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Letter

Polymer solar cells based on inkjet-printed PEDOT:PSS layer

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ABSTRACT

In this article, we have demonstrated solar cell performance of the inkjet-printed PEDOT:PSS layer and the roles of additives in device efficiency. The newly proposed PEDOT:PSS inks with additives of glycerol and surfactant show the improved surface morphology and high conductivity resulting in the enhanced photovoltaic performance. Using the optimized ink formulation of PEDOT:PSS, we have demonstrated a 3.16% efficient solar cell with an inkjet printing.

1. Introduction

During the past decade, there has been an intensive search for cost-effective photovoltaics [1–3]. As an alternative to inorganic solar cells, polymer solar cells could provide a significant cost reduction since their low temperature processing may allow for the printing of large area solar cells on flexible substrates at low fabrication cost [4]. Progress in the field of polymer solar cells is rapid [5,6]. The performance of polymer solar cells has been improved by using new materials [7], new structures [8] and new techniques in devices. Recently, several printing techniques have been used to fabricate various polymer based organic devices. Among them, inkjet printing is a commonly used technique for the controlled deposition of solutions of functional materials in specific locations on a substrate. It facilitates easy and fast deposition of polymer films over a large area. Moreover, it may be suitable for the large scale production of various electronic devices. In addition, inkjet printing is very promising because the polymer devices can be fabricated easily, due to their compatibility with various substrates and already complete patterning. Inkjet printing has been extensively used in the fields of polymer light emitting diodes (LEDs), and thin film transistors (TFT) [9–12]. Inkjet printing technology has also been used for fabricating polymer:fullerene bulk heterojunction solar cells, but not many results have been reported. Aernouts et al. developed polymer solar cells with an active layer of P3HT:PCBM using inkjet printing [13]. Steirer group recently reported inkjet-printed thin film electrodes for polymer.

Poly(3,4-ethylenedioxythiophene) doped with poly(4-styrenesulfonate) (PEDOT:PSS) has attracted much attention and has been widely used as an antistatic coating

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material, as electrodes for capacitors or photodiodes, and as a hole transport layer in organic LEDs during the last decade [14–17]. PEDOT:PSS is optically transparent and easily processed using simple coating methods such as spin-coating [18–20]. Many researchers reported on the conductivity modification of PEDOT:PSS by adding several additives such as polyols, metals and different solvents [21–23]. The increase in conductivity of the PEDOT:PSS improves characteristics such as electromagnetic radiation shielding and electrical transport. In spite of such a potential use of PEDOT:PSS, few studies dealing with a PEDOT:PSS printing technique have been reported. Steirer et al. only reported inkjet-printed thin film electrodes of PEDOT:PSS for polymer solar cells [24].

In this paper, we report on the performance of bulk heterojunction polymer solar cells with an inkjet-printed PEDOT:PSS layer. The morphological and electrical studies and device performance of the inkjet-printed PEDOT:PSS layer in polymer solar cells are discussed in this article.

Table 1
Formulation details of the PEDOT:PSS inks with additives.

Inks	PEDOT:PSS (g)	Glycerol		EGBE	
		g	wt.%	g	wt.%
1	7.194	–	–	–	–
2	7.194	0.431	6	–	–
3	7.194	0.431	6	0.014	0.2
4	7.194	0.431	6	0.028	0.4

2. Experimental

PEDOT:PSS was purchased from Bayer (Baytron P AI 4083) and used alone, as well as mixed with additives of glycerol and ethylene glycol butyl ether (EGBE) to make inks for printing. (Details are given in Table 1.) The polymer solar cell device was fabricated with a configuration of indium tin oxide (ITO)/PEDOT:PSS/P3HT:PCBM/LiF-Al. Patterned ITO glass was cleaned with chloroform, acetone and isopropyl alcohol using an ultrasonication method, and then treated with an O_2-plasma. After solvent cleaning, the PEDOT:PSS thin films were coated by using inkjet printing (UJ2100, Unijet, Korea) and dried for 20 min at 140 °C. An active layer of P3HT:PCBM (mixed solution of 1:0.7 wt.%) was cast on top of the PEDOT:PSS film by spin-coating and dried for 1 h at 50 °C in a nitrogen atmosphere. To complete the device, LiF was evaporated on the active layer to about 0.7 nm thicknesses, and then Al evaporated to about 150 nm thicknesses under vacuum (10^{-6} torr). This device was encapsulated to measure the solar cell performance. The current versus voltage (I–V) characteristics of the solar cell devices in the dark and under white light illumination were measured with an AM 1.5G solar simulator (300 W, Newport, USA) and 100 mW/cm^2 conditions, adjusted with a standard PV reference cell (2 × 2 cm, a monocrystalline silicon solar cell, calibrated at NREL, Colorado, USA) with a Keithley 2400 source-measure unit. In order to avoid the underestimation of the area of the devices due to cross conduction of

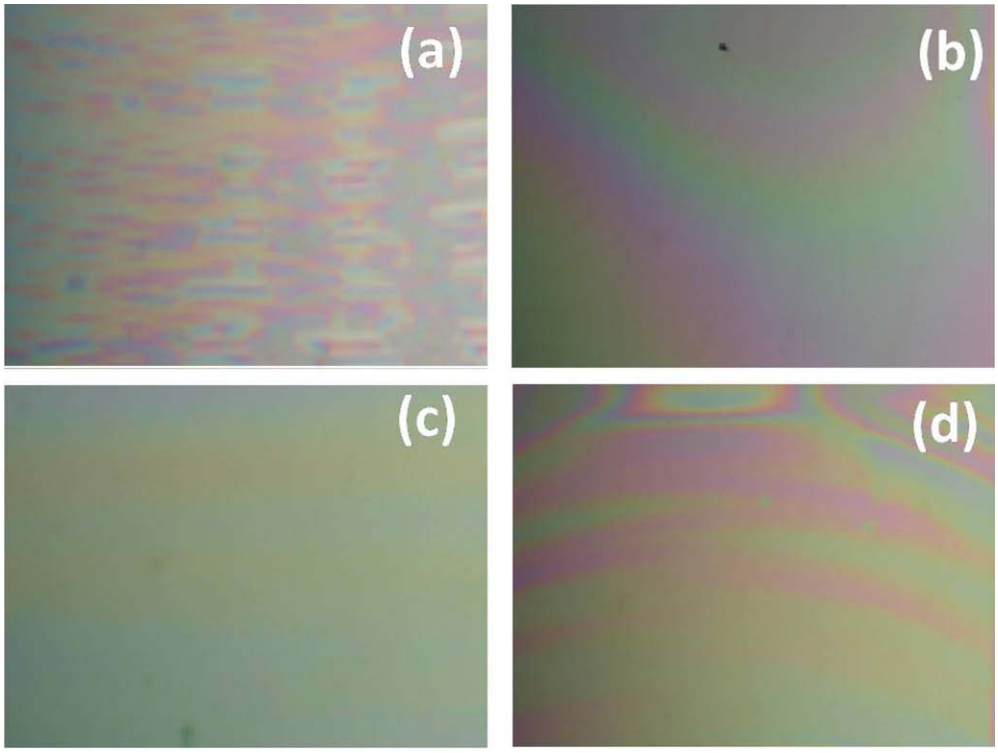

Fig. 1. Polarization microscope images of inkjet-printed PEDOT:PSS films (a) without additives (pure PEDOT:PSS): ink 1, with (b) glycerol (6 wt.%): ink 2, (c) glycerol (6 wt.%), and EGBE (0.2 wt.%): ink 3, (d) glycerol (6 wt.%) and EGBE (0.4 wt.%): ink 4.

a highly conducting PEDOT:PSS used in this study, we used a black mask fitted to the active area (3 × 3 mm) of the device [25,26]. The surface topography and morphology of the inkjet-printed PEDOT:PSS thin films were analyzed using polarization microscopy (JEOL-2010), surface profiler (SNU Precision SIS3747) and atomic force microscopy (AFM, VECCO, 613R1). All the characterizations were performed at room temperature.

3. Results and discussion

Polarization microscopy images of the inkjet-printed PEDOT:PSS films were completed to examine film morphology and thickness uniformity at the millimeter length scale (Fig. 1). As shown in Fig. 1a, the surface of the inkjet-printed films appeared non-uniform for PEDOT:PSS ink without any additives (ink 1 in Table 1). It appears to be composed of discontinuous clusters which do not stick to ITO substrates. The PEDOT:PSS accumulates in the center of the substrate due to spreading and wetting on the substrate and the drying behavior of the inkjet-printed films. The surface anchoring forces want to align the PEDOT:PSS parallel to the bottom surface and perpendicular to the top surface of the film. The elastic forces work against the resulting vertical distortions of the director field. Inkjet-printed PEDOT:PSS film with 6 wt.% glycerol (ink 2) gives better uniformity than film from ink 1 as shown in Fig. 1b. The colors shown in the images are due to the Newton colors of thin films which depend on the thickness of the film. Fig. 1c shows an image of PEDOT:PSS film with glycerol 6 wt.% and 0.2 wt.% EGBE added (ink 3). This ink had the best uniform film thickness and density. This

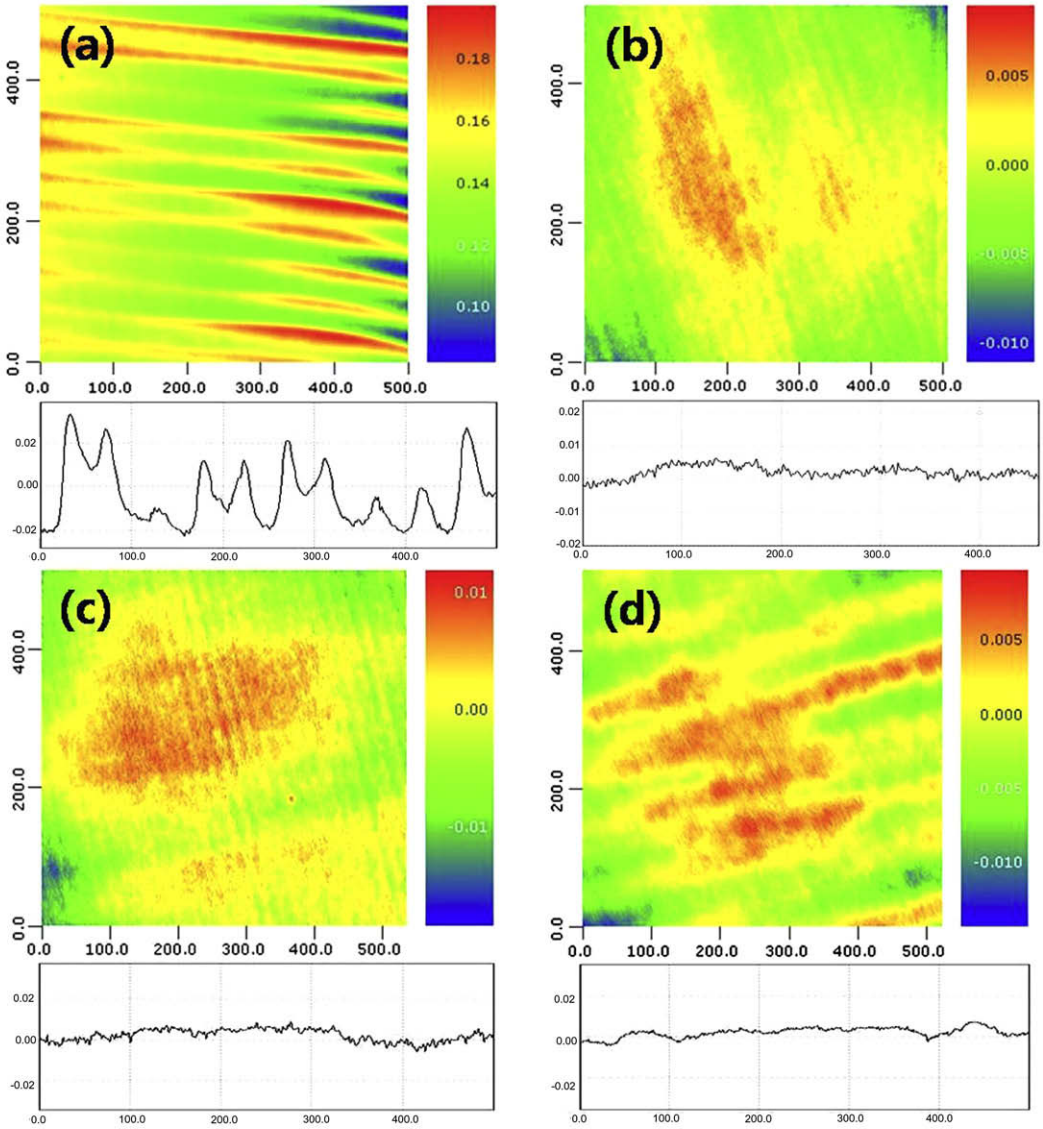

Fig. 2. Surface profile images of inkjet-printed PEDOT:PSS films (a) without additives (pure PEDOT:PSS): ink 1, with (b) glycerol (6 wt.%): ink 2, (c) glycerol (6 wt.%), and EGBE (0.2 wt.%): ink 3, (d) glycerol (6 wt.%) and EGBE (0.4 wt.%): ink 4.

may be due to the EGBE surfactant in the dispersion which minimizes the interfacial tension between the PEDOT:PSS and glycerol, allowing the pitch size (distance between individual droplets from the inkjet head) to be smaller than the droplet diameter. When the EGBE ratio is increased to 0.4 wt.%, the formation of the film seems to be disturbed, and film uniformity decreases as shown in Fig. 1d.

Fig. 2 shows the surface profile images of inkjet-printed PEDOT:PSS films without and with additives. A significant distinction in the film surface profile was observed in inkjet-printed PEDOT:PSS films. The surface profile image of the inkjet-printed PEDOT:PSS film without any additives (ink 1 in Table 1) shows significantly rough surface in 500 μm length scale. The surface roughness was dramatically improved in the inkjet-printed PEDOT:PSS film with adding 6 wt.% glycerol (ink 2). With adding of additional EGBE surfactant of 0.2–0.4 wt.% (ink 3 and 4), the surface roughness were slightly changed and smoother surface

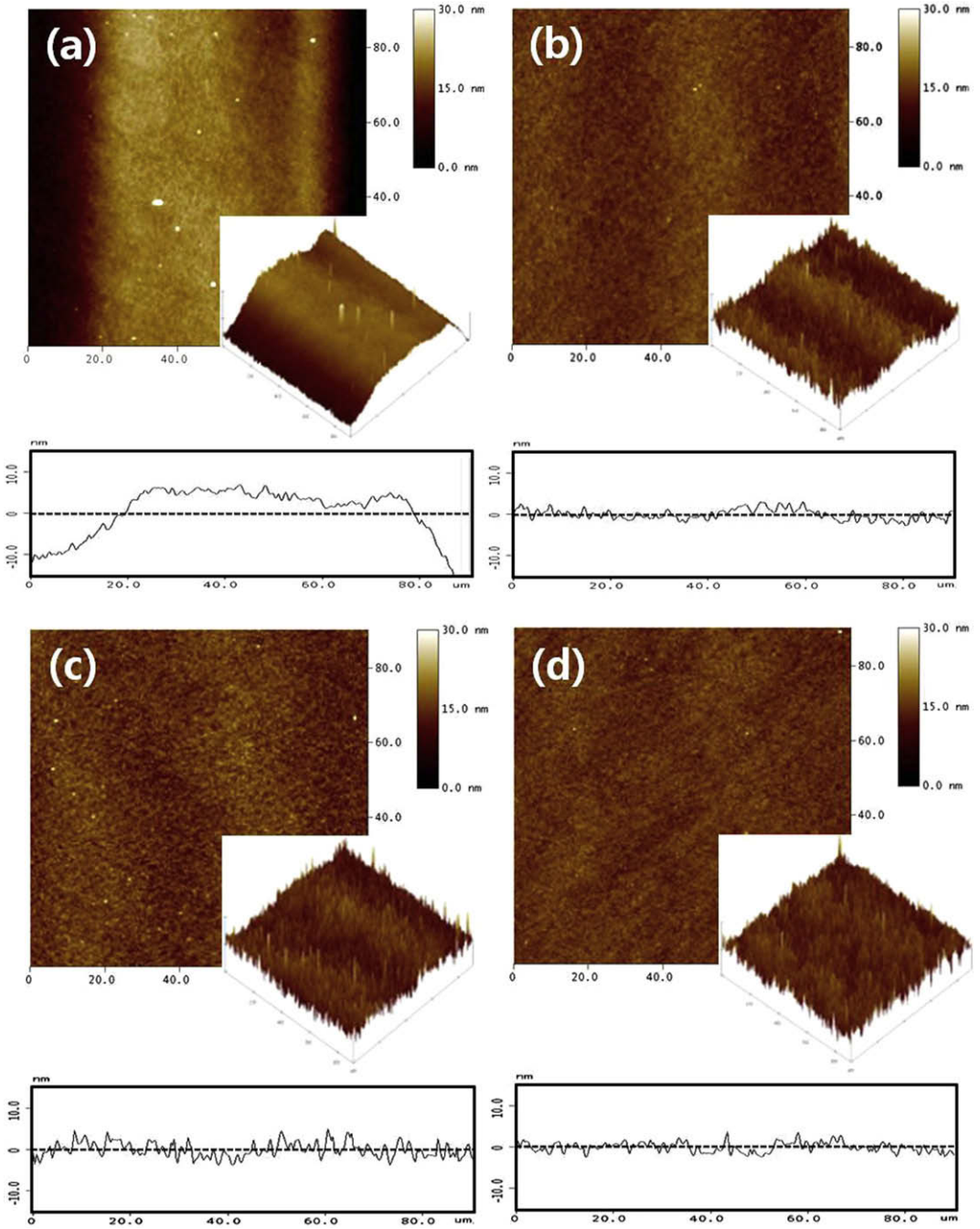

Fig. 3. AFM images of inkjet-printed PEDOT:PSS films (a) without additives (pure PEDOT:PSS): ink 1, with (b) glycerol (6 wt.%): ink 2, (c) glycerol (6 wt.%), and EGBE (0.2 wt.%): ink 3, (d) glycerol (6 wt.%) and EGBE (0.4 wt.%): ink 4.

profiles were obtained. The surface morphology was further studied with AFM. Fig. 3 represents the AFM images of the inkjet-printed PEDOT:PSS films without and with additives in different amounts. Similarly with a surface profile result, the inkjet-printed PEDOT:PSS film from ink 1 without any additives shows relatively rough surface morphology with an rms roughness of 6.67 nm. The AFM images of the inkjet-printed PEDOT:PSS films from ink 2 and ink 3 with additives provide significantly reduced roughness profiles with similar rms roughness values of 1.64 and 1.63 nm. The rms roughness of inkjet-printed PEDOT:PSS film from ink 4 was slightly reduced up to 1.36 nm. A non-uniform surface roughness and profile, especially in the PEDOT:PSS film without additives (ink 1), may affect the interfaces between PEDOT:PSS and the photoactive layer, and therefore the performance of the inkjet-printed solar cell devices [9].

Fig. 4 shows the conductivity results of the PEDOT:PSS films with and without additives. The conductivity was enhanced in the inkjet-printed PEDOT:PSS film by the addition of 6 wt.% glycerol (ink 2) and with further addition of 0.2 wt.% EGBE (ink 3). The conductivity of PEDOT:PSS increased from 7.82×10^{-1} to 1.52×10^{2} S/cm for PEDOT:PSS by adding 6 wt.% glycerol and to 1.64×10^{2} S/cm by adding 0.2 wt.% EGBE. However, the conductivity decreases to 1.28×10^{0} S/cm when EGBE is increased to 0.4 wt.%. The addition of glycerol to the aqueous PEDOT:PSS dispersion is known to enhance the conductivity of the thin films by several orders of magnitude, depending on its concentration [27]. The conductivity of the PEDOT:PSS is strongly dependent on the film morphology and its chemical structure. F. Zhang et al. recently reported that PEDOT:PSS with glycerol shows higher performance in solar cells than pure PEDOT:PSS film due to the swelling and aggregation of colloidal PEDOT-rich particles that ultimately facilitate conduction in the film [36]. Several reports show that the dramatic effect of glycerol as a processing additive is due to the reorganization and stabilization of the PEDOT and PSS chains during subsequent thermal annealing of the films by a plasticizing effect [28–35]. In our study, the addition of glycerol and surfactant EGBE may also affect the morphology and physical structures of inkjet-printed PEDOT:PSS film. Here, we propose a hypothesis to explain the basic principles of molecular interactions between the surfactant, glycerol and the PEDOT:PSS film. Normally PEDOT:PSS film originates from a core-shell type framework, as shown in Fig. 2d, where PSS molecules are located around the PEDOT units through ionic interaction. Similarly, upon addition of glycerol, the polar functionality (–OH) in the glycerol molecule might directly interact with cationic species of PEDOT. Probably stronger ionic interactions between the glycerol and PEDOT are responsible for the highly conductive network formation in glycerol added PEDOT:PSS, when compared to PSS and PEDOT in pure PEDOT:PSS film. A mild repulsive force may be exerted between the PSS and glycerol units. The level of conductive network formation is further extended by an incorporation of 0.2 wt.% EGBE surfactant, which has both a polar alcoholic (–OH) group and a nonpolar alkyl group (butyl) at the other end. However, with a higher weight percentage of EGBE surfactant, the conductive network formation is significantly suppressed by the formation of hydrophobic areas. The alkyl group in the EGBE surfactant aggregates along with PSS units to form hydrophobic domains that will decrease the surface poten-

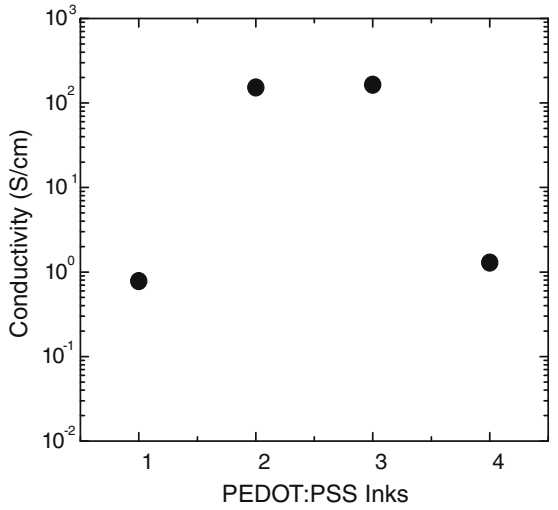

Fig. 4. Conductivity measurements for inkjet-printed PEDOT:PSS films (1) without additives (7.82×10^{-1} S/cm), with (2) glycerol (6 wt.%) (1.52×10^{2} S/cm), (3) glycerol (6 wt.%) and EGBE (0.2 wt.%) (1.64×10^{2} S/cm), (4) glycerol (6 wt.%) and EGBE (0.4 wt.%) (1.28×10^{0} S/cm).

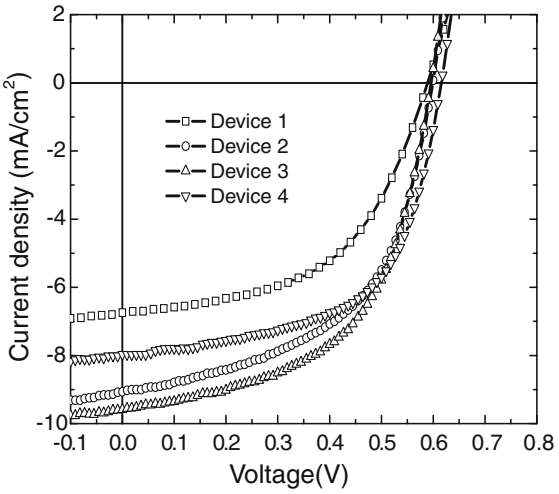

Fig. 5. Current-density versus voltage (*J–V*) characteristics of solar cells with different inkjet-printed PEDOT:PSS layers in the dark and under simulated AM1.5 illumination of 100 mW/cm^2.

Table 2
Summary of solar cell device characteristics with different inkjet-printed PEDOT:PSS layers.

Devices	Voc (V)	Jsc (mA/cm^2)	FF (%)	EFF (%)
1	0.589	6.746	52.63	2.09
2	0.599	9.063	53.70	2.92
3	0.595	9.593	55.28	3.16
4	0.615	7.972	59.06	2.90

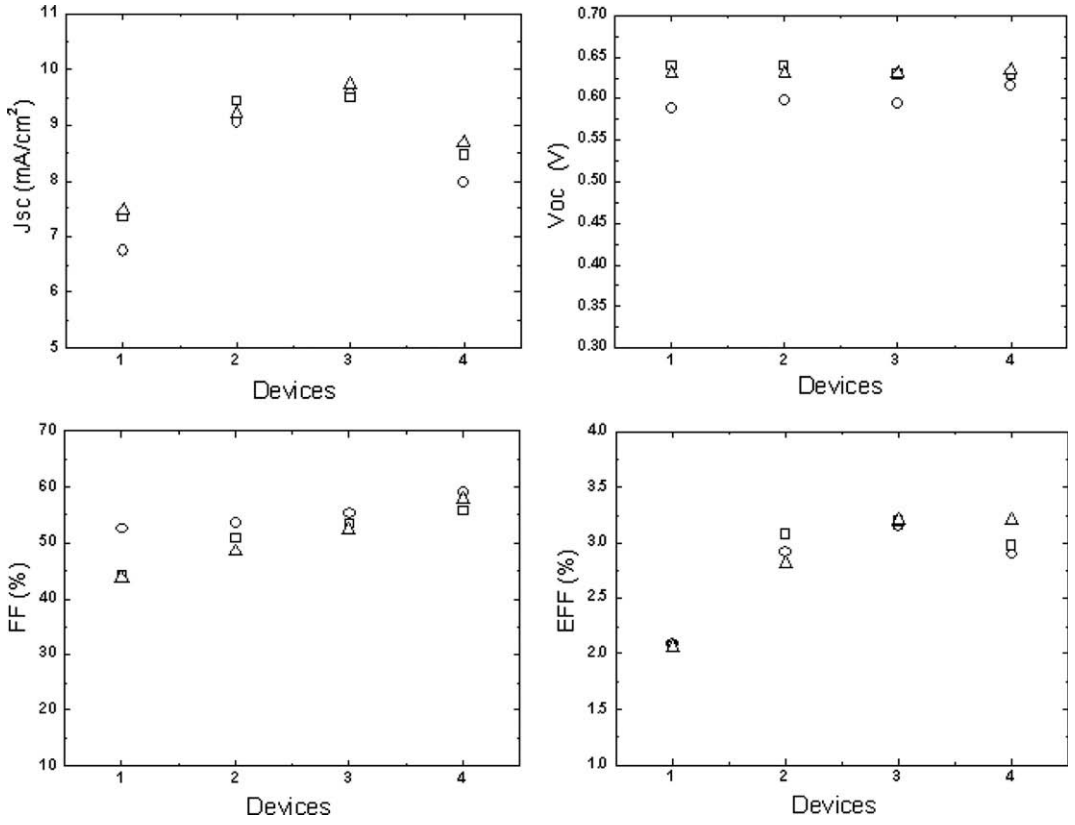

Fig. 6. Photovoltaic characteristics of three solar cell devices by inkjet printing of PEDOT:PSS inks prepared in the different batches.

tial of the PEDOT:PSS film in order to reduce conductivity. The work is still underway to find an exact mechanism.

To study the effect of additives on solar cell device performance, polymer bulk heterojunction solar cells (device 1–4) from different PEDOT:PSS inks (inks 1–4 as shown in Table 1) have been fabricated in the configuration of ITO/PEDOT:PSS inks/P3HT:PCBM/LiF-Al by inkjet printing. Current-density versus voltage (*J–V*) characterization has been performed in the dark and under simulated illumination as shown in Fig. 5. The resulting characteristics are shown in Table 2. Without any additives (device 1), the device performance was very poor showing low power conversion efficiency (EFF), circuit current density (Jsc) and fill factor (FF). This is due to the roughness surface profile as indicated in surface morphology results and low conductivity of PEDOT:PSS layer. The Jsc, FF and EFF of the device 2 from inkjet-printed PEDOT:PSS with glycerol were more than that of the pure PEDOT:PSS (device 1). Especially, Jsc was dramatically enhanced in device 2. This enhancement in the Jsc as well as device efficiency may be due to the improvement of the surface morphology and the improved charge collection by increased conductivity of the PEDOT:PSS with glycerol compared with pure PEDOT:PSS [37,38]. This may also be explained by the swelling and aggregation of colloidal PEDOT-rich particles which form a highly conductive network in the films [36,39]. The device performance (device 3) further improved with the addition of 0.2 wt.% EGBE surfactant from 2.92% to 3.16% in efficiency. Jsc and FF values were also enhanced in device 3. The conductivity of PEDOT:PSS film in this device is almost the same as glycerol added to PEDOT:PSS (device 2), but the surface roughness is optimal compared to other films. When the amount of EGBE in the PEDOT:PSS film is increased from 0.2 to 0.4 wt.%, it decreases the conductivity of the film, therefore efficiency and Jsc decrease in device 4.

In order to investigate the reproducibility of solar cell devices with inkjet-printed PEDOT:PSS layers, we have prepared several solar cell devices from inkjet-printed PEDOT:PSS inks in the different batches and their solar cell properties were measured. Fig. 6 shows the photovoltaic characteristics of three solar cell devices. All devices show good reproducibilities in Voc, Jsc, FF and efficiency. The best solar cell performance was obtained in device 3.

4. Conclusion

We have demonstrated solar cell performance of the inkjet-printed PEDOT:PSS layer and the roles of additives in device performance. We have used glycerol and EGBE surfactant as additives for improve the surface morphology and conductivity of PEDOT:PSS inks. The newly proposed ink formulation of PEDOT:PSS increases the photovoltaic performance such as Jsc, FF and efficiency of inkjet-printed PEDOT:PSS resulting in a reliable print head with optimum wetting, spreading and drying. Using the newly developed

ink formulation of PEDOT:PSS (ink 3) with glycerol and optimized EGBE surfactant, we have demonstrated a 3.16% efficient and reliable solar cell with an inkjet-printed PEDOT:PSS layer (device 3). This high photovoltaic performance indicates the potential of inkjet printing for the mass production of organic photovoltaics.

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