



## Cesium compounds as interface modifiers for stable and efficient perovskite solar cells



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### ABSTRACT

The presented work demonstrates the development of highly stable low temperature processed Cesium compound incorporated ZnO electron transport layer (ETL) for perovskite solar cells (PSCs). Cesium compounds such as CA (cesium acetate) and CC (cesium carbonate) modified ETLs are employed for fabricating highly efficient (PCE: ~ 16.5%) mixed organic cation based MA<sub>0.6</sub>FA<sub>0.4</sub>PbI<sub>3</sub> PSCs via restricted volume solvent annealing (RVSA) method. Here, CA ETL demonstrates a 50 meV upshift in Fermi level position with respect to CC ETL, contributing to higher n-type conductivity and lower electron injection barrier at the interface. Furthermore, CA ETL also exhibits profound influence on the perovskite microstructure leading to larger grain size and uniform distribution. Cesium acetate incorporated devices exhibit about 82% higher PCE compared to conventional CC devices. In addition to higher photovoltaic performance, CA devices exhibit mitigated photo-current hysteresis phenomena compared to CC devices, owing to suppressed electrode polarization phenomena. Besides, the stability of the CA devices are 400% higher than the conventional CC devices, retaining almost 90% of its initial PCE even after a month-long (30 days) systematic degradation study. The mechanism behind superior performance and stability is investigated and discussed comprehensively.

### 1. Introduction

In recent years, low temperature processed perovskite solar cells (PSCs) have demonstrated immense prospect for mass production in roll-to-roll process with flexible substrates [1–5]. In particular, PSCs, incorporating solution processed ZnO thin films as electron transport layer (ETL) provide a facile, low-cost device fabrication pathway [3,6,7]. However, the low temperature processed ZnO ETL exhibits energetic disorder induced deep trap states (as deep as 0.2 eV below the conduction band [8]) due to the chemisorption of oxygen [9,10], which causes the electrons from perovskite LUMO (Lowest Unoccupied Molecular Orbital) to hop between these trap states [9,11] before being finally collected by the cathode electrode. The electron hopping phenomena in the deep trap states of ZnO film can lead to trap-mediated recombination [9,12,13], which is a major process limitation of such low temperature processed ETL. To deal with this complication, the trap-state passivation of low temperature processed ZnO film has been reported by inserting a secondary organic ETL layer [PCBM ([6,6]-

phenyl C61 butyric acid methyl ester)] [12] in between the ZnO and perovskite layer as a form of interfacial engineering or by modifying the ZnO surface with Al doping [13,14] via Burstein-Moss mechanism [15].

Despite being notable endeavours towards trap-state passivation of ZnO ETL for PSCs, the reported studies [12–14] demonstrate some process limitations requiring further research attentions into this direction. Firstly, small molecular buffer layer like PCBM, in conjunction with ZnO film [12] has been reported to either aggregate or diffuse during the perovskite annealing process [16], which exposes the perovskite layer to the underlying ZnO film and thus effectively eliminates the benefit associated with the trap-state passivation. Besides, PCBM ETL based PSCs have been reported to demonstrate low device stability due to chemisorption of oxygen and water in PCBM film [17]. The photovoltaic performance reported with PCBM/ZnO bilayer ETL PSC is also relatively low (highest PCE: 12.20%) [12]. On the other hand, PSCs incorporating Al doped ZnO (AZO) ETL demonstrate relatively lower J<sub>SC</sub> compared to pristine ZnO ETL based PSCs [13,14] owing to lower light transmittance through the AZO film, in contrast with ZnO ETL

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[13]. In this regard, it is intriguing to explore the ZnO surface modification with cesium based compound like cesium acetate (CA), which has been reported to exhibit superior conductive property compared to pristine ZnO film [18] that can compensate the lower transmittance for the doped ZnO film and contribute to enhanced device  $J_{SC}$ , as reported for organic solar cell devices [18]. So far, for perovskite solar cells, cesium carbonate (CC) ETL has been incorporated as a surface modifier along with high temperature (500 °C) processed TiO<sub>2</sub> ETL [19,20]; however, the compatibility of CC based surface modification along with low temperature processed ZnO ETL is yet to be explored. Furthermore, to date, no perovskite study has been conducted incorporating CA doped ZnO as ETL, although CA doped ZnO ETL bids fair to be a promising replacement for pristine ZnO ETL due to its enhanced conductive property [18] and conceivable beneficial role in trap state passivation of pristine ZnO film in Burstein-Moss effect [21]. It is, thus, intriguing to investigate the effectiveness of ZnO surface modification with cesium compounds for perovskite solar cells and to delve into the charge transport property [22–24], inherent electrode polarization and concomitant photo-current hysteresis characteristics [25] and device aging phenomena [26] of such low temperature processed devices. Our current work is aimed to close these knowledge gaps.

In this work, we have reported surface modification of low temperature processed sol-gel ZnO ETL with cesium compounds (CA and CC) for fabricating highly efficient (highest PCE: 16.45%) mixed organic cation based MA<sub>0.6</sub>FA<sub>0.4</sub>PbI<sub>3</sub> PSC in restricted volume solvent annealing (RVSA) method [27]. The photovoltaic performance, photo-current hysteresis and device aging phenomena in CA and CC ETL based PSCs have been systematically investigated and compared. Enhanced device performance with CA devices has been explained with elaborate surface morphology, topography and hydrophobicity characterization, material workfunction and electron injection barrier investigation with ultraviolet photoelectron spectroscopy (UPS) and X-Ray photoelectron spectroscopy (XPS) measurement, along with charge transport and trap-assisted recombination analysis by electrochemical impedance spectroscopy (EIS). The mitigated hysteresis phenomenon with CA devices has been elucidated in terms of inherent electrode polarization process. A systematic month-long degradation study has been conducted to comprehend the device stability of the fabricated PSCs. Augmented device stability with CA PSCs has been investigated with frequency-dependent capacitive response and Mott-Schottky characterization of the aged devices.

## 2. Experimental details

### 2.1. Device fabrication

ITO/glass substrates were cleaned sequentially with Hellmanex III, DI water, Acetone and Isopropanol with duration of 10 min for each. For CC ETL, at first, sol-gel processed ZnO film was deposited on top of ITO/glass substrate in a process reported in our earlier works [9,28]. In brief, 0.48 M sol-gel ZnO solution was prepared by dissolving zinc acetate dihydrate in 2-methoxyethanol with an additive ethanolamine by vigorous stirring for 24 h. ZnO precursor solution was spin coated on ITO/glass substrate at 4000 rpm for 60 s and then annealed on a hotplate at 140 °C for half an hour. For CC ETL, 0.5 wt% CC in DI water was spincoated over the ZnO layer at 3000 rpm for 30 s and dried at 100 °C. The process was repeated once, as demonstrated in a previous perovskite literature with TiO<sub>2</sub> ETL [20]. For further referencing in our manuscript, by CC ETL, we will denote the ZnO/Cs carbonate bilayer ETL. For CA ETL, a 0.09 M cesium acetate (> 99.99% trace metal basis, sigma aldrich) solution with 2-methoxyethanol solvent was prepared by vigorous stirring for 4 h at 80 °C. Later, the aforementioned 0.48 M sol-gel ZnO solution was separately doped with the stock solution of cesium acetate to obtain five different solutions having the dopant concentration of 0, 1, 2, 3, 4 and 5 wt%. Unless otherwise stated, by CA ETL, we will refer to the 2% (optimized) cesium acetate doped ZnO ETL (the

details of the ETL optimization process have been explained in subsequent device performance section) in our work. All the cesium acetate solutions were spin-cast and annealed on ITO/glass substrate in a similar manner as sol-gel ZnO ETL. For both the CA and CC ETL devices, the mixed organic cation based perovskite (MA<sub>0.6</sub>FA<sub>0.4</sub>PbI<sub>3</sub>) precursor solution was prepared using PbI<sub>2</sub> (1 M), MAI (0.6 M) and FAI (0.4 M) powder in anhydrous DMF (*N,N*-dimethylformamide) solvent and the solution was stirred at 70 °C for 24 h. The perovskite precursor solution was filtered with 0.45 μm PTFE (polytetrafluoroethylene) filter and deposited on the ETL coated substrates with pipettes for spin-coating. A dry N<sub>2</sub> gas stream was blown over the central part of the film dynamically (during the spinning at 2500 rpm) after 9 s of the commencement of spin-casting in nucleation aided gas-assisted method [29]. After the spin-coating, the substrates were annealed at 100 °C for 10 min on hotplate in RVSA method [27]. In brief, a glass slide was placed on top of the substrates during the annealing session, which acted as a confining barrier for methyl amine gas to escape from perovskite surface and thus preventing thermal degradation of perovskite on alkaline ZnO film [30]. For HTL (hole transport layer), 73.3 mg/ml Spiro-OMeTAD in chlorobenzene was doped with 17.5 μL Li-TFSI (520 mg/ml in Acetonitrile) and 28.8 μL 4-TBP. The Spiro-OMeTAD layer was spin-casted on the perovskite film with 3000 rpm for 30 s. Finally, 100 nm Ag layer was deposited on the HTL coated substrate by thermal evaporation with an evaporation rate of 2 Å/s under a vacuum condition of 1 × 10<sup>-6</sup> mbar. The device area was fixed to be 4.5 mm<sup>2</sup> with the use of a metal mask. So, the overall device structures were: ITO/CA or CC ETL/MA<sub>0.6</sub>FA<sub>0.4</sub>PbI<sub>3</sub> perovskite/Spiro-OMeTAD/Ag (Fig. 5(A)).

### 2.2. Device characterization

The current–voltage characteristics of the devices were measured with a NREL calibrated Keithley 2400 Source Meter under 100 mW/cm<sup>2</sup> (AM 1.5G) simulated sunlight using a black, non-reflective aperture (4.5 mm<sup>2</sup>) mask over the cells to avoid overestimation of the device current densities associated with the active device area. For optical characterization like transmittance, reflectance and absorbance measurement, a UV–VIS–NIR spectrometer (Perkin Elmer–Lambda 950) was used. X-ray diffraction (XRD) with CuKα radiation was performed by step-scanning with a step size of 0.02°. Surface topology view was captured by Carl Zeiss AURIGA Cross Beam SEM and the surface roughness was measured with Bruker Dimension ICON SPM AFM machine. Contact angle measurement was conducted using Ramé-hart contact angle goniometer (Model 200) and the contact angles were determined using DROPimage advanced software. XPS measurement was conducted in ESCALAB250Xi instrument (Thermo Scientific, UK) with background pressure of 2 × 10<sup>-9</sup> mbar using a mono-chromated AlKα ( $h\nu = 1486.68$  eV) anode (120 W, 13.8 kV, 8.7 mA). UPS measurement was carried out in ESCALAB250Xi instrument (Thermo Scientific, UK) using the He I photon line ( $h\nu = 21.22$  eV) of a He discharge lamp under UHV condition (4 × 10<sup>-10</sup> mbar). The impedance analysis was conducted with an Autolab PGSTAT-30 equipped with a frequency analyzer module in the frequency range from 1 MHz to 1 Hz. AC oscillating amplitude was as low as 20 mV (RMS) to maintain the linearity of the response.

## 3. Results and discussion

### 3.1. Material and optical characterization of ETL films

Deposited CA and CC ETL films have been investigated with XPS elemental analysis to ensure the incorporation of Cs atoms in spin-coating process for the surface modification of ZnO film. Fig. 1(A) and (B) present the XPS survey spectra of CC and CA ETL, respectively, demonstrating the respective elemental peaks. Corresponding peak binding energies, peak width and elemental atomic ratio in CC and CA ETL films have been tabulated in Table S1 and Table S2, respectively.

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