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Stable small-molecule organic solar cells with 1,3,5-tris(2-*N*-phenylbenzimidazolyl) benzene as an organic buffer

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Abstract

We demonstrate in this paper that crystallization of bathocuproine (BCP) is the main reason for the instability of fullerene-based devices with BCP buffer by *in-situ* measurement of current degradation in oxygen and by polarized light microscopy. In order to improve the performance of organic solar cells, 1,3,5-tris(2-*N*-phenylbenzimidazolyl) benzene (TPBI) takes the place of BCP. Organic solar cells with power conversion efficiency 2.32% under 75 mW/cm^2 AM1.5G simulated illumination and shelf-lifetime over 1800 min in atmosphere without encapsulation are achieved. The improved performance is ascribed to the better stability and higher electron mobility of TPBI than that of BCP.

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Keywords: Organic solar cell; Lifetime; Crystallization; TPBI; BCP

1. Introduction

Since generating electricity from the most plentiful source – the sun – can be expensive due to the high price of producing traditional silicon-based solar cells, organic solar cells have attracted much attention due to their low-cost, light weight and mechanical flexibility [1–10]. During the development of organic solar cells, the introduction of organic buffer has proved critical for the cells' performance [11–17]. Forrest and co-workers improved the efficiency of the cell by introducing exciton blocking layer (EBL) tris(acetylacetonato) ruthenium(III) (Ru (acac)$_3$) and bathocuproine (BCP). In their opinion, the EBL buffer keeps the excitons in the active layer, reduces the penetration of hot vaporized cathode atoms and protects the organic layers from the damage during the deposition of cathode [6,17]. Recently, the best efficiency of organic solar cells with BCP organic buffer has reached 5.7%, which shows great potential for commercial implication [10,18]. However the lifetime of organic solar cells with BCP buffer is not satisfactory. In air and without encapsulation it takes only about 20 min for the efficiency of the cells to decrease to half the initial values. Very few works have been done to improve the stability of such organic solar cells. Song et al. have found doping the BCP buffer with Alq can improve the shelf-lifetime of the cell [19]. The crystallization of BCP was suspected to be the reason for the instability of such cells but few direct evidence was given [12,20].

In this work, degradation of fullerene(C$_{60}$)-based devices is studied by *in-situ* monitoring their current in oxygen. We find the insertion of BCP buffer accelerates the degradation of current. By using polarized light microscopy, direct images of BCP buffer's crystallization are shown, which give direct support to the view that the instability of BCP is the main reason for the accelerated degradation of current in fullerene-based devices and poor shelf-lifetime of organic solar cells with BCP buffer. We obtain the organic solar cell with power conversion efficiency of 2.32% and shelf-lifetime more than 1800 min by replacing the BCP buffer with 1,3,5-tris(2-*N*-phenylbenzimidazolyl) benzene (TPBI). The improved performance may be attributed to TPBI's better stability and higher electron mobility than BCP [21]. The better stability is in favor of shelf-lifetime and higher electron mobility is good for the efficiency of the cell.

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2. Experiment details

The present copper phthalocynine (CuPc)/C_{60} organic solar cells and C_{60}-based devices are fabricated on the pre-cleaned glass substrates coated with transparent conducting indium tin oxide (ITO) anode. The sheet resistance is about 30 Ù/square. The substrates are heated to about 200 °C in air after solvent cleaning. And then the substrates for organic solar cells are loaded into a high vacuum chamber (5×10^{-6} Pa) and the substrates for C_{60}-based devices are loaded into another high vacuum chamber (1×10^{-5} Pa). Organic films are deposited after cooling down the substrates to room temperature. The cathode is aluminum (Al), *in-situ* deposited with shadow mask. Organic solar cells and C_{60}-based devices are all of 9 mm^2 area, with 3-mm-wide ITO crossed over by 3-mm-wide Al bar. The image in Fig. 2 is taken by polarized light microscopy 18 h after thin film device deposition. The organic films are deposited on the cleaned glass coated with ITO, using the same deposition procedure mentioned above. Two polaroid sheets with perpendicular polarized direction are used in the polarized light microscopy. One sheet is to produce polarized light and the other is used to detect the light pass through the sample.

The *in-situ* current degradation process is monitored 3 h after the fabrication of the C_{60}-based devices by Keithley 2600. Highly pure (99.99%) oxygen is introduced into the chamber until the pressure reaches atmospheric pressure during current monitoring. Power conversion efficiencies of organic solar cells are measured under illumination of Oriel solar simulator producing an AM1.5G spectrum. The intensity of irradiation is measured with a calibrated broadband optical power meter (verified by a standard crystalline silicon solar cell). The current–voltage (I–V) characteristics are measured by Keithley 2400. All the measurements of organic solar cells are carried out in air at room temperature without encapsulation.

3. Results and discussion

Fig. 1 shows the degradation process of C_{60}-based devices measured *in-situ* in the chamber filled with pure oxygen (99.99%). The solid square line and solid circle line represent the devices with structures of ITO/C_{60}(100 nm)/BCP(6 nm)/Al (device A) and ITO/C_{60}(100 nm)/Al (device B) respectively. One may note from Fig. 1 that an abrupt decrease of current is observed in the initial 200 s in the two devices. Such fall of the current can be attributed to the penetration of oxygen into the C_{60} layer. It was shown that the penetrated oxygen in the layer may create deep electron traps resulting in deceasing of electron mobility and current of the device [22–27]. After 200 s, the current degradation rate of device B becomes slower than that of device A with BCP buffer. About 1800 s later, 58% current of device B remains while only 25% current for device A. The degradation difference between the two samples shows the inserted BCP buffer accelerates the current degradation rate in C_{60}-based devices. The instability of BCP has been considered as the main reason for the poor lifetime of organic semiconductor devices with BCP layer but very little research on the instability of BCP in device has been reported. Here polarized light microscopy is used to observe the crystallization of ITO/C_{60}(100 nm)/ BCP (10 nm) (device C) and ITO/C_{60}(100 nm)/TPBI(10 nm) (device D). Before image observation, the two devices are kept in air for 18 h. Fig. 2 shows the polarized light microscopy image of device C. White area can clearly be seen, which means crystallization happened in this device. Polarized light microscopy image of device D only shows a completely black square (not shown here), which means no crystallization in this device. The only difference between device C and device D is that BCP layer is replaced by TPBI layer. Thus the crystallization area in device C is formed by the BCP organic layer. Moreover, areas of crystallized BCP grow with time (not shown here). These images demonstrate that it is easy for BCP to crystalize in atmosphere and TPBI is much more stable than BCP. In our opinion, the crystallization of BCP has two effects on the C_{60}-based devices: 1) The interface between C_{60} and Al cathode, where BCP is inserted, is damaged during the process of crystallization. It is more difficult for carriers to transport through this damaged interface. 2) The gaps caused by crystallization become the channels for oxygen penetrating into C_{60}, inducing the traps for the electrons in C_{60} layer. As a result, the current of the C_{60} device with BCP buffer decreases considerably. It is then obvious why lifetime of semiconductor devices such as organic light emitting devices and organic solar cells with BCP layers are so poor. Hence, organic buffers with stable performance in atmosphere are crucial for the lifetime of C_{60}-based organic solar cells and organic light emitting devices.

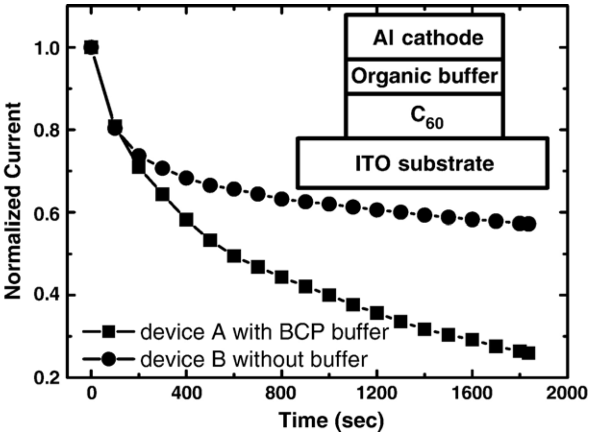

Fig. 1. Current degradation of C_{60}-based devices measured in oxygen without encapsulation. The solid circle and solid square lines represent the devices with structures of ITO/C_{60}(100 nm)/Al and ITO/C_{60}(100 nm)/BCP(6 nm)/Al respectively. ITO and Al are respectively the anode and cathode under forward bias. The initial currents for the two devices are 3±0.1 mA. The solid circle and solid square lines are monitored under 0.75 V and 1 V respectively. The inset shows the structure of the C_{60}-based devices.

Specially, for fabricating organic solar cells with high power conversion efficiency, organic buffers with wide band gap and high carrier mobility are needed [6,17,19]. TPBI is a promising organic buffer for organic solar cells due to its wide band gap, high carrier mobility and good stability [21]. Fig. 3 shows the I–V characteristics of an organic solar cell with a TPBI buffer both in dark and under illumination. The structure of the cell is ITO/CuPc (20 nm)/C_{60}(50 nm)/TPBI(6 nm)/Al, with its parameters being optimized by numerical calculation [28]. From the inset of Fig. 3, we can obtain the short-circuit current density (J_{sc}), open-circuit