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닥터블레이드 코팅 인쇄공정을 이용한 고분자 태양전지

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Doctor Blade-Coated Polymer Solar Cells

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초록: 본 연구에서는 대면적 용액 인쇄장비인 닥터블레이드 코터를 이용하여 형성된 P3HT:$PC_{71}BM$ 및 PBDTTT-EFT:$PC_{71}BM$ 벌크헤테로 정션을 기반으로 하는 고분자 태양전지를 보고한다. 블레이드 코팅 인쇄공정으로 제작된 정구조와 역구조의 P3HT:$PC_{71}BM$ 고분자 태양전지로부터 기존 스핀코팅법으로 제작된 태양전지 성능보다 우수한 2.75, 3.03%의 광전변환효율을 얻을 수 있었을 뿐만 아니라, 개선된 소자 성능의 균일도가 확보됨을 확인하였다. 나아가 블레이드 코팅 공정을 이용하여 3.10%의 광전변환효율을 나타내는 PBDTTT-EFT:$PC_{71}BM$ 기반의 플렉시블 고분자 태양전지를 구현함으로써 블레이드 코팅법이 향후 대면적 고속 롤투롤 프린팅 인쇄공정에 효과적으로 활용될 수 있음을 제시하였다.

Abstract: In this work, we report polymer solar cells based on blade-coated P3HT:$PC_{71}BM$ and PBDTTT-EFT:$PC_{71}BM$ bulk heterojunction photoactive layers. Enhanced power conversion efficiency of 2.75 (conventional structure) and 3.03% (inverted structure) with improved reproducibility was obtained from blade-coated P3HT:$PC_{71}BM$ solar cells, compared to spin-coated ones. Furthermore, by demonstrating 3.10% efficiency flexible solar cells using blade-coated PBDTTT-EFT:$PC_{71}BM$ films on the plastic substrates, we suggest the potential applicability of blade coating technique to the high-throughput roll-to-roll fabrication systems.

Keywords: polymer solar cells, doctor blade-coating, printing process, flexible solar cells.

Introduction

Polymer solar cells (PSCs) have attracted considerable interest because of their exceptional advantages such as lightweight, flexibility, low-temperature solution-processability. Since the first discovery of the bulk heterojunction photovoltaic cells in 1995,[1] remarkable progress has been made in improving the performance of PSCs.[2-6] Generally, bulk heterojunction consists of a blend of two organic semiconductors, an electron donating (*p*-type) conjugated polymer and an electron accepting (*n*-type) small molecules, where interpenetrating networks of electron donors and acceptors efficiently dissociate excitons, resulting in charge carriers generation.

Due to the intensive research efforts in the development of materials comprising bulk heterojunction, optimization of device architectures, and processing techniques, the power conversion efficiency (PCE) of state-of-the-art bulk heterojunction-based PSCs has increased tremendously in the past few years and recently reached up to over 10% from a unit cell, which offers their potential for the commercialization.[7-9]

Most widely used process for the quick and easy preparation of these bulk heterojunction films has been a spin-coating

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method.[10-12] Although spin-coating is a suitable technique for the fabrication of laboratory-scale small-area devices, it has limitations to be used for the high throughput and large-area production because of serious undesired material loss (most of the excess solution is ejected during high-speed rotation), high fabrication cost, and variation in film thickness between center and edge part of the coated films due to the radial flow of the solution and shear thinning.

Recently, as alternatives, advanced coating techniques which are compatible with roll-to-roll mass production have been introduced such as flexographic printing, blade-coating, ink-jet printing, spray-coating, flatbed and rotary screen-printing.[13-20] Among them, a doctor blade-coating method features an appealing merit for a potential up-scaling in that it allows a preparation of precisely defined uniform film thickness (d) in large-area which is mainly controlled by the gap size of the blade to the surface (g), the concentration of the used solution (c), and the density of the used material in the film (ρ), following the empirical relationship as below:[13]

$$d = (1/2)\ g\ (c/\rho)$$

In addition, it shows minimal solution ink waste during the coating process where all amount of solution is utilized, and is easily transferable to roll-to-roll coating system as well.

In this study, we demonstrate doctor-blade coated poly(3-hexylthiophene) (P3HT): [6,6]-phenyl C71-butyric acid methyl ester ($PC_{71}BM$) bulk-heterojunction-based PSCs with both conventional and inverted architectures showing enhanced performances compared to those of spin-coated ones. Furthermore, we also suggest potential applicability of blade-coating technique towards roll-to-roll processes by demonstrating a flexible PSC solar cell based on blade-coated poly[4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)-benzo[1,2-b:4,5-b0]dithiophene-2,6-diyl-alt-(4-(2-ethylhexyl)-3fluorothieno[3,4b]thiophene-)-2-carboxylate-2-6-diyl] (PBDTTT-EFT):$PC_{71}BM$ bulk heterojunction films on the plastic substrates.

Experimental

P3HT, PBDTTT-EFT (electron donating polymers), and $PC_{71}BM$ (electron accepting small molecule) were purchased from Rieke metals, 1-materials, and nano-C, respectively. All the used solvents, zinc acetate dihydrate, and ethanolamine were purchased from Sigma-Aldrich and all chemicals were used without further purification.

Glass/indium-tin-oxide (ITO) and poly(ethylene terephthalate) (PET)/ITO were used as substrates for the rigid and flexible solar cells, respectively. Before device fabrication, all the substrates were rinsed by sonication in detergent, deionized water, acetone and isopropyl alcohol in sequence. After drying under nitrogen stream, the substrates were subjected to UV plasma for 5 min for further cleaning. After then, to modify ITO electrode surface, poly(3,4-ethylenedioxythiophene):poly(styrene-sulfonate) (PEDOT:PSS, Baytron PVP AI 4083, pre-filtered using a 0.45 μm filter) or ZnO films was formed by spin-coating on the substrates, and the substrates were annealed at 150 ºC for 20 min and 200 ºC for 40 min for PEDOT:PSS and ZnO films, respectively, followed by slow cooling to room temperature (25 ºC). The ZnO films were prepared using a zinc acetate dihydrate solution in ethanol. Ethanolamine was added as a stabilizer in equal concentration to zinc acetate dihydrates.

P3HT:$PC_{71}BM$ and PBDTTT-EFT:$PC_{71}BM$ were blended in chlorobenzene with 1:1 and 1:1.5 weight ratios, respectively, and using these solutions each bulk heterojunction film was coated on the PEDOT:PSS or ZnO-coated substrates. P3HT:$PC_{71}BM$ and PBDTTT-EFT:$PC_{71}BM$ bulk heterojunction layers were blade-coated from homogeneous solution at a speed of 25 mm s^{-1} using a knife-coating device (KP-3000H, KIPAE), as schematically described in Figure 1(a). After 30 min evaporation of solvent from prepared wet film in room temperature, the P3HT:$PC_{71}BM$ films were annealed at 150 ºC for 15 min. For the comparison, spin-coated solar cells were prepared as references. All film coating processes were carried out in an ambient condition. Finally, LiF (1 nm)/Al (100 nm), for conventional structure device, or MoO_3 (10 nm)/Ag (100 nm), for inverted structure devices, electrodes were deposited by thermal evaporation under a vacuum pressure of 2×10^{-6} Torr. The defined active areas of solar cells were 0.1 and 1.0 cm^2 for P3HT:$PC_{71}BM$ and PBDTTT-EFT:$PC_{71}BM$ devices, respectively. Current density-voltage (J-V) characteristics of the photovoltaic devices were measured using a Keithley 2400 source-meter unit. The photocurrent was measured under AM 1.5G illumination at an intensity of 100 mW cm^{-2}. UV-vis absorption spectra were obtained using an Agilent 8457 UV-vis spectrophotometer.

Results and Discussion

The conventional and inverted solar cell structures and energy level diagram of the materials used in this study are

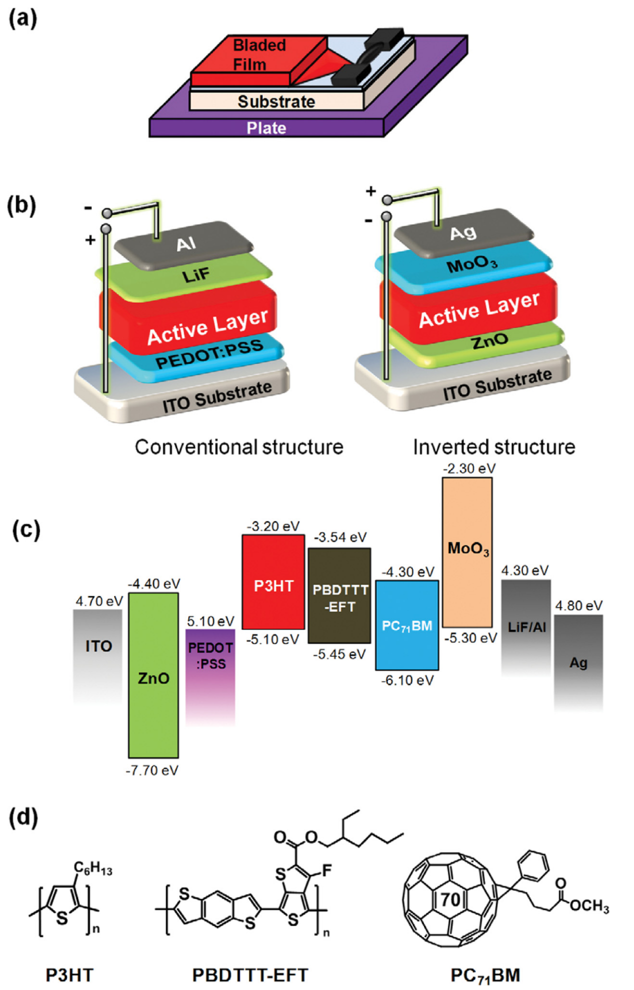


Figure 1. Schematic diagrams of (a) blade-coating; (b) solar cell device architectures used in this study; (c) energy levels; (d) molecular structure of the component materials.

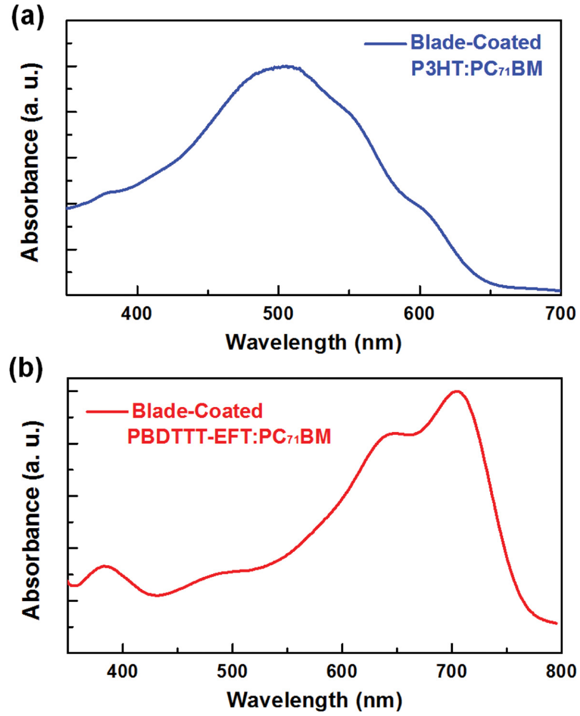


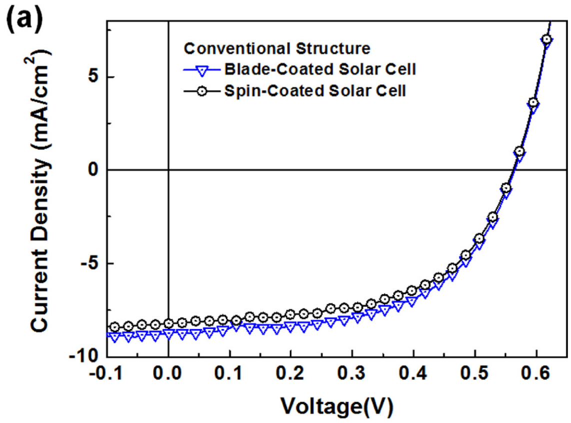
Figure 2. Absorption spectra of blade-coated (a) P3HT:$PC_{71}BM$; (b) PBDTTT-EFT:$PC_{71}BM$ films.

presented in Figure 1(b) and (c), respectively.[21,22] Device fabrication methods are described in the experimental section in detail.

First, in order to explore the feasibility of a blade-coating technique for the bulk heterojunction photoactive film formation, we blade-coated blend solutions (polymer:$PC_{71}BM$) on the substrate and performed UV-Vis absorption spectrum measurements. The absorption spectra of blade-coated P3HT:$PC_{71}BM$ and PBDTTT-EFT:$PC_{71}BM$ films in Figure 2 reveals broad-band light absorbing (350~650 and 350~800 nm for P3HT:$PC_{71}BM$ and PBDTTT-EFT:$PC_{71}BM$ films, respectively) capability of each film.

Figure 3 shows the current density (J)–voltage (V) characteristics of PSCs based on P3HT:$PC_{71}BM$ bulk heterojunction films fabricated by blade-coating method. Spin-coated cells were additionally prepared as reference devices to compare (20 mg/mL concentration of P3HT:$PC_{71}BM$ (1:1 weight ratio) solution was used and the average film thickness is 120 nm measured by atomic force microscopy (AFM)).

Interestingly, the PSCs fabricated by two different coating methods resulted in different photovoltaic properties. The open circuit voltage (V_{OC}), short circuit current density (J_{SC}), fill factor (FF) and PCE of conventional structured solar cells are 0.56 V, 8.22 mA cm^{-2}, 0.56, and 2.58% and 0.57, 8.76 mA cm^{-2}, 0.55, and 2.75%, for spin- and blade-coated films, respectively as presented in Figure 3(a). Improvement in PCE from blade-coated devices are attributed to the enhanced J_{SC}, which is speculated to originate from the enhanced organization of donor-acceptor network because blade-coating provides much longer molecular organization (solvent-drying) time in the wet film state (30 min), compared to spin-coating where solvent evaporate in very short time (< 60 s) during high speed (1500 rpm) spinning. This trend of PCE improvement by blade-coating is also observed from inverted structure devices as well. Figure 3(b) shows that the V_{OC}, J_{SC}, FF and PCE of spin-coated inverted structure solar cells are 0.58 V, 8.73 mA cm^{-2}, 0.57, and 2.89% while those of blade-coated ones are 0.57, 9.68 mA cm^{-2}, 0.55, and 3.03%, respectively.



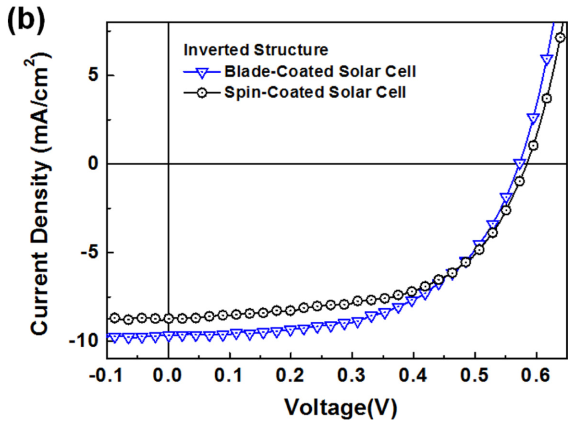


Figure 3. *J-V* curves of P3HT:$PC_{71}BM$ solar cells based on (a) conventional; (b) inverted structures (triangles: blade-coated solar cells and circles: spin-coated solar cells).

The average values with standard deviations of photovoltaic parameters (V_{OC}, J_{SC}, FF, and PCE) from all the measured devices are summarized in Table 1. Here we note that, as shown in Table 1, standard deviations of J_{SC} and PCE values from blade-coated devices are much (2.7-5.3 times) lower than those from spin-coated devices in both conventional and inverted structures. This result indicates that more uniform films with constant thickness can be effectively achieved through a blade-coating method, which allows reliable and constant electrical signals. This beneficial film-formation property in large area suggests that blade-coating technique is highly compatible with ultimate roll-to-roll device fabrication that requires reproducible PCE without significant deviation from any point in large-area films.

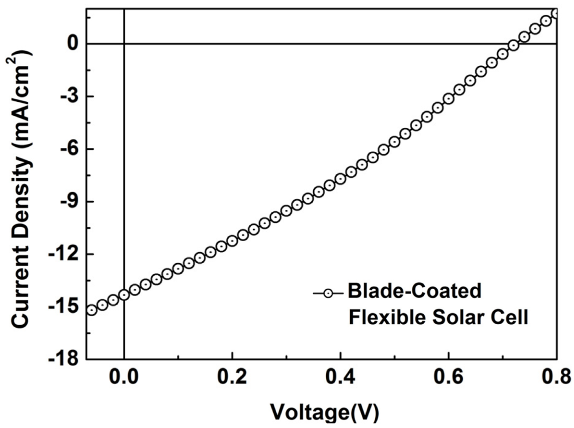


Figure 4. *J–V* curve of flexible PBDTTT-EFT:$PC_{71}BM$ solar cell.

Most high-efficiency PSCs being reported are fabricated on the rigid glass substrates, which means they do not take a full advantage of the processing merits of organic or polymer solution inks. From a manufacturing point of view, the development of PSCs on the flexible plastic substrates using printing technology is highly desired in order to expand potential fields of PSCs.

Based on the obtained results above, we have further examined the general applicability of a blade-coating technique to the different polymers and fabrication of flexible devices. As a proof-of-concept, a flexible PSC was demonstrated by constructing conventional type solar cells using a blade-coated PBDTTT-EFT:$PC_{71}BM$ bulk heterojunction film on the ITO-coated plastic PET substrates.

Figure 4 shows *J-V* characteristics of the fabricated solar cells. Encouragingly, a decent PCE of 3.10% (V_{OC}: 0.72 V, J_{SC}: 14.33 mA cm^{-2}, and FF: 0.30) was achieved from larger active area (1.0 cm^2). Limited photovoltaic performances originated from the high sheet resistance (100 ohm/square, c.f. sheet resistance of ITO on glass is 10 ohm/square) of ITO on flexible PET substrates. Investigation on the further improvement

Table 1. Summary of Performance of Spin- and Blade-coated P3HT:$PC_{71}BM$ Solar Cell Devices with Conventional and Inverted Structures

Structure	Coating method	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF	PCE (%)
Conventional structure	Spin-coating	0.56±0.01	8.03±0.32	0.56±0.01	2.51±0.06
	Blade-coating	0.56±0.01	8.73±0.06	0.56±0.01	2.73±0.02
Inverted structure	Spin-coating	0.57±0.01	8.85±0.16	0.55±0.01	2.77±0.08
	Blade-coating	0.57±0.01	9.71±0.06	0.55±0.01	3.03±0.03

of blade-coated flexible PSCs is in progress by designing and adopting embedded grid-type electrodes on the substrates.

Conclusions

We have reported blade-coated polymer solar cells featuring simple, fast, and low-cost fabrication process. Blade-coated P3HT:PC_{71}BM polymer solar cells showed improved power conversion efficiencies up to 2.75 (conventional structure) and 3.03% (inverted structure) with enhanced performance reliability, compared to those of spin-coated ones. Moreover, 3.10% flexible PBDTTT-EFT/PC_{71}BM polymer solar cells were also demonstrated by applying blade-coating method onto the plastic substrates. These results indicate that blade-coating not only can effectively improve photovoltaic properties of bulk heterojunction-based polymer solar cells but also is a very compatible process with the high-throughput roll-to-roll technology for the fabrication of high-efficiency wearable solar cells.

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