Interfacial modification of cathode with low-work-function metal or *n-type* metal oxide for an efficient inverted organic solar cell

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During the past decade, organic solar cells (OSC) have attracted great attention because of light weight and potentially low cost from printing at low temperature on flexible substrates. In spite of high power conversion efficiency (PCE), traditional bulkheterojuncion (BHJ) architecture has limitations in device stability due to air-sensitive low-work-function (LWF) metal cathode such as Al. Diffusion of oxygen into the active layer through pinholes and gain boundaries in Al cathode causes the degradation of the active layer, leading to device instability in air. Moreover, the degradation of indium tin oxide (ITO)/poly (3,4-ethylene dioxythiophene):(polystyrene sulfonic acid) (PEDOT:PSS) interface is inevitable because of the strong acidic nature of PEDOT:PSS. One approach to solve this issue is using inverted structure where the charge separation and collection nature of electrode is reversed. The reversed polarity of charge collection allows the use of high-work-function (HWF) metal as top electrode as well as the removal of ITO/PEDOT:PSS interface. In an inverted structure, transparent conductive oxide (TCO) such as ITO or fluorine-doped tin oxide (FTO) serves as the cathode and a HWF metal as the anode. However, TCO cannot serve as cathode directly. It requires interfacial modification with functional buffer layer for efficient electron extraction and hole blocking. We demonstrated that interfacial modification of TCO with LWF metal or *n-type* metal oxide semiconductor lowers the work-function of TCO, allowing to extract electrons effectively from polymer:fullerene blend.

We constructed inverted structure cells (ITO/LWF metal/P3HT:PCBM/MoO_3/Ag) in which various LWF metals (1 nm) with different work-functions were deposited on ITO to adjust the work-function of transparent electrode. It was observed that both J_{sc} and V_{oc} are a function of the work-function of the metal applied on the ITO surface. Without modification on ITO, the cell is a hole-only device, exhibiting nearly no photovoltaic effect. A very low V_{oc} (0.12 V) is due to a small difference between the work function of the ITO electrode (~ 4.8 eV) and the valence band of MoO_3 layer (~ 5.3 eV). Similarly, HWF metal, Ag (~ 4.2 eV) applied on the ITO surface results a small V_{oc} and Jsc. In contrast, LWF metals (Al, Ca, Mg) applied on the ITO surface lead to very good photovoltaic performances of the inverted cells. The highest V_{oc} (0.65 V) and photocurrent are from the inverted cells with ITO modified by Ca and Mg. A low work function Ca or Mg (~ 2.8 eV) lowers the work-function of ITO, favoring the ohmic contact between LUMO of PCBM for electron extraction. Moreover, lowering the workfunction of ITO makes a large potential difference between two electrodes, leading to high V_{oc} according to metal-insulator-metal (MIM) model of OSC. We also varied the thickness of Ca from 0 to 3 nm and studied the performance of the inverted OSC. Although the inverted cell without Ca shows almost no photovoltaic effect, the efficiency of the cell increases significantly by inserting just a 0.5 nm of Ca. The thickness of Ca 1 nm yields the optimum performance of the cell. Ca thicker than 1 nm deteriorates the performance of the cell due to optical loss in thicker film. We observed that the air stability of the inverted cell was significantly improved as compared to the conventional cell. The shelf lifetime which is defined as the degradation time of PCE from the original value to half of it, of inverted cell (ITO/Ca/P3HT:PCBM/MoO_3/Ag) is about 15 days whereas that of conventional cell (ITO/MoO_3/P3HT:PCBM/Ca/Ag) is only 2 days. The conventional cell with (ITO/PEDOT:PSS/ P3HT:PCBM/Al) structure is even worse and the shelf lifetime is only 1 day.

We also fabricated inverted cell using n-type metal oxide film derived from solgel technique as functional buffer layer. We constructed the inverted cell with architecture (FTO/ZnO/P3HT:PCBM/MoO_3/Ag) where FTO is modified with *n-type* ZnO. The conduction band of ZnO (4.2 eV) is able to extract electron effectively from LUMO of PCBM (4 eV) while the valence band of ZnO (7.5 eV) blocks the hole injecting into FTO cathode, reducing the recombination of charge carriers at the electrode. In addition to low cost and large area fabrication from solution processing, the other advantages of metal oxide over LWF metal is that the optical transmittance can be tuned by manipulation the grain size of the crystalline film without changing the thickness. In our experiment, we observed that reducing the concentration of sol makes the grain size of crystal smaller, in turn, increases the optical transmittance of film. Hence, the inverted cell with ZnO film derived from 0.1M sol gives higher efficiency than the cell with ZnO film derived from 0.5M. We further improved the efficiency of inverted cell by doping ZnO film with appropriate indium content. In our experiment, 1% indium doped ZnO (IZO) gives higher efficiency than un-doped ZnO buffer layer due to enhancement in charge collection which is contributed from higher conductivity and lower work-function, without sacrificing the roughness of the buffer layer.

In summary, interfacial modification with buffer layer is essential to achieve highly efficient invert solar cell. We have demonstrated LWF metals and n-type metal oxides as interfacial buffer layer in the inverted cell. The invert OSC employed with Ca, ZnO and IZO buffer layers yields power conversion efficiency of 4.01%, 3.09% and 3.3% respectively.