Towards high efficiency solution processable inverted bulk heterojunction polymer solar cells using modified indium tin oxide cathode

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ABSTRACT

High efficiency inverted regioregular poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl C_{61}-butyric acid methyl ester (PCBM)-based polymer solar cells (PSCs) using an indium tin oxide (ITO) cathode, modified with a solution-processed ionic liquid-functionalized carbon nanoparticles (ILCNs) layer, was demonstrated. ILCNs-modified ITO cathode has a very good thermal stability and a superior surface electronic property suited for application in polymer solar cells. A power conversion efficiency (PCE) of 3.2% was obtained for inverted PSCs measured under AM1.5G illumination of 100 mW/cm^2, which is comparable to PCE of a reference P3HT:PCBM-based solar cell having a conventional structure. There was almost no deterioration in the performance of inverted PSCs that were aged over a post-annealing temperature range from 100 to 200 °C. The work function of ILCNs-modified ITO cathode annealed at different temperatures was also measured using ultraviolet photoelectron spectroscopy. It was found that the work function of 4.4 eV, measured for a bare ITO electrode, decreased to 3.8 eV when it was modified with ILCNs, and was not dependent on the post-annealing temperature.

1. Introduction

The development of the emerging polymer solar cell technology has attracted a lot of interests due to its great potential of low-cost non-vacuum process photovoltaic technology. Polymer solar cells (PSCs) can be flexible, large-area and prepared using solution processable technologies. PSCs have enjoyed significantly development in the past decades. The power conversion efficiency (PCE) of 4–5% for bulk heterojunction (BHJ) PSCs using regioregular poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl C_{61}-butyric acid methyl ester (PCBM) blend system has been achieved. A PCE of 6.0% was reported for BHJ polymer solar cells using low-bandgap alternating co-polymers of

poly (2,7-carbazole) derivatives with deeper highest occupied molecular orbital (HOMO) energy and [6,6]-phenyl C_{70}-butyric acid methyl ester [1]. PCE of 6.77% was reported recently for heterojunction PSCs [2]. New device processes based on the control of film morphology, optimization of the active layer thickness [3], modification of electrode using surface plasmonic effect to boost the light absorption [4,5], and use of p- and n-types metal oxides [6–11] to improve the charge collection efficiency were demonstrated.

In a conventional P3HT:PCBM-based polymer solar cell, the hole-transporting layer, poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) is spin-coated on top of indium tin oxide (ITO) surface to prevent electron leakage and to aid in hole extraction. The active layer of P3HT:PCBM is sandwiched between an ITO/PEDOT:PSS anode and a low work function metal cathode. However,

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PEDOT:PSS layer is detrimental to ITO anode and the active polymer layer due to its acidic nature. In conventional PSCs, the top cathode, often made with a low work function metal cathode, such as calcium or barium cathode, is easily oxidized even with a delicate encapsulation, leading to reduced device lifetime [12]. The p- and n-types transparent metal oxides have been recently introduced as anode and cathode contacts in PSCs, providing greater process freedom for new device structures including inverted PSCs [6–8,10,11]. The use of transparent metal oxides can also offer a better choice to fabricate inverted PSCs. More importantly, the inverted PSCs can overcome some disadvantages of the regular PSCs with PEDOT:PSS anode contact layer. Therefore, several inverted polymer solar cell structures have been developed. For example, p-type metal oxide, such as vanadium oxide (V_2O_5) [11,13] and molybdenum trioxide (MoO_3) [10] were deposited on top of the active layer as a hole selective layer before a less air-sensitive and high work function metal was deposited as a back hole collecting electrode [8,10]. Solution-processed ZnO [7] and TiO_x [6] when applied as electron selective layer have been reported to achieve 2.58% and 3% PCE, respectively. However the high temperature annealing needed to improve the film properties of these metal oxides is not compatible with the active polymer layer.

Liao et al. [14] demonstrated that work function of ITO electrode was decreased from 4.5 to 3.06 eV by spin-coating an ultrathin cesium carbonate (Cs_2CO_3) onto ITO surface. The Cs_2CO_3 layer can be decomposed into low work function cesium oxide by annealing under 150 °C, which is consistent with the fabrication procedures of the active polymer layer. The PCE of inverted PSCs with Cs_2CO_3-modified ITO cathode reaches 4.2% after annealing, which is comparable to the regular structure device on the same system. However, Cs_2CO_3 is very sensitive to moisture and the property of Cs_2CO_3-modified ITO cathode can be easily degraded due to air-leakage through the edges of the encapsulation. Solution-processed V_2O_5 as an anode interlayer without annealing have been reported, the PCE of devices made with V_2O_5 modified ITO anode was shown to increase from 2.5% to 3.56% compared to PSCs without the V_2O_5 interlayer [11]. This solution-processed V_2O_5 is relatively insensitive to moisture and oxygen and its advantage of non-annealing treatment, as compared to a post-annealing treatment required for solution-processed TiO_x [6] and ZnO [7], offers a simple and effective approach for fabrication of low-cost and large-area PSCs.

In this work, a thermally stable, transparent cathode of ionic liquid-functionalized carbon nanoparticles (ILCNs)-modified ITO was developed. A layer of ILCNs was solution-processed and its low annealing temperature offers additional advantage for fabrication of PSCs. The ILCNs was used to modify ITO electrode; the work function of the modified ITO electrode decreased from 4.5 to 3.8 eV after spin-casting a ~1–3 nm thick ILCNs film on top of the ITO electrode. The PCEs of inverted PSCs made with modified ITO cathode increased to 3.2%, after post-annealing at a temperature of 120 °C, which is comparable to that of a reference PSC using the same system [15,16].

2. Experimental

The ILCNs was synthesized by the electrochemical exfoliation of graphite electrode in 1-butyl-3-methylimidazolium tetrafluoroborate ([C4mim]$^+$[BF4]$^-$) and water mixture [17]. The ILCNs consists of ionic liquid molecules and graphite-like carbon nanoparticles held together by hydrogen bonding, van der Waals forces, π–π stacking interactions or/and covalent interactions in a gel-like matrix. The transmission electron microscopy image shows that the average size of ILCNs is below 4 nm [15]. The details of ILCNs synthesis and its properties have been reported [15,17]. In this work, the ILCNs layer was spin-coated on the surface of ITO-coated glass substrates (15 Ω/sq), pretreated with UV-ozone, and followed by annealing with different temperature in the glove box with an O_2 level and a H_2O level <2 ppm. P3HT (Sigma–Aldrich) and PCBM (American Dye Source) were dissolved in 1,2-dichlorobenzene with 1:0.8 wt. ratio. ILCNs were dissolved in ethanol. P3HT:PCBM film was spin-coated on top of the ILCNs-modified ITO in the glove box. The P3HT:PCBM film was spin-coated at 800 rpm for 60 s, and then kept in a petri dish for slow growth. After 12 h, P3HT:PCBM films were annealed at 120 °C for 10 min. The 5 nm thickness MoO_3 and 100 nm Al metallic layers were thermally deposited with a background pressure of 5×10^{-7} Torr. The active area of PSCs is 3.0 mm × 3.0 mm. Current density–voltage (J–V) characteristics of PSCs were measured in nitrogen under AM1.5G illumination of 100 mW/cm^2 (SAN-EI Electric Xe-Lamp controller). The surface work function of bare ITO and ILCNs-modified ITO cathode was examined using ultraviolet photoelectron spectroscopy with Helium line (21.2 eV).

3. Results and discussion

The atomic force microscopy (AFM) image measured for ILCNs layer on ITO surface is shown in Fig. 1(a). The ILCNs film was spin-coated at the speed of 1500 rpm for 60 s. The average thickness of the ILCNs layer was estimated to be 2.8 nm with corresponding rms roughness of ~0.85 nm, as shown in Fig. 1(b). The optical transmission spectra of ILCNs films spin-coated at 1500 and 2500 rpm, respectively onto ITO/glass substrates are shown in Fig. 1(c). The transmission spectra measured for ILCNs-modified ITO glass substrate show a slight decrease in the light wavelength range from 350 to 450 nm, as the thickness of ILCNs over layer increases. The overall transparency of the ILCNs-modified ITO glass substrates is almost identical to that of the bare ITO glass over the light wavelength from 450 to 800 nm. This reveals clearly that modification of the ILCNs layer on ITO electrode does not affect its transparency. This is in agreement with the results showing that absorption in PSCs made with ILCNs-modified ITO glass is almost the same as PSCs with bare ITO glass.

In order to carry out a systematic study of the effect of the ILCNs-modified ITO cathode on the performance of inverted P3HT:PCBM-based PSCs, a set of structurally identical polymer solar cells made with ITO cathode modified differently by ILCNs was fabricated. To get optimal
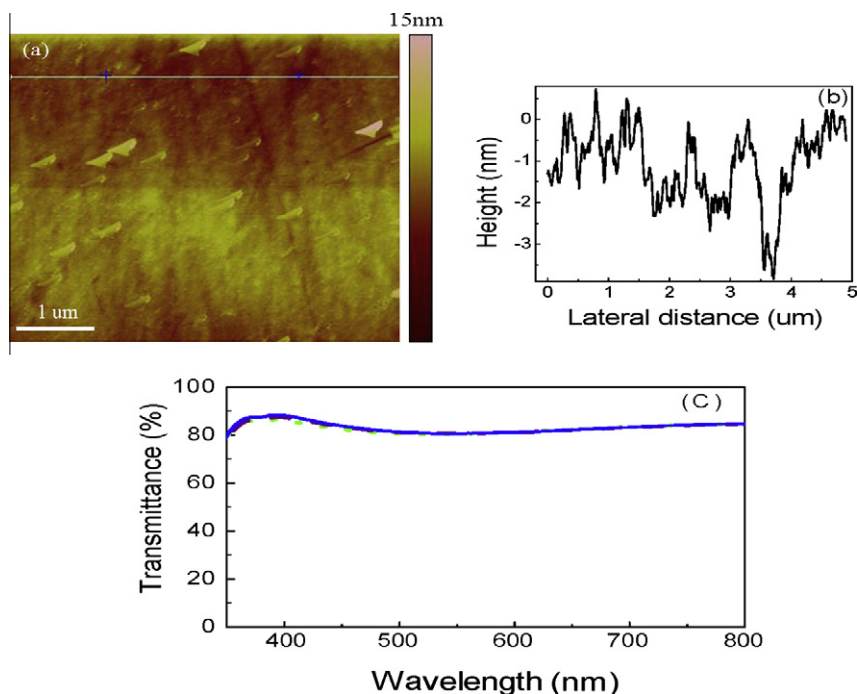
Fig. 1. (a) AFM images measured for ILCNs-modified ITO surface. (b) Topographical height of ILCNs layer on ITO. (c) Optical transmission spectra measured for ITO surface modified with ILCN layers prepared at different spin-coating speeds of 1500 rpm (dot), 2500 rpm (dash) and pure ITO (solid).

thickness of ILCNs layer, the ILCN films were spin-coated at 1500, 2000 and 2500 rpm for 60 s, respectively, followed by annealing at 120 °C for 10 min. The layer thickness of ILCNs prepared at different spin-casting speeds was estimated to be 1–3 nm using AFM. However, the PCE of devices within these spin-coating speed range is close and the optimal device of PCE is 3.20% at the spin-coating speed of 2000 rpm. The results reveal that the PCE of devices is insensitive to thickness of ILCNs layer. This is probably attributed to the sp^2-bonded aromatic structure of carbon nanoparticles and the formation of the electric double layers between ITO and the active layer. The sp^2-bonded aromatic structure of carbon nanoparticles can transport electrons and decrease tunneling barrier height at the interfacial contacts [18]. The ions of ILCNs are expected to form electric double layers with large polarization fields at the interface between the active layer and ILCN, as well as between ILCN and ITO cathode [19]. The presence of electric double layers and carbon nanoparticles helps to reduce the electron injection/extraction barrier and, unlike the tunnel theory [20], is not significantly sensitive to barrier height and tunnel thickness.

The schematic energy diagram of an inverted PSC is shown in the inset of Fig. 2a. The thickness of P3HT:PCBM blend layer and MoO_3 is 200 and 5 nm, respectively. Fig. 2a shows J–V characteristics corresponding to PSCs prepared with ILCNs-ITO cathode that was pre-annealed at different temperatures. The ILCNs films were annealed at 120 °C (device A), 160 °C (device B) and 200 °C (device C) for 10 min after spin-casting ILCNs solution at 2000 rpm for 60 s. As-prepared ILCN-ITO cathode, which was done at room temperature (RT) without the post-annealing treat-

ment, was also used for the control PSC (device D) for comparison study. The PCE of PSCs with ITO-only cathode is far lower than that of PSCs with ILCNs-ITO cathode, which is attributed to the higher interface barrier and the elevated reverse saturation current, as shown in Fig. 2(b). Fig. 3 presents the statistical graph of PCE of PSCs made with ILCNs-modified cathode that was annealed at different temperature. The PCE of inverted PSCs made with ILCNs-modified ITO under optimum annealing temperature of 120 °C can reach up to 3.2% and the highest efficiency of 3.37% was obtained for PSCs made with ITO-cathode pre-annealed at 160 °C. The PCE of PSCs made with ILCNs-modified ITO cathode that was annealed over the temperature from 120 and 160 °C is slightly higher than efficiency of PSCs made with the cathode that was at 200 °C (device C). It is noted that PCE of device C is comparable to the efficiency of devices A, B and D, suggesting that ILCNs-modified cathode has a very good thermal stability suitable for application in inverted PSCs. In addition to its thermal stability, the nature of the solution processability also makes ILCNs practically more attractive over the materials commonly used for electrode modification, such as TiO_x, ZnO and Cs_2CO_3. This is because the performance of inverted PSCs made with ITO, modified with these materials, is very sensitive to the annealing temperature. The solution-processed ILCNs-modified ITO can be also easily integrated with the fabrication of PSCs using solution processable materials.

In order to understand the changes in the surface properties of ILCNs-modified ITO cathode, the surface hydrophobic property of ILCNs-modified ITO was measured using contact angle measurement, and the ILCNs-modified
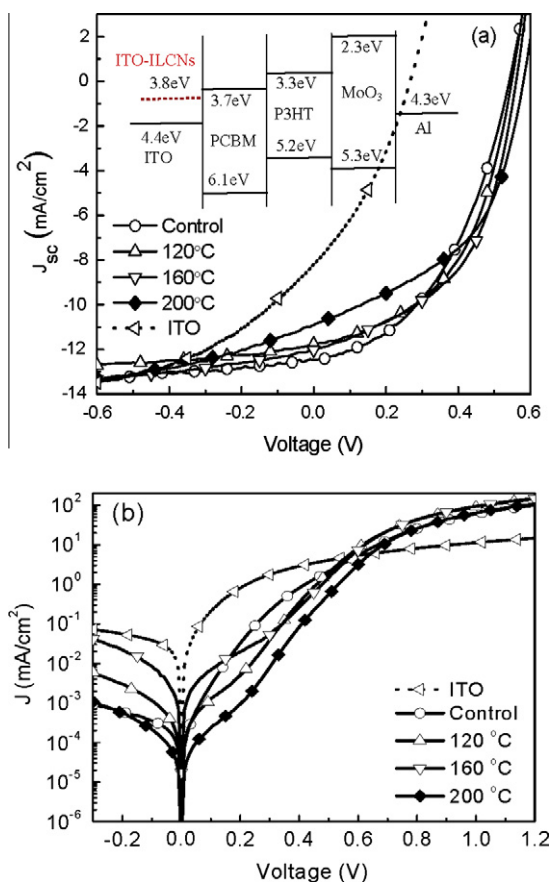
Fig. 2. (a) The *J–V* characteristics of PSCs made with ITO-only cathode (◁), ILCNs-modified ITO cathodes prepared at different pre-annealing temperature, for example, the as-prepared ILCNs layer at room temperature (Control ○), annealed at temperatures of 120 °C (△), 160 °C (▽) and 200 °C (♦). The inset illustrates the schematic energy diagram of an inverted PSC studied in this work. (b) The *J–V* characteristics measured for the PSCs in the dark condition.
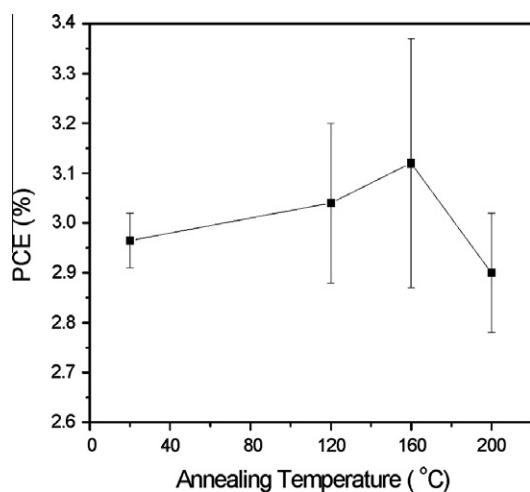
Fig. 3. PCE of devices made with ILCNs-modified ITO cathode as a function of pre-annealing temperature.

ITO cathode was studied using UPS measurements to determine the electronic structures on both bare ITO and ILCNs-modified ITO surfaces. Fig. 4(a) shows the secondary electron edge in UPS spectra measured for ILCNs-modified ITO surface, which can provide information of the work function of ILCNs-modified ITO surface. The work function of modified ITO cathode as a function of ILCNs annealing temperature is further presented in Fig. 4(b). As shown in Fig. 4(b), the surface hydrophobic property of ILCN films gradually increased with the post-annealing temperature. The increase in the contact angle seen in ILCNs surface is ascribed to the ionic liquid deficiency in ILCNs, due to the increase in the annealing temperature. The work function of UV-ozone treated ITO surface was 4.4 eV. The work function of the bare ITO decreased to about 3.8 eV when its surface was modified with a thin layer of ILCNs. The 0.6 eV decrease in work function of ILCNs-modified ITO electrode suggests that ILCNs-modified ITO can be an effective cathode for application in inverted PSCs. It was found that the work function of ILCNs-modified ITO further decreased to 3.7 eV after annealing at 200 °C for 10 min. However, the PCE of device C annealed at 200 °C was a little lower, which means that other possible factors such as hydrophobic property may affect the morphology of the
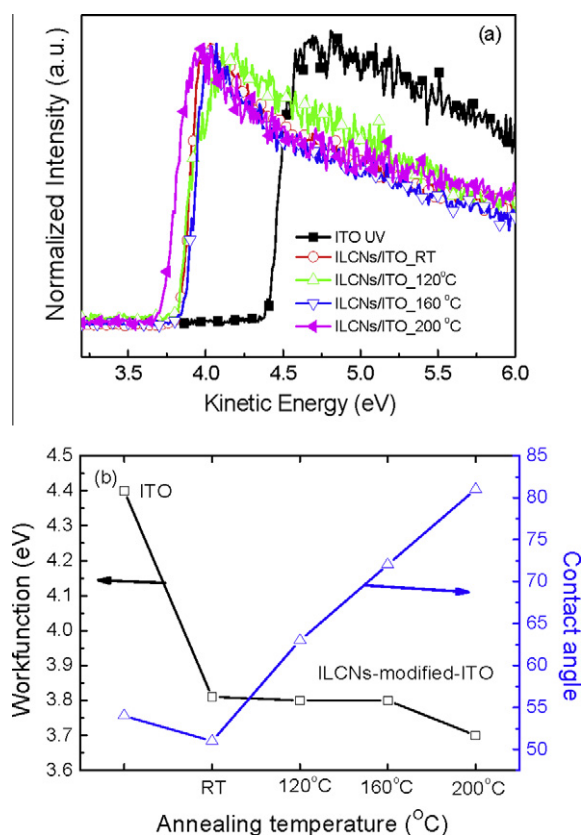
Fig. 4. (a) Evolution of secondary electron edge in UPS spectra measured for ILCNs layer modified ITO annealed at different temperatures; (b) Work function (□) and the contact angle (△) of modified-ITO cathode as a function of ILCNs annealing temperature, the values of work function and the contract angle obtained for a bare ITO are also plotted for comparison.

active polymer layer and the interface barrier between cathode electrode and P3HT:PCBM blend layer [14].

4. Conclusion

In summary, a high performance solution processable ILCNs-modified ITO cathode was developed. ILCNs-modified ITO cathode has very good thermal stability and a surface work function of 3.8 eV. Transparent ILCNs-modified ITO cathode was used for P3HT:PCBM-based inverted polymer solar cells, resulting in a PCE of 3.2% measured under AM1.5G illumination of 100 mW/cm^2. The device performance of the inverted PSCs is comparable to that of a reference PSC having the same material system and device structure [15,16]. The ILCNs-modified ITO cathode developed here has the advantages of solution processability, thermal stability and the desired electronic properties, and is superior to the cathode contacts that are modified using traditional materials such as TiO$_x$, ZnO and Cs$_2$CO$_3$, for application in inverted polymer solar cells.

Acknowledgement

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