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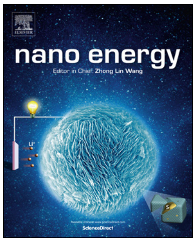

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RAPID COMMUNICATION

Efficiency improved for inverted polymer solar cells with electrostatically self-assembled BenMeIm-Cl ionic liquid layer as cathode interface layer

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Abstract
The interlayer inserted between active layer and ITO has been a key issue for improving electron extraction in inverted polymer solar cells (IPSCs), while the ideal interlayer for IPSCs has not been well developed. In this work, we presented a spontaneous vertical phase separation (SVPS) self-assembled bilayers structure with BenMeIm-Cl ionic liquid (IL) interfacial bottom layer and a photoactive top layer via a single spin-coated step of BenMeIm-Cl IL and organic donor-acceptor composite and achieved a PCE as high as 8% based on IPSCs with PTB7 as the donor. The presence of BenMeIm-Cl IL reduces the work function of ITO and leads to a better energy-level matching for efficient charge-transfer. The driving force of SVPS self-assembled structure is from the relative surface energy difference between organic materials and BenMeIm-Cl ILs, together with their interactions with the substrates. This self-assembled process procedure pave the way to simplify the manufacturing of low-cost and large-area organic electronic devices.

Introduction

Bulk heterojunction polymer solar cells (BHJ-PSCs) have tremendously attracted attention as a renewable energy

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source owing to their advantages of easy fabrication, low cost, light weight, and the feasibility to fabricate flexible devices [1-3]. Considering the aspects of its commercialization, the typical inverted polymer solar cells (IPSCs), consisting of a BHJ photoactive layer between indium tin oxide (ITO) as a bottom cathode and a high work function (WF) metal as a top anode, is an advantageous approach due to its superior long-term stability [4-6]. To fabricate efficient IPSCs, a cathode interface layer (CIL) must be introduced between the ITO cathode and the photoactive layer to reduce the WF of the ITO cathode and to lower the energy barriers for efficient charge-transfer, because of an energy-level mismatch between the high WF of the ITO cathode (approximately 4.8 eV) and the lowest unoccupied molecular orbital (LUMO) levels of fullerene derivatives [7,8].

To date, a variety of cathode interfacial materials have been applied to shift and modify the energy level of the ITO electrode, such as metal oxides (TiO_2, ZnO), metal carbonates (Cs_2CO_3) [9-10], titanium chelate (TIPD, TOPD) [11] and water/alcohol soluble polyelectrolytes (PEI, PFN) [4,12-17]. However, IPSCs using metal oxides typically require a high annealing temperature (over 200° C) to yield a high charge carrier mobility; the use of water/alcohol soluble polyelectrolytes creates a critical problem in the large-scale printing processes of IPSCs. Because the thickness of polyelectrolytes interlayer has to be controlled at the nanometer scale to minimize its insulating effect [18,19].

Thus, the ideal interlayer material available for cost-effective large-scale roll-to-roll manufacturing of the ultrathin and uniform CILs approach is imperative. Different from interfacial layer used before, our group has presented that ionic liquid (IL) offers unique properties that make them important candidates for CILs, such as low temperature fabrication, variety category, simple synthesis and environment-friendly nature [20]. What is more, the thickness of ILs as CIL can be effectively controlled by doping them in photoactive solution via a spontaneous self-assembled structure [21-23].

In this paper, we used entirely cation-anion combinations BenMeIm-Cl ionic liquid as a CIL in P3HT:$PC_{61}BM$, PBDTTT-C:$PC_{71}BM$ and PTB7:$PC_{71}BM$ BHJ-IPSCs and demonstrated that the insert of BenMeIm-Cl IL layer leads to an efficiency enhancement from $<1\%$ to 8% based on PTB7 as the donor via the spontaneous vertical phase separation (SPVS) self-assembled approach [24-27]. The utilization of a SPVS process in organic composites, consisting of BHJ photoactive materials and interface material, is unique for the formation of both the photoactive top layer and ultrathin and uniform cathode interface bottom layer through only single-step solution processing [28-30].

From device characteristics, surface energy calculation and time of flight secondary ion mass spectrometry (TOF-SIMS) analysis, we confirmed that the self-assembled BenMeIm-Cl IL layer acts as an ideal CIL, which reduces the WF of ITO from 4.8 to 4.4 eV and decreases the energy barrier between ITO and fullerene. The controllable thickness of BenMeIm-Cl ILs bottom layer and a BHJ photoactive top layer have been obtained via the SVPS self-assembled process procedure, which is a facile and efficient approach to improve photovoltaic performance.

Experimental section

Materials

BenMeIm-Cl ionic liquid (Alfa Aesar) with a molecular weight of 208.69 g/mol was dissolved in methanol with a weight concentration of 0.1 wt%. Poly(3-hexylthiophene-2,5-diyl)(P3HT) and [6,6]-phenyl-C61-butyric acid methyl ester ($PC_{61}BM$) (weight-averaged molecular weight, $M_w < 50{,}000$ g/mol, RiekeMetals Inc.), Poly[4,5-b']dithiophene)-2,6-diyl-alt-(4-(2-ethylhexanoyl)-thie-no [3,4-b] thiophene))-2,6-diyl](PBDTTT-C) and poly(thieno [3,4-b]thiophene-alt-benzodithiophene) (PTB7) (Solarmer Materials), fullerene derivatives [6,6]-phenyl-C71-butyric acid methyl ester ($PC_{71}BM$) (Solenne BV), O-dichlorobenzene (99%) and 1,8-diiodoctane (98%) were purchased from Sigma-Aldrich Inc. All materials were used as received.

Preparation of the BHJ and BenMeIm-Cl IL:BHJ films

For the preparation of the P3HT:$PC_{61}BM$ solution, 20 mg of P3HT, 20 mg of $PC_{61}BM$, and 1 ml of o-dichlorobenzene (O-DCB) were mixed. The PBDTTT-C:$PC_{71}BM$ solution consisted of a blend of PBDTTT-C and $PC_{71}BM$ (1:1.5 by weight) in O-DCB solvent with a 1,8-diiodooctane additive (3% by volume) with a total concentration of 12 mg/ml. The PTB7:$PC_{71}BM$ solution consisted of a blend of PTB7 and $PC_{71}BM$ (1:1.5 by weight) in CB solvent with a DIO additive (3% by volume) with a total concentration of 10 mg/ml. We prepared the BenMeIm-Cl IL: BHJ solutions by mixing 50ul of the dilute BenMeIm-Cl IL solutions and 0.5 ml of the different BHJ solutions(IL:BHJ, 1:10). Also, we have explored the effect of the mixing ratios of BenMeIm-Cl IL:BHJ material (IL:BHJ, 1:5 or 1:20).

Device fabrication

IPSCs was fabricated with the structures of ITO/BHJ/MoO_3/Ag (ITO devices), ITO/IL/BHJ/MoO_3/Ag (IL/BHJ devices) and ITO/IL:BHJ/MoO_3/Ag (IL:BHJ devices). The ITO glass with a sheet resistance of 10 Ω/sq (AimCore Technology Co.Ltd) was cleaned by sequential ultrasonic treatment in detergent, deionized water, acetone, isopropanol and ethanol, ultraviolet-ozone chamber treatment for 20 min, finally, they were transferred to the nitrogen-filled glove-box for the following process. For the fabrication of ITO/IL/BHJ/MoO_3/Ag the BenMeIm-Cl IL solution was then spin-coated onto the substrates at a speed of 4000 rpm for 1 min and an acceleration of 1000 rpm/s with a thickness about 15 nm, followed by annealing at 100 °C for 10 min on a hot plate. Subsequently, the BHJ solutions were spin-coated onto the IL layer at 1000 rpm, 1500 rpm, and 4000 rpm for P3HT:$PC_{61}BM$, PBDTTT-C:$PC_{71}BM$ and PTB7:$PC_{71}BM$, respectively. The P3HT:$PC_{61}BM$ film was dried in covered glass petri dishes for solvent annealing, the PBDTTT-C:$PC_{71}BM$ and PTB7:$PC_{71}BM$ films without any post-processing. For the fabrication of ITO/IL:BHJ/MoO_3/Ag. The IL:BHJ solutions were spin-coated onto the ITO at 1000 rpm, 1500 rpm, and 4000 rpm for P3HT:$PC_{61}BM$, PBDTTT-C:$PC_{71}BM$ and PTB7:$PC_{71}BM$, respectively. The IL:P3HT:$PC_{61}BM$ film was dried in covered glass petri dishes for solvent annealing and the IL:PBDTTT-C:$PC_{71}BM$ and IL:PTB7:$PC_{71}BM$ films without any post-processing. Finally, a 5 nm MoO_3 layer and a 100 nm Ag