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Enhanced absorbance and electron collection in inverted organic solar cells: Optical admittance and transient photocurrent analyses

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ABSTRACT

Optical admittance analysis reveals that light absorption in inverted organic solar cells (OSCs), based on the same polymer blend layer of regio-regular poly(3-hexylthiophene):[6,6]-phenyl-C61-butyric acid methyl ester (PCBM), is always greater than their regular geometry OSCs fabricated using an ITO/poly(3,4-ethylene dioxythiophene):(polystyrene sulfuric acid) anode. Transient photocurrent measurements elucidate that interfacial exciton dissociation at the cathode interfaces of Al-modified ITO/PCBM (inverted cell) and Al/PCBM (regular cell) is not equivalent. It is shown that the reverse configuration allows improving the absorbance of the cell, favoring charge collection at cathode/PCBM interface and also possessing a dawdling degradation behavior as compared to a control regular OSC in the accelerated aging test.

1. Introduction

Organic solar cells (OSCs) are a promising alternative photovoltaic technology to conventional inorganic solar cells due to their low cost solution process fabrication capability. A broad range of distinct device technologies based on organic small molecules and polymeric photoactive materials are being developed very rapidly. Power conversion efficiency (PCE) of >9.2% [1] for single junction OSCs and ~10% for tandem OSCs have been demonstrated recently [2]. Apart from the encouraging results in achieving high PCE for OSCs, realizing stabile OSC performance over a long operation lifetime also attracts a significant research effort. The commonly used bulk heterojunction (BHJ) OSCs, forming so called regular OSC structure, have a donor/acceptor blend sandwiched between a front transparent indium tin oxide (ITO) anode and a reflective rear metal cathode. In regular OSCs, a hole-transporting buffer layer of poly(3,4-ethylene dioxythiophene):(polystyrene sulfuric acid) (PEDOT:PSS) is often deposited on ITO surface to assist in hole transport and hole extraction at the ITO/organic interface. It has been shown that the use of acidic PEDOT:PSS hole-transporting layer is not the best choice for efficient operation of OSCs over a long period of time, due to the deterioration in the contact property at ITO/PEDOT:PSS interface [3]. The upper metallic cathode in regular OSCs often undergoes a gradual oxidation resulting in a thermally unstable cathode/organic interface [4].

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A comprehensive study on the degradation mechanisms of the regular structured OSC, based on the blend of regioregular poly(3-hexylthiophene) (P3HT):[6,6]-phenyl-C61-butyric acid methyl ester (PCBM) system, has been performed. The unbalanced charge mobility in the photoactive layer, due to oxygen-induced charge traps, is one of the degradation mechanisms [5]. In a previous work, we identified two distinguishable degradation pathways in the regular OSC [6]. One is associated with a localized failure related to the moisture encroachment in the charge generation area, inducing the charge recombination and thus eliminating the photocurrent. The other is dominated by an inevitable initial oxidation at the organic/cathode interface due to the presence of residual moisture and oxygen, leading to lowering PCE of OSCs. The degradation caused by the interfacial passivation could be avoided by the removal of the low work function cathode. This implies that the reverse configuration with a relatively environmental sensitive cathode/organic interface away from the top contact in the cell is preferred compared to the regular OSC.

Inverted OSCs, having an organic functional photoactive layer sandwiched between a front transparent cathode and a rear anode, are preferable for efficient cell operation. In this device configuration, a PEDOT:PSS hole transporting layer is not existent, avoiding the use of acidic PEDOT:PSS on ITO surface. In inverted OSCs, ITO surface is modified with a suitable low work function interlayer serving as a transparent cathode, for example, solution-processable ZnO [7], TiO_2 [8] and Cs_2CO_3 [9], low work function metals of Ca [10] and Al [11], and surface dipole-inducing materials [12]. However, the optical advantages, interfacial exciton dissociation at the cathode/organic interface and operational stability of the inverted OSCs have not yet been studied systemically. In this work, we show that the reverse configuration allows improving the absorbance of the cell, therefore its PCE. Transient photocurrent measurements indicate that interfacial exciton dissociation at the cathode/organic interfaces of Al-modified ITO/PCBM (inverted cell) and PCBM/Al (regular cell) is not equivalent. PCBM on Al-modified ITO forms a more abrupt interface than the energetic Al deposited on PCBM. X-ray Photoelectron Spectroscopy (XPS) analyses suggest that an ultrathin Al on ITO is partially oxidized, resulting in a reduction in ITO surface work function and acting as an effective transparent cathode. The operation stability of inverted OSCs, fabricated with a pair of an ultrathin Al-modified ITO front cathode and a MoO_3/Ag anode, was demonstrated by accelerated aging test in air.

2. Experimental

OSCs reported in this work were fabricated on ITO/glass substrates with a sheet resistance of ~15 Ω/square. The ITO substrates were pre-cleaned by ultrasonication in detergent solution, de-ionized water, acetone and isopropanol for 10 min sequentially. For the inverted OSCs, the surface of ITO/glass substrates was modified with ~1.2 nm thick Al, deposited by thermal evaporation in vacuum with a base pressure of $<1.0 \times 10^{-4}$ Pa at an evaporation rate of 0.1 Å/s. The ITO/glass substrates were not subjected to the oxygen plasma treatment before or after the surface modification enabling a simpler OSC fabrication process. The Al-modified ITO substrates were then transferred to an adjacent glove box with O_2 and H_2O levels below 1.0 ppm, which is connected to the evaporator. A pre-prepared polymer blend of P3HT (Rieke Metals) and PCBM (Nano-C), dissolved separately in 1,2-dichlorobenzene solution in a weight ratio of 1:0.8, was spin-coated on ultrathin Al-modified ITO front transparent cathode. The resulting inverted OSCs have a structure of ITO/Al (~1.2 nm)/P3HT:PCBM (200 nm)/MoO_3 (5 nm)/Ag (100 nm) and an active area of 3.0 mm × 3.0 mm. A control regular OSC with a structure of ITO/PEDOT:PSS (40 nm), Clevios P VP AI 4083/P3HT:PCBM (200 nm)/Al (100 nm) was also made for comparison study. Current density–voltage (J–V) characteristics of OSCs were measured under AM1.5G illumination at 100 mW/cm^2 (SAN-EI Electric XEC-301S solar simulator). Light intensity of the solar simulator was calibrated using a monosilicon detector (with KG-5 visible color filter) to minimize the spectral mismatch. After the control and the inverted OSCs were fabricated, they were kept inside N_2-purged glove box to stabilize for 3 days prior to the cell encapsulation. The encapsulated OSCs were then removed from the glove box for aging test in air. The accelerated lifetime measurements were carried out by continuous light soaking using a calibrated AM1.5G solar simulator, with light intensity of 100 mW/cm^2 under open-circuit condition at 60 ± 5 °C.

3. Results and discussion

J–V characteristics of the inverted and control regular OSCs are plotted in Fig. 1(a), insets in Fig. 1(a) are the cross-sectional views of the inverted OSC and control regular cell. It is shown that the open-circuit voltage (V_{OC}), short-circuit current density (J_{SC}) and fill factor (FF) of the inverted OSC increased from 0.59 V to 0.60 V, 9.98 mA/cm^2 to 10.30 mA/cm^2 and 0.63 to 0.68, respectively, making up for an overall 13% increase in PCE from 3.67% to 4.16%. The enhancement in PCE of the inverted OSC comes primary from a steady improvement in J_{SC} and FF, as can be seen in Fig. 1(a). This suggests that light absorption and photo-generated carrier transporting are more favorable in the reverse configuration of the cell, although the same photoactive layer thickness was used in both types of the cells. In P3HT:PCBM-based BHJ OSCs, an undesirable PCBM-rich blend layer appeared at the anode/organic interface, formed by the segregation of fullerene from the P3HT:PCBM blend due to its relatively poorer solubility in the organic solvent [13]. The presence of a PCBM-rich region at the PEDOT:PSS/P3HT:PCBM interface induces an adverse interfacial barrier for hole extraction in regular OSCs. In the reverse configuration, the removal of the interfacial barrier at the Al-modified ITO/PCBM-rich interface favors the electron collection, as compared to the hole collection at the PEDOT:PSS/PCBM-rich interface in the regular OSC. This can be seen by a reduced series resistance (R_S) in the cell, e.g., from 8.7 Ω for a control regular OSC to 7.1 Ω for an inverted OSC.