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# Fabrication and Characterization of Halide Perovskite ($CH_3NH_3PbI_3$) Absorber Layer Using Two-Step Deposition Technique

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***Abstract:*** *The processing method in perovskite solar cells plays an important role in film layer roughness, suppressing morphological defects such as voids and improving the structural formation of perovskite-based absorber. In this study, the perovskite absorber layers were prepared by dipping and loading based on two-step method. FTO substrate etching, compact $TiO_2$ and mesoporous $TiO_2$ preparation, lead iodide ($PbI_2$) preparation and annealing conditions remain the same using the two thin film growth methods. X-ray diffraction (XRD), Atomic Force Microscope (AFM), and Field emission scanning electron microscope (FESEM) were used to characterize the $CH_3NH_3PbI_3$ layers for each technique. The $CH_3NH_3PbI_3$/mp-$TiO_2$/c-$TiO_2$/FTO/glass fabricated by loading shows surface roughness and root mean square (rms) value of 0.031 µm and 5.76 nm respectively. While the lead-based absorber layer fabricated using dipping shows 0.029 µm and 5.20 nm as surface roughness and root mean square (rms) value respectively. The loading method exhibits higher surface roughness with reduced morphological defects compared with the layer fabricated by dipping technique. Lead-based perovskite absorber layer using two–step method by loading technique can reduce morphological defects and enhance photovoltaic performance in perovskite absorber layer.*

***Keywords:*** *absorber layer, deposition, halide perovskite, lead, two-step technique*

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## I. Introduction

Lead (Pb)-based halide perovskite solar cells have shown significant improvement of power conversion efficiency (PCE) from initial efficiency of 3.8 % (Kojima *et al.*, 2009) to 22.7% (NREL, 2018) in just nine years. The highest theoretical power conversion efficiency achieved by perovskite ($CH_3NH_3PbI_3$) is 31.4 % (Yin *et al.*, 2014). This remarkable performance is achieved due to unique properties of organic-halide perovskite to exhibit ambipolar transport, high absorption co-efficient, charges carrier mobility, long diffusion length, direct and tunable band gap, simple methods of fabrication (Eperon *et al.*, 2014, Chen *et al.*, 2015, and Green *et al.*, 2014). Organic-lead halide perovskite absorber material can be fabricated by one –step or two step deposition techniques. In one-step method, all the precursors of the perovskite (either in 1:1 stoichemetry or 3:1 stoichemetry ratio) are dissolved in a common solvent (such as DMF or DMSO). The required percentage weight of the solution should be around 40 % for a suitable perovskite layer.

Though, the one-step method is commonly used for the fabrication of perovskite layer, the perovskite material formed found with reduced morphology and contains voids which can results in quick recombination (Kajal and Power, 2018, Chen *et al.*, 2018). While in two-step deposition method, the precursors of the metal halide is first deposited and annealed then followed by dipping the coated substrate into methyl-ammonium iodide solution (for a short period of time) for the formation of the organo-metal halide perovskite layer. This method gives better morphology control over the one-step deposition method (Im *et al.*, 2014). However, to improve the surface roughness of the mesoscopic perovskite absorber layer is still a common challenge among the researchers. In the conventional technique, lead II iodide (PbI$_2$) was prepared and deposited onto a mesoporous coated layer by spin coating. After annealing, the coated PbI$_2$ was dipped in a solution of methyl-ammonium iodide (MAI) in 2-propanol and formed high quality CH$_3$NH$_3$PbI$_3$ for the perovskite solar cells with efficiency of 9.5% (Bi *et al*., 2013).

In contrast to one-step deposition method, an improved performance was achieved for the perovskite solar cells fabricated by two-step deposition method (Burschaka *et al*., 2013). After that, many perovskite solar cells were prepared and reported using the two-step deposition methods (Chen *et al*., 2015, Mo *et al*., 2017, Mehdi *et al.*, 2018, Chen, *et al.,* 2018,). In the two-step dipping method, solution concentration and dipping time are the two major factors affecting the morphology and photovoltaic properties of the final perovskite absorber layer. Xu *et al* (2016) have reported a two –step spin coating method with controlled morphology of the perovskite absorber layer. The method was also used by Ling *et al.* (2018) by dissolving PbI$_2$ in a mixed solvent (DMF:DMSO) and then spin coated onto a mp-TiO$_2$ and then annealed. After that, CH$_3$NH$_3$I solution was directly spin coated onto the coated PbI$_2$ layer. The device exhibited 10.7 % power conversion efficiency. The two-step spin coating depicted that the morphology and the photovoltaic performance of the perovskite film largely depend on the concentration of CH$_3$NH$_3$I solution (Park *et al*., 2016). In this work, the perovskite absorber layers were prepared by dipping and loading based on two-step method. FTO substrate etching, compact TiO$_2$ and mesoporous TiO$_2$ preparation, lead iodide (PbI$_2$) preparation and annealing conditions were remain the same for both CH$_3$NH$_3$PbI$_3$ layers. The final perovskite layers were characterized using Atomic Force Microscope (AFM), Field Emission Scanning Electron Microscope and the (FESEM), X-Ray Diffraction (X-RD).

## II. Materials

FTO-coated glass (15< Ω.sq$^{-1}$, Zhuhai Kaivo Optoelectronic Technology Co. Ltd. China), Zinc powder (45 µm, Merk Germany), Hydrochloric (HCl) acid, isoproponol, titanium diisopropoxide bis (acetylacetonate) (75 wt % in isopropanol), titanium IV oxide (P-25), Lead II iodide (Sigma Aldrich), Dimethyl-formamide (DMF) solvent (Sigma Aldrich), and methyl-ammonium iodide (Sigma Aldrich)

## III. Method

Fluorine-doped tin oxide (FTO) - coated glass sheets (15< Ω.sq$^{-1}$, Zhuhai Kaivo Optoelectronic Technology Co. Ltd. China) were cut into 15 cm X 20 cm and patterned by etching with zinc powder and 2 M HCl acid. The etched FTO were cleaned by ultrasonic bath with de-ionized (DI) water, acetone, ethanol and finally with DI water again at 10 minutes each and then dried under nitrogen flow. Finally, the FTO glass is subjected to oxygen plasma treatment for 5 minutes to remove the remaining organic residues and make the surface hydrophilic. The FTO were coated with a dense compact TiO$_2$ blocking layer prepared by mixing 0.6 ml of titanium diisopropoxide bis (acetylacetonate) (75 %, Adrich) diluted in 8 ml isopropanol inside a fume hood. The c-TiO$_2$ was spin coated on top of the substrates with 3000 rpm for 30 s, annealed at 125°C for 5 min and then sintered at 450°C for 30 min. After cooling to room temperature, the TiO$_2$ paste was coated on the surface of the compact TiO$_2$ layer by doctor blading and heated inside a furnace at 500°C for 30 min and then transferred to a glove box for perovskite layer deposition. The active layer was deposited using the two step deposition technique. First, the dipping method, PbI$_2$ precursor solution was prepared by dissolving PbI$_2$ (462 mg) in 1 ml DMF and stirred at 70°C inside glove box overnight. For the first technique, the PbI$_2$ solution was spin coated on the three FTO/c-TiO$_2$/mp-TiO$_2$ coated substrates at 3000, 5000, and 6500 rpm for 30s each and annealed at 125°C for 10 min. Then the PbI$_2$ coated substrates were immersed inside methyl-ammonium iodide slution (10mg/ml in 2-propanol) for 1 min each. After dipping time passed, the substrates were spin coated again at the same spin coating parameters and annealed at 100°C for 10 min for each. For the loading method, MAI was loaded after spin coating the PbI$_2$ at the same spin coating speeds. X-ray diffraction measurement on perovskite film was performed with EMPYREAN PANalytical diffractometer operating at 40 kV and 40 mA employing Cu – Kα radiation ($\lambda$ = 1.54060 Å) to investigate the desired perovskite layer (CH$_3$NH$_3$SnI$_3$) formation while the morphology and topography analysis were obtained using Field Emission Scanning Electron Microscope (NOVA NANOSEM 230 model) and Atomic Force Microscope (QUESANT-USA-250 by tapping mode) respectively.

## IV. Results And Discussion

The X-ray diffraction (XRD) measurements started from 10° (2θ) to 80° (2θ). Figure 1 shows that the commercial PbI$_2$ was successfully converted into perovskite in tetragonal crystal structure and agreed with the patterns obtained by Oku *et al*., 2015 and Guo *et al.,* 2016. However, quite a few peaks originated from PbI$_2$ 12.5° as observed in CH$_3$NH$_3$PbI$_3$ (a) and 12.33°, and 12.59° observed in CH$_3$NH$_3$PbI$_3$ (b) even with an intensity higher than the perovskite peaks as clearly observed in CH$_3$NH$_3$PbI$_3$ (b). This indicates incomplete conversion of PbI$_2$ into perovskite. Additional MAI solution might be required for CH$_3$NH$_3$PbI$_3$ (a) and increase in loading time for CH$_3$NH$_3$PbI$_3$ (b) to obtain a fully converted PbI$_2$ into CH$_3$NH$_3$PbI$_3$.

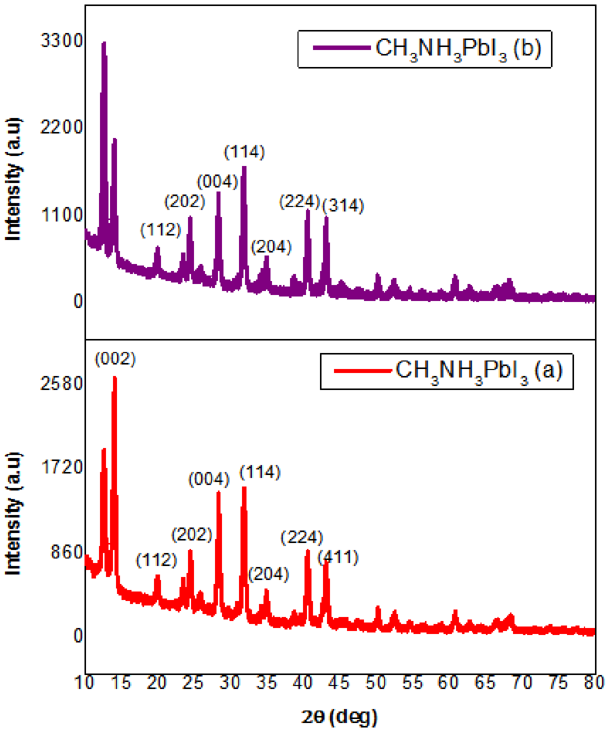
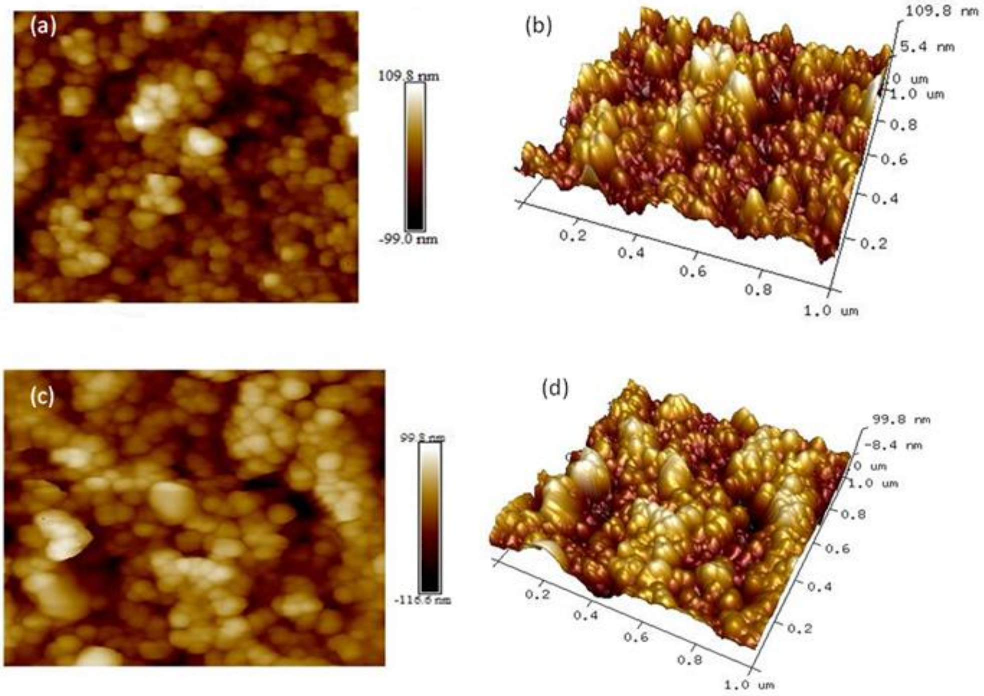


**Figure 1.** X-rd of the perovskite layer $CH_3NH_3PbI_3$ (a) by dipping (b) loading

Figure 2 (a) and (b) show the 2D and the 3D micrographs of $CH_3NH_3PbI_3$/mp-$TiO_2$/c-$TiO_2$/FTO/glass fabricated by dip-coating with surface roughness and root mean square (rms) value of 0.029 µm and 5.20 nm respectively. Similarly figure 2 (c) and (d) indicate the 2D and the 3D micrographs of $CH_3NH_3PbI_3$/mp-$TiO_2$/c-$TiO_2$/FTO/glass synthesized based on loading with surface roughness and rms value of 0.031 µm and 5.76 nm respectively obtained by AFM using the tapping method. The increased surface roughness and rms value observed in the perovskite structure based on loading method indicates smoother surface.



**Figures 2** (a) 2D topographical image of $CH_3NH_3PbI_3$ prepared by dipping method (b) 3D topography image of $CH_3NH_3PbI_3$ prepared by dipping (c) 2D topography image of $CH_3NH_3PbI_3$ prepared by loading and (d) 3D topography image of $CH_3NH_3PbI_3$ prepared by the loading method

Figures 3 a - f show the field emission scanning microscope (FESEM) micrographs of the $CH_3NH_3PbI_3$ film prepared by the dipping and the loading techniques. At the surfaces, all the samples exhibit uneven small cuboids and voids. The observed voids were reduced with the increased in the spin speed in the loading methods in contrast to the dipping method. Hence, the loading method can be optimized to reduce the voids formation in perovskite solar cells.

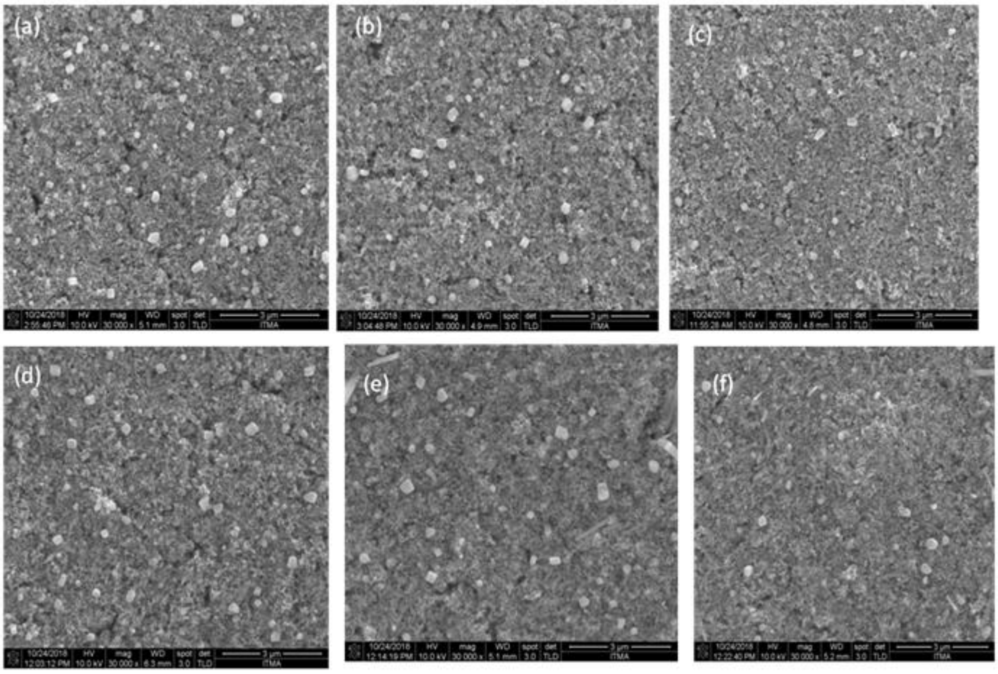


**Figure 3.** FESEM micrographs of $MAPbI_3$ deposited by dipping at (a) 3000 rpm, (b) 5000 rpm, and (c) 6500 rpm and FESEM micrographs of $MAPbI_3$ deposited by loading at (d) 3000 rpm, (e) 5000 rpm, and (f) 6500 rpm

The yellow and dark brown color shown in figure 4 (a) and (b) confirmed the formation of $PbI_2$ and $MAPbI_3$ respectively on a microscope glass slides.

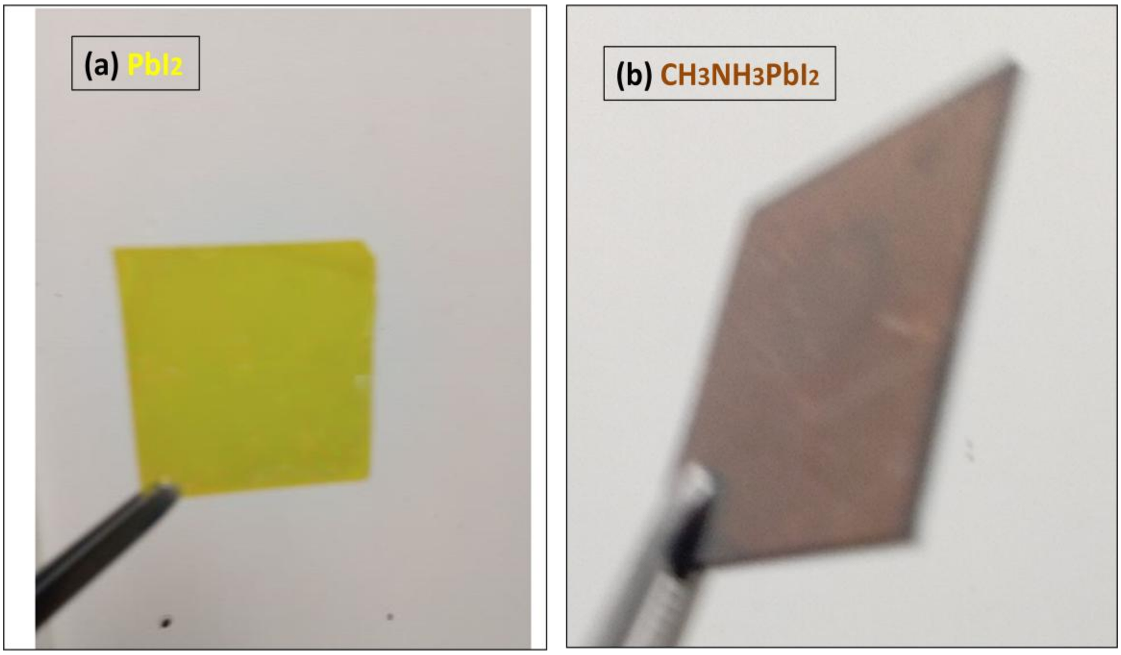


**Plate 1**.(a) Spin coated $PbI_2$ (yellow color) and (b) converted $CH_3NH_3PbI_3$ perovskite (brown color)

## V. Conclusion

In this work, methyl-ammonium iodide (MAI) was deposited onto lead iodide ($PbI_2$) using dipping and loading method for the formation of the methyl-ammonium lead iodide on mesoporous device in planar structure; FTO/c-TiO$_2$/mp-TiO$_2$/CH$_3$NH$_3$PbI$_3$. The effect of spin coating speed on the morphology of the perovskite crystals was observed. The fabricated device by loading shows smoother surface with high surface roughness and root mean square (rms) value in contrast to the device deposited using the dipping technique. This study could help in improving the structural formation and surface morphology of lead-based perovskite absorber layers in perovskite solar cells using the two-step deposition method.

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