

# Solution-processed-MoO<sub>3</sub> hole extraction layer on oxygen plasma-treated indium tin oxide in organic photovoltaics

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## ABSTRACT

Effects of oxygen plasma (O<sub>2</sub> plasma) treatment of ITO on the characteristics of solution-processed molybdenum oxide (MoO<sub>3</sub>) hole extraction layer in bulk hetero-junction organic photovoltaics (OPVs) are studied. The chemical composition of O<sub>2</sub> plasma-treated ITO was determined using monochromatic X-ray photoelectron spectroscopy (XPS). The valence band energies were investigated by ultraviolet photoemission spectroscopy (UPS) measurements. XPS and UPS measurements reveal that O<sub>2</sub> plasma treatment of bare ITO film was found to incorporate the polar surface species such as (O<sub>2</sub>)<sup>2-</sup>, resulting in an increase of both workfunction from 4.62 to 5.05 eV and polar surface energy from 27 to 38 mN/m. The high work function results in efficient hole transport at the ITO/MoO<sub>3</sub> interfaces. The highly polar surface is readily available for uniform coating of MoO<sub>3</sub> on ITO. Electrical conductivity of oxidized ITO changes four orders of magnitude from  $2.4 \times 10^{-2}$  to  $4.08 \times 10^2$  S/cm, depending on O<sub>2</sub> plasma pressure conditions. Thus, the ITO/MoO<sub>3</sub> interface dominates the series resistance of OPVs fabricated with poly(3-hexylthiophene) and phenyl-C61-butyric acid methyl ester (P3HT:PCBM). The presence of (O<sub>2</sub>)<sup>2-</sup> states in the ITO/MoO<sub>3</sub> interface in OPVs is suggested to play a significant role in controlling the device lifetime as well as the efficiency of OPV.

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## 1. Introduction

Polymer solar cells (PSCs) have attracted much attention as a potential alternative to conventional inorganic based photovoltaics as a future renewable energy source due to their low-cost, and mechanically flexible substrates as well as the possibility of using roll-to-roll fabrication processes [1–6]. To date, advanced PSCs have shown a power conversion efficiency (PCE) approaching 10%, but still have limited value for practical applications [7]. Therefore, interface engineering has attracted interest due to its potential to create highly efficient PSCs by limiting hole extraction between the anode and the active layer. The work function of the anode material is the key factor for efficient hole extraction, because the large highest occupied molecular orbital (HOMO) level of the donor material (i.e. P3HT, ~5.2 eV) requires a high work function anode [8–13]. Although indium–tin oxide (ITO) is the most widely used anode material, work function is too low to afford sufficient built-in-potential for collection of holes. To obtain better interfacial properties between the active layer and the anode, poly(3,4-

ethylenedioxythiophene)/poly(styrenesulfonate) (PEDOT:PSS) is commonly used as a hole extraction layer (HEL) [14–18]. Although a thin layer of PEDOT:PSS aligns the work function between ITO and the donor material, the high acidity (pH~1) of this material causes the dissociation of indium–tin-oxide into In and Sn atoms at the surface of the ITO [15,16]. The In and Sn atoms can diffuse into the photo-active layer upon thermal annealing [17]. Moreover, PEDOT:PSS films formed by spin coating are not micro-structurally and electrically uniform [18]. This leads to inhomogeneous charge transport, resulting in “dead zones” in some regions. These issues illustrate the need for a chemically stable and mechanically uniform HEL to replace PEDOT:PSS for PSCs.

In previous reports, various vacuum deposited transition metal oxides with high work functions, such as V<sub>2</sub>O<sub>5</sub>, MoO<sub>3</sub>, NiO and WO<sub>x</sub>, have been introduced to replace PEDOT:PSS [19–24]. However, it was found that the atomic composition of the oxide could change with the deposition rate during thermal evaporation, leading to a non-uniform distribution of the work function across the substrate. In addition, those materials unavoidably require high cost vacuum deposition, increasing the fabrication cost. Recently, solution processed reduced graphene oxide (r-GO) has been used to replace the PEDOT:PSS [25–29]. Even though this solution process is compatible with future roll-to-roll fabrication, the hydrazine solvent is highly toxic and explosive, so significant precautions should be taken when dealing with it. Sun et al.

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developed a chlorination method on ITO to remove the PEDOT:PSS layer [30,31]. However, the device degraded faster than a conventional device because of unstable physisorbed chlorinated functional groups on the ITO surface.

In order to overcome aforementioned problems, solution processed transition metal oxides have attracted attention. Of the transition metal oxides, one most promising candidate to emerge is  $\text{MoO}_3$ .  $\text{MoO}_3$  has several advantages such as being feasible for solution processing, and reproducible, having easily accessible chemistry, and providing excellent electronic property (work function  $> 4.9$  eV) [32]. Up to now, several methods have been reported for the development of solution processed  $\text{MoO}_3$  modified ITO layers in organic photovoltaics [32–37]. The first employs acidified solution of ammonium molybdate that was spin coated onto ITO and heat treated at  $160^\circ\text{C}$ . However, the  $\text{MoO}_3$  film results in unfavorably large aggregates with size of 100 nm [33]. The second method utilizes polymer stabilizers and requires annealing at high temperatures of  $200^\circ\text{C}$ . The third method involved dissolving  $\text{MoO}_3$  in hydrogen peroxide, which was then diluted with polyethylene glycol and 2-methoxyethanol [35]. But, the annealing temperature of  $275^\circ\text{C}$  is too high for application in organic photovoltaics. Recently, low temperature metal–organic precursor based solution is developed using  $\text{Mo}(\text{CO})_3(\text{EtCN})_3$  precursor dissolved in acetonitrile solution [37]. Although low temperature processing is realized, long aging time ( $> 12$  h) is disadvantage of this method. Another fast and cost-effective method involved synthesis by a thermal decomposition technique, using ammonium heptamolybdate  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$  as the precursor [36].  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$  was dissolved in deionized water and heated at  $80^\circ\text{C}$ . The preparation of the  $\text{MoO}_3$  solution is extremely simple, employing deionized water as a solvent and a low temperature process under ambient conditions. In order to coat this  $\text{MoO}_3$  solution on ITO, it is necessary to modify the ITO surface with large polar surface energy because of the hydrophilic nature of  $\text{MoO}_3$  solution. However, the effect of surface modification of ITO for solution processed  $\text{MoO}_3$  has not been investigated at all either chemically or physically.

In this work, we demonstrate a highly efficient and stable PSC structure with solution processed  $\text{MoO}_3$  layer on  $\text{O}_2$  plasma modified ITO anode. It is found that the amount of surface oxygen can be tuned by  $\text{O}_2$  plasma treatment, resulting in a variation of workfunction, surface energy, electrical conductivity, and then, device performances. The best cell efficiency of 3.43% was achieved by employing  $\text{MoO}_3$  on 1000 mTorr  $\text{O}_2$  plasma treated ITO. In addition, the new device structure is proved to have a improved lifetime compared with a conventional PEDOT:PSS device. Based on these results, the effects of chemical composition on the power conversion efficiency and stability are discussed.

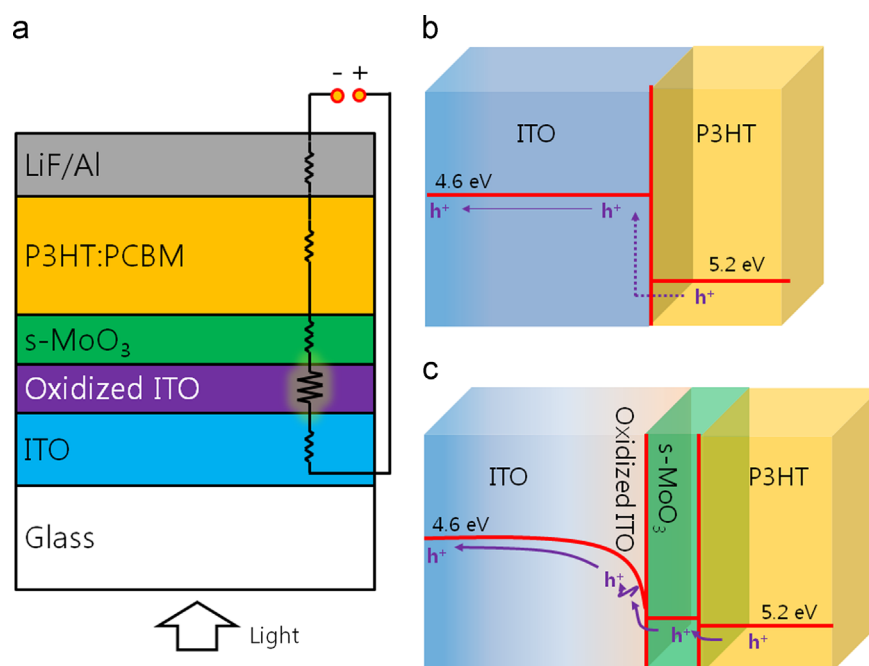
## 2. Experimental

### 2.1. Preparation of the $\text{MoO}_3$ solution

The  $\text{MoO}_3$  solution was prepared by ammonium molybdate tetrahydrate  $((\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O})$ , Aldrich, 99.98%, 0.1 g dissolved in deionized water (5 ml) at  $80^\circ\text{C}$  for 1 h in air. The 0.1 wt%  $\text{MoO}_3$  solution was made by dilution of 95 ml DI water [36].

### 2.2. Device fabrication

The PSC devices were fabricated as described below. Glass coated by ITO (160 nm thick,  $\sim 15 \Omega/\text{sq}$ ) was used as the starting substrate.  $\text{O}_2$  plasma treatment is conducted in vacuum chamber at a base pressure of  $1 \times 10^{-3}$  Torr. Various operating pressures of 50 mTorr, 100 mTorr, 200 mTorr and 1000 mTorr are applied onto ITO surface for 1 min. After  $\text{O}_2$  plasma treatment, the substrates were coated by  $\text{MoO}_3$  solution at 4000 rpm for 40 s using a spin coater manufactured by Dong-A Inc. Then, the air-dried  $\text{MoO}_3$  film is annealed at  $90^\circ\text{C}$  for 10 min. As for the control device, the PEDOT:PSS layer was spin-coated at 5000 rpm for 1 min and dried at  $200^\circ\text{C}$  for 10 min. After hole extraction layer coating, samples were transferred to an  $\text{N}_2$ -filled glove box ( $< 0.1$  ppm  $\text{O}_2$  and  $\text{H}_2\text{O}$ ). Regioregular poly(3-hexylthiophene) (P3HT, purchased from Rieke



**Fig. 1.** (a) Device structure with solution processed  $\text{MoO}_3$  hole extraction layer, (b) schematic illustration of a hole extraction process from P3HT to ITO anode and (c) schematic illustration of a hole extraction process from P3HT via solution processed  $\text{MoO}_3$  and oxidized ITO to ITO anode.

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