular orbits (LUMO) energy levels have been developed and assembled with the most representative donors P3HT, showing

* Corresponding authors. Fax: +86 10 51683933.
E-mail addresses: fjzhang@bjtu.edu.cn (F. Zhang), jianzhang@dicp.ac.an (J. Zhang), whtang@mail.njust.edu.cn (W. Tang).

0927-0248/$ - see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.solmat.2011.09.006

higher open circuit voltage (V_{oc}) and PCE [22,23]. However, the low absorption of $PC_{60}BM$ and its derivatives in the visible light range is not conducive to further improving the performance of PSCs. To address this short fall, [6,6]-phenyl-C-71-butyric acid methyl ester ($PC_{70}BM$) and its derivatives are selected as the electron acceptors to improve light absorption in the visible light range, leading to more exctions in the active layer [24]. It is worth mentioning that the performance of PSCs should be codetermined by the following parameters, including absorption, the extent of phase separation and the balance of charge carrier transporting. Recently, Xi et al. also reported that the cells with C_{70} as the electron acceptor and copper phthalocyanine (CuPc) as electron donor show an increased photovoltaic performance compared with the cells with C_{60} as the electron acceptor and CuPc as electron donor [25]. In this paper, two series of P3HT-based PSCs with different electron donors were investigated under the same conditions. The effects of $PC_{70}BM$ and $PC_{60}BM$ on the performance of PSCs were comparatively studied by the absorption spectra, the extent of phase separation, external quantum efficiency (EQE) and saturation photocurrent density.

2. Experimental details

The indium tin oxide (ITO) coated glass substrates (sheet resistance 15 Ω/□) were cleaned consecutively in ultrasonic baths containing acetone, ethanol and de-ionized water and dried by high speed nitrogen gas. The cleaned substrates were treated by UV–ozone for 10 min to improve the work function of ITO. A thin layer of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) was spin-coated on the substrates at the speed of 3000 round per minute (RPM) for 40 s. The substrates coated with PEDOT:PSS thin film were transferred to a hot plate and annealed at 150 °C for 10 min. Photovoltaic materials P3HT, $PC_{60}BM$ and $PC_{70}BM$ were purchased from Sigma-Aldrich and dissolved in chloroform to prepare 10 mg/ml stock solution without further purification, respectively. Then $PC_{60}BM$ and $PC_{70}BM$ solutions were mixed with P3HT with the same volume ratio, respectively. Their blended solutions were spin-coated on PEDOT:PSS coated ITO substrates and then annealed at 120 °C for 10 min under atmosphere conditions. Subsequently, the substrates coated with different active layers were transferred to a vacuum chamber to prepare the aluminum (Al) cathode under 5×10^{-3} Pa. The thickness of Al cathode is about 100 nm and the active area is about 0.09 cm^2 through foursquare shadow mask.

The absorption spectra of all above-mentioned films were measured on Shimadzu UV-3101 PC spectrometer. The photoluminescence spectra were measured on Perkin Elmer LS55 fluorescence spectrometer. The current density–voltage (J–V) characteristics of PSCs were measured and recorded by Keithley source meter 2410 in dark and under illumination at 100 mW/cm^2 using a 150 W Xenon lamp. The EQE spectra were measured on Zolix Solar Cell Scan 100. The optical microscope photographs were captured by a Nikon Eclipse TE2000-S inverted microscope. The morphology and structure of the blended thin films were investigated with atom force microscopy (AFM) using a multimode Nanoscope IIIa operated in tapping mode. All measurements were carried out at room conditions. The chemical structures of the used photovoltaic materials and schematic diagram of cells are shown in Fig. 1.

3. Results and discussion

Photon harvesting is the first key issue to obtain high performance PSCs. The absorption spectra of pure $PC_{70}BM$, pure $PC_{60}BM$ and P3HT blended with $PC_{70}BM$ or $PC_{60}BM$ thin films after annealing treatment at 120 °C for 10 min are shown in the Fig. 2a. It is apparent that the blended P3HT:$PC_{70}BM$ film shows a stronger absorption in the visible range than P3HT:$PC_{60}BM$ film due to the contribution from $PC_{70}BM$ molecule. The pure $PC_{70}BM$ thin films exhibits relatively strong absorption from 400 to 700 nm range and longer wavelength absorption at 362 nm compared with $PC_{60}BM$ at 338 nm in the UV light range. Recently, Nicolaidis et al. reported that about 13% of J_{sc} arises from the contribution of the fullerene component in the P3HT:$PC_{60}BM$ (1:1) system under air mass (AM) 1.5 illumination conditions [26]. It means that the photocurrent generated by light that is absorbed by the fullerene component needs to be considered when evaluating the performance of PSCs systems containing PCBM. Therefore, $PC_{70}BM$ should give more contribution on the J_{sc} in the P3HT:$PC_{70}BM$ (1:1) system due to its stronger and broader absorption range in the visible light range compared with $PC_{60}BM$. Fig. 2b shows absorption spectra variation of P3HT:$PC_{60}BM$ and P3HT:$PC_{70}BM$ thin films before and after annealing treatment. The absorption P3HT:$PC_{70}BM$ films after annealing treatment is much stronger than that of P3HT:$PC_{60}BM$ films, which favors more photon harvesting and the improvement of based-P3HT:$PC_{70}BM$ PSCs performance. The annealing treatment on the active layer or the devices has been extensively carried out in order to improve the performance of PSCs, especially for the P3HT:PCBM system [20,27–30]. The main contributions of annealing treatment could be summarized as the following points: i) increase P3HT crystallization, which may affect its highest occupied molecular orbit (HOMO) level and particularly the nature of film morphology nears the film-air interface [29]; ii) enhance absorption intensity and range of P3HT as well as improve interchain and intrachain orders of P3HT [31,32]; iii) reorganize and form a phase segregated 3D structure of donor and acceptor molecules enhancing the charge transfer efficiency [33]; iv) enhance charge carrier mobility and the photoluminescence (PL) intensity of P3HT thin films [34,35]; vi) optimize interfacial contact between the metal electrode and the active layer

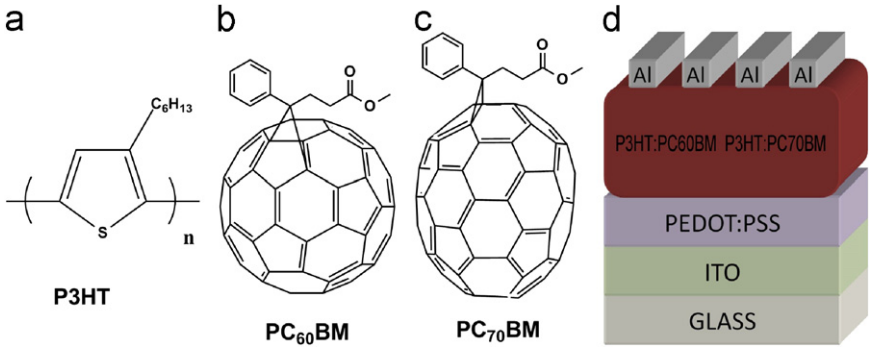

Fig. 1. Chemical structure of used photovoltaic materials and the schematic configuration of PSCs.