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Improved performance of MEH-PPV/ZnO solar cells by addition of lithium salt

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Abstract

The paper reports the improved performance by addition of lithium bis(trifluoromethanesulfonyl)amide (LiTFSI) to poly(2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene) (MEH-PPV) in the hybrid solar cells consisting of MEH-PPV as an electron donor and vertically aligned ZnO nanorod array as an electron acceptor. Results show that, with increasing the weight ratio R of LiTFSI/MEH-PPV, the charge transfer efficiency at MEH-PPV/ZnO interface, the device short circuit current (J_{sc}) and open circuit voltage (V_{oc}) get increased for $R \leqslant 2/10$, but decreased when $R > 2/10$, resulting in a peak power conversion efficiency of $\eta = 0.48\%$ for $R = 2/10$ at AM 1.5 illumination (100 mW/cm^2). It is revealed that the increased J_{sc} is due to the improved charge transfer between the MEH-PPV and ZnO as a result of the interaction between LiTFSI and MEH-PPV, while the increased V_{oc} and the decreased charge recombination are attributed to the increased hole mobility of MEH-PPV; moreover, the decreased J_{sc} and V_{oc} at high R values are attributed to the morphology degradation in the active layer due to the high LiTFSI content.

Keywords: Zinc oxide; Solar cell; MEH-PPV; Modification; LiTFSI; Photovoltaics

1. Introduction

Polymer-based solar cells (PSCs) have been extensively investigated (Pivrikas et al., 2011; Huang et al., 2011; Deng et al., 2010; Yap et al., 2011) due to its low-cost, flexibility and light-weight. An encouraging power conversion efficiency (η) up to 7% has been realized by using fullerenes as organic electron acceptors (A) for such devices (Chen et al., 2009; Liang et al., 2010). A potential alternative to such all-organic solar cell is to use inorganic nanomaterials as electron acceptors instead of the fullerenes, due to their advantages of good electron mobility and friendly environmental stability. However, the state-of-the-art efficiency of the hybrid PSCs ($\eta = 2$–3%) (Takanezawa et al., 2007; Lin et al., 2009; Dayal et al., 2010) is not high yet. During the photovoltaic process, the conjugated polymer serving as an electron donor (D) absorbs light to generate excitons; once the photogenerated excitons are separated at the D/A interface, the electrons and holes need to be transported across the layers composed of nanomaterials and conjugated polymer to the electrodes in order to generated photocurrent. Subjected to the low carrier mobility (ca. 10^{-1}–10^{-9} cm^2 V^{-1} s^{-1}) (Coakley and Mcgehee, 2004; Skompska, 2010) and the short exciton diffusion length (~10 nm) (Nunzi, 2002) in conjugated polymers, the recombinative carrier loss at the D/A interface becomes an important efficiency-limiting factor in PSCs. Therefore, modifying the packing morphology of polymer chains is

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expected to enhance the carrier mobility in the polymer domain and further to reduce interfacial charge recombination.

In order to suppress the interfacial charge recombination, various efforts have been made to optimize the morphology and structure of the nanomaterials. For example, application of vertically aligned one-dimensional nanostructure arrays to PSCs (Mor et al., 2009; Bi et al., 2010; Hames et al., 2010), instead of disordered nanoparticles, offers the straightforward pathways for electron transport and maintains stably the spatial distribution of the D/A interfaces, resulting in a less charge recombination and a better device performance. The morphology in polymer phase has a significant influence on the performance of solar cells (Campoy-Quiles et al., 2008). Post-treatments, such as thermal (Ma et al., 2005; Hiorns et al., 2006) and solvent (Li et al., 2005, 2007) annealings, have been applied to improve the crystallization of polymer in efficient PSCs. Additionally, interface modification is also a strategy for improving the performance of PSCs (Kudo et al., 2007; Lin et al., 2008), normally resulting in the increase in both short circuit current (J_{sc}) and open circuit voltage (V_{oc}). However, the device performance is still not satisfying, and it is of great interest to find new ways to improve the performance of PSCs.

Recently, it is found that lithium bis(trifluoromethanesulfonyl)amide (LiTFSI) can serve as an additive to improve the photovoltaic performance of various dye-sensitized solar cells (DSCs) (Haque et al., 2004; Snaith and Grätzel, 2006) and the hybrid PSCs based on the simple blends of TiO_2 nanoparticles and poly(2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene) (MEH-PPV) (Barkhouse et al., 2010). In the cases of DSCs, the LiTFSI effects have been suggested to adjust the energetic and electronic properties of nanocrystalline TiO_2 phase (Durr et al., 2006), to enhance the electron diffusion coefficients in nc-TiO_2 electrodes (Kudo et al., 2007) and the electrolyte conductivity (Xia et al., 2008; Fukuri et al., 2006), and to inhibit the interfacial charge recombination in solid-state DSCs (Krüger et al., 2001). Barkhouse et al. (2010) applied LiTFSI, along with 4-tert-butyl-pyridine, to MEH-PPV/TiO_2 solar cells via different addition methods, including the pretreatment of nanoparticles, the co-deposition of polymer, nanoparticles and lithium salt and the post-treatment of the D/A active layer, and the authors attributed the improved V_{oc} and J_{sc} values to the increased hole mobility in MEH-PPV with the presence of LiTFSI.

Recently, polymer solar cells based on ZnO have also been widely studied, For example, Krebs et al. (2008) reported a simple device prepared in air condition based on ZnO nanoparticles; Waldo et al. (Beek et al., 2006) fabricated the solar cells consisting of ZnO nanoparticles and poly(3-hexylthiophene) (P3HT) and reached the efficiency of 0.9% by thermal annealing; Ravirajan et al. (2006) used dye Z907 to modify ZnO nanorod and achieved an efficiency of 0.2% in P3HT/ZnO devices. However, more efforts are still needed to enhance the ZnO devices. In this paper, we apply LiTFSI as an additive to the polymer layer in the hybrid PSCs consisting of vertically aligned ZnO nanorod arrays and MEH-PPV, and reveal the dependence of the device performance on the LiTFSI content in the polymer phase.

2. Experimental section

2.1. Device fabrication

MEH-PPV (Avg. $M_n = 40{,}000–70{,}000$, Aldrich), lithium bis(trifluoromethanesulfonyl)amide (LiTFSI) (97%, Aldrich) were commercially obtained. Chlorobenzene (AR, Sinopharm Chemical Reagent Co., Ltd.) was used as solvent for solar cell preparation, and was distilled under reduced pressure before use. The vertically aligned ZnO nanorod array (170 nm in length and 30–40 nm in diameter) was grown in 10 min on the ZnO dense layer coated on indium tin oxide (ITO) conducting glass ($\leqslant 15\ \Omega/\square$, Shenzhen Laibao Hi-Tech Co., Ltd., China) by electrochemical deposition, as described previously (Bi et al., 2010). The aligned ZnO nanorod array was first annealed in air at 100 °C and 220 °C for 10 min, respectively. Solar cells were fabricated by the procedure reported previously (Bi et al., 2010), where the polymer layer was deposited on the top of ZnO nanorods by spin-coating (3000 rpm, 30 s) the MEH-PPV-LiTFSI solution, followed by annealing at 150 °C under N_2 atmosphere for 30 min to ensure the polymer infiltration into the interspaces between nanorods. The weight ratio R (=1/10, 2/10, 4/10 and 6/10) of LiTFSI/MEH-PPV in the devices was controlled by adding a defined amount of LiTFSI (dissolved in acetonitrile with a concentration of 0.2 g/mL) to the MEH-PPV solution in chlorobenzene (10 mg/mL). For the cell fabrication, the PEDOT:PSS was filtered with a 0.45 μm filter and added isopropanol (50% in volume). A gold electrode (100 nm thick) of $1 \times 4\ mm^2$ defined the active area of each device.

2.2. Characterization

The MEH-PPV film for FT-IR studies was obtained by drying a MEH-PPV solution in chloroform (5 mg/mL) at room temperature, while MEH-PPV-LiTFSI films for FT-IR measurements were prepared by drying the MEH-PPV solution with addition of LiTFSI in chloroform. The R values in the MEH-PPV-LiTFSI films were controlled to be the same to those in the solar cells. All the FT-IR samples were dried at 80 °C for 1 h under vacuum before measurements. FT-IR spectra were recorded on a Nicolet Magna-IR^{TM} 750 spectrometer with a maximum resolution of 0.1 cm^{-1}. The absorption and room temperature photoluminescence (PL) properties were measured in ambient conditions, and the samples were prepared as the same as that in solar cell fabrication. The absorption spectra were recorded with a Shimadzu UV-2550 spectrophotometer, while PL measurements (excitation at 500 nm) were performed on a Hitachi F7000 spectrofluorophotometer. The steady-state $J–V$ curves of solar cells under AM