# The deficiency of CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> solar cells performance under high relative humidity

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Abstract—With the consideration of humidity effect, the deficiency of CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> solar cells performance under high relative humidity is predicted. The efficiency limitation was studied in order to enhance the perovskite solar cell (CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>) performance. To understand this convincing prediction, perovskite solar cells were synthesis, fabricated and characterized in high humidity condition. The role of humidity in degradation and then decline the perovskite solar cell performance are also clarified due to the humidity sensitive nature of these perovskite, their thin films are often prepared in-situ which may hinder their mass production.

Keywords—Moisture, degradation, stability

# 1. Introduction

Organometal halide perovskite has increased rapidly from 3.8% in 2009[1] up to 20.1% in 2014[2-4], making them prominent in photovoltaic (PV) technology. These materials have captivated many researches due to high absorption coefficient, direct band gap and high carrier mobility [5-8]. Furthermore perovskite solar cells could achieve high efficiency and low cost [9, 10]. In spite of tremendous efficiency, practical applications are almost impossible due to degradation of perovskite solar cells.

The quality of the perovskite film plays a main role in the fabrication of high performance perovskite solar cells[11]. The formation of high quality perovskite films depends on the atmospheric conditions present during crystal growth. The relative humidity (RH) is a key factor in both the growth and the decomposition of perovskite crystals due to the hygroscopic nature of CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>

Here we demonstrate the efficiency limitation of perovskite solar cells under uncontrollable humidity. The perovskite solar cells were fabricate under high humidity condition using one step deposition. In order to improve the performance of perovskite solar cells at high humidity, we need to understand the mechanism of degradation at high humidity.

#### 2. EXPERIMENTAL

### Synthesis of perovskite solution at high humidity

Methylamine (CH<sub>3</sub>NH<sub>2</sub>) and hydroiodic acid (HI) were stirred at  $0^{\circ}$ c for 2 hours. After the reaction, the solvent of the solution was evaporated using rotary evaporator at  $70^{\circ}$ c for  $1\sim2$  Hours. Crystallization of the CH<sub>3</sub>NH<sub>2</sub>I was generated by the reaction. The yellowish raw product CH<sub>3</sub>NH<sub>2</sub>I was washed with diethyl ether few times to become white precipitate and dried in an oven at  $70^{\circ}$ c for 24 h. To form CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> precursor solution, CH<sub>3</sub>NH<sub>3</sub>I and PbI<sub>2</sub> were dissolved in 30, 40, 50 and 60 wt% equimolar solution of anhydrous N,N dimethylformamide (DMF), at a 1:1 molar ratio of MAI to PbI<sub>2</sub>.

# Fabrication of perovskite solar cell at high humidity

FTO glass that are used as a substrate to deposit perovskite films were sequentially cleaned with detergent, acetone and ethanol by sonicating for 15 min each. Compact layer (CL) was synthesis using  $TiCl_4$  and spin coated on the FTO glass at 1500rpm for

20s. Mesoporous  $TiO_2$  (mp -  $TiO_2$ ) paste was diluted in absolute ethanol at a volumetric ratio (1:2) and was spin coated onto the cleaned glass slides at 2000 rpm for 40 s to form a mesoporous scaffold layer. The films were dried on the hotplate at  $100^{\circ}c$  for 15 min prior to annealing at  $450^{\circ}C$  for 30 min in air to evaporate organic binder in the  $TiO_2$  paste. The  $CH_3NH_3PbI_3$  precursor solution was synthesized by dissolving  $CH_3NH_3I$  and  $PbI_2$  (1:1 molar ratio) in 40 wt % solution of anhydrous DMF and stirring at  $80^{\circ}c$  for 3 h. To improve surface coverage of perovskite, the  $TiO_2$  coated glass substrates were preheated at  $100^{\circ}c$ . This solution was spin casted onto the mp- $TiO_2/glass$  films at 2000 rpm for 40 s and sintered at  $100^{\circ}c$  for 1 h and  $125^{\circ}c$  for 15 min to form  $CH_3NH_3PbI_3$  crystals. The deposition was carried out at room temperature ( $25-30^{\circ}c$ ) and a high humidity (70-80%). 20mL of spiro OMeTAD solution in 75mg/ml of chlorobenzene, $8\mu l$  of tert-Butylpyridine (TBP) +  $14.2\mu l$  lithiumbis (trifluoromethanesulphonyl)imide) (LiTFSI) and 525 mg/ml acetonitrile was spin - coated onto FTO/CL/mp -  $TiO_2/CH_3NH_3PbI_3$  at 2000 rpm for 40s. A platinum layer was evaporated under high vacuum onto spiro-MeoTAD layer to complete the device fabrication.

#### 3.RESULTS AND DISCUSSIONS 2 ABS FTO/TiO,/CH,NH,Pbl, - 40% FTO/TiO<sub>2</sub>/CH<sub>3</sub>NH<sub>3</sub>Pbl<sub>3</sub> - 30% Relative PL intensity PL FTO/TiO<sub>2</sub>/CH<sub>3</sub>NH<sub>3</sub>Pbl<sub>3</sub> - 40% FTO/TiO<sub>3</sub>/CH<sub>3</sub>NH<sub>3</sub>Pbl<sub>3</sub> - 40% b) a) Absorbance (a.u) Absorbance (a.u) FTO/TiO<sub>2</sub>/CH<sub>3</sub>NH<sub>3</sub>Pbl<sub>3</sub> - 50% FTO/TiO<sub>3</sub>/CH<sub>3</sub>NH<sub>3</sub>Pbl<sub>3</sub> - 60% 400 500 600 700 800 900 400 500 600 700 900 Wavelenght (nm) Wavelenght (nm)

Figure 1 : a) Absorbance spectra for CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> with different concentration of DMF b) Absorbance and PL spectra of CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> with 40% of DMF

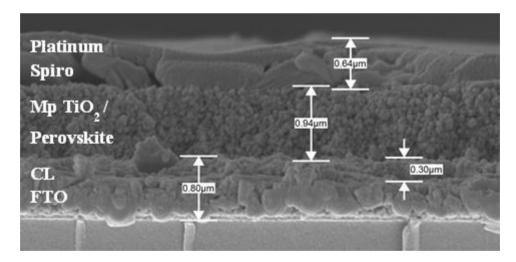


Figure 2: Cross-sectional FESEM image of the device consisting of FTO-Glass/cl-TiO<sub>2</sub>/mpTiO<sub>2</sub>/perovskite/Spiro/Pt

Table 1 : Electrical characteristics for CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> perovskite solar cell at high humidity (R.H 70 -80%)

	2 2 21	$\mathcal{E}$	J \ /
FF	Voc (V)	Jsc (mA/cm <sup>2</sup> )	η%
0.22	0.49	6.85	0.55

Perovskite solutions (CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>) were prepared with different concentration of solvent DMF (Fig. 1 (a)). The absorbance of 40% of DMF is the highest and was used to study the limitation of efficiency at high humidity conditions (Rel. H 70 –80%). The absorbance and PL spectra of 40% of DMF were compared in Fig.1 (b). The absorbance peaks of CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> is located at ~760 and ~480 nm which also matches with previous literature [12]. The presence of perovskite is also confirmed from the emission peak related to perovskite at ~770 nm through PL spectra. Fig.2 shows the cross – sectional image of perovskite solar cell device. The perovskite solar cells full devices were fabricated at room temperature (25 –30°C) and a high humidity (70 – 80%). The device exhibits open – circuit voltage (Voc) = 0.485 V, short – circuit current (Jsc) =  $6.85 \text{ mA/cm}^2$ , and fill factor (FF) = 0.22, corresponding to a power conversion efficiency (PCE) of 0.55% under a standard one sun of simulated solar radiation (AM1.5) (Table 1). Even, moisture introduction is helpful to perovskite growth but uncontrolled humidity can lead to deteriorate performance of solar cell devices[13]. The partial solvation of the MA ion and "self- healing" of the perovskite crystal is happened when the moisture is controlled due to reduction of surface traps [14, 15]. However, perovskite crystal is known for its water solubility will decompose in excess humidity [16, 17]. Other than that, XRD results show a small amount of PbI<sub>2</sub> phase present in crystal after annealing at high humidity indicating decomposition of CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> crystal[13]. Furthermore, the nature of CH<sub>3</sub>NH<sub>3</sub>I in perovskite is hygroscopic materials which would cause to accumulation of moisture within grain boundaries. A dense film with large crystal size of CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> (size up to 200 to 250 nm) was growth in high humidity condition compared with perovskite films synthesized in inert atmosphere with smaller crystal size and large grain boundary density which previously reported[18]. These defects introduce strong energetic disorder which induces recombination and impede the charge transport and lowers photovoltaic performance[13].

#### 4. CONCLUSIONS

In conclusion, the deficiency of  $CH_3NH_3PbI_3$  solar cells under high relative humidity is predicted. Firstly, the decomposition of  $CH_3NH_3PbI_3$  due to  $CH_3NH_3I$  is very sensitive to moisture and proved by the presence of  $PbI_2$ . Second, the efficiency limit of perovskite solar cell full devices fabricated in the ambient air (70 - 80%) which is 0.55%. All of these results due to the uncontrollable of humidity, which still needs more experimental studies and evidences.

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