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Citation: *Appl. Phys. Lett.* **100**, 253303 (2012); doi: 10.1063/1.4729932

View online: <http://dx.doi.org/10.1063/1.4729932>

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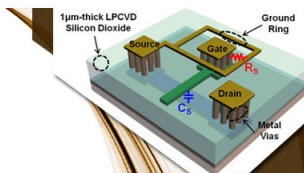
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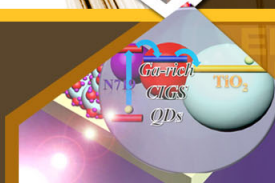
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## Solution processed LiF anode modification for polymer solar cells

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(Received 18 May 2012; accepted 1 June 2012; published online 21 June 2012)

The indium-tin-oxide/active layer interface is critical to the performance of organic solar cell devices. In this study, submonolayer films of LiF nanoparticles are deposited on the electrode surface with the assistance of polymeric micelle reactors, with controlled nanoscale surface coverage. Incorporation of the solution-processed bi-layer electrodes into a conventional poly(3-hexyl-thiophene): [6,6]-phenyl C<sub>61</sub>-butyric acid methyl ester device shows significant improvement in device performance, especially when used in combination with a poly(3,4-ethylenedioxythiophene: poly(styrene sulfonate) layer. The nearly 5× improvement in the short circuit current and decrease in the contact resistance is mostly likely related to the increase in surface work function from the use of LiF nanoparticles. The results strongly indicate that engineering of the interfaces is a useful tool for future device optimization. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4729932>]

One of the primary advantages of organic electronics, such as solar cells, is the potential for low-cost mass production of large-area devices.<sup>1–3</sup> Current state-of-the-art organic solar cells (OSCs) are based on fully solution-processed polymer blends, using reel-to-reel (R2R) approaches for upscaling to production-scale manufacturing lines.<sup>2–4</sup> These R2R processes are not compatible with costly and time-consuming vacuum deposition of inorganic electrodes.<sup>5</sup> To effectively take advantage of ambient processing, non-vacuum approaches for electrode fabrication are highly desirable. Much progress has been achieved in recent years on producing electrodes from solution.<sup>5–8</sup> An important aspect of enabling power conversion efficiencies (PCE) and stability that will surpass the 10–10 targets (10% PCE, 10-year stability) for commercializability<sup>2</sup> is interface engineering at the electrodes to optimize the short circuit current density ( $J_{sc}$ ), the open-circuit voltage ( $V_{oc}$ ), fill factor ( $FF$ ), and contact resistances ( $R_s$ ).

Surface modification of the indium-tin-oxide (ITO) anode has been widely used for both organic light emitting diodes (OLEDs) and OSCs to improve the device performance. Introducing a discontinuous interlayer of metals, such as Au,<sup>9</sup> nanopatterned Ag,<sup>10</sup> or Pt (Ref. 11), and oxides, such as AgOx,<sup>12</sup> MoO<sub>3</sub>,<sup>13</sup> or ZnO nanoparticles,<sup>14</sup> has been seen to greatly enhance the hole collection efficiency in organic solar cells. Though the mechanism are not fully understood, the presence of an abrupt energy step at the interface between the electrode and the active layers or the improvement of wetting with surface roughening are two potential explanations for the observed effects. In this letter, we report an increased PCE for polymer based solar cells using a discontinuous layer of solution processed LiF nanoparticles as an anode modification on ITO electrodes.

LiF nanoparticles were produced and deposited on ITO substrates using the reverse micelle technique, as described elsewhere.<sup>15</sup> Substrates with and without nanoparticles were sonicated in isopropyl alcohol/acetone/methanol baths for 10 min each, before being treated with UV-ozone for 30 min. Diluted poly(3,4-ethylenedioxythiophene: poly(styrene sul-

fonate) (PEDOT:PSS, Clevios P VP Al083) was spin coated at 5000 rpm (30–40 nm) and annealed at 150 °C for 20 min under inert atmosphere. Poly(3-hexyl-thiophene) (P3HT, Rieke Metals, 50 000 MW) and [6,6]-phenyl C<sub>61</sub>-butyric acid methyl ester (PCBM, Sigma Aldrich) were cast in a 1:1 weight ratio from 1,2-dichlorobenzene. Spin coating at 600 rpm for 60 s produced films of approximately 120 nm thickness. The samples were allowed to dry slowly under coverage by a petri dish to obtain a solvent saturated environment, followed by a thermal treatment at 120 °C for 10 min on a hot-plate under a N<sub>2</sub> environment. A top cathode of 100 nm Al/1 nm LiF was sequentially thermally evaporated atop the absorber film in a Balzers vacuum system (vacuum better than  $1 \times 10^{-6}$  mbar). Note that none of the samples were annealed after electrode evaporation.

Current-voltage curves were measured using a Keithley 2400 measurement unit under simulated AM 1.5 global solar irradiation (Oriel sun simulator) with 100 mW/cm<sup>2</sup> to extract the basic solar cell characteristics from devices of approximately 0.45 cm<sup>2</sup> size. The final device architecture was ITO/interlayer/P3HT:PCBM/LiF/Al, where the interlayer was either LiF nanoparticles (sol-LiF NPs), PEDOT:PSS, or both together (see Figure 1). To minimize variations in the results that may arise, all devices were produced on ITO from the same manufacturer during the same batch processing.

Figure 1 shows the current-density voltage (J-V) characteristics under AM 1.5G filtered illumination. The introduction of LiF nanoparticles at the ITO surface has a dramatic effect on the short circuit current density ( $J_{sc}$ ), with a nearly 5× increase, as described in Table I. However, the open circuit voltage ( $V_{oc}$ ) is nearly halved, leading to only a two-fold improvement in the power conversion efficiency (PCE) compared to base devices using only a PEDOT:PSS layer.<sup>16</sup> By using both the nanoparticle layer and PEDOT:PSS, the  $V_{oc}$  increases to 0.6 V, the typically observed value for P3HT:PCBM solar cells.<sup>17,18</sup> Simultaneously, the devices maintain the improved  $J_{sc}$ , leading to a dramatic overall increase in the PCE (6×), yielding a value of 3.9%, with  $J_{sc} = 11.2$  mA/cm<sup>2</sup>,  $V_{oc} = 610$  mV, and  $FF = 59\%$ .

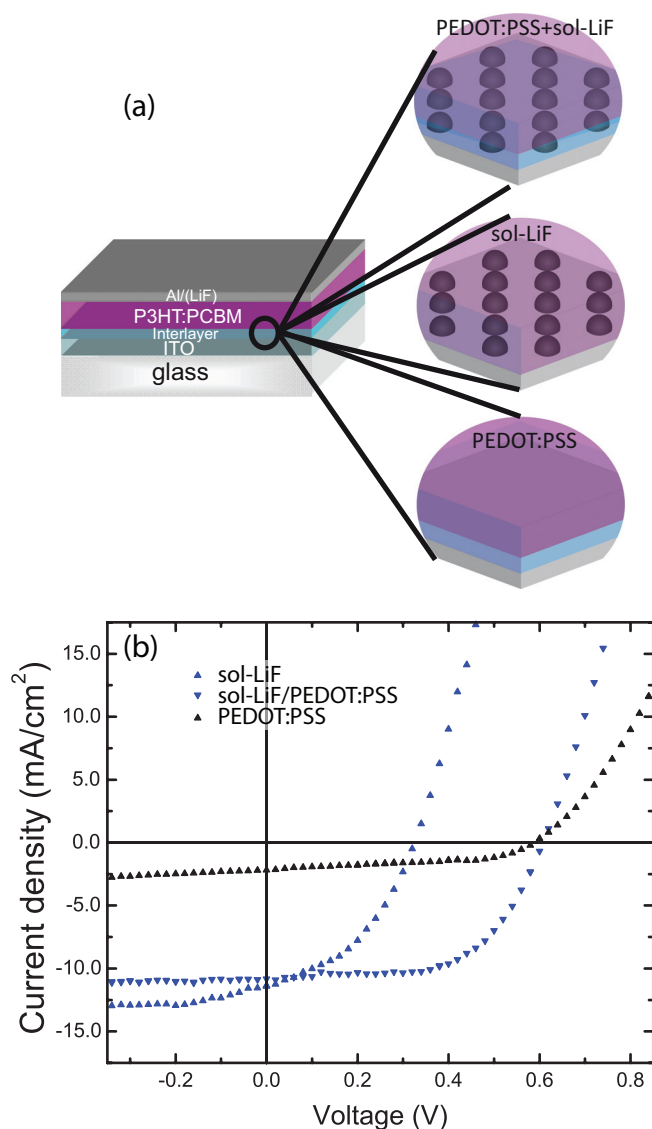


FIG. 1. Typical illuminated current-voltage ( $J$ - $V$ ) curves for polymer-fullerene photovoltaic cells with various anodes.

In addition to these standard derived parameters, real solar cells tend to have parasitic series ( $R_s$ ) and shunt resistances ( $R_{sh}$ ), which can lead to significant changes in the observed PCE (Ref. 19). For ideal solar cell behaviour,  $R_{sh}$  should be infinite and  $R_s$  zero. The shunt resistance, extracted<sup>20</sup> using the slope of the  $J$ - $V$  curve at  $V=0$ , is generally associated with leakage currents in the device. Using nanoparticles alone yields  $R_{sh}$  values 25% of those with PEDOT. This is possibly related to the discontinuous nature of the nanoparticle film, which only covers 14% of the ITO surface.<sup>15</sup> However, the use of PEDOT recovers the high

TABLE I. Solar cell performance of the illuminated diodes with anode modifications. Device values are normalized to that of the control device with PEDOT:PSS to emphasize the differences.

Sample	$J_{sc}$	$V_{oc}$	$FF$	PCE	$R_{sh}$	$R_s$	$n$
sol-LiF	4.9	0.6	0.9	2.4	0.25	0.34	1.3
sol-LiF/PEDOT	4.8	1	1.2	6	1	0.54	0.9
PEDOT	1	1	1	1	1	1	1
sol-LiF/PEDOT (redeposited)	4.7	1	1	5	0.95	0.77	1.6

shunt resistance of the control device, indicating that the PEDOT:PSS layer can act as a buffer to the roughness of the underlying electrode.<sup>21</sup>

The series resistance, which arises from resistance to current flow out of the device, can be determined by a number of methods.<sup>22</sup> We have chosen the method of Ishibashi,<sup>23</sup> which is based on a single  $J$ - $V$  measurement using the constant illumination level method.<sup>24</sup> As organic devices are highly prone to variability and rapid degradation,<sup>25</sup> this single measurement approach was preferred to eliminate potential sources of error that may result from multiple measurements as required by most other techniques. Using this approach,  $R_s$  and ideality factor ( $n$ ) were extracted for all the devices. The incorporation of nanoparticles significantly decreased the observed series resistance, to only 34% that of the control device. Though the use of PEDOT increased the series resistance, measured  $R_s$  of the combination of PEDOT:PSS and the nanoparticles was still almost 50% less than with PEDOT:PSS alone.  $R_s$  can arise from 3 possibilities: (i) contact resistance between the electrode and the active layer, (ii) the bulk resistance of the polymer film, or (iii) the bulk resistance of the contacts.<sup>26</sup>

Though the bulk resistance of the contact may have been affected by deposition, four-point probe measurements of the surface resistivity of the bare ITO and nanoparticle covered surfaces showed no significant differences,<sup>15,24</sup> suggesting little impact on the electrodes themselves. A non-uniform electric field arising from the nanoparticles is also possible; however, scanning Kelvin probe measurements indicate that it is not less uniform than the ITO surface itself (Ref 24), with a smooth surface potential similar to that observed for discontinuous Pt films by Shen *et al.*<sup>11</sup>

In regard to the polymer bulk resistances, for the P3HT:PCBM layer, it is assumed to be unchanged as all devices were treated to the same annealing conditions. The difference in the series resistance between the bare LiF-nanoparticle ITO and PEDOT:PSS covered may be attributed to an increase in the bulk resistance within the polymer layer, as PEDOT:PSS appears to be a source for deep-traps in the device.<sup>24</sup> As this resistance already exists for the control device, the major contribution to the observed 50% decrease in  $R_s$  is related to the contact resistance between the nanoparticles and the active layers.

In addition to the dramatic impact on the parasitic resistances, the major impact of the nanoparticles is on the short circuit current. The  $J_{sc}$  is a direct measure of the number of electrons that can be extracted to the external circuit under illumination.<sup>20</sup> It is controlled by the number of absorbed photons leading to exciton formation, the efficiency of exciton conversion into positive and negative polarons, and the efficiency of charge transport to and extraction at the electrodes. Figure 2 shows the optical transmittance of both anodes over the visible range, performed under ambient conditions from 200–800 nm, as LiF has high optical transparency from UV-to extreme IR,<sup>27</sup> the transmissivity of the LiF nanoparticle-coated ITO showed little attenuation at all wavelengths. All values of transmittance are within 2.5% of that of ITO at all wavelengths and are well within the range of ITO used in solar cells.<sup>28</sup> The visible change in the spectrum shape below 400 nm is likely a function of LiF

absorption at those wavelengths.<sup>27</sup> As polymer solar cells are prone to UV degradation,<sup>25,29,30</sup> suppression of these wavelengths may actually be beneficial to the stability of the solar cells. Regardless, light in this range of wavelengths corresponds to low spectral irradiance under AM1.5G, and a minimum in the absorbance spectrum for P3HT:PCBM blends;<sup>31</sup> therefore, it is not expected to significantly contribute to the exciton generation efficiency of the polymer film. As the nanoparticle film is discontinuous, it is also unlikely to act as an effective optical spacer.

Given that the polymer blend films are the same for all devices and the optical transmission is unaffected by the LiF nanoparticles, only changes in the charge transport and charge collection efficiencies are causes for the dramatic increase in  $J_{sc}$  with the nanoparticle interlayer. Previous studies using nanoparticles have shown improved performance and stability as a result of nanoparticle dispersion in the hole transport layers.<sup>32,33</sup> However, solvent removal and re-deposition of the PEDOT:PSS and P3HT:PCBM layers leads to comparable device performance as freshly deposited layers (see Table I, device curves not shown). Therefore, the particles are fixed to the ITO surface, and detachment and dispersion effects can be ruled out as a major contributing factor. The nanoparticle film can thus be considered as equivalent to a surface modification of the ITO. Other groups have also observed significant increases to  $J_{sc}$  with ITO surface modifications.<sup>12,34,35</sup> For the devices described in this study, there are two possible reasons for the improvement—a global work function change or roughness-induced wetting.

The modification of the interfacial energy has been previously proposed to alter the charge collection efficiency.<sup>35</sup> Khodabakhsh *et al.* used self-assembled monolayers to modify the ITO surface, achieving similar increases in the  $J_{sc}$  with no modification of the  $V_{oc}$ . They show that tailoring the interfacial energy step between the ITO and the active layers can lead to a  $4.6\times$  increase in the  $J_{sc}$ , which is comparable to the measured values in this study ( $5\times$  and  $4.8\times$  for sol-LiF NPs). We have previously measured the surface work function modification of the sol-LiF NP layer,<sup>15</sup> which led to an increase in the ITO work function of 0.17 eV. The proposed

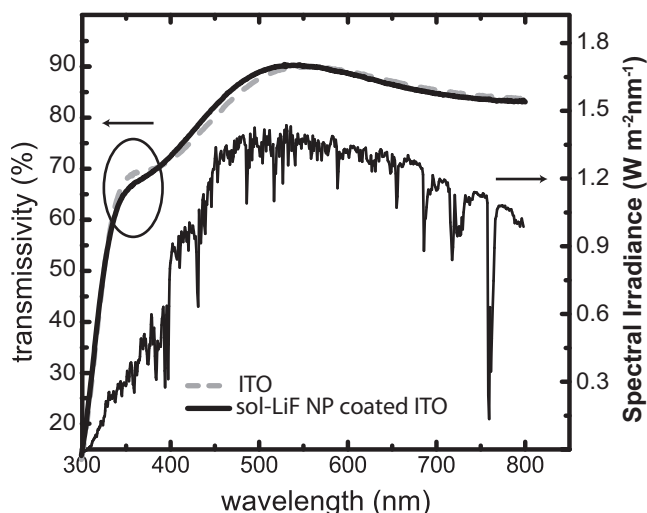


FIG. 2. Optical transmission of the solution processed LiF nanoparticle modified ITO and bare ITO with respect to the AM1.5G spectra.

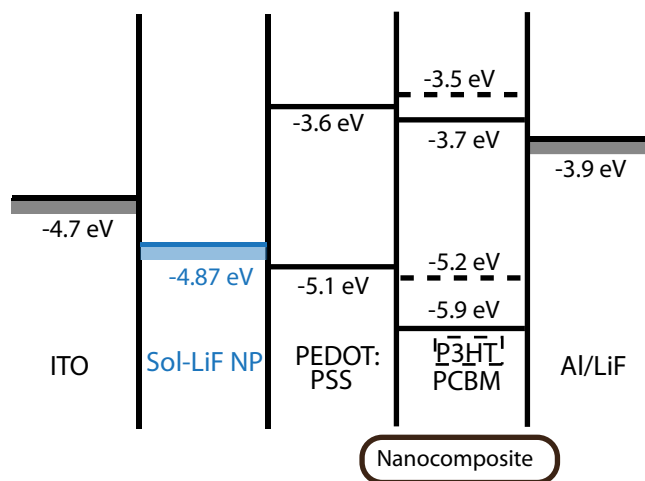


FIG. 3. Proposed energy level diagram indicating the interfacial energy barrier created by the solution processed LiF nanoparticle array. Values for P3HT and PCBM are taken from Ref. 41 and for PEDOT:PSS from Ref. 42.

energy level diagram<sup>36</sup> in Figure 3, shows nanoparticles acting as an intermediate step between the ITO and the active layers.

Another possible explanation is improved wetting of the polymer films on the ITO surface due to the presence of islands, roughening the surface.<sup>37</sup> Increased wetting of the active layers plays a major role in charge injection,<sup>38,39</sup> and roughness enhanced charge injection has also been observed with discontinuous Pt layers in OLEDs.<sup>11</sup> The PEDOT:PSS film in particular visually appeared to adhere better to the nanoparticle-coated ITO than the bare substrate (not shown). This improved adhesion could also explain the observed decreased series resistance with nanoparticles compared to a bare ITO surface.<sup>40</sup>

In conclusion, we have shown an improved PCE for polymer-fullerene bulk heterojunction devices, mainly through an enhancement of the  $J_{sc}$ , with an array of LiF nanoparticles produced from a reverse polymeric micelle technique. The discontinuous surface provided by the nanoparticles showed  $\sim 5\times$  increase in the  $J_{sc}$ , but poor  $V_{oc}$  when used alone. With both nanoparticles and PEDOT:PSS at the ITO surface, both  $V_{oc}$  and  $J_{sc}$  are high, leading to a  $6\times$  improvement in the PCE compared to PEDOT:PSS alone. Coating the ITO surface with LiF nanoparticles could be an effective, stable surface modification that ensures good wetting contact between the electrode and the active layers, and a stable high work function surface for enhanced charge collection in photovoltaic cells.

The authors would like to acknowledge the support of Dr. O. Gurlu at Istanbul Technical University. A.T. acknowledges the support by a Marie Curie Reintegration Grant within the 7th European Community Framework Programme. T.A. acknowledges a BIDEB 2210 scholarship from TÜBİTAK. Partial funding was provided by TÜBİTAK Grant No. 110T023.

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