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Optimizing ZnO nanoparticle surface for bulk heterojunction hybrid solar cells

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Abstract

The performance of hybrid solar cells composed of polymer and ZnO is mainly hindered by the defects of ZnO. Here, we investigate the effects of ZnO nanoparticle surface modification with poly(ethylene oxide) (PEO) on the performance of bulk heterojunction hybrid solar cells based on poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV) and ZnO nanoparticles. The reference device using ZnO nanoparticles as electron acceptor shows an open-circuit voltage (V_{OC}) of 0.83 V, a short-circuit current (J_{SC}) of 3.00 mA/cm², a fill factor (FF) of 0.46 and a power conversion efficiency (PCE) of 1.15%. After modification with very small amount of PEO, the PCE will be enhanced, which is attributed to less surface traps of ZnO nanoparticles with PEO modification. With optimized PEO (0.05%) modified ZnO nanoparticles as electron acceptors, the device typically shows a V_{OC} of 0.86 V, a J_{SC} of 3.84 mA/cm², a FF of 0.51 and a PCE of 1.68% due to less recombination loss of carriers, smaller series resistance, and improved the electrical coupling between ZnO nanoparticle and MEH-PPV. However, further increase PEO content to 0.3% will deteriorate device performance.

Keywords: Hybrid solar cells, Surface modification, Trap, ZnO

1. Introduction

Polymer solar cells have been attractive candidates for green energy sources due to their potential advantages of low cost and large area processing [1-7]. The bulk heterojunction structure composed of interpenetrating network of polymer donor and electron acceptor has greatly promoted the development of polymer solar cells [8]. In the past two decades, a large variety of polymer donor materials have been tested [9-15]. In contrast to polymer donors, the diversity of electron acceptors remains rather small. Both inorganic and organic electron acceptors are used, the latter are mainly fullerene derivatives [16-18]. Although power conversion efficiency (PCE) of polymer solar cells with these fullerene derivatives electron acceptors reached up to 9%, the complicated synthesis process and easy oxidation of fullerene in ambient still hinder their practical application [17-20]. Alternatively, inorganic nanocrystals such as CdSe, TiO₂ and ZnO can be used as electron acceptors combined with polymer donor in hybrid solar cells, which exhibit higher electron mobility and ambient stability with low cost [21-27]. Among these inorganic nanocrystals, ZnO is believed to be one of the most promising electron acceptors due to its environmental friendliness and low crystallization temperature. However, the intrinsic surface defects of ZnO nanocrystals make the final power conversion efficiency of hybrid solar cells lower than their fullerene based counterparts. These defects would trap photo-excited electrons, which not only enlarges series resistance (R_s) for electron transport and weaken electronic coupling with polymer donor in hybrid solar cells, but also results in severe back charge recombination due to the lower energy offset between the trap state and highest occupied electron orbit (HOMO) of polymer donor. Surface modification of ZnO surface using various organic

molecules with functional groups is an effective way to passivate the surface traps [28, 29]. Currently, much attention has been paid to investigate the effects of surface modified ZnO as electron transport layer on polymer solar cells containing fullerene derivatives as electron acceptors. Hau et al. used a carboxylic acid functionalized fullerene to modify the surface of ZnO electron transport layer, which reduced the surface defects, improved electronic coupling of ZnO/organic layer and consequently improved the short circuit current density (J_{SC}) and fill factor (FF) of the device [28]. Hsieh et al. inserted a crosslinked fullerene between ZnO electron transport layer and active layer, which can also effectively passivate the shunts in ZnO film, restrain the back charge recombination and improve the device performance [29]. However, little efforts were paid to investigate the effects of surface modification of ZnO nanoparticles on bulk heterojunction hybrid solar cells based on polymers (as electron donor) and ZnO (as electron acceptor).

Herein, we report enhanced performance of bulk heterojunction hybrid solar cells composed of poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV) and ZnO by using poly(ethylene oxide) (PEO) modified ZnO nanoparticles as electron acceptors where PEO molecules coordinate to the surfaces of ZnO nanoparticles by sharing the lone electron pairs of oxygen in PEO with ZnO. In this case, the surface traps of ZnO nanoparticles are effectively passivated, which provide improved electrical coupling between ZnO and polymer as well as paths for electron transport and collection. The restrained trap-assisted recombination loss of carriers and reduced R_S contribute to improved performance of bulk heterojunction hybrid solar cells.

2. Experimental

2.1 Synthesis of ZnO nanoparticles.

MEH-PPV was purchased from Canton OLEDKING Optoelectronic Materials Co. Ltd. and PEO (weight average molecular weight (M_w) = 600 000) was purchased from BDH Chemicals.

ZnO was synthesized following the previous work [30]. 4 g of zinc acetate dihydrate (>99%) was dissolved in 160 mL methanol at 60°C under vigorous stirring. 2 g of KOH (>85%) was dissolved in 80 mL methanol. The KOH solution was dropped into the zinc acetate dihydrate solution in 10 min under vigorous stirring. The solution temperature was held at 60 °C and stirred for 4 h, and then the heating and stirring were removed to allow particles to precipitate for additional 12 h. The precipitate was cleaned by centrifugation of the dispersion and washed twice with 50 mL of methanol. The washed ZnO nanoparticles were dissolved in chlorobenzene (CB) to form 70 mg/ml ZnO CB solution. Surface modification of ZnO by PEO is achieved by adding the desired amount of PEO molecules into ZnO solution.

2.2 Fabrication of hybrid solar cells.

The device used in this work has a structure of ITO/PEDOT:PSS/poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV):PEO modified ZnO/Al. ITO-coated glass substrates were first cleaned with detergent and deionized water, then dried by nitrogen flow. A 45 nm thick PEDOT:PSS layer was spin coated on top of the ITO substrates as hole transport layer. A solution containing a mixture of MEH-PPV:ZnO (1:3, weight ratio) or MEH-PPV:PEO modified ZnO in chlorobenzene (CB):methonal (9:1, volume ratio) was spin-cast on top of the hole transport layer to produce a 80-nm-thick active layer. Finally, Al (80 nm) was deposited atop the active layer by thermal

evaporation in a vacuum of 4×10^{-6} Torr to complete the device fabrication. The cell active area was 5 mm^2 , which was defined by the overlapping area of the ITO and Al electrodes. The solar cells were characterized using a Keithley 2400 source meter under simulated AM 1.5G solar illumination (100 mW cm^{-2}), with a GG 420 nm UV filter between the light source and the solar cells. External quantum efficiency (EQE) of the devices was collected by a Keithley 485 picoammeter under illumination of monochromatic light at short circuit condition.

2.3 Other characterization.

The thickness of MEH-PPV:PEO modified ZnO layer was measured using a Dektak 6M Stylus Profiler. Atomic force microscopy (AFM) images were recorded on Dimension 3100 system (Digital Instruments/Veeco) in tapping-mode. The dynamic light scattering experiment was performed on ALV light scattering system. Steady-state emission (PL) spectra of MEH-PPV:PEO modified ZnO blend films on glass substrate were recorded as follows: an Oriel optical liquid light guide was located as close to the sample as possible, and connected to the entrance slit of the spectrometer. A Newton EM-CCD Si array detector cooled to $-60 \text{ }^{\circ}\text{C}$ in conjunction with a Shamrock sr 303i spectrograph from Andor Tech. served as the emission detection system. The system was wavelength calibrated by an Argon lamp to a resolution higher than 0.5 nm.

Transient absorption measurements (TA) were carried out by a standard pump-probe setup. In brief: laser pulses (800 nm, 80 fs pulse length, 1 kHz repetition rate) were generated by a femtosecond laser system (Mai-Tai) with a regenerative amplifier (Spitfire, both Spectra physics). The pulses were converted by using an optical parametric amplifiers (Topas, Light conversion) to 440 nm (excitation) and 575 nm (probe). In order

to construct transient absorption signal, every second excitation pulse is blocked. Hence the probe pulse intensity can be recorded by a photodiode for the excited and non-excited sample. Transient absorption measurements were carried out on MEH-PPV:ZnO films without electrolyte and electrodes, placed in the nitrogen atmosphere. The samples were excited by the photon flux of 5×10^{12} photons/cm² (corresponds to ~ 2 μ J/cm²).

3. Results and discussion

Fig. 1 shows the chemical structures of polymer donor MEH-PPV and surface modifier PEO. The effects of PEO modification to ZnO nanoparticle surface on the performance of the hybrid solar cells are investigated. Fig. 2 shows the illuminated J-V curves of the devices with various amounts of PEO surface modifier under 100 mW/cm² of AM 1.5G condition with performance parameters listed in Table 1. The reference device without PEO shows an open-circuit voltage (V_{OC}) of 0.83 V, a J_{SC} of 3.0 mA/cm², an FF of 0.46, giving a final PCE of 1.15%. The device performance was considerably improved when PEO modified ZnO is used as electron acceptor. The optimum device is achieved when using 0.05% PEO modified ZnO (weight ratio of PEO to ZnO) as electron acceptor, which displays a V_{OC} of 0.86 V, a J_{SC} of 3.84 mA cm⁻², an FF of 0.51 and a PCE of 1.68%. However, further increase PEO loading would degrade the device performance. Device with PEO content of 0.3% showed a decreased J_{SC} of 2.21 mA cm⁻² and a reduced FF of 0.39, giving a final PCE of 0.74%. The origin of performance variation can be revealed by analyzing series resistance (R_s) and shunt resistance (R_{sh}) of the hybrid solar cells extracted from the illuminated J-V characteristics. Twelve devices in each configuration were fabricated and the averaged device performance parameters are summarized in Table 1. The optimum device using modified ZnO with 0.05% PEO as

electron acceptor shows a smaller R_s and higher R_{sh} ($R_s = 37 \Omega \text{ cm}^2$, $R_{sh} = 1.8 \text{ k}\Omega \text{ cm}^2$) compared to the reference device ($R_s = 70 \Omega \text{ cm}^2$, $R_{sh} = 1.05 \text{ k}\Omega \text{ cm}^2$). The reduced R_s of the device with PEO modified ZnO as electron acceptors is favorable for charge transport and collection, which explains the improved FF and J_{SC} . The increased R_{sh} indicates restrained recombination loss of charge carriers due to the current leakage pathways in the bulk active layer. This is verified by dark J - V curves as shown in Fig. 2a. It is obvious that the device with 0.05% PEO modified ZnO as electron acceptors shows considerably restrained leakage current and higher built-in potential at forward bias compared to the reference device, resulting in an enhanced V_{OC} . When PEO content is increased up to 0.3%, however, all the device parameters degrade with R_s increased to $90 \Omega \text{ cm}^2$ and R_{sh} decreased to $0.99 \text{ k}\Omega \text{ cm}^2$ due to large energy barrier for charge collection and pronounced carrier recombination within the device. Fig. 2b shows external quantum efficiency (EQE) of the devices, that is, the efficiency of electrons generated per incident photon increases first and then decreases with the increment of PEO content. The maximum EQE value appears in 0.05% PEO modified device over the whole absorption spectrum of MEH-PPV.

Because of very high surface-to-volume ratio of nanoparticles, surface states play an important role in such materials. It is generally accepted that surface traps of ZnO nanocrystals have a significant adverse effect on the performance of hybrid solar cells. [31,32]. Energy of the traps is usually located within the bandgap of ZnO as schematically shown in Fig. 3. Electrons which are transferred from MEH-PPV will be efficiently trapped and consequently R_s for electron transport is increased. Due to the energy barrier between the trap states of ZnO and the top electrode Al for electron

collection, the trapped electrons are likely to recombine with holes in the HOMO level of MEH-PPV, leading to leakage current or a smaller R_{sh} . When PEO is used to modify ZnO nanocrystal surface, however, PEO molecules coordinate to the surface of ZnO by sharing the lone electron pair of oxygen in PEO with ZnO, and therefore degenerate the population of trap states [32]. In this case, the trapping of electrons and R_s are considerably decreased, which lead to enhanced J_{sc} and FF. Moreover, the back charge transfer recombination from trap states to HOMO level of MEH-PPV is also restrained, which contributes to increased R_{sh} and V_{oc} .

The effect of PEO on the topography of the active layer is investigated with an Atomic Force Microscopy (AFM). As depicted in Fig. 4, MEH-PPV:0.05% PEO modified ZnO film shows similar smooth surface morphology to that of the pristine MEH-PPV:ZnO film, which ensures comparable contact with Al cathode and contact resistance. However, when PEO content is further increased up to 0.3%, the active layer shows very rough surface morphology. The root mean square (RMS) roughness of MEH-PPV:0.3% PEO modified ZnO film is increased from 4 nm to 40 nm compared to the MEH-PPV:ZnO film. After modification, the surface of ZnO nanoparticles becomes more hydrophilic [32], which causes larger ZnO aggregates in nonpolar CB:methanol solution before film formation, as can be seen from dynamic light scattering (DLS) results in Fig. 5. Moreover, the more hydrophilic surface of PEO modified ZnO nanoparticle renders them less compatible with MEH-PPV in solution. These two factors lead to large phase separation and rough surface of MEH-PPV:PEO modified ZnO film. First of all, this reduces the interface area between MEH-PPV and ZnO domains, and consequently decreases the exciton dissociation efficiency due to a short exciton

diffusion length (about 10 nm). To validate this assumption, PL spectra were recorded for the MEH-PPV:PEO modified ZnO films as shown in Fig. 6. As can be seen, the quenching of the intrinsic emission from MEH-PPV by ZnO was obviously weakened when the PEO content is 0.3%, which indicates less interface area between MEH-PPV and ZnO for exciton dissociation. Secondly, the insulating PEO molecules may form a barrier layer restraining exciton dissociation and the charge transport between ZnO nanoparticles, which is evidenced by increased series resistance and reduced fill factor with PEO content up to 0.3%. Furthermore, pinholes are often produced within the rough active layer, which allow the evaporated aluminium atoms to be in direct contact with anode and consequently result in local shunting. The poor contact between cathode Al and the rough active layer is another possible reason for the shunts. These shunts in rougher active layer greatly reduced the R_{sh} to $0.99 \text{ k}\Omega \text{ cm}^2$ and thus increased the recombination loss for the free carriers. Therefore, as the PEO content was increased up to 0.3%, the reduced exciton dissociation efficiency, the restrained electron transport and increased leakage current lead to reduced device performance.

In order to investigate the effect of PEO addition on the charge transfer dynamics between MEH-PPV and PEO modified ZnO, we carried out transient absorption spectroscopy measurements. The observed signal (see Fig. 7) is dominated by the MEH-PPV absorption bleach, which reflects the concentration of the excitons in the polymer [33]. The pristine MEH-PPV films on glass, shows a longest exciton lifetime of 180 ps. The exciton lifetime is sharply decreased when ZnO is incorporated into MEH-PPV matrix due to electron transfer from LUMO of MEH-PPV to that of ZnO. When PEO content is lower than 0.05%, similar exciton decay dynamics are observed for MEH-

PPV:PEO modified ZnO blends. It indicates the charge transfer process is not influenced by small PEO content based on the fact these two films show similar surface morphology and microstructure. However, MEH-PPV:0.3%PEO modified ZnO film shows a prolonged exciton lifetime of 85 ps, which originates from inefficient exciton dissociation. As previously discussed, the large phase separation between 0.3% PEO modified ZnO and MEH-PPV reduces the exciton dissociation efficiency. Besides, too much PEO content may also prohibit the electron transfer from MEH-PPV to ZnO. These lead to reduced J_{SC} and FF of the device using 0.3% PEO modified ZnO as electron acceptor.

4. Conclusion

In conclusion, the effects of PEO modified ZnO as electron acceptor on the performance of hybrid solar cells composed of MEH-PPV and ZnO are investigated. It is found that the device using small amount of PEO (<0.05%) modified ZnO as electron acceptor shows considerably reduced series resistance and increased shunt resistance due to the passivated surface traps of ZnO electron acceptor. As a result, the device performance is improved due to favorable electron transport and restrained back charge transfer recombination. The optimum device using 0.05% PEO modified ZnO as electron acceptor shows a V_{oc} of 0.86 V, a J_{sc} of 3.84 mA/cm², a FF of 0.51 and a PCE of 1.68%.

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Captions

Fig. 1. Chemical structures of (a) MEH-PPV and (b) PEO.

Fig. 2. (a) The illuminated J - V characteristics (open symbols) and dark J - V characteristics (filled symbols), (b) EQE data of hybrid solar cells composed of MEH-PPV: PEO modified ZnO blends.

Fig. 3. The schematic diagrams of energy level of the devices using (a) pristine ZnO, and (b) PEO modified ZnO as electron acceptor.

Fig. 4. The topography images of MEH-PPV:PEO modified ZnO films (a) ZnO, (b) 0.05% PEO modified ZnO, and (c) 0.3% PEO modified ZnO.

Fig. 5. DLS results of 0% and 0.3% PEO modified ZnO in CB:Methanol solution.

Fig. 6. PL spectra of MEH-PPV:PEO modified ZnO blend films on top of glass substrates.

Fig. 7. TA spectra of MEH-PPV:PEO modified ZnO blend films on top of glass substrates.

Table 1 The performance parameters of the hybrid solar cells based on MEH-PPV:PEO modified ZnO blends.

PEO/ZnO (wt%)	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF	R_s Ω cm ²	R_p k Ω cm ²	PCE (%)
0	0.83	3.00	0.46	70	1.05	1.15
0.01	0.85	3.64	0.49	50	2.00	1.52
0.05	0.86	3.84	0.51	37	1.80	1.68
0.3	0.90	2.11	0.39	91	0.99	0.74

Fig.1

Fig.2

Fig.3

Fig.4

Fig.5

Fig.6

Fig.7