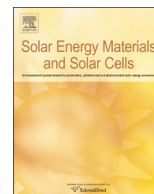




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## Vertical phase separation and light-soaking effect improvements by photoactive layer spin coating initiation time control in air-processed inverted organic solar cells



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### ABSTRACT

Inverted type organic solar cells have been regarded more promising over normal type, owing to a favorable vertical phase separation and air-processability. Many techniques, such as thermal or solvent annealing, slow growth method, melting bi-layers etc. have been employed to improve the morphology of photoactive layer, which is one of the advantages of inverted type OSCs. As a result, the device performance is greatly enhanced which is also reflected in the current-density versus voltage curve. However, some of the methods presented above are difficult and costly to perform. In addition, inverted OSCs still employ certain metal oxide electron-transporting layers, which impose UV activation time due to light-soaking effect. Here we show a facile method that can control the vertical phase separation as well as minimize the light-soaking effect. By leaving the photoactive solution with a low volatile solvent in air before spin coating, conductive polymers (donor) and fullerene derivatives (acceptor) were separated vertically in a way that their charge extraction is enhanced. Besides, oxygen and impurities at the contact on ETL were removed by leaving the solution for a certain period. Mechanisms of these improvements were evidenced by various analytical techniques and empirical tests using different materials in different environments. We anticipate this finding can expedite the OSC research and its usage in all air-processed inverted OSCs.

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### 1. Introduction

Research in organic solar cells (OSCs) has drawn a great deal of attention as an alternative energy generation for its low-cost solution processability, flexible application, and high efficiency of around 10% for a non-tandem device [1]. Above all, the inverted type has shown more promising aspects such as higher stability, air-processability, and more favorable vertical phase separation [2–6]. Avoiding a direct contact of acidic poly(3,4-ethylenedioxythiophene)–polystyrenesulfonic (PEDOT:PSS) from ITO electrode and utilizing gold electrode with low work function ensure higher stability and air processability. Electron donor and acceptor species in a photoactive bulk heterojunction layer, such as an archetypal example of poly(3-hexylthiophene):[6,6]-phenyl C<sub>61</sub>-butyric acid methyl ester (P3HT:PCBM) blends will favor the inverted structure due to the surface energy difference between PCBM and P3HT [7,8]. The P3HT:PCBM blends on electron-transporting layer (ETL) induces more P3HT on the top and more PCBM at the

bottom. Therefore, the resulting structure will benefit from better charge flow at the interfaces between ETL, photoactive layer, and hole-transporting layer [9]. Researchers have so far been exploiting tendency of P3HT to crystallize for controlling the alignment of conjugated polymer chains [10,11] through myriad ways. These are namely post-annealing treatments [12,13], appropriate solvent choice [14–16], slow drying of spin-coated films [17–19], melting of bilayers, and etc. [20]. However, those methodologies take long time and sometimes are difficult to perform. Also there is a significant drawback for the inverted type OSCs called ‘light-soaking effect’. Under general circumstances, the current-density versus voltage (*J–V*) curve of solar cells is ‘J-shaped’ and can be rationalized through the diode equation; however, an inflection point appears especially for inverted devices causing the curve to be ‘S-shaped’. Such characteristics are also called ‘kink’ and this results in decreasing fill factor (FF) and power conversion efficiency (PCE) [21–23]. This is observed only in the light curve [24]. This can be overcome by exposing the cells to a combination of illumination and temperature [25]. A certain period of UV activation on ETL metal oxides restrains the ‘S-curve’ and increases PCE [26,27]. This is because electrons on valence band of the metal oxide get excited

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to fill up any trap sites created and increase the electron number on conduction band, which enhance the transfer rate. However, during the process, OSCs are imposed with several problems: a long UV exposure time can damage and reduce the performance and it limits the use of any substrate with low UV transmission [28]. The origin of the 'S-curve' is still not understood clearly, but we know, it can be attributed to the limited donor–acceptor electron transfer rate of intermolecular charge hopping which is largely caused by electron traps at the interface and morphology of domains in the photoactive layer [29–34]. Since those traps are induced by surface-adsorbed oxygen, PCE of air-processed inverted OSCs imperatively lags behind the anaerobically fabricated normal type OSCs. In order to fully exploit the inverted OSCs' air processability, it is crucial that the interfaces are free of oxygen adsorption.

Here in this work, we report a new methodology of controlling spin coating initiation time that improves the contact at the interfaces of ETL by removing oxygen and impurities, and inducing a more favorable vertical phase separation of the photoactive layer, at the same time. In effect, this facile method reduces light-soaking time, and increases  $J_{SC}$  and FF. Accordingly, a PCE of 3.54%, which is 12% higher than the reference with 3.15%, is achieved and this result is comparable to that of anaerobically fabricated normal type OSCs. Reduced UV activation time of 3 min is achieved, which is 17 min shorter than 20 min from the reference. The mechanism behind these improvements has been studied through diverse analytical techniques and discussed in this work. This phenomenon is displayed in other ETL, ZnO, and other organic material, methano indene fullerene (MIF) [35] as long as low volatile solvents such as ortho-dichlorobenzene (ODCB) are used.

## 2. Experimental

### 2.1. Device fabrication

ITO substrates ( $22 \times 38 \text{ mm}^2$ ) with a sheet resistance of  $6 \Omega/\text{square}$  (Kuramoto Co., Ltd.) were firstly etched using Zn and 1 M HCl, followed by sonicating the substrates sequentially in cleaning surfactant (Semi Clean, M-Lo), water, acetone and 2-isopropanol for 15 min each. The substrates were then dried in an oven at  $70^\circ\text{C}$ . Prior to metal oxide deposition, ITO substrates were exposed to UV/ $\text{O}_3$  for 20 min. The  $\text{TiO}_2$  films and ZnO sol–gel films were prepared using the method reported by Kuwabara and Heeger [36,5], respectively. The metal oxides were baked at  $150^\circ\text{C}$  before depositing the photoactive layer to dry and improve conductivity. This minimizes the light-soaking time of the OSC [27].

For the P3HT:PCBM photoactive layer deposition, a poly(3-hexylthiophene) (regioregular, Sigma Aldrich Chemical Co., Inc.) and [6,6]-phenyl C61-butyl acid methyl ester and [6,6]-phenyl C71-butyl acid methyl ester in 16:3 ratio (mix-PCBM, Frontier Carbon Co., Nanom spectra E124) solution with a donor:acceptor ratio of 5:3 and concentration of 40 mg/ml in ortho-dichlorobenzene (anhydrous, 99%, Sigma Aldrich Chemical Co., Inc.) was prepared [37]. The solution was left stirring for 2 h at  $65^\circ\text{C}$ .

For P3HT:MIF photoactive layer deposition, P3HT (regioregular, Sigma Aldrich Chemical Co., Inc.) and MIF (Synthesized) solution with a donor:acceptor ratio of 1:1 and concentration of 50 mg/ml in ODCB (anhydrous, 99%, Sigma Aldrich Chemical Co., Inc.) was prepared [35]. The solution was left stirring for 2 h at  $65^\circ\text{C}$ .

The prepared photoactive layer solution was then spin coated on the metal oxide layers at a speed of 850 rpm for 45 s to give films of approximately 300 nm. The films were then immediately placed in a petri-dish for 40 min to allow slow evaporation of the solvent.

A PEDOT:PSS dispersion in water (CleviosPVP, Heraeus Precious Metals GmbH & Co.) containing 0.5 wt% polyoxyethylene(6)

tridecyl ether (Sigma Aldrich Chemical Co., Inc.) was spin coated on top of the active layer to form the hole transport layer with a 30 nm thickness. Approximately 200 nm thick Au layer was thermally evaporated at pressure of  $3 \times 10^{-3} \text{ Pa}$ , with the use of a shadow mask, which defined the device active area as  $1 \text{ cm}^2$ . All processes, except for Au deposition, were performed in air and the devices were not encapsulated. All devices were thermally annealed at  $150^\circ\text{C}$  for 10 min.

### 2.2. Photovoltaic characterization

$J$ – $V$  characteristics were measured using a software-controlled source meter (Keithley 2400) under dark conditions and 1 Sun AM1.5G simulated sunlight irradiation ( $100 \text{ mW cm}^{-2}$ ) using a solar simulator (EMS-35AAA, Ushio Spax Inc.), which was calibrated using a silicon diode (BS-520BK).

### 2.3. Optical characterization

UV–vis absorption spectra were measured on JASCO V-670 spectrometer (Nihon bunko) at room temperature (298 K) in a  $1 \times 1 \text{ cm}^2$  glass substrate.

### 2.4. Surface characterization

Contact angle measurements were collected on a FAMAS (Kyowa Products) where  $3 \mu\text{L}$  droplets were applied to the surface and left equilibrating for 5 s before measuring the contact angle. A minimum of 10 droplets were measured for each samples. Core-level photoemission measurements of S 2s and 2p, and C 1s were performed by X-ray photoemission spectroscopy (XPS; PHI 5000 Versaprobe) using monochromatic Al  $K\alpha$  radiation. The XPS resolution was estimated to be  $\sim 1 \text{ eV}$  and the energy offset was calibrated using the surface C 1s peak. Atomic force microscope (AFM) topography images were recorded using a Bruker Multi-mode AFM operating in tapping mode. Silicon AFM probes were used that had a nominal frequency of 70 kHz.

## 3. Results and discussion

### 3.1. Photovoltaic performance and light-soaking time

We fabricated inverted OSCs using the P3HT:PCBM with different waiting times before spin coating. Reference device with immediate spin coating, 5 min waiting time, 10 min waiting time, and 20 min waiting time were employed. Table 1 shows photovoltaic performance of the devices. PCE is the highest when 10 min waiting time is applied due to the enhancement of  $J_{SC}$  and FF – it should be noted that the most optimal waiting time varied in every experiment but it was between 5 min and 10 min everytime. While  $J_{SC}$  increases continuously with the waiting time, FF increases and decreases back after 5 min waiting time. Increase in  $J_{SC}$  means that the longer we leave the solution, the better the dissociation of excitons. Improved vertical phase separation is surmised to be the reason. Notwithstanding high  $J_{SC}$ , series resistance ( $R_s$ ) increases after 10 min of the waiting time to decrease FF, which undercuts the PCE. The solution left in air for a long time being oxidized is suspected to be the reason.

Table 1 also shows that the light-soaking time reduces as the waiting time increases. Ultimately, it decreases down to less than 1 min when the waiting time is 20 min. The corresponding  $J$ – $V$  curves under one sun during the light-soaking time show the S-curves appearing in the beginning and disappearing gradually (Fig. 1a–e). The dynamic inflection phenomenon can be explained by distribution of oxygen within the device. The initial oxygen

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