

## EFFECT OF TREATMENT CONDITION ON PEROVSKITE FILM FOR PEROVSKITE SOLAR CELL APPLICATION

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### ABSTRACT

*In this study, the Perovskite material  $CH_3NH_3PbI_3$  was prepared using two-step sequential solution deposition technique. The treatment condition for Perovskite film including dipping duration, reaction temperature and annealing temperature was studied. Crystal structure, grain size, and purity of the prepared material were examined using XRD and SEM methods. The results indicate that controlling treatment condition has a significant effect on the crystallinity and purity of Perovskite film. Under suitable condition, the obtained Perovskite material has a tetragonal structure and grain size ranges from 200 to 400 nm. The Perovskite film was then applied as a light-harvesting material in Perovskite solar cell. The device exhibits a power conversion efficiency of 5.18% with  $J_{SC}$  of  $13.6 \text{ mA cm}^{-2}$ ,  $V_{OC}$  of 0.83 V, and fill factor of 45.9%.*

**Keywords:** Perovskite solar cells, Perovskite materials, two-step sequential solution deposition, treatment condition, power conversion efficiency.

### 1. INTRODUCTION

In recent years, Perovskite solar cells (PSCs) have emerged as a promising candidate to replace conventional Silicon-based solar cells. Since the first PSC was successfully fabricated in 2009 [1], research on this area has significantly increased lead to a continuous improvement in power conversion efficiency (PCE) of the devices, with a reported performance of 25.2% in 2020 [2].

Perovskite material is the term used to describe any material has similar structure with calcium titanium oxide. For solar cell application, methyl ammonium lead trihalide ( $CH_3NH_3PbX_3$ ) is most commonly used as light harvesting material, due to its outstanding properties such as broad-spectrum absorption, high carrier mobility and suitable band gap [3-5].

Figure 1 shows structure of a mesoscopic PSC [6]. In this structure, a compact  $TiO_2$  blocking layer is applied to reduce the recombination process occur in the device. Mesoporous  $TiO_2$  is used as an

electron transport layer, and Perovskite material is penetrated inside the pores and covered on top of mesoporous  $TiO_2$  layer (capping layer). Finally, a layer of hole transport materials (HTM) is deposited to transport holes to the back contact [7, 8].

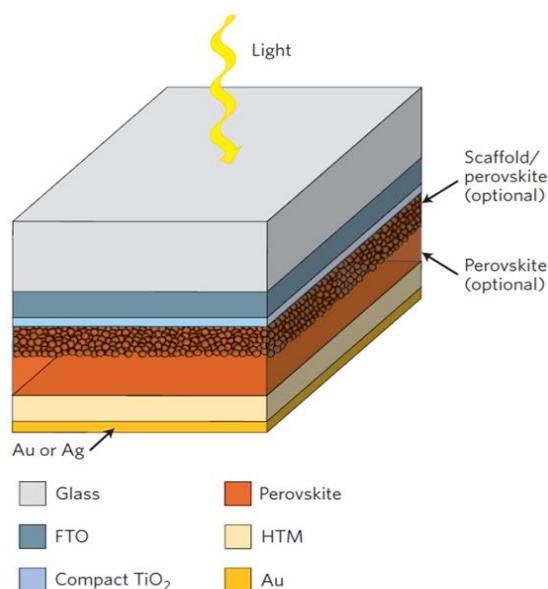
Perovskite is the most important component in PSCs, since it is the light-harvesting material in the photovoltaic devices. In this research, the Perovskite layers were prepared following the two-step sequential deposition technique. The effect of treatment condition for Perovskite film was investigated, included dipping time, dipping and annealing temperature. The suitable condition was selected for application in a photovoltaic device.

### 2. EXPERIMENTAL

#### 2.1 Materials

All following chemicals were used as received without further purification: hydroiodic acid (HI, 57 wt.% in water, Aldrich), methylamine (40% in methanol, TCI), acetonitrile (Aldrich), chlorobenzene (Aldrich), 1-butanol (Aldrich), titanium

diisopropoxide bis(acetylacetonate) (75% in 2-propanol, Aldrich), zinc powder (Aldrich), bis(trifluoromethane)sulfonimide lithium salt (LiTFSI, 98%, Alfa Aesar), (2,2',7,7'-tetrakis (*N,N*-di-*p*-methoxyphenylamino)-9,9'-spirobifluorene (spiro-MeOTAD, 98%, TCI), and 4-*tert*-butylpyridine (*t*BP, 96%, Aldrich).



**Figure 1.** Mesoscopic structure of Perovskite solar cell.

Methylammonium iodide ( $\text{CH}_3\text{NH}_3\text{I}$  or MAI) was prepared according to the reported process[9]. In short, hydroiodic acid (30 mL, 0.227 mol,) and methylamine (27.8 mL, 0.273 mol) were stirred in an ice bath for 2 hours, resulting solution was evaporated at 50 °C for 1 hour and the synthesized chemical  $\text{CH}_3\text{NH}_3\text{I}$  was collected. The precipitate was washed three times with diethyl ether and dried under vacuum for 12 hours.

### 2.3 Method

Perovskite layers were prepared following the two-step sequential deposition technique. First, a precursor solution of  $\text{PbI}_2$  in DMF (462  $\text{mg mL}^{-1}$ ) was spin-coated onto the FTO-coated  $\text{TiO}_2$  films. Then, the coated films were annealed at a temperature of T1 to remove the excess solvent. The dried films were sequentially immersed in a solution of  $\text{CH}_3\text{NH}_3\text{I}$  in 2-propanol (10  $\text{mg mL}^{-1}$ ) at a

temperature of T2. The prepared films were then rinsed with 2-propanol and annealed once again at a temperature of T3.

For PSC fabrication, FTO substrates were cleaned sequentially with deionized water, ethanol, and acetone, followed by etching by zinc powder and hydrochloric acid solution to prevent direct contact between working and counter electrodes.

A compact  $\text{TiO}_2$  blocking layer was deposited on top of the FTO substrates by spin-coating method using a solution of 0.15 M titanium diisopropoxide bis(acetylacetonate) in 1-butanol at a speed of 2000 rpm for 30 sec, followed by heating at 125 °C for 5 min. The films were then cooled down to room temperature and a similar process was repeated 2 times. The coated films were sintered at 450 °C for 30 min and allowed to cool to room temperature. After that, a mesoporous  $\text{TiO}_2$  layer was sequentially deposited by spin-coating a slurry of commercial  $\text{TiO}_2$  particles diluted in ethanol. The mesoporous  $\text{TiO}_2$  films were sintered at 450 °C for 30 min and cooled down to prepare for the deposition of Perovskite films. Next, the hole transport layer was deposited on top of the Perovskite films by spin-coating a solution of spiro-MeOTAD (0.068 M), LiTFSI (0.018 M) and *t*BP (0.05 M) in the mixed solvent of chlorobenzene and acetonitrile (chlorobenzene/ acetonitrile = 1: 0.1, v/v) at 2000 rpm for 30 sec. Finally, a 100 nm-thick Au was deposited on top of the device to form the back contact by thermal evaporation in a high vacuum system.

### 2.3 Characterizations

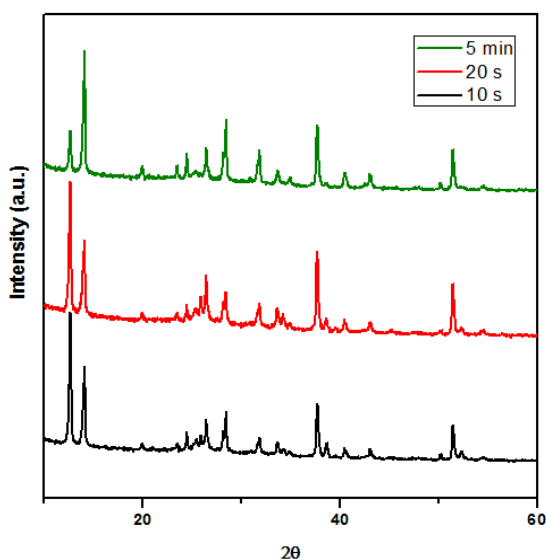
The optical extinction spectra were measured using an Agilent 845X UV-vis/near-infrared spectrophotometer. The crystallographic properties were analyzed using a PANalytical X-ray diffractometer (XRD,  $\text{CuK}\alpha$  radiation). Cross-sectional and top-view images were captured using a Hitachi S-4800 scanning electron microscope (SEM). Photovoltaic characterization was performed under standard global condition

(AM 1.5G) simulated sunlight (PEC-L11, Peccell Technologies, Inc.).

### 3. RESULTS AND DISCUSSION

#### 3.1 Effect of dipping time on the purity of Perovskite films

Perovskite layers were prepared following method described in section 2. After spin-coating a precursor solution of  $\text{PbI}_2$  in DMF onto the prepared FTO-coated  $\text{TiO}_2$  layers, the  $\text{PbI}_2$ -coated films were annealed at a temperature of  $100^\circ\text{C}$  to remove the excess solvent. Then the dried films were immersed in a solution of  $\text{CH}_3\text{NH}_3\text{I}$  in 2-propanol ( $10\text{ mgmL}^{-1}$ ) for 10 s, 20 s or 5 min. After dipping process, the color of the film changes immediately from yellow to dark brown, indicating the formation of  $\text{MAPbI}_3$  following the reaction:



**Figure 2.** XRD spectra of Perovskite films with different dipping time.

Fig. 2 shows the XRD spectra of  $\text{MAPbI}_3$  layers with different dipping time. The results indicate more  $\text{MAPbI}_3$  was formed and less  $\text{PbI}_2$  remained by increasing the duration of dipping process. However, continue increase dipping time leads to the decomposition of the Perovskite film, thus a dipping time of 5 min was selected for further experiment.

#### 3.2 Effect of temperature treatment on crystallinity and purity of Perovskite films

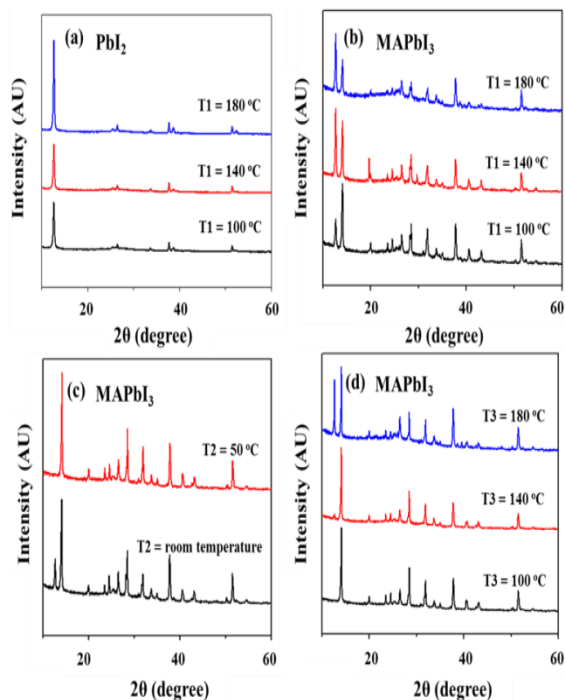
In this section, the effect of temperature treatment on the crystallinity and purity of Perovskite films was studied. First,  $\text{PbI}_2$ -coated films were annealed at different temperature ( $T_1 = 100^\circ\text{C}$ ,  $140^\circ\text{C}$  or  $180^\circ\text{C}$ ).

Figure 3a shows the XRD of the  $\text{PbI}_2$  films deposited onto  $\text{TiO}_2/\text{FTO}$  substrates with different annealing temperature and Fig. 3b shows the corresponding XRD of the films after dipping process. The appearance of a series of strong peaks is observed, which is in good agreement with standard reference data on the tetragonal phase of the  $\text{MAPbI}_3$  Perovskite [7]. However, all results show that the transformation from  $\text{PbI}_2$  to  $\text{MAPbI}_3$  were incomplete, indicated by the presence of the peak at  $12.64^\circ$  (the (001) peak of the unreacted  $\text{PbI}_2$ ). This peak shows a higher intensity at a corresponding higher temperature ( $140^\circ\text{C}$  and  $180^\circ\text{C}$ ), probably due to the increasing crystallinity of the  $\text{PbI}_2$  films (as shown in Fig. 3a), which make the reaction more difficult to happen.

It is important to complete the transformation of  $\text{PbI}_2$  and MAI to  $\text{MAPbI}_3$  since the presence of  $\text{PbI}_2$  can drastically reduce the performance of the cells. To boost the reaction, the dipping process was carried out at a higher temperature ( $T_2 = 50^\circ\text{C}$ ); a similar process was carried out at room temperature for comparison. As seen in Fig. 3-c, the peaks attributed to  $\text{PbI}_2$  disappear, indicating the complete reaction of  $\text{PbI}_2$  with MAI.

To further investigate the effect of temperature treatment on the crystallinity and purity of deposited Perovskite films, we applied different annealing temperatures ( $T_3 = 100^\circ\text{C}$ ,  $140^\circ\text{C}$  or  $180^\circ\text{C}$ ) after dipping process. The results reveal that increased sintering temperatures do not lead to increased Perovskite purity; on the contrary, the Perovskite film tends to be destructed at a

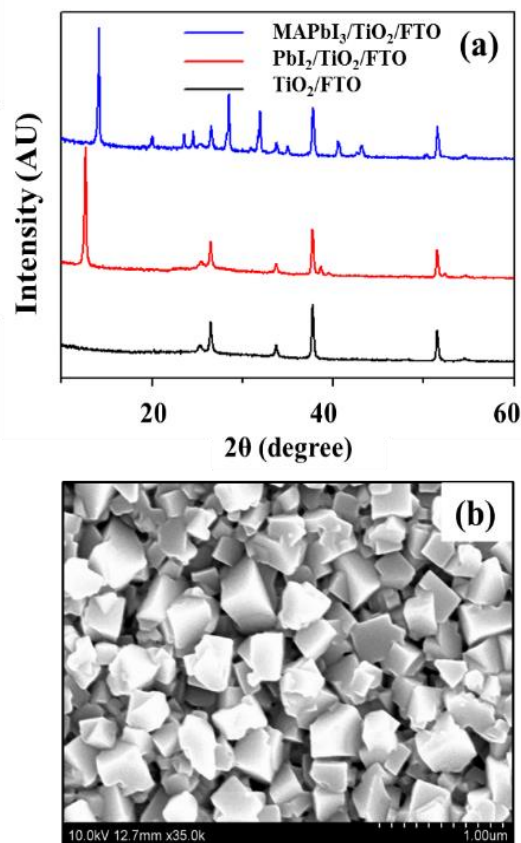
high temperature (the peak attributed to  $PbI_2$  reappears as seen in Fig. 3d).



**Figure 3.** XRD spectra (a)  $PbI_2$  deposited onto FTO-coated  $TiO_2$  films annealed at different temperatures, (b) corresponding films after the reaction with MAI, (c) Perovskite films prepared at different reaction temperatures, and (d) Perovskite films annealed at different temperatures.

From the obtained results, we selected the conditions for the next experiments as follows:  $T_1 = T_3 = 100\text{ }^\circ\text{C}$  for annealing processes of  $PbI_2$  and  $MAPbI_3$  films and  $T_2 = 50\text{ }^\circ\text{C}$  for the reaction of  $PbI_2$  and MAI.

Fig. 4a shows the XRD spectra of  $TiO_2$  mesoporous layer,  $PbI_2$  layer and Perovskite layer deposited onto  $TiO_2$  mesoporous layer fabricated under optimal treatment condition. The quality of the Perovskite film is further evaluated using the SEM technique. Fig. 4b shows that the prepared Perovskite film is fully covered on the substrates, with the grain size ranges from 200 to 400 nm. The tetragonal crystal structure of  $CH_3NH_3PbI_3$  is well observed.



**Figure 4.** (a) XRD spectra of  $TiO_2$  ML,  $PbI_2$  layer, and Perovskite layer deposited onto  $TiO_2$  mesoporous, all coated onto FTO substrates, (b) top-view SEM image of Perovskite  $MAPbI_3$  deposited onto FTO-coated  $TiO_2$  mesoporous layer.

### 3.3 Application of Perovskite film in PSCs

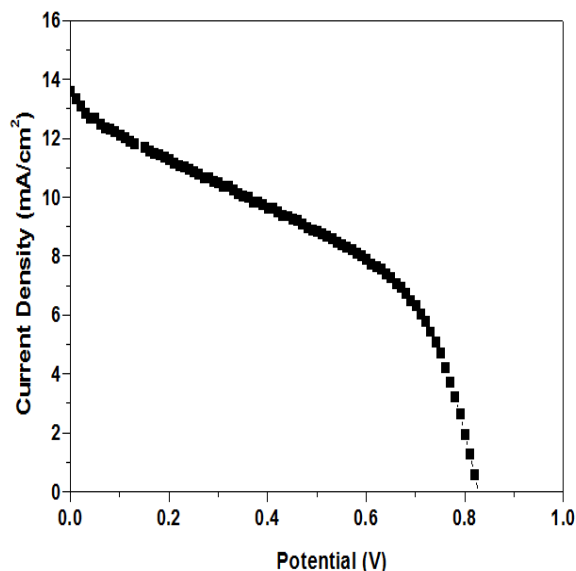
The Perovskite films under selected treatment condition was applied as light-harvesting material in Perovskite solar cells. Current-voltage characteristic of the device was measured using a solar simulator (AM 1.5G). The overall PCE of a solar cell is calculated using the following equation:

$$PCE = \frac{J_{sc}V_{oc}FF}{P_{in}}$$

where  $J_{sc}$  is the short-circuit photocurrent density,  $V_{oc}$  is the open-circuit photovoltage,  $P_{in}$  is the intensity of the incident light, and FF is the fill factor [10, 11].

**Table 1.** Photovoltaic parameters of PSC

$J_{SC}$ (mA cm <sup>-2</sup> )	$V_{OC}$ (V)	FF (%)	PCE (%)
13.6	0.83	45.9	5.17



**Figure 5.** Current-voltage characteristic of PSC.

Table 1 and Fig.5 shows the photovoltaic parameters of PSC. The device has a  $J_{SC}$  of 13.6 mA cm<sup>-2</sup>,  $V_{OC}$  of 0.83 V, and FF of 45.9%, giving an overall PCE of 5.18%.

#### 4. CONCLUSION

In conclusion, the Perovskite layer was prepared with the suitable treatment condition for high crystallinity and high purity includes:

- (1) annealing temperature  $T_1 = 100$  °C,
- (2) reaction temperature  $T_2 = 50$  °C,
- (3) post-annealing temperature  $T_3 = 100$  °C.

The Perovskite layer was then successfully applied in Perovskite solar cell with an overall power conversion efficiency of 5.18%, with  $J_{SC} = 13.6$  mA cm<sup>-2</sup>,  $V_{OC} = 0.83$  V, and FF = 45.9%. Further study on optimization process can be conducted to obtain device with better performance.

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#### REFERENCES

- [1] Kojima, A., et al., Organometal Halide Perovskites as Visible-Light Sensitizers for Photovoltaic Cells. *Journal of the American Chemical Society*, 2009. 131(17): p. 6050-6051.
- [2] <https://www.nrel.gov/pv/cell-efficiency.html>. 2020.
- [3] Shaikh, J.S., et al., Perovskite solar cells: In pursuit of efficiency and stability. *Materials & Design*, 2017. 136(Supplement C): p. 54-80.
- [4] Djurišić, A.B., et al., Perovskite solar cells - An overview of critical issues. *Progress in Quantum Electronics*, 2017. 53(Supplement C): p. 1-37.
- [5] Park, N.-G., M. Grätzel, and T. Miyasaka, *Organic-Inorganic Halide Perovskite Photovoltaics*. Springer, 2016.
- [6] Green, M.A., A. Ho-Baillie, and H.J. Snaith, The emergence of Perovskite solar cells. *Nature Photonics*, 2014. 8(7): p. 506-514.
- [7] Burschka, J., et al., Sequential deposition as a route to high-performance Perovskite-sensitized solar cells. *Nature*, 2013. 499(7458): p. 316-319.
- [8] Zhou, H., et al., Interface engineering of highly efficient Perovskite solar cells. *Science*, 2014. 345(6196): p. 542-546.
- [9] Kim, H.-S., et al., Lead Iodide Perovskite Sensitized All-Solid-State Submicron Thin Film Mesoscopic Solar Cell with Efficiency Exceeding 9%. *Scientific Reports*, 2012. 2: p. 591.

- [10] Hagfeldt, A., et al., Dye-Sensitized Solar Cells. *Chemical Reviews*, 2010. 110(11): p. 6595-6663.
- [11] Chan, D.S.H. and J.C.H. Phang, Analytical methods for the extraction of solar-cell single- and double-diode model parameters from I-V characteristics. *IEEE Transactions on Electron Devices*, 1987. 34(2): p. 286-293.

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