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## **Ionic-liquid-functionalized carbon nanoparticles modified cathode for efficiency enhancement in polymer solar cells**

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The power conversion efficiency (PCE) of regioregular poly(3-hexylthiophene) (P3HT) and {6,6}-phenyl C<sub>61</sub>-butyric acid methylester (PCBM) based polymer solar cells was increased using an ionic liquid-functionalized carbon nanoparticles thin film (ILCNs)-modified cathode. An ILCN interlayer was prepared by the electrochemical exfoliation of graphite electrode. The PCE of P3HT:PCBM based polymer solar cells with a conventional aluminum (Al)-only cathode was increased by 20-30% when the structural identical devices were made with an ILCNs-modified Al cathode, measured under AM1.5G illumination of 100 mW/cm<sup>2</sup>. The photocurrent response characteristics and the impedance spectroscopy analyses reveal that the presence of an ILCN interlayer between Al cathode and the polymer photoactive blend has a similar function as LiF in terms of cathode modification. However, ILCN interlayer approach is superior to LiF, as it is solution-processed making it possible to open up new low cost fabrication concepts and achieve low cost benefit.

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Polymer solar cells are attractive alternatives to silicon-based solar cells due to their ability towards low cost, large area and eventually roll-to-roll printing technologies. The cell parameters such as short-circuit current density ( $J_{sc}$ ), open-circuit voltage ( $V_{oc}$ ), and fill factor (FF) are affected by a myriad of factors such as the morphology, thickness of the active layer, and work function of electrodes.<sup>1,2</sup> To enhance the performance of polymer solar cells, modified layers such as LiF and Au/LiF<sup>3</sup> were thermally deposited on top of active layers before depositing Al cathode. These successive vacuum deposition steps greatly increase the cost and complexity of fabrication. To realize low cost and vacuum-free printing techniques for polymer solar cells, solution processable materials such as TiO<sub>x</sub><sup>4</sup> and poly(ethylene oxide)<sup>1</sup> have been developed to modify the cathode for improving the power conversion efficiency (PCE).

Ionic liquids (ILs) have been applied for dye-sensitized solar cells (DSCs)<sup>5</sup> due to their unique properties such as negligible vapor pressure, high ionic conductivity, low toxicity. A quasi-solid-state DSC with an ionic gel electrolyte containing ILs and carbon nanotubes was developed to circumvent the step of hermetic sealing.<sup>5</sup> Conjugated polyelectrolytes have been applied for light-emitting devices.<sup>6,7</sup> Hence, such quasi-solid state ionic gel electrolyte is expected to be potentially useful in polymer-based solar cells.

We developed an ionic liquid-functionalized carbon nanoparticles (ILCNs) hybrid film which was synthesized by the electrochemical exfoliation of graphite electrode in 1-butyl-3-methylimidazolium tetrafluoroborate ([C4mim]<sup>+</sup>[BF<sub>4</sub>]<sup>-</sup>) and water mixture (40:60). This modified method produced ILCNs, which is different from previous reports of ionic liquid-functionalized graphene sheets.<sup>8</sup> The shape and size of the exfoliated products can be controlled by tuning the water to IL composition in the electrolyte. The detail chemical and physical experiments and properties will be reported elsewhere. Such ILCNs consist of ionic liquid molecules and graphite-like carbon nanoparticles held

together by hydrogen bonding, van der Waals forces,  $\pi$ - $\pi$  stacking interactions or/and covalent interactions in a gel-like matrix.<sup>8,9</sup>

The transmission electron microscopy (TEM) images in Fig. 1a show that ILCNs are carbon nanoparticels with average sizes below 4 nm. The X-ray photoelectron spectroscopy (XPS) spectrum of the ILNCs is shown in Fig. 1b, a well-defined peak at 400.9 eV due to the presence of nitrogen (N1s) can be seen. This peak can be deconvoluted into two components at 400.24 eV and 401.38 eV, implying that two different types of nitrogen bonding environment in the imidazolium ion-decorated carbon nanoparticles.<sup>8</sup> The atomic force microscopy (AFM) phase image of ILCNs film is shown in Fig. 1c. The ILCNs film was fabricated by drop-casting ILCNs solution on top of the blended film of the regioregular poly (3-hexylthiophene) (P3HT) and {6,6}-phenyl C61-butyric acid methylester (PCBM). It is obvious that the phase image of ILCNs-modified P3HT:PCBM films is different from that of pure P3HT:PCBM film (the inset of Fig. 1c).

Conjugated carbon materials such as graphene<sup>10</sup> and carbon nanotubes<sup>9</sup> demonstrate superior mechanical properties and electrical conductivities. The  $sp^2$ -bonded aromatic structure provides low tunneling barrier height at the interfacial contacts.<sup>11</sup> 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 Al cathode.<sup>7</sup> The presence of interfacial electric field helps to reduce the electron injection/extraction barrier. We found that the PCE of polymer P3HT:PCBM based solar cells using ILNCs-modified cathode can be improved up to 30% as compared to that using Al-only cathode measured at AM1.5G illumination of 100 mW/cm<sup>2</sup>.

The polymer solar cell structure is shown in the inset of Fig. 2a. The poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) and P3HT:PCBM thickness were 40 nm and 200 nm, respectively, and the active area of device was 0.11 cm<sup>2</sup>. The PEDOT:PSS (Baytron VPAI4083) was spin coated on top of the ITO substrates (10  $\Omega$ sq<sup>-1</sup>) and then annealed at 140 °C for 15 min under ambient atmospheric condition. 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 films were spin coated on top of PEDOT:PSS film in the glove box (<2 ppm O<sub>2</sub> and

H<sub>2</sub>O). The 0.7 nm thickness LiF or/and 100 nm Al metallic layers were thermally deposited with a background pressure of  $5 \times 10^{-7}$  Torr. Current–voltage characteristics were measured in nitrogen under AM1.5G illumination of 100 mW/cm<sup>2</sup> (SAN-EI Electric Xe-Lamp controller). The impedance spectroscopy (IS) data was recorded using an impedance analyzer (Autolab PGSTAT100) in the frequency range from 0.1 Hz to 1 MHz at the oscillating voltage of 10 mV.

In order to carry out a systematic study of the effect of the ILCN interlayer on the performance of P3HT:PCBM polymer solar cells, a set of solar cells with four different device architectures, as summarized in Table 1, was fabricated. For devices A,B, C and D, the P3HT:PCBM film was spin coated at 800 rpm for 80 second and annealed at 120 °C for 10 min for the fast-grown films. However, the performance of polymer solar cells can be improved by controlling the film morphology with the slow growth method.<sup>2, 12</sup> In addition, the Voc and the PCE of polymer solar cells based on pure Al cathode is more sensitive to the Al deposition condition compared to polymer solar cells using modified cathode such as LiF/Al.<sup>13</sup> Therefore, devices E, F and G were also fabricated with slow growth method (Table 1). The P3HT:PCBM film was spin coated at 800 rpm for 60 sec, and then kept in a petri dish for slow growth. After 12 hours, ILNC film was spin coated on top of P3HT:PCBM film and annealed at 120 °C for 10 min.

Figure 2 shows the current density-voltage (J-V) curves corresponding to the representative devices. The Voc of device E is only 0.46 V, which is lower than that of device A with Voc 0.56 V. One possible reason is that the samples were heated during the evaporation of Al, this can result in changes to the morphology of the films or to the interface of P3HT:PCBM/Al.<sup>13</sup> However, the Voc of devices based on ILCN or/and LiF modified electrodes is almost the same even with different Al deposition condition. The PCE (2.47%) of device F is 29% higher than that (1.91%) of device E. The Jsc or/and FF of devices fabricated using the slow growth method (Fig. 2b) are usually higher than the same type of devices made with fast grown film (Fig. 2a). Our results show that the PCE of polymer solar cells with slow growth can be greatly improved compared to the same type of devices with fast growth. Figure 3 presents the statistical graphs of characteristics of four types of device with fast growth. From these preliminary data, the PCE of devices based on ILCN layer exhibit improvement in

the range of 20-30% over devices using pure Al electrode, independent of the different film fabrication procedure and Al deposition condition.

The J-V curves of the devices in the dark with the slow growth were shown in the inset of Fig. 2b. The J-V curves of devices using Al cathodes exhibited higher reverse and leakage current than the structurally identical solar cells made with LiF or ILCN modified cathode. This reveals that the ILCN and LiF act as protective layers to prevent the diffusion of Al into the active layer.<sup>1</sup> In addition, the short circuit current density measured for the devices made with ILNC or LiF/Al is higher than that of devices with pure Al as a cathode at high forward bias, which indicates that the decrease of interface barrier after cathode modification due to the formation of electric dipole layer.<sup>1, 7</sup>

Impedance spectroscopy was also applied to derive insights into the interfacial properties and the charge carrier dynamics of our devices.<sup>14-16</sup> The different contact potential for electrodes modified by different methods is expected to affect carrier collection and carrier accumulation, resulting in differences in the device capacitance. The impedance spectra of three sets of devices in the dark are shown in Fig. 4. The complex impedance plot ( Fig. 4a and 4c) exhibits an arc in the fourth quadrant at the low frequency range in the moderate voltage (0.5V), indicating the negative capacitance exists in device E.<sup>15, 16</sup> However, the  $-\text{Im}(Z)$  values are always positive at any voltages and frequencies in devices F and G (Fig. 4b and 4d). Using the equivalent circuit model in the inset of Fig. 4c to fit the Cole-Cole plot, we found that this model is suitable for devices F and G (Fig. 4b and 4d). For device E, the fit is good at high voltage of 0.9 V. But the fit is poor at low frequency for moderate voltage of 0.5 V because of its negative capacitance behavior. In the model,  $R_s$  is due to contact resistance at the electrode.  $R_1C_1$  semicircle at high frequencies is related to the bulk resistance and the  $R_2C_2$  semicircle at low frequencies results from the depletion region between the active layer and cathode.<sup>14</sup> The negative capacitive behavior is consistent with reports by Garcia-Belmonte which attributed it to the Schottky behavior at P3HT:PCBM/Al.<sup>14</sup> In the case of the P3HT:PCBM/Al contact, electron collection might be blocked to some extent due to high barrier height under moderate forward bias, which can result in the negative capacitive behavior when the minority carriers (electrons) are far lower than the dopant density. However, the electron collection barrier of device B and C is low due

to the modification by ILCN and LiF, this is consistent with the absence of the negative capacitive phenomenon at the range of voltages and frequencies studied.

In summary, we have demonstrated that the PCE of P3HT:PCBM based polymer solar cells can be readily improved 20-30% by insert an ILCN interlayer between polymer blend and Al contact. The ILCN layer can be prepared by drop-casting or spin-coating using an ionic-liquid-functionalized carbon nanoparticles gel. The photocurrent response and impedance spectroscopy results measured for polymer solar cells using the cathode contacts of ILCN/Al and LiF/AL indicate that ILCN interlayer plays a similar role as LiF in lowering the electron collection barrier at polymer/cathode interface. The solution-processed ILCN is potentially superior to LiF as a cathode modifier for application in the low cost, large area and eventually flexible polymer solar cells.

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## Figure captions

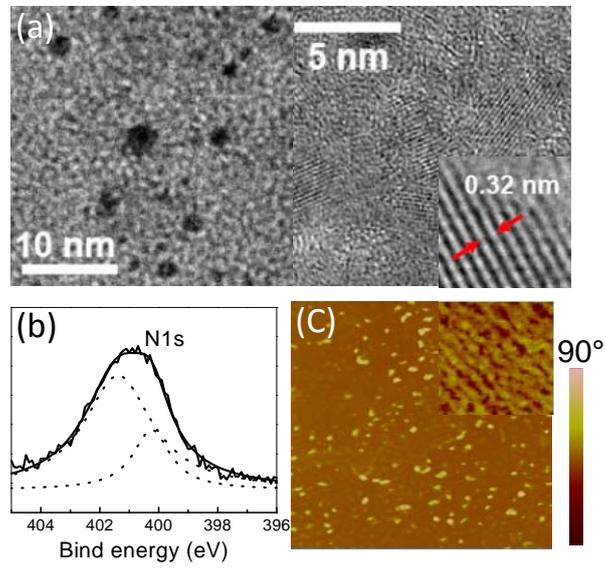
**Fig. 1** (a) TEM micrographs of ILCNs under different magnifications, (b) XPS N1s region (c) AFM phase image of ILCNs on top of the P3HT:PCBM film. The inset in (a) is the HR-TEM image which shows a lattice constant of 0.32nm for the graphite-like carbon nanoparticles. The inset in (c) is the AFM phase image of pure P3HT:PCBM film.

**Fig. 2** The J-V characteristics of different types of the representative device. (a) Device A ( $\nabla$ ), B ( $\triangleleft$ ), C ( $\triangle$ ) and D ( $\blacksquare$ ) with fast-grown film; (b) device E (solid) and F (dash) with slow-growth film. The inset of (a) is the device structure with ILCN modification. The inset of (b) is the J-V curves of devices E (solid), F (dash) and G (dot) in the dark.

**Fig. 3** Device parameters and scatter plot derived from four types of devices with fast-grown film. The cathode composition is Al (device A), ILCN/Al with drop-casted film which are allowed to stand for 20 s (device B) and 40 s (device C), respectively, and LiF/Al (device D).

**Fig. 4** Bias dependence of Cole-Cole plots of (a) device E, (b) device F and (d) device G. (c) the zoom of device e at 0.5 V. The solid lines are fitting lines from the equivalent circuits in the inset of (c).

**Table 1** Different types of polymer solar cells used in this study.



**Fig. 1**

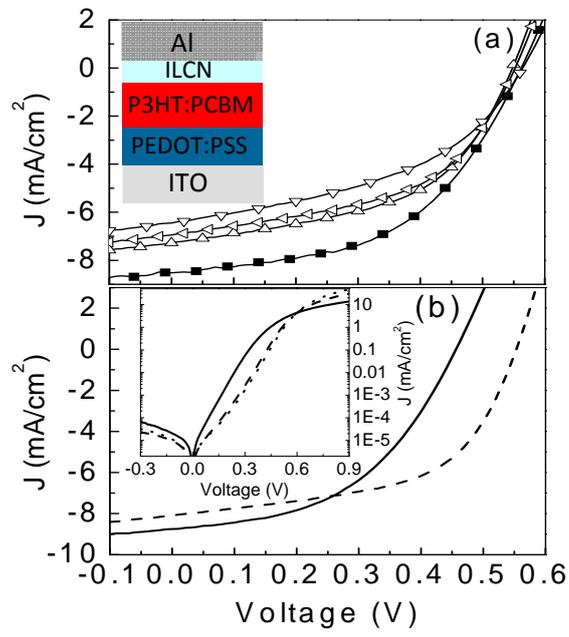
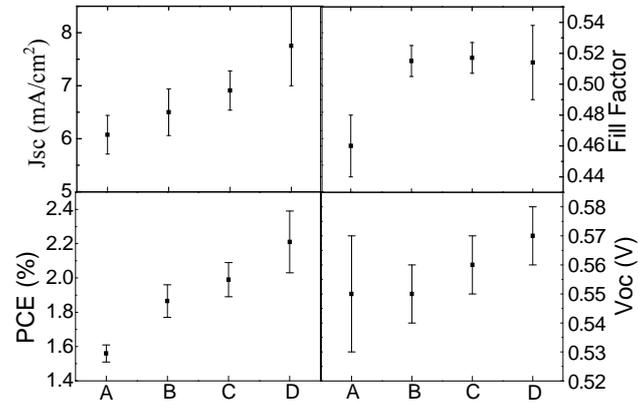
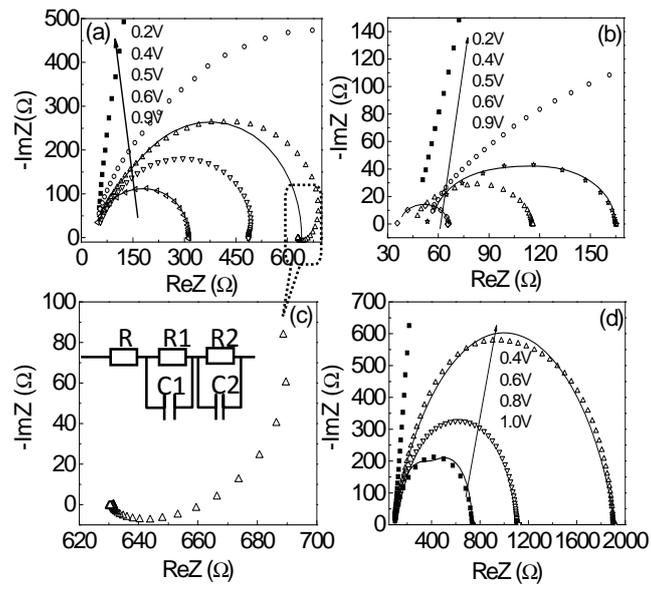


Fig. 2



**Fig. 3**



**Fig. 4**

Device	Cathode	Fabrication condition
A	Al	Fast-grown P3HT :PCBM blend films. ILCN solution drop-casted onto blend films to stand for 20 sec (B) and 40 sec (C) before blow drying.
B	ILCN/Al	
C	ILCN/Al	
D	LiF/Al	
E	Al	Slow-grown P3HT :PCBM blend films. ILCN layer was spin coated onto blend films in device F.
F	ILCN/Al	
G	LiF/Al	

**Table 1**