Interface modification for highly efficient organic photovoltaics

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We present highly efficient inverted polymer:fullerene bulk-heterojunction solar cells by incorporation of a nanoscale organic interfacial layer between the indium tin oxide (ITO) and the metal oxide electron-conducting layer. We demonstrate that stacking of solution-processed organic and metal oxide interfacial layers gives highly charged selective low ohmic cathodes. The incorporation of a polyoxyethylene tridecyl ether interfacial layer between ITO and solution-processed titanium oxide (TiOx) raised the power conversion efficiency of inverted organic photovoltaics to 3.6%, an improvement of around 15% in their performance over comparable devices without the organic interfacial layer. © 2008 American Institute of Physics.

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During the past decade, there has been an intensive search for cost-effective photovoltaics.1,2 Among all alternative technologies to inorganic solar cells, polymer solar cells have the potential for the most significant cost reduction since they can be printed at low temperatures on flexible substrates.3 At present, bulk-heterojunction structures based on blends of regioregular poly(3-hexylthiophene) RR-P3HT, and a highly soluble fullerene derivative [(6,6)-phenyl-C61-butyric acid methyl ester) PCBM, have been among the material systems with the highest reported efficiencies.4,5

For the superstrate device architecture, solar cells based on glass/indium tin oxide (ITO)/poly(3,4-ethylenedioxythiophene) (PEDOT):poly(styrene-sulfonate) (PSS)/RR-P3HT:PCBM/ITO, and a highly soluble fullerene derivative [(6,6)-phenyl-C61-butyric acid methyl ester) PCBM, have been among the material systems with the highest reported efficiencies.4,5 These PCE values were much higher compared to that reported for RR-P3HT:PCBM in the substrate (“inverted”) architecture.6–9 The development of highly efficient inverted solar cells is an interesting architecture since it allows us to study fundamental processes in bulk-heterojunction architecture, including the vertical phase segregation of polymer/fullerene composites as well as the charge selectivity of the interfacial contacts.10 Another potential advantage of this technology is its more natural compatibility with metal grid electrodes, which may become a likely replacement for ITO-based electrodes. Thus, identification of engineering methods to further improve the PCE of the inverted solar cells is of relevance.

Previous attempts to make bulk-heterojunction organic solar cells with inverted layers have resulted in device performance which was below the state of the art performance of the superstrate architecture (PCE of less than 3% was achieved).6–9 One of the main challenges of inverted solar cells is the high charge selectivity for electron extraction at the bottom electrode. We have recently reported on solution-processed titanium oxide (TiOx) as a highly charge selective interfacial layer. Solution processing of TiOx on top of ITO gave fairly optimized charge selectivity and allowed to manufacture inverted organic solar cells with a PCE of up to 3.1%.10 In our previously reported inverted structure glass/ITO/TiOx/RR-P3HT:PCBM/PEDOT:PSS/Au, the electrons are extracted at the bottom electrode (ITO/TiOx) and the holes are extracted at the top electrode (PEDOT:PSS/Au).10

In this letter, we report further performance improvement of inverted solar cells by incorporating an interfacial layer between ITO and TiOx to improve the quality of the TiOx electron extraction layer. The new proposed structure is based on glass/ITO/interfacial layer/TiOx/PR-P3HT:PCBM/PEDOT:PSS/Au (see Fig. 1). The replacement of top metal electrode from Au to a higher reflective metal such as Ag is expected to give lower absorption losses at the top electrode.

The photoactive layer of the devices is a blend of RR-P3HT:PCBM in o-xylene sandwiched between the two extracting electrodes. Devices were processed as reported earlier and measured with and without the influence of ultraviolet (UV) light. The current density–voltage (J–V) characteristics were measured with a Keithley source measurement unit (SMU 2400). For illumination, a calibrated Steuernagel solar simulator was used providing an AM 1.5G spectra at 100 mW/cm2. The Steuernagel solar simulator is equipped with metal halogenide lamps. The mismatch factor

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It is clear that ITO alone does not provide an electron selectivity and a high leakage current in the reverse direction. The solar cells under investigation had a typical active area of 20 mm². The active area of the devices was defined by scribing the hole conducting layer along the outline of the Ag electrode. This patterning step is required to suppress artificial photocurrent contributions from outside the active device area, i.e., preventing lateral current collection via the hole conducting buffer layer. Due to the tolerances in the mechanical patterning process, we estimate an uncertainty of up to 5% in the determination of the active area. That may lead to an efficiency overestimation by a similar amount.

In the present study, polyoxyethylene tridecyl ether (PTE) [C₁₃H₂₇(OCH₂CH₂)₁₂OH, Aldrich] was used as an organic interfacial layer to improve the quality of the TiOₓ layer (see Fig. 1). The organic interfacial layer (0.1 wt % in water) was doctor bladed onto the glass/ITO substrate and resulted to an ultrathin layer with an estimated thickness of less than 10 nm.

The device architectures studied are summarized as follows. Our control devices based on TiOₓ interfacial layer as electron selective contact (glass/ITO/TiOₓ/PR-P3HT:PCBM/PEDOT:PSS/Ag) are compared with device architectures which had PTE interfacial layer between the ITO and the TiOₓ electron selective contact (glass/ITO/PTE/TiOₓ/PR-P3HT:PCBM/PEDOT:PSS/Ag). Finally, both sets of devices are compared to solar cells without any electron selective layer at all (glass/ITO/RR-P3HT:PCBM/PEDOT:PSS/Ag).

Figure 2 shows the representative J-V measurements of the solar cells in the dark (upper plot) and under illumination (lower plot). The J-V data under illumination are measured with and without the influence of UV light. Similar to previous observations, we have observed an increase in the device performance when UV light is present. We will discuss this point in more details in a separate publication.

The dark J-V curve for the inverted solar cell without an electron selective interfacial layer (glass/ITO/RR-P3HT:PCBM/PEDOT:PSS/Ag) shows low current in the forward direction and a high leakage current in the reverse direction. It is clear that ITO alone does not provide an electron selective contact for the extraction of electrons and blocking of holes. By using low temperature solution-processed TiOₓ (glass/ITO/TiOₓ/RR-P3HT:PCBM/PEDOT:PSS/Ag) as interfacial layer, the electron selectivity of the bottom contact improves significantly. A high current in the forward direction as well as low leakage currents are achieved. The improved carrier selectivity is also reflected in the fill factor (FF) of the corresponding cells in the light J-V data (see Fig. 2, lower plot).

The best selectivity (highest injection current and low leakage current) is observed for solar cells using a combination of PTE and TiOₓ (glass/ITO/PTE/TiOₓ/RR-P3HT:PCBM/PEDOT:PSS/Ag). This is also followed from a detailed analysis of the J-V curves according to the one-diode model. The insertion of a thin PTE layer (glass/ITO/PTE/TiOₓ/RR-P3HT:PCBM/PEDOT:PSS/Ag) reduces the serial resistance of the glass/ITO/TiOₓ/RR-P3HT:PCBM/PEDOT:PSS/Ag solar cells from 3 to 1 Ω and increases the shunt resistance from 14 to 31 kΩ. The combination of reduced serial resistance and increased shunt resistance is reflected in the higher FF observed for these diodes.

Figure 3 summarize the performance parameters of the solar cells studied under UV illumination. Data are presented...
in box plots (see Fig. 3). Three series of cells [without electron selective layer (ITO), with TiO$_x$ electron selective contact (ITO/TiO$_x$), and with a combination of PTE and TiO$_x$ (ITO/PTE/TiO$_x$)] with 16 solar cells each were investigated. The 50% of the cells with TiO$_x$ electron selective contact have a PCE of 3.2% or higher, a value which is slightly better compared to our previous published data based on a similar structure.\textsuperscript{10} As discussed in the introduction, we attribute the small improvement in performance to the higher reflectivity of the Ag back electrode compared to an Au back electrode. Solar cells without any electron selective layer have a median PCE in the range of 1.6%. The best device performance was achieved with a combination of PTE and TiO$_x$ as electron selective contact, with 50% of the cells having a PCE higher than 3.6%. We note that the data presented here have been collected from the same experimental run but were confirmed and reproduced in several other independent runs.

Since the PTE is an ultrathin, insulating layer and is not a functional layer but a passive layer. The electron selective layer of the ITO/PTE/TiO$_x$/RR-P3HT:PCBM/PEDOT:PSS/Ag device is still the TiO$_x$ layer. To further investigate the effect of PTE interfacial layer on ITO/PTE/TiO$_x$ interface, we performed photogenerated-current-voltage measurements as described in detail elsewhere\textsuperscript{13} of the solar cells under study to investigate changes in the built in voltage ($V_{bi}$) by PTE interface modification. The photogenerated-current-voltage measurements identified no difference in $V_{bi}$ for the devices using ITO/TiO$_x$ and ITO/PTE/TiO$_x$ as electron selective contact. For both cases, the $V_{bi}$ was found to be 0.64 V, thus the interface modification does not alter the work function of the bottom electrode.\textsuperscript{14}

Thus, the underlying mechanism of the improved electron selectivity by incorporation of PTE in the ITO/TiO$_x$ interface (ITO/PTE/TiO$_x$/RR-P3HT:PCBM/PEDOT:PSS/Ag organic photovoltaics) can be related to an improvement of the overall surface quality (roughness and/or surface energy) of the ITO/PTE/TiO$_x$ bottom electrode. Indications that the surface morphology of the TiO$_x$ is altered when coated on the top of PTE compared to ITO are found from atomic force microscopy studies (Fig. 4). Although the surface roughness of the TiO$_x$ coated on the top of ITO and PTE has the same rms value of 2.2 nm, the distance between the peaks and valleys is different. We attributed the improvement in the electron selectivity of the ITO/PTE/TiO$_x$ bottom electrode to PTE coating step, allowing better wetting of the TiO$_x$ precursor solution. Excellent wetting of the TiO$_x$ layer is essential to guarantee homogeneous hydrolysis and electrode properties and can also provide more intimate interface with the photoactive layer.

In summary, we presented a detailed study on the role of stacking solution-processed organic and metal oxide interfacial layers, PTE interfacial layer on the device performance of inverted bulk heterojunction polymer:fullerene based solar cells. PTE interface modification clearly alters the functionality of the electron selective bottom electrode (ITO/PTE/TiO$_x$). The improved selectivity of the electron selective bottom contact with the incorporated PTE interfacial layer between ITO and TiO$_x$ is reflected in the FF values of the corresponding solar cell device. Due to better electron selectivity, better FF value is achieved. By incorporating a PTE interfacial layer between ITO and TiO$_x$, a PCE of 3.6% for inverted bulk-heterojunction polymer:fullerene solar cells has been achieved.


