



Efficiency improvement of polymer solar cells by iodine doping

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ABSTRACT

A series of poly(3-hexylthiophene) (P3HT)/(6,6)-phenyl C₆₀ butyric acid methyl ester (PCBM) bulk hetero-junction polymer solar cells were fabricated with different iodine (I₂) doping concentrations. The short circuit current density (J_{sc}) was increased to 8.7 mA/cm² from 4 mA/cm², meanwhile the open circuit voltage (V_{oc}) was decreased to 0.52 V from 0.63 V when the iodine doping concentration is 5%. The optimized power conversion efficiency of polymer solar cells (PSCs) with iodine doping is about 1.51%, which should be attributed to the better charge carrier transport and collection, and the more photon harvesting due to the red shift of absorption peaks and the widened absorption range to the longer wavelength. The morphology and phase separation of polymer thin films were measured by atomic force microscopy (AFM). The phase separation of P3HT and PCBM has been distinctly increased, which is beneficial to the exciton dissociation. The photocurrent density of PSCs with iodine doping was increased compared with the PSCs without iodine doping under the same effective voltage.

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1. Introduction

Polymer solar cells (PSCs) have attracted much attention as one of the promising choices for green and renewable energy source because of their low production cost, light weight, mechanical flexibility. The power conversion efficiencies (PCE) of PSCs has been up to 7% for the poly(3-hexylthiophene) (P3HT) doping with (6,6)-phenyl C₆₀ butyric acid methyl ester (PCBM) system under the standard solar spectrum AM1.5G [1,2]. Many effective approaches have been carried out to improve the performance of solar cells, such as the synthesis of new narrow band gap materials for better photon harvesting, optimization of phase segregation in the bulk heterojunction (BHJ) layers, interfacial modification for better charge carrier collection, and design of novel configuration cells [3–9]. It is known that the performance of PSCs is still lower compared with inorganic solar cells, which results from the relatively narrow absorption range in the visible light, short exciton diffusion length, low charge carrier mobility and poor phase separation of the active layer [10]. One limitation to the improvement of PCE of PSCs is the relative narrow absorption range of organic semiconductor in the visible light range, which makes the large mismatch with solar spectrum. To improve the active layer's light harvesting capability, many researches have been carried out to explore small band gap materi-

als or combine different organic materials with complementary absorption spectra in one device [11–15]. Another limitation is considered as the low charge carrier mobility in organic materials [16]. Zhao et al. reported the 1,2-dichlorobenzene (DCB) vapor treatment can induce P3HT self-organizing into ordered structure leading to enhanced absorption and high hole mobility [17]. Li et al. studied the effects of annealing temperature and time on the device performance for devices annealed before and after cathode deposition. Thermal annealing condition was found very important for improving short circuit current, fill factor, and therefore the efficiency of the device [18]. In 1977, Heeger's group reported that the conductivity of polyacetylene (PA) is increased in many magnitudes orders after doping I₂ or AsF₅ into PA, even nearly to that of metal ($Cu \ 6 \times 10^3 \text{ s/m}$) [19]. The Nobel Prize in Chemistry for 2000 was awarded jointly to Heeger, MacDiarmid and Shirakawa due to their outstanding contribution for the discovery and development of conductive polymer polyacetylene. Subsequently, lots of papers reported the positive effect of I₂ on the conducting characteristics of polymer and the performance of organic optoelectronic devices [20–22]. Li et al. reported that the photocurrent of solid state dye sensitized solar cells was increased to 148 $\mu\text{A}/\text{cm}^2$ from 27 $\mu\text{A}/\text{cm}^2$ by iodine doping in conjugated polymer [23]. Schon et al. reported an efficient organic photovoltaic diodes based on doped pentacene [24]. The incorporation of bromine and iodine as dopant is beneficial to the photovoltaic properties in several ways: (i) the conductivity of pentacene is increased; (ii) the optical absorption edge is shifted to 1.4 eV; (iii) the quantum efficiency is enhanced [24]. Meanwhile, ultrathin interfacial layers also play a very

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important role the improvement of organic optoelectronic devices [4,5]. Recently, we reported the effect of ultra thin MoO₃ layer and illumination intensity on the performance of OSCs, it was found that the MoO₃ 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 MoO₃ layer compared to the devices without the MoO₃ interfacial layer under different illumination intensities [25]. The energy level alignment between donor and acceptor interfaces will strongly determine the exciton dissociation [26]. However, the detailed understanding of these dynamic processes is not completely articulated, especially the balance between light absorption and charge carrier transport dependence on the molecular arrangement, energy level alignment at the interfaces, and the relationship between charge carrier collection and phase separation of donor/acceptor.

In this paper, we studied the effect of iodine doping on the performance of PSCs with P3HT:PCBM as the active layer. The UV–visible absorption peak of P3HT:PCBM shows distinctly red shift from 490 nm to 560 nm before and after doping iodine, which is better matched with the solar spectrum. The red shift of absorption peak is beneficial to improve photon harvesting in the visible light range, resulting in more exciton generation. The phase separation of P3HT and PCBM was also increased due to the iodine doping, which will favor exciton dissociation into free charge carriers and charge carrier transport and/or collection. Therefore, the short circuit current density (J_{sc}) was increased to 8.7 mA/cm² and power conversion efficiency (PCE) arrived to 1.51% when the iodine doping concentration is 5%.

2. Experimental details

Indium tin oxide (ITO) coated glass substrates with a sheet resistance of 60 Ω/square (purchased from Shenzhen Jinghua Display Co. Ltd.) 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 min 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 s. Then PEDOT:PSS-coated ITO substrates were annealed for 10 min at 100 °C in the atmosphere. Polymer materials P3HT and PCBM (Aldrich) were dissolved in chloroform with concentration 10 mg/ml and 8 mg/ml and mixed together with equal volume ratio. Analytic iodine were dissolved in chloroform with concentration 3 mg/ml, then different doping concentration P3HT:PCBM:I₂ solutions were prepared and used as the active layer of PSCs. The lithium fluoride (LiF) thin layer (1 nm) was deposited on the active layer under 5×10^{-3} Pa vacuum level. The aluminum (Al) cathode, consisting of 100 nm thickness and active areas about 0.09 cm², was deposited by thermal evaporation through foursquare shadow mask under the same vacuum level. All cells were annealed at 120 °C for 10 min under ambient conditions.

The absorption spectra and the Fourier Transform infrared spectroscopy (FTIR) spectra of all the polymer thin films with different doping concentrations were measured by Shimadzu UV-3101 PC spectrometer and Shimadzu FTIR-8400S, respectively. The morphology and phase of P3HT:PCBM and P3HT:PCBM:I₂ were investigated by atomic force microscopy (AFM) using a multimode Nanoscope IIIa operated in tapping mode. The current–voltage (I – V) characteristics of PSCs were measured both in dark and under illumination at 100 mW/cm² by using a 150 W Xenon lamp. All measurements were carried out at the atmosphere and room temperature. The chemical structure of used polymer materials and schematic diagrams of cells are shown in Fig. 1.

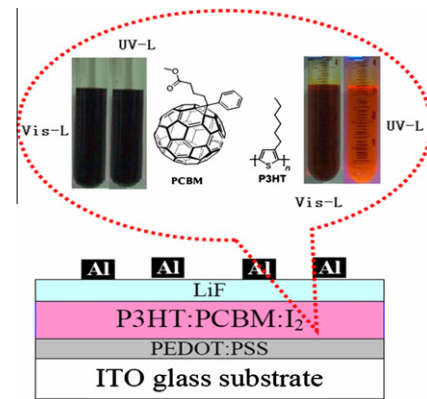


Fig. 1. Schematic diagram of polymer solar cells and chemical structure of P3HT and PCBM, the images marked with ultraviolet light (UV-L) or visible light (Vis-L) are PCBM and P3HT solution in chloroform under ultraviolet (UV) light and ambient conditions, respectively.

3. Results and discussion

The UV–visible absorption spectra of P3HT:PCBM, P3HT:PCBM:I₂ thin films which with and without annealing treatment were measured and are shown in Fig. 2. It is apparent that there are two main absorption bands for the blended polymer thin films without annealing treatment, one peak about 334 nm corresponds to the absorption of PCBM, and the other is a broad absorption band peaking at 520 nm with two weaker vibronic shoulder absorption peak at about 560 nm and 610 nm, which is attributed to the absorption of P3HT [27]. Interestingly, the distinguished red

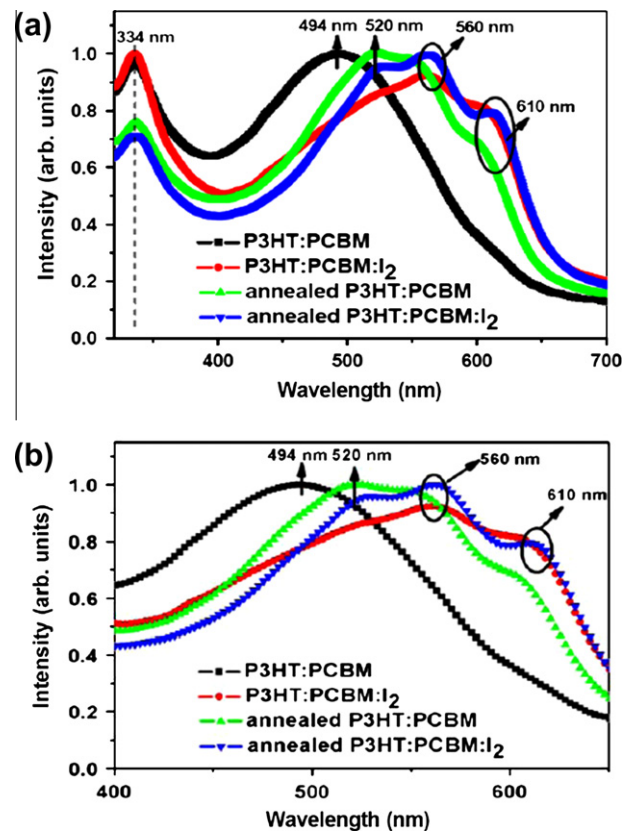


Fig. 2. (a) UV–visible absorption spectra of P3HT:PCBM and P3HT:PCBM:I₂ thin films before and after annealing treatment and (b) the zoom-in image from 400 nm to 650 nm.

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