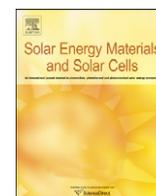




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## Polymer solar cells using chlorinated indium tin oxide electrodes with high work function as the anode

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### ABSTRACT

This paper reports polymer solar cells (PSCs) using chlorinated indium tin oxide (Cl-ITO) substrates with high work function as the anode. There is no conducting polymer buffer layer between the Cl-ITO anode and the active layer in these PSCs. PSCs with P3HT:PCBM (P3HT=poly(3-hexylthiophene), PCBM=[6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester) exhibited high photovoltaic performance, short-circuit current density ( $J_{sc}$ ) of 9.91 mA/cm<sup>2</sup>, open-circuit voltage ( $V_{oc}$ ) of 0.57, fill factor (FF) of 0.69, and photovoltaic efficiency of 3.90% under AM1.5G illumination immediately after the device fabrication. The photovoltaic performance is comparable to that of normal PSCs with a conducting polymer buffer layer. But the photovoltaic efficiency of PSCs with Cl-ITO degrades quickly. The photovoltaic efficiency dropped to 3.43% and 3.24% just 10 and 20 min after the device fabrication, respectively. The reasons for the photovoltaic degradation were studied by ultraviolet photoelectron spectroscopy (UPS) and X-ray photoelectron spectroscopy (XPS). The work function of Cl-ITO decreases with time. The decrease in the work function of Cl-ITO is attributed to Cl desorption from the surface of ITO.

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### 1. Introduction

Polymer solar cell (PSC) is regarded as the next-generation solar cells owing to their low fabrication cost and high mechanical flexibility [1,2]. They can be fabricated through a roll-to-roll process, and their stability has been improving [3–9]. The photovoltaic performance of PSCs has been raised by the development of new donor and acceptor materials [10–16]. The electrodes are also important for the practical application of PSCs, such as the stability and cost [17–20]. Indium tin oxide (ITO) is usually used as the transparent electrode of PSCs. It has a work function of 4.4–4.7 eV [21,22], which matches with neither the highest occupied molecular orbital (HOMO) level of polymer donor nor the lowest unoccupied molecular orbital (LUMO) level of organic acceptor, so that bare ITO cannot be used as an electrode for the charge collection. Two strategies have been adopted to modify the work function of ITO. One way is to insert a buffer layer like poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) [23–26]. PEDOT:PSS has a work function of 5.1 eV, so that ITO/PEDOT:PSS can effectively collect holes. Another approach is to lower the work function by adding a buffer layer like oxides [27–32] or modifying the surface of ITO for the electron collection [33–40]. ITO with low work function has been used as the cathode of inverted PSCs. Recently, Helander et al. [41] reported a novel

method to significantly increase the work function of ITO. They could increase the work function of ITO up to 6.1 eV by covering the ITO with a monolayer of chlorine and demonstrated high-performance organic light-emitting diodes (OLEDs) using the chlorinated ITO (Cl-ITO) as the anode.

In this work, Cl-ITO electrodes without a PEDOT:PSS buffer layer were used as the anode of solution-processed PSCs. PSCs with poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester (PCBM) can have a photovoltaic efficiency of 3.90% under AM1.5G illumination, which is comparable to that of a normal PSC with ITO/PEDOT:PSS as the anode. But the photovoltaic efficiency of PSCs with Cl-ITO degrades quickly. The degradation is attributed to Cl desorption from the ITO surface.

### 2. Experimental section

#### 2.1. Fabrication of polymer solar cells

ITO glass with a sheet resistance of 15 Ω/sq was purchased from Nikko Materials Co. PSCs with device architecture glass/Cl-ITO/P3HT:PCBM/LiF/Al were fabricated by the following process. ITO substrates were cleaned sequentially with Decon 90 detergent, de-ionized water, acetone, and iso-propanol. Each rinsing step was carried out in an ultrasonic bath for 10 min. The cleaned and dried ITO substrates were treated with UV-ozone (Jelight 42–220 UVO cleaner) for 15 min. The chlorination was performed through a process similar to that reported by Helander et al. [41].

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ITO substrates together with 100  $\mu\text{l}$  1,2-dichlorobenzene (DCB) were put in a closed Petri dish. They were exposed to UV light generated by a Jelight 42–220 UVO cleaner for 10 min. These ITO substrates were subsequently treated with UV-ozone for additional 3 min to eliminate residual chlorocarbon segments on the ITO surface. These chlorinated ITO (Cl-ITO) substrates were then transferred into a glove box filled with dried nitrogen. The active layer was formed on Cl-ITO by spin coating a DCB solution consisting of 20  $\text{mg ml}^{-1}$  P3HT and 20  $\text{mg ml}^{-1}$  PCBM at 500 rpm for 90 s. The P3HT:PCBM films were slowly dried in closed Petri dishes at room temperature. They had a thickness of about 220 nm. The devices were completed by thermally depositing a 7 Å-thick LiF layer and successively a 120 nm-thick Al layer in a vacuum of  $1 \times 10^{-6}$  mbar. Each device had an area of 0.11  $\text{cm}^2$ . The PSCs were encapsulated with UV-curable epoxy glue (Epotech OG112-6, Epoxy Technology Inc.) and glass sheets in the glove box. They were taken out for the electrical testing in air.

## 2.2. Characterizations of materials and devices

Ultraviolet photoelectron spectra (UPS) and X-ray photoelectron spectra (XPS) were acquired with a Kratos Axis Ultra X-ray photoelectron spectroscopy (Kratos Analytical) equipped with a monochromatized Al  $K\alpha$  X-ray source. The pressure of the chamber was  $10^{-9}$  Torr. The thicknesses of the P3HT:PCBM films were measured using an Alpha-Step IQ surface profiler. The AFM images were acquired with a Veeco NanoScope IV Multi-Mode AFM in tapping mode.

The photovoltaic performance of the devices was measured with a computer-programmed Keithley 2400 source/meter under Newport's Oriol class A solar simulator, which simulated the AM1.5G illumination ( $100 \text{ mW/cm}^2$ ) and was certified to the JIS

C 8912 standard. The devices were stored in Petri dishes in dark for the investigation of the photovoltaic stability.

## 3. Results and discussion

### 3.1. Photovoltaic performance

As Helander et al. observed, Cl-ITO can have a high work function [41]. PSCs were fabricated using Cl-ITO without a PEDOT:PSS buffer layer. The photovoltaic current density ( $J$ )–voltage ( $V$ ) curves of a PSC with Cl-ITO is shown in Fig. 1.  $J$ – $V$  curves of a normal PSC, glass/ITO/PEDOT:PSS/P3HT:PCBM/LiF/Al, and a control PSC, glass/ITO/P3HT:PCBM/LiF/Al, are also presented for comparison. The values of the short-circuit current density ( $J_{sc}$ ), open-circuit voltage ( $V_{oc}$ ), fill factor (FF), power conversion efficiency (PCE), series resistance ( $R_s$ ), and shunt resistance ( $R_{sh}$ ) of all the devices are summarized in Table 1. The PSC with Cl-ITO exhibited high photovoltaic performance.  $V_{oc}$  (0.57 V) and PCE (3.90%) are almost the same as that of the normal PSC with ITO/PEDOT:PSS. Thus, Cl-ITO with high work function can effectively collect holes. The photovoltaic performance of the PSC with Cl-ITO is significantly higher than that of the control PSC with bare ITO as the anode.  $V_{oc}$  of the control PSC is 0.48 V as the result of the low work function of the bare ITO.

The different photovoltaic performances of these PSCs can be understood in terms of their  $R_s$  and  $R_{sh}$  values.  $R_s$  and  $R_{sh}$  of the PSC with Cl-ITO are almost the same as that of the normal PSC. This also indicates that Cl-ITO can form an ohmic contact with the active P3HT:PCBM layer. The high  $R_s$  value of the control PSC with bare ITO can be attributed to the non-ohmic contact between bare ITO and the active layer.

The different photovoltaic performances of PSCs with bare ITO and Cl-ITO are not due to the effect of the ITO surface modification on the morphology of the active layer but the contact between the anode and the active layer. As shown in Fig. 2, no remarkable change can be observed on the ITO surface after the Cl modification. The P3HT:PCBM layer on bare ITO has almost the same morphology of that on Cl-ITO.

### 3.2. Degradation of the photovoltaic performance

The freshly fabricated PSCs with Cl-ITO have high photovoltaic efficiency. However, we observed that their photovoltaic efficiency decreased rapidly with time. As shown in Fig. 3, the photovoltaic performance remarkably degrades only after 10 min after the device fabrication. Both  $J_{sc}$  and  $V_{oc}$  drop. It becomes even worse after 60 min. Fig. 4 presents the changes in  $J_{sc}$ ,  $V_{oc}$ , FF, and PCE of the PSC with Cl-ITO with time.  $J_{sc}$  and  $V_{oc}$  decrease rapidly with time. Consequently, PCE drops to 3.43% and 3.24% only after 10 and 20 min, respectively. The photovoltaic stability is remarkably worse than the normal PSC with ITO/PEDOT:PSS as the anode.

Presumably, the poor stabilities in  $J_{sc}$  and  $V_{oc}$  of the PSC with Cl-ITO are related to the stability of the interface between ITO and the P3HT:PCBM active layer. The stability in the work function of Cl-ITO was studied by UPS. The work function of Cl-ITO may

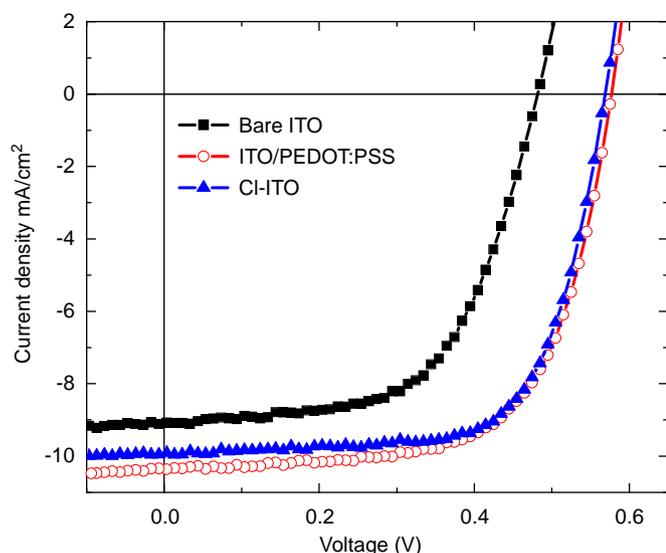


Fig. 1.  $J$ – $V$  curves of PSCs with bare ITO (■), ITO/PEDOT:PSS (○), and Cl-ITO (▲) as the anodes under AM1.5G illumination.

**Table 1**  
Photovoltaic performance of PSCs with different anodes.

Anode	$J_{sc}$ ( $\text{mA/cm}^2$ )	$V_{oc}$ (V)	FF	PCE (%)	$R_s$ ( $\Omega/\text{cm}^2$ )	$R_{sh}$ ( $\Omega/\text{cm}^2$ )
Bare ITO	9.08	0.48	0.59	2.57	4.0	750
ITO/PEDOT:PSS	10.36	0.58	0.65	3.90	2.0	1032
Cl-ITO	9.91	0.57	0.69	3.90	2.0	1300

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