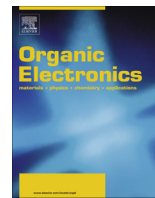




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# Morphology construction of vertical phase separation for large-area polymer solar cells



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## ABSTRACT

Although the power conversion efficiency (PCE) of small-area polymer solar cells (PSCs) has now surpassed 10% upon various optimizations, it is still a challenge to improve the performance of large-area device partially due to the problems encountered in film morphology optimization and incompatibility of using these optimizations for size scale-up. Herein, we reported a method to effectively improve the morphology of photoactive layer and thus device efficiency under ambient atmosphere by using spray coating technique. It was found that by finely adjusting the parameters of the instrument, and the properties of the “electronic ink”, the dynamics of solvent evaporation after film deposition could be controlled. By resorting to a few techniques for morphology characterization, it confirmed that the resulting blend film showed desirable vertical phase separation where polymer enriched near the anode and PCBM adjacent to the cathode. The graded composition is beneficial for the efficient charge transportation as well as eventual charge collection. By using PBDT-TFQ/PC<sub>71</sub>BM composite as an example, the exceptional high PCEs of 4.6% and 4.1% were achieved for the devices with the size of 1.0 and 10.2 cm<sup>2</sup>, respectively. In comparison to conventional device fabrication process, this method is not only simple without additional treatment steps, but also dramatically increases the device efficiency, which opens a new way for fabricating highly efficient large-area PSCs.

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## 1. Introduction

Polymer solar cells (PSCs) have drawn significant attention owing to their outstanding advantages of light weight with flexibility, solution processability through various techniques, and low-cost production over large area [1,2]. Due to high reproducibility and precision [3], the spin coating technique is the most used method for fabrication of small-area device (typically few square millimeters), and much effort has been devoted to the optimization of fabrication conditions [4,5], development of post-treatment methods [6–10], and synthesis of new conjugated polymers [11–13]. To date, the power conversion efficiency (PCE) of small-area PSC devices has reached over 10% threshold [14,15].

It is well recognized that besides the synthesis of new conjugated polymers, the morphology of the active layer plays the most

important role in determining the device PCE [7,16]. Therefore, different post-treatment methods, such as thermal annealing [6,7], solvent annealing [8], and processing additives [9,10], etc., have been created allowing further enhancement in PCE. In general, the optimization of the film morphology should be started from both lateral and vertical directions, and the vertical morphology is of utmost importance because the charge carriers transport to corresponding electrodes along this direction [17–20]. Unfortunately, most of the methods focus on former aspect, and although solvent vapor annealing [21], solvent-soaking treatment [22], and methanol-fluxing treatment [17,23] were recently developed to tailor the vertical phase morphology, these methods are directed to the spin-coated small-area polymer solar cells.

The ultimate goal of the research in polymer solar cells is to scale-up the size of the device to fabricate modules in real applications. Until now, various techniques, such as inkjet printing [24,25], slot-die coating [26,27], screen printing [28–30], doctor blading [31], gravure printing [32–34], and spray coating [19,35–48], have been developed to prepare the large-area polymer solar cells, and promising efficiencies have been obtained

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for each technique. However, in comparison to small-area device, the low homogeneity of the blend film and the thus resulting defects (such as disconnected and short-circuited areas) during large-scaling process heavily limit the module's PCE promotion [49,50]. Although the treatment methods mentioned above could improve the film morphology to some extent, the difference in efficiencies between small and large size devices still could not be made up. In addition, these current post-treatment methods are also not applicable for large-area polymer solar cells due to energy consuming, operation complexity, and environmental concerns.

For the fabrication of large-area polymer solar cells, the morphology control is much more complicated because it depends not only on the instrument type but also on the operation parameters [51–53]. Our experience on flexible and scalable polymer solar cells in the last few years shows that it is possible to precisely regulate the morphology of the active layer (especially along the vertical direction) by selecting appropriate instrument and finely adjusting the operation parameters, and thus greatly increase the PCE [54]. To demonstrate this strategy, in this study, the ultrasonic spray coating technique was utilized, and the “electronic ink” composed of poly{4,8-bis(2'-ethylhexyloxy)-benzo[1,2-b:4,5-b']-dithiophene-alt-[5,8-bis(5'-thiophen-2'-yl)-6,7-difluoro-2,3-bis-(3'-hexyloxyphenyl)quinoxaline]} (PBDD-TFQ) [55] as electron donor and [6,6]-phenyl-C<sub>71</sub>-butyric acid methyl ester (PC<sub>71</sub>BM) as electron acceptor was selected to prepare the active layer. After precise adjustment of the operation conditions (especially the ink flow rate and the number of spray passes) and the properties of the solution (with and without processing additive), it was found that the active layer with desired vertical component distribution could be obtained while the lateral phase structure was kept unchanged. The efficiency of the large-area devices with the size of 1.0 and 10.2 cm<sup>2</sup> based on this technique reaches as high as 4.6% and 4.1%, respectively. This method, the principle of which could be applicable for other techniques, is simple, cost-effective, and easy to operate with no need of any post-treatment steps, and shows great potentials in the fabrication of large-area polymer solar cells.

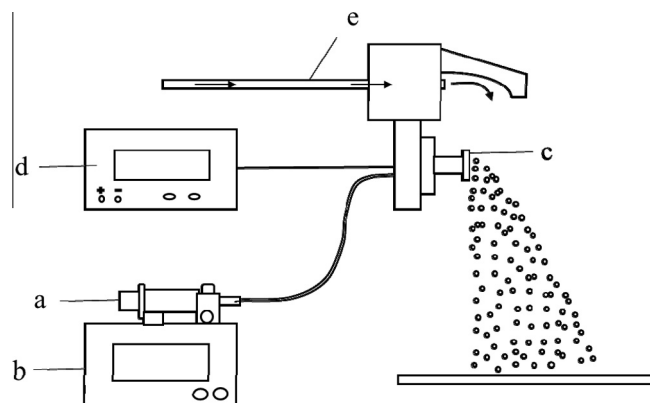
## 2. Experimental section

### 2.1. Materials

PBDD-TFQ ( $M_n = 35 \text{ kg mol}^{-1}$ , PDI = 2.0) was prepared according to the previous literature [55]. PC<sub>71</sub>BM, 1,8-diiodooctane (DIO) and chlorobenzene (CB, anhydrous, 99%) were purchased from Sigma-Aldrich. PEDOT:PSS (Clevios P VP AI 4083) was purchased from H.C. Stark company.

### 2.2. Spray coater

Ultrasonic spray coating systems (ExactaCoat W4301) was purchased from Sono-Teck Corporation (Fig. 1). For spraying, the ink is pumped to the nozzle at a settled flow rate and broken into micro scale droplets by the ultrasonic vibration, and then the droplets are directed toward the substrates by the carrier gas. In the process, the variety of parameters including carrier gas pressure, nozzle scan speed, ultrasonic power, nozzle to substrates distance, flow rate of the ink and the number of spray passes over the substrate can be manipulated. The carrier gas pressure can vary from 0 to 23.4 psi. The maximum nozzle scan speed is 200 mm s<sup>-1</sup>. The maximum ultrasonic power is 5.5 watt. The nozzle to substrates distance can vary from 6 to 12 cm. Flow rate depends on the capacity of the syringe used and the speed at which the syringe plunger is moved forward. For the 10 ml syringe that is used in our experiment, the maximum flow rate is 20.9 ml min<sup>-1</sup>. For the



**Fig. 1.** Schematic diagram of spray-coater. (a) Syringe, (b) auto-solution injection pump: controlling the injected flow rate of the ink, (c) ultrasonic nozzle: atomizing the ink into droplet, (d) ultrasonic generator: supplying power and controlling frequency of the nozzle, (e) carrier gas controller: controlling gas pressure to deposit solution onto the substrate.

films in the following discussion, the parameters including carrier gas pressure, nozzle scan speed, ultrasonic power, and distance between nozzle and substrates are fixed at 23.4 psi, 30 mm s<sup>-1</sup>, 3.5 watt, and 6 cm, respectively. And, the flow rate of the electronic ink and the number of spray passes are varied from 0.12 to 0.35 ml min<sup>-1</sup> and 2 to 6, respectively. Correspondingly, the films are named as Film LH, Film MM and Film HL (Table 1), of which the former letter represents the flow rate and the latter letter represents the number of spray passes. L, M, and H represent low, medium and high values of the corresponding spray parameters, respectively. For example, Film LH means the film is deposited under the low flow rate of 0.12 ml min<sup>-1</sup> and the high number of spray passes of 6.

### 2.3. Device fabrication

The organic ink was prepared by dissolving PBDD-TFQ:PC<sub>71</sub>BM (1:1, w/w) in a mixture of 1,8-diiodooctane (2 vol%) and chlorobenzene (98 vol%), the total solid concentration is 4 mg ml<sup>-1</sup>. The PEDOT:PSS ink was prepared by diluting PEDOT:PSS with deionized water and isopropanol in the ratio of 18:9:73 by volume [42,56].

The PSCs were prepared on pre-patterned ITO-coated glass with a sheet resistance of ca. 15 Ω per square. The ITO substrates were cleaned sequentially in detergent, deionized water and isopropanol. After UV ozone treatment for 30 min, a ca. 30 nm PEDOT:PSS layer was spray deposited onto the substrate and annealed at 150 °C for 20 min to remove the residual solvent and enhance the conductivity. The photoactive layers with a thickness of ca. 120 nm were spray deposited onto the PEDOT:PSS layer from the organic ink in air and then thermal annealed at 140 °C for

**Table 1**  
Blend film spray parameters.\*

	Flow rate (ml min <sup>-1</sup> )	Number of spray passes
Film LH	0.12	6
Film MM	0.17	4
Film HL	0.35	2

\* Note:(a) Sample solution is PBDD-TFQ and PC<sub>71</sub>BM (1:1, weight ratio) in a solvent mixture of 1,8-diiodooctane (DIO, 2 vol%) and chlorobenzene (CB, 98 vol%), the total solid concentration is 4 mg ml<sup>-1</sup>.(b) Other parameters: carrier gas pressure is 23.4 psi, nozzle scan speed is 30 mm s<sup>-1</sup>, ultrasonic power is 3.5 watt, distance between nozzle and substrates is 6 cm.

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