

# Organic photovoltaic devices incorporating a molybdenum oxide hole-extraction layer deposited by spray-coating from an ammonium molybdate tetrahydrate precursor

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## ABSTRACT

Polymer bulk heterojunction solar cells have been constructed using a thin film molybdenum oxide (MoOx) hole extraction layer that was fabricated by thermally annealing an ammonium molybdate tetrahydrate precursor layer deposited in air by ultrasonic spray-coating. Onto this layer was spray cast a PCDTBT:PC<sub>71</sub>BM film that acted as the active light-harvesting and charge-transporting layer. We optimise the processing steps used to convert the spray-cast MoOx precursor and show that the temperature at which it is annealed is critical to achieving high device efficiency as it both facilitates the removal of trapped solvent as well as driving its chemical conversion to MoOx. We demonstrate that by optimising the spray-casting and annealing process, we are able to create solar cell devices having a peak power conversion efficiency of 4.4%.

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## 1. Introduction

The manufacturing and materials costs of solar cells provide barriers to the growth in the adoption of photovoltaic electricity generation, and limit the returns on investment in generation capacity. Polymer organic cells still promise potential significant cost reductions through the possibility of high volume, low temperature and vacuum-less cell processing by roll-to-roll processing [1]. In order for polymer organic photovoltaic cells to become commercially viable, improvements in the manufacturability, efficiency and lifetime of devices need to be achieved [2]. Rapid improvements in the power conversion efficiency (PCE) of organic photovoltaic (OPV) devices have been seen, with single junction OPVs now exceeding 9% [3]. This has in part been due to a better understanding of the

properties required by donor and acceptor materials in order to achieve high efficiencies and also the ability to synthesise these required materials [4,5]. Currently new donor materials such as Poly[N-9'-heptadecanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)] (PCDTBT) and similar derivatives are being synthesised with properties close to that of an ideal donor [4,6,7]. However many of these new donors differ from older materials such as poly(3-hexylthiophene-2,5-diyl) (P3HT) in the fact that their highest occupied molecular orbitals (HOMOs) are deeper [4,7,8]. This general increase in the depth of the HOMO level has required the development of new electrode materials to facilitate the efficient extraction of holes from materials such as PCDTBT [9,10]. One such electrode modification material is the metal oxide molybdenum oxide [11,12]. We henceforth refer to molybdenum oxide as MoOx as the molybdenum in thin films of this material can exist in a variety of different oxidation states.

At present, most OPV devices fabricated in a research environment have been created using deposition

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techniques such as spin coating from solution or vacuum based deposition techniques to deposit both the active semiconducting and hole extracting interfacial layers [11–13]. Whilst spin-coating is a high-precision technique that permits films to be fabricated having excellent uniformity and control over thickness, it is not compatible with high-volume manufacturing processes. Recently, attention has turned to the use of spray-coating to deposit materials for organic-electronics. Ultrasonic spray-coating is a solution based deposition technique that is easily scalable and has been shown to be able to deposit organic active layers within OPVs while retaining high efficiencies [14–18]. Spray-coating has also been used to deposit the hole-extracting polymer PEDOT:PSS [19], with spray-pyrolysis (a technique in which precursor solutions are sprayed onto a preheated substrate) being used to deposit metal oxide films [20]. There appears therefore to be significant scope to explore the application of spray-based techniques to deposit a range of functional materials for thin-film electronics applications, as a number of groups have shown that metal oxide films can be prepared from solution via a range of precursors [21–24]. Many of such processes require thermal annealing to convert the precursor into the metal-oxide, although the precursor ammonium molybdate tetrahydrate ( $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ ) can also be initially converted to MoOx *in solution* by heating, with the aqueous solutions being cast to form a MoOx film [25]. Notably however such thin films still require thermal annealing; a process that is presumably necessary to remove adsorbed water.

Here, we report the fabrication of OPVs using the sequential deposition of a metal oxide hole extraction layer and an active semiconductor layer with both layers deposited by ultrasonic spray-coating. To fabricate a MoOx hole extraction layer, we have used the precursor material ammonium molybdate tetrahydrate ( $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ ) that was then thermally annealed to convert it to MoOx. We characterise the various films using X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), spectroscopic ellipsometry and atomic force microscopy (AFM), and discuss their electronic structure, oxidation state, thickness and surface morphology. We also use such films as the hole-extraction layer in OPV devices and comment on device efficiency. We show that by optimising the deposition condition and annealing temperature, we can fabricate spray-cast devices that have a peak (average) power conversion efficiency of 4.4 (4.1)%.

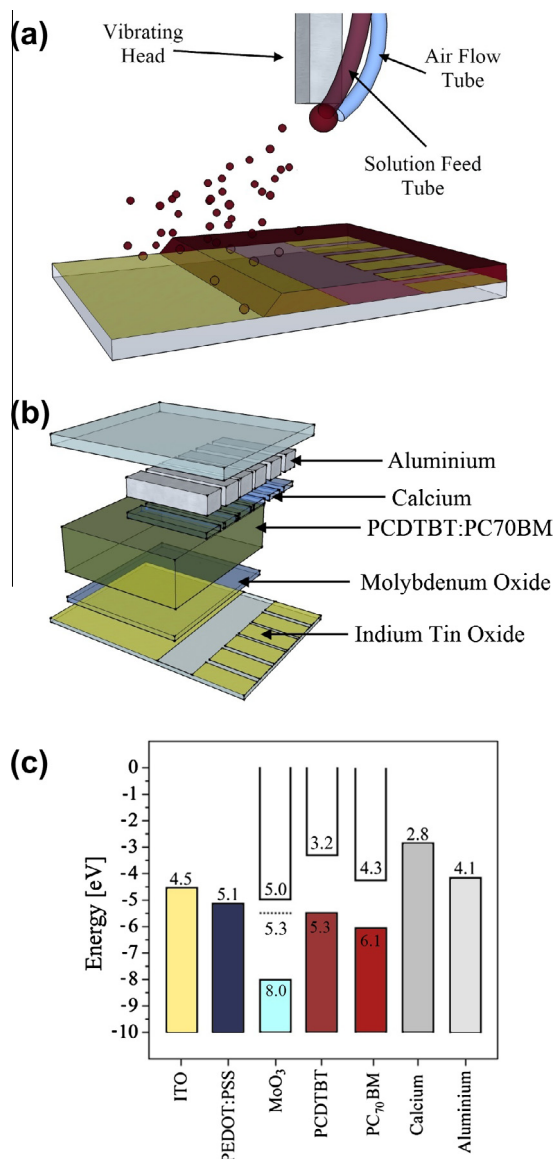
## 2. Experimental

Ammonium molybdate tetrahydrate (99.98%) was purchased from Sigma Aldrich, chlorobenzene (99.95%) was purchased from Sigma Aldrich. PCDTBT was synthesized according to a previously reported method [7], and had a  $M_w$  of 26.5 kDa with a PDI of 2.18. PC<sub>71</sub>BM was purchased from Ossila Ltd and had a purity of 95% (5% PC<sub>61</sub>BM). Aluminium, calcium and molybdenum oxide pellets (99.95% purity) were purchased from Testbourne Ltd.

Samples for use in XPS, UPS and AFM were prepared on unpatterned indium tin oxide (ITO) substrates while OPVs

were prepared on pre-patterned ITO substrates, (both purchased from Ossila Ltd). Samples for ellipsometry were prepared on a Si (100) wafer. All substrates were cleaned by sonicating in hot deionized (DI) water/Hellmanex, rinsed in DI water followed by hot isopropyl alcohol and then dried using nitrogen gas. Finally, substrates were exposed to a UV-ozone plasma to remove any remaining organic residue from the surface before the deposition of the MoOx precursor layer.

Spray-coating of the MoOx precursor and OPV active layer was performed using a Prism ultra-sonic spray-coater supplied by Ultrasonic Systems Inc. (USI). Fig. 1(a) shows a schematic representation of the spray coating process.



**Fig. 1.** (a) Schematic representation of the ultrasonic spray coating system, (b) the device architecture where films are deposited onto pre patterned ITO coated substrates, and (c) shows a flat band diagram of the energy levels within standard PCDTBT:PC<sub>71</sub>BM OPV device.

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