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Letter

Annealing-free, air-processed and high-efficiency polymer solar cells fabricated by a dip coating process

Ziyang Hu, Jianjun Zhang *, Shaozhen Xiong, Ying Zhao

Institute of Photo-Electronic Thin Film Devices and Technology of Nankai University, Key Laboratory of Photo-Electronic Thin Film Devices and Technology of Tianjin, Tianjin 300071, PR China
Key Laboratory of Opto-Electronic Information Science and Technology for Ministry of Education, Tianjin 300071, PR China

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ABSTRACT

We have used dip coating method to fabricate polymer solar cells (PSC) with an active layer composed of a blend of poly(3-hexylthiophene) and [6,6]-phenyl-C61 butyric acid methyl ester. With optimized conditions, pinhole-free and highly self-assembly active films were obtained, resulting in a narrow distribution of the device parameter. The performance of the dip coated devices (4.03%) is comparable to that of the spin coated devices (4.00%). Moreover, we show that dip coating is a feasible technology to deposit all solution processable layers of PSC, including the hole-transporting layer poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) as well and demonstrate dip coated hole-transporting layer and active layer devices with an efficiency of 3.49%. Our research may provide an alternative way for preparation of roll-to-roll processed organic electronics.

In recent years, polymer solar cells (PSCs) have emerged as an alternative to conventional Si-based solar cells due to their advantages of low cost, ease of fabrication and their potential for the manufacture of flexible and large area solar cells [1–3]. In particular, polymer bulk heterojunction (BHJ) solar cells based on interpenetrating networks of an electron donor and an acceptor, with a large-area donor and acceptor interface, resulting in an efficient photo-induced charge separation, have gained considerable interest. Currently, the major issues in the field of PSC research have been narrowed down to two aspects. First, the device efficiency and stability must be improved. Second, a roll-to-roll compatible, high-yielding process must be developed. Great efforts have been made to improve the power conversion efficiency (PCE) of the PSCs by synthesizing various donor and acceptor materials and optimizing their nanomorphology. To date, BHJ structured PSCs have exhibited PCEs of >7% [4,5]. Therefore, considering the stable rise of efficiencies, the development of novel solution processes that are compatible with low-cost mass production is one of the crucial requirements for practical application. Various methods for fabrication of PSCs have been suggested, including ink-jet printing [6], spray coating [7–9], brush painting [10], and screen printing [11,12]. Each method possesses its own advantages better than the spin coating method. The careful optimization of the film-deposition conditions have been used to achieve PCEs of 3–5%, which are close to those for the PSCs using the spin coating method with the same materials [6,9,10].

Dip coating process is a commonly used method for conventional dyeing and can provide easy and fast deposition of polymer films over large area. It can be a suitable technology for large scale production of organic solar cells. A particular advantage of dip coating process compared to other spray coating and inkjet print processes is the prompt and single pass formation of the film. Furthermore, the formed film by dip coating process is free-pinhole. It is well known that organic materials, such as poly(3-hexyl-

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* Corresponding author at: Institute of Photo-Electronic Thin Film Devices and Technology of Nankai University, Key Laboratory of Photo-Electronic Thin Film Devices and Technology of Tianjin, Tianjin 300071, PR China. Tel./fax: +86 22 23508032.

E-mail address: jjzhang@nankai.edu.cn (J. Zhang).

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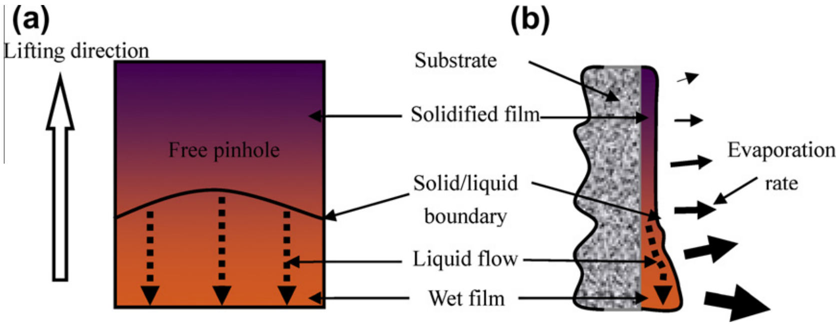

Fig. 1. Schematic evolution of the liquid layer during the slow natural drying process: (a) top view of the coverage of the substrate; (b) side view of the coverage of the substrate. The evaporation rate of the solvent was increased from the top to the bottom of the substrate, which was indicated by the size of the arrows.

thiophene) (P3HT) and [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM), can be effectively crystallized when the solvents are slow drying [13–15]. The fabrication of high efficiency PSCs was also reported using brush and roller painting combined with the slow drying process [10,16]. Therefore, it is expected that dip coating, which is accompanied by a natural drying process, may effectively induce the crystallization of P3HT and PCBM, and consequently yield enhanced solar cell performance.

In this work, we demonstrate the use of dip coating technology as a fabrication tool for highly efficient BHJ solar cells. With optimized conditions, PSC showed a PCE of 4.03% under AM 1.5 100 mW/cm^2 illumination, even though the device was fabricated in air without any annealing treatment. The performance of the dip coated PSCs was comparable to that of the spin coated device (4.00%) fabricated in air without any annealing treatment. Furthermore, PSC with the dip coated hole-transport and active layers were fabricated and showed an efficiency of 3.49%.

ITO-coated glass substrates were cleaned with a special detergent followed by ultrasonication in acetone and isopropyl alcohol and then kept in a 70 °C oven overnight. For conventional spin coated devices, the detailed process of the spin coated devices can refer to our previous work [17]. For dip coated PEDOT:PSS (Baytron P VP AI 4083) layer, PEDOT:PSS was first diluted by the deioned water with the ratio of 1:1. Then, the substrate was upright soaked fully, allowing full coverage of the aqueous solution. Lastly, the substrate was taken off and then left to dry for 1 min under a gentle air flow. The PEDOT:PSS film was completely dried in a 135 °C oven for 20 min. For dip coated active layer, P3HT and PCBM were dissolved in chlorobenzene to make 10 mg mL^{-1} and 8 mg mL^{-1} solutions, respectively. The substrate coated PEDOT:PSS film was upright soaked fully, allowing full coverage of the P3HT: PCBM solution. Then, the substrate was taken off with a pulling speed of ~3 mm s^{-1}, allowing the liquid flow by the self-gravity of the solution. After the solvent evaporates, a free-pinhole solid film was left on the substrate. We judged the complete drying of the dip coated film by the transition of the film color. The liquid film was brown. When the solvent was evaporated, the solidified film became purple. The dip coated and spin coated fimls have the similar thicknesses (~200–230 nm). The schematic evolution of the liquid layer during the slow natural drying process is illustrated in Fig. 1. The following process for the finished device fabrication was the same as the spin coated device. The morphology of the active layer films were observed by AFM (Seiko SPA-400 SPM UNIT). The photovoltaic performance was measured under ambient condition in air. The current density–voltage (*J*–*V*) characteristics were measured with a Keithley 4200 sourcemeter under AM 1.5 G (100 mW cm^{-2}) simulated by a Newport-Oriel solar simulator. The light intensity was calibrated using a certified photodiode to each measurement.

As shown in Fig. 2, in the case of an optimized spin coated device (SCSC), an excellent performance was observed with an open-circuit voltage (V_{oc}) of 0.61 V, a short-circuit current density (J_{sc}) of 9.28 mA cm^{-2}, a fill factor (FF) of 0.70, and a PCE of 4.00%. The FF of 0.70 and PCE of 4.00% are among the highest values reported for PSCs composed of P3HT:PCBM fabricated in air without any pre-or post-treatment [18,19]. This excellent performance can be attributed to the slow solvent-evaporation method, which results in an increased hole mobility and balanced charge transport of the active layer. In contrast to the dip coated device (SCDC) without any pre-or post-treatment, the device showed a similar efficiency of 4.03% with a V_{oc} of 0.58 V, a J_{sc} of 10.69 mA cm^{-2}, and an FF of 0.65. The result is also comparable to the previous highest reports which were obtained by spray or print coating process [6,9,10,16]. In addition, PSCs (DCSC) with the dip coated hole-transport and spin coated active layers were fabricated; and PSCs (DCDC) with the dip coated hole-transport and active layers were also fabricated. All of the results are present in Table 1.

To rationalize the measured values of J_{sc}, we also calculated the J_{sc} from the incident photon-to-current efficiency (IPCE) measured using the same devices as shown in Fig. 2(b). When the J_{sc} values from IPCE were compared with the device values, the two values were nearly equal to within the range experimental errors. The PCEs of the PSCs fabricated by the dip coating process are compared with those from the spin coating process in Table 1. Though the values of V_{oc} and FF of the dip coated PSC are relatively low, the main reason for the equal PCE of the spin coated PSC is its slightly increased J_{sc}. Although the

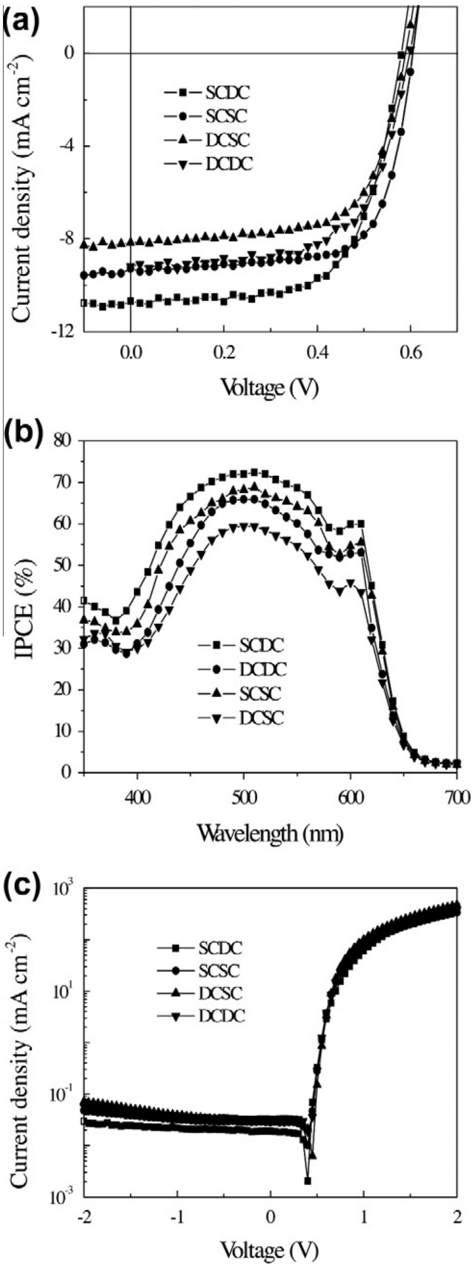

Fig. 2. (a) Representative *J*–*V* curves of solar cells fabricated by different process under light; (b) the corresponding IPCE spectra; (c) representative *J*–*V* curves of solar cells in the dark. All the devices are fabricated in air at room temperature of 20 °C without any pre- or post-treatment.

Table 1
Summary of device performance for various processes in this work.

Process	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)
SCSC	0.61	9.28	70	4.00
SCDC	0.58	10.69	65	4.03
DCSC	0.59	8.16	66	3.16
DCDC	0.60	9.18	63	3.49

factors affecting device performance have not been completely identified yet, it has generally been accepted that the performance is influenced by the morphology of the active layer, the balance between hole and electron mobility, and the interface of layers in PSC. Fig. 2(c) shows the dark *J*–*V* log-linear plot of the devices. The dark *J*–*V* curves illustrate the excellent rectification behavior of the devices prepared from dip coating and spin coating. An extremely low leakage current, indicating a high shunt resistance, is observed under reverse bias, suggesting that a good coverage for the PEDOT:PSS and P3HT:PCBM layers on the substrates. This is consistent with the high FFs observed in these devices under illumination. This result again confirmed that the high quality films could be obtained from the dip coating process. The slope of the dark *J*–*V* curve between 0.3 V and 0.7 V represents the diode behavior of the solar cells as governed by the diode ideality factor (n) and saturation current (J_0). For BHJ solar cells the ideality factor correlates with the number of distributed interfaces within the blend [20]. The similar values of n and J_0 derived from the dark *J*–*V* characteristics also indicated the well-established contact between the electrodes and the active layer. In previous studies, it has found that the ideality factor reflects the recombination behavior of the BHJ distributed interfaces [20]. The fact that the ideality factors are almost the same in all devices suggests that the film morphology is similar in all cases. In addition, the formed excellent films including PEDOT:PSS and P3HT:PCBM blend prepared by dip coating resulted in a narrow distribution of the relevant device parameters as shown in Fig. 3.

It is well known that the morphology of the PSCs plays an importance role in device performance. The film morphology was examined by AFM (Fig. 4). It is very clear to observe that a rough surface is formed in the dip coated film. The surface roughness of the dip coated film is larger than that of the spin coated one: the average root-mean-square (RMS) roughness is 12.76 nm and 7.29 nm for dip coating and spin coating, respectively. In previous reports [7,8,21], it is pointed out that the rough surface of the film could affect the interfaces of the active layer and therefore the device performance. This roughness has a negative impact on FF of the resulting solar cells, often limited to values below 60%. However, in our experiments the roughness surface may effectively reduce the charge-transport distance and increase the J_{sc} value. At the same time, the metal electrode on the rough surface can reflect normally incident light to random directions and then the path length of light in the active layer can be increased, leading to more efficient light harvesting [22–24]. This increased path length and reduced the charge-transport distance could lead to the increase of IPCE, as shown in Fig. 2(b).

As many groups have reported improved efficiencies of ~4–5% by pre-or post-heat treatment of spin coated devices, resulting in an enhanced degree of ordering. We also attempted to improve the efficiency of our spin coated and dip coated devices by applying a heat treatment to the as-prepared active layers. However, there is no substantial improvement in the device performance. We may conclude that the dip coating process allows the well self-organization and crystallization crystal in the active layer. Also, the

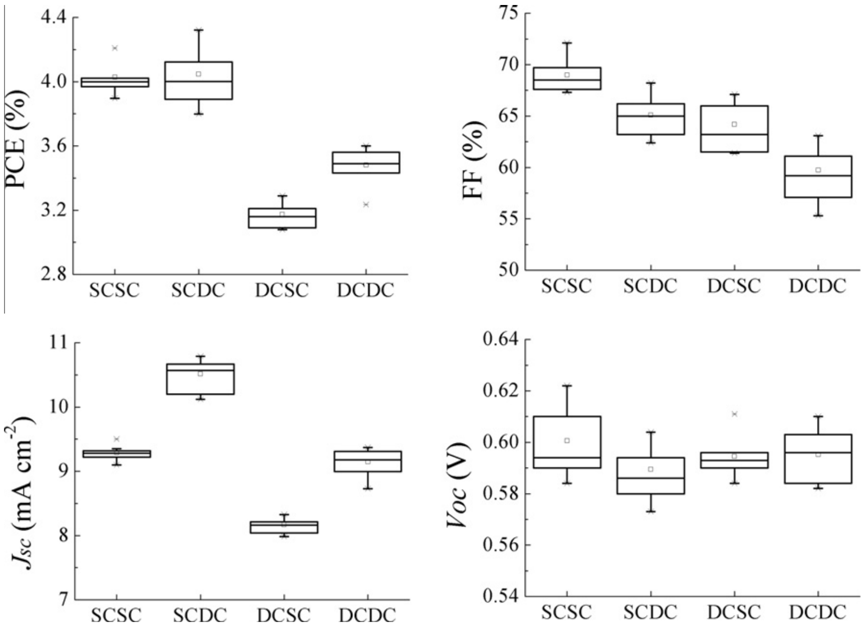

Fig. 3. Average PCE, FF, J_{sc} and V_{oc} for solar cells with different process, bars represent maximum and minimum values of 16 devices.

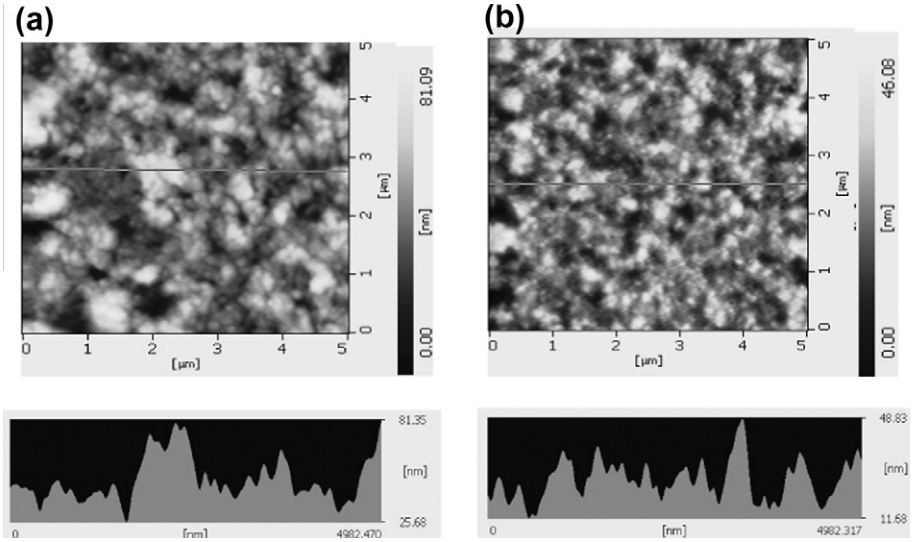

Fig. 4. AFM images of P3HT:PCBM films showing a 5 μm × 5 μm surface area by different coating: (a) dip coating (RMS = 12.76 nm); (b) spin coating (RMS = 7.29 nm). The white line across the AFM images indicates the height profiles.

effect of the remained solvent in the active layer is negligible. The achievement of high efficiency PSCs without additional post-treatment is indispensable for their industrialization, which may provides a very promising feature for the development of annealing-free PSCs for commercialization.

In conclusion, we have investigated a simple dip coating technique as a promising method for the mass production of low-cost and large-area flexible solar cells. This method has many advantages including the absence of a vacuum system to support the substrate, fast processing and good compatibility with roll-to-roll systems. High efficiency, air-processed and annealing-free PSCs fabricated by dip coating process have been achieved. In addition, without any thermal treatment, additional additive, the dip coating process may be applied in wide areas. In short, the dip coating process follows the basic process of the roll-to-roll processing; our research may provide an alternative way for preparation of roll-to-roll processed organic electronics.

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