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High performance airbrush spray coated organic solar cells via tuning the surface tension and saturated vapor pressure of different ternary solvent systems

Ding Zheng, Jiang Huang, Yifan Zheng, Junsheng Yu *

State Key Laboratory of Electronic Thin Films and Integrated Devices, School of Optoelectronic Information, University of Electronic Science and Technology of China (UESTC), Chengdu 610054, PR China

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ABSTRACT

In this work, thieno [3,4-b] thiophene/benzodithiophene (PTB7): [6,6]-phenyl C71-butyric acid methyl ester ($PC_{71}BM$) based organic solar cell (OSC) with a new record of power conversion efficiency (PCE) of ~7.62% has been realized using airbrush spray (AS) coating method in air ambient which can be well compatible with large-scale fabrication. By investigating the physical mechanism of AS coated blend films, a series of ternary solvent systems (TSS) are used to simultaneous optimize the surface tension and the saturated vapor pressure of solution. Therefore, different TSS further controls the morphology of PTB7:$PC_{71}BM$ blend films precisely and systematically. It is elucidated that the chlorobenzene (CB)/o-Xylene (o-Xy)/1, 8-diiodoctane (DIO) TSS with a ratio of 37:60:3 vol.% could lead to a homogeneous surface morphology with a decreased aggregation domain size of active layer. In addition, the high fill factor, increased $PC_{71}BM$ absorption and internal quantum efficiency indicate the formation of bicontinuous interpenetrating and fully percolated networks with nanostructured phase separation in BHJ blend films. Ultimately, the AS coated OSCs based on the TSS of CB/o-Xy/DIO gains a 34% enhancement in *PCE*, compared with the conventional CB/DIO solvent based OSCs.

1. Introduction

Organic solar cells (OSCs) possess potential advantages of environmentally friendly, lightweight, flexibility, large-scale manufacturing and low cost-effect [1–4]. Recently, the state-of-arts single junction OSCs with power conversion efficiency (*PCE*) approaching 9–10% have been achieved via interfacial engineering [5], device optimization [6] and rational material synthesis, e.g., p-type polymers PTB7 [7], PTB7-Th [8], PPDT2FBT [9] and PffBT4T-2OD [10]. However, the above mentioned OSCs are all fabricated based on conventional spin coating method, which is not capable of large-scale fabrication due to its significant waste of materials and limitation on the rigid substrates [11–14]. Until now, a variety of alternative deposition methods have been emerged including roll-to-roll [15], blade coating [16] and ink-jet printing [17] et al. Although a large volume of researches using these techniques have been devoted in maintaining the *PCE* as high as those based on spin coating, the obvious declines of *PCE* could be observed for most of bulk heterojunction (BHJ) systems, e.g., P3HT:$PC_{61}BM$ and PTB7:$PC_{71}BM$ systems [18–25]. The intrinsic reason lies on the lack of driving force during fabricating BHJ active layer, leading to the larger aggregation domains and poorer phase separation comparing with spin coating method.

To circumvent this problem, airbrush spray (AS) coating method is a preeminent candidate of spin coating method, which naturally brings much stronger driving force during the processing of BHJ film by dispersing the solution into atomized droplets via high speed flew rate of N_2 flow [18]. Previous insightful researches have revealed that AS coating method provides the precious control on film morphology including aggregation domain size and phase separation [26]. However, it is still tough to realize the high OSC performance, when indiscriminately utilizing the optimized conditions of spin coating to AS coating process, due to their quite different natures of film growth. Numerous physical properties of the solution, such as the surface tension (*ST*), volatility and wettability, directly affect the AS processes of atomization, flying and deposition [27,28]. For instance, the photovoltaic performances of OSCs based on PTB7:$PC_{71}BM$ BHJ system with high *PCE*s up to 7–9% from spin coating method decrease to the *PCE* of 5–6% when using AS coating method [29,30]. It is found that the conventional BHJ system only with a single solvent and additive cannot perfectly

* Corresponding author.
E-mail address: jsyu@uestc.edu.cn (J. Yu).

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match with the AS coating method due to the simplex physical property of solution, which usually results in large aggregation domains as well. Therefore, to constrain the adjustment of the droplets size and take control of the "coffee-ring" effect [31], it is imperative to construct a pertinent system of solvent for specific BHJ to effectively manipulate the growth process and film morphology, which is one of the crux matters to realize the maintained preferable *PCE* of AS coated OSCs.

Herein, to solve the issues mentioned above, a series of ternary solvent system (TSS) consisting of two solvents and an additive with different physical properties based on AS coating method is proposed, and the dynamics of film formation and morphology adjustment according to the physical properties of TSS are investigated in detail. By optimizing the composition of ternary solvent, the aggregation domains of BHJ film are significantly decreased characterized by atomic force microscope (AFM). The optimal microscopic morphology and charge transportation in BHJ layer are responsible for the maintained high fill factor (*FF*) of OSCs. As a result, high performance AS coated OSC in air ambient with an outstanding *PCE* of ~7.62% comprised of PTB7:$PC_{71}BM$ BHJ is achieved via controlling morphology of blend film by TSS.

2. Experimental

The chemical structure of organic materials, device architecture of OSCs and fabrication schematic diagram are shown in Fig. 1. The inverted OSCs are constructed as ITO/ZnO (40 nm)/PTB7:$PC_{71}BM$ (95 nm)/MoO_3 (15 nm)/Ag (100 nm). ITO-coated glass substrates with a sheet resistance of 10 Ω/sq were consecutively cleaned in an ultrasonic bath containing detergent, acetone, deionized water and ethanol for 15 min each step, and then dried at 80 °C for 1 h prior to use. After drying, the substrate was treated by UV light for 10 min. The ZnO precursor was prepared by dissolving zinc acetate dihydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$, Aldrich, 99.9%, 1 g) and ethanolamine ($NH_2CH_2{\cdot}CH_2OH$, Aldrich, 99.5%, 0.28 g in 2-methoxyethanol ($CH_3OCH_2CH_2OH$, Aldrich, 99.8%, 10 ml) under vigorous stirring for 12 h for the hydrolysis reaction in air. A 40 nm ZnO electron transfer layer (ETL) was spin-cast from the precursor solution on top of the clean ITO glass substrate, and annealed at 200 °C for 1 h in air [32]. Then, the BHJ active layer was cast from a solution with PTB7:$PC_{71}BM$ ratio of 1:1.5 wt.% in ternary solvent at a concentration of 10 mg/ml. PTB7:$PC_{71}BM$ blend films fabricated by AS coating process in air, an air brush was powered by N_2 gas, the injected flow rate of PTB7:$PC_{71}BM$ solution was 1.16 μl/s and the pressure of N_2 stream was 0.6 MPa. The nozzle was kept at 12 cm distance from the substrate. In this AS condition, the 95 ± 5 nm PTB7:$PC_{71}BM$ film was deposited. Then, a MoO_3 (99.98%, Aldrich) layer was deposited onto the substrates at a rate of 1–2 Å/s at a pressure of 3×10^{-3} Pa in vacuum, followed by the deposition of Ag anode at a rate of about 10 Å/s under a pressure of 3×10^{-3} Pa without breaking the vacuum. The morphology of the active layer was characterized by AFM (MFP-3D-BIO, Asylum Research), and metallographic microscope (DMM-300C, Caikon). Current density–voltage (*J*–*V*) curves under illumination were measured with Keithley 4200 programmable voltage–current source. A light source integrated with a Xe lamp (CHF-XM35, Beijing Trusttech Co. Ltd.) with an illumination power of 100 mW/cm^2 was used as a solar simulator [4]. All the measurements were carried out in air at ambient circumstance without encapsulation.

3. Result and discussion

3.1. Physical mechanism of AS coated blend films

In the first step of AS fabrication process, the solution is atomized and dispersed into droplets driven by low pressure N_2 gas. The process of liquid broken into droplets under the action of low-pressure N_2 gas is illustrated in Fig. 2a, which obeys the Bernoulli equation as Eq. (1) [33]:

$$P_0 + \rho gh + 0.5\rho v^2 = C \tag{1}$$

where P_0 is the environmental pressure, ρgh is the pressure generated by gravity. These two terms are known as static pressure. 0.5 ρv^2 is the dynamic pressure associated with fluid flow velocity.

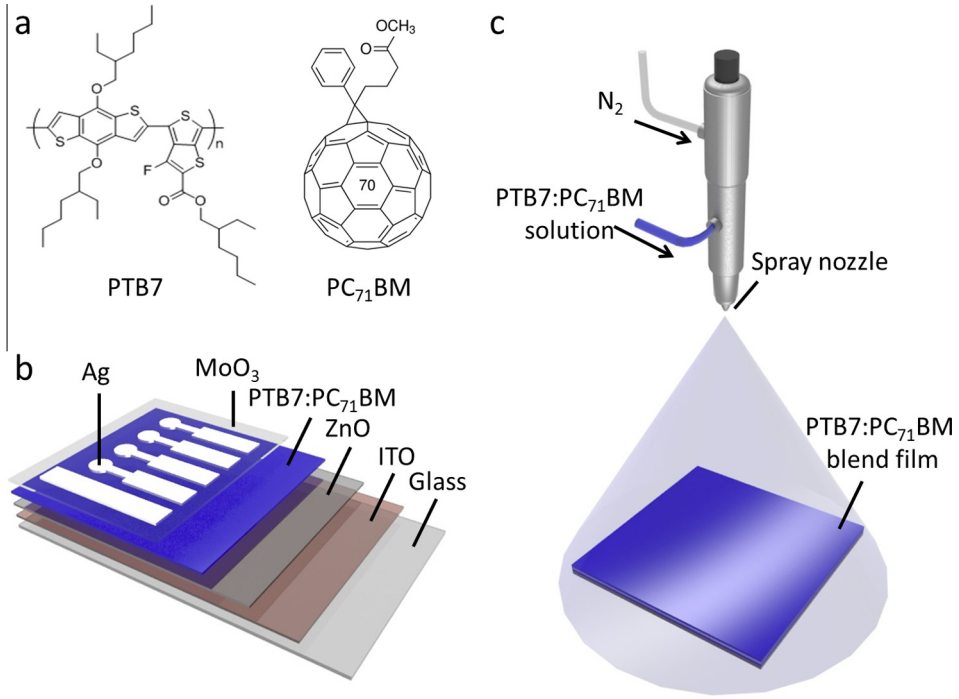

Fig. 1. (a) Chemical structures of PTB7 and $PC_{71}BM$. (b) Device architecture of OSC. (c) AS coating schematic diagram.