

Fabrication and Characterization of Halide Perovskite (CH₃NH₃SnI₃) Absorber Layer

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Abstract: Lead-based perovskites have attracted great attention as a new type of photovoltaic materials. However, the toxicity of lead causes concerns about future large scale applications. Therefore, it is imperative to find environmentally- friendly divalent metal to replace lead (Pb). Sn²⁺ metal cation is the most possible alternative candidate to replace Pb²⁺. However, the tendency of Sn²⁺ to oxidize into Sn⁴⁺ state distort the neutrality between cations and anions in the perovskite structure leading to instability of tin perovskite solar cells. In this paper, X-Ray Diffraction (X-RD), Field Emission Scanning Electron Microscope (FESEM) and Photoluminescence spectroscopy (PL) were used to investigate the properties of tin-based perovskite absorber layer fabricated in FTO/c-TiO₂/mp-TiO₂/CH₃NH₃SnI₃ architecture using one step- deposition method. The results show that tin-based perovskite absorbing layer could be promising candidate to replace lead-based perovskite absorber. Better film coverage in CH₃NH₃SnI₃ can be attained by smoothing and optimizing the layer thickness by varying the precursor concentrations and spin coating parameters.

Keywords: absorber layer, halide, methyl-ammonium, tin II iodide, perovskite.

I. INTRODUCTION

The need for an alternative energy source and the increasing threat of global warming resulted from burning fossil fuels are great future challenges. The sun is the ultimate origin of most of the energy presently available on earth. The amount of solar intensity received by the earth in an hour is almost equal to the total energy consumed by man on earth in one year [1]. Achieving cost effective, easily processable, efficient and versatile solar cell has always been a challenge for the scientific community [2]. Projection results show that the global energy demand will increase to 16 terawatt (TW) in the year 2030 from 13 terawatt (TW) in 2013 [3]. Carbon emission is still need to be reduced. 60 – 80 % of the carbon emission reduction is required to limit the climate change [3]. Hence, clean energy such as solar energy is the best option.

Utilizing the solar energy supplied by the sun is a key approach to provide sustainable energy by direct conversion of sunlight into electricity using solar cells.

Alternative material for the fabrication of high efficient solar cells has been proposed called “perovskites” based on the general composition ABX₃. Typically, organic-cation (A) include (methyl-ammonium ‘MA’, formamidinium ‘FA’), with a range of divalent metal cations (B) being utilized such as Ge²⁺, Fe²⁺, Mn²⁺, Pb²⁺, Sn²⁺, e.t.c. These cations have been mixed with halide anions (X) include Cl⁻, Br⁻ and I⁻. Combining A- cation, B-cation and X-anion different ratios, various perovskite materials can be obtained [4]. Direct substitution either of the cations or anions may results in distorted perovskite structure or non perovskite. Goldschmidt Tolerance Factor (GTF) is a dimensionless empirical index which can predict regular crystal structure of a perovskite [5]. Generally, tolerance factor, *t*, of 0.9 – 1.0 has an ideal cubic structure.

The organic-inorganic halide perovskite solar cells have shown significant improvement of power conversion efficiency (PCE) from initial efficiency of 3.8 % [6] to about 22.7 % [7]. This outstanding performance is achieved due to exceptional properties of organic-halide perovskite; high absorption co-efficient, charges carrier mobility, long diffusion length, direct and tunable band gap, simple methods of fabrication [8], [9]. Despite these outstanding properties, the major issue of concern for perovskite-based solar cells is the used of toxic metal lead (Pb) in the light absorbing layer. The toxic nature of lead might obstruct the possible large-scale applications of this new class of solar cells. Institute for Health Metrics and Evaluation (IHME) estimated that lead (Pb) ingestion is responsible for 9.3 % of world intellectual disorder, 4.0 % of the world problem of heart diseases and 6.6 % of the world problem of stroke [10]. The estimated concentration of lead in a perovskite module is 0.55 % which

is higher than the agreed RoHS (0.1 %) [11]. For this reason, interest has recently turned towards replacing lead by less toxic or non toxic metals. Among the possible alternative to lead (Pb), tin (Sn) is proposed. Sn^{2+} metal cation is the most possible alternative candidate to replace Pb^{2+} because of its similar electronic configuration [12] and close effective ionic radius (Sn^{2+} : 115 pm) to lead (Pb^{2+} : 119 pm) [5].

However, the efficiency of tin-based perovskite solar cells is still very low. This might be due to the tendency of Sn^{2+} to oxidize into Sn^{4+} state, and this oxidation process might distort the neutrality between cations and anions in the perovskite structure leading to instability of tin perovskite solar cells [13], [14], [11] and [15]. Despite the fast progress of the performance of halide perovskite solar cells, there is still need for further improvement. The study of structural and optical properties of tin-based perovskite absorbing layer has great potential to considerably enhance the stability and power conversion efficiency of lead-free perovskite solar cells. In this work, X-Ray Diffraction (XRD), Field Emission Scanning Electron Microscope (FESEM) and Photoluminescence spectroscopy (PL) were used to investigate the properties of tin-based perovskite absorber layer fabricated in FTO/c-TiO₂/mp-TiO₂/CH₃NH₃SnI₃ architecture using one step- deposition method.

II. MATERIALS

The materials used are; FTO-coated glass ($15 < \Omega \cdot \text{sq}^{-1}$, Zhuhai Kaivo Optoelectronic Technology Co. Ltd. China), Zinc powder (45 μm , Merk Germany), Hydrochloric (HCl) acid, isopropanol, titanium diisopropoxide bis (acetylacetonate) (75 wt % in isopropanol), titanium IV oxide (P-25), Dimethyl-formamide (DMF) (Sigma Aldrich) solvent, tin II iodide (Sigma Aldrich), acetonitrile, 2,2,7,7'-tetrakis-(*N,N*-di-*p*-methoxyphenylamine)9,9'-spirobifluorene (spiro-OMeTAD), (Sigma Aldrich), chlorobenzene (Sigma Adrich), bis(trifluoromethylsulfonyl)-imide Lithium salt (Li-TFSI) Sigma Adrich).

III. EXPERIMENTAL PROCEDURE

Etching and Cleaning of the FTO Substrate

Fluorine-doped tin oxide (FTO) - coated glass sheets ($15 < \Omega \cdot \text{sq}^{-1}$, Zhuhai Kaivo Optoelectronic Technology Co. Ltd. China) were cut 15 X 20 mm and patterned by etching with zinc powder and 2 M HCl acid. Firstly, the active area of the FTO sheets were covered with a scotch tape leaving the desired area to be etched uncovered. 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 with 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.

Perovskite Layer Synthesis

The perovskite active layer CH₃NH₃SnI₃ was prepared by dissolving 372 mg of tin-II-iodide (SnI₂) and 159 mg commercial methyl-ammonium iodide (MAI) in 1 ml of *N,N*-dimethyl-formamide (DMF). The mixture was stirred with magnetic stirrer on a hot-plate for about six hours to enable the tin precursor fully dissolved inside glove.

Fabrication Procedure

The cleaned and patterned FTO were coated with a dense compact TiO₂ blocking layer prepared by mixing 0.6 ml of titanium diisopropoxide bis (acetylacetonate) (75 %, Aldrich) diluted in 8 ml isopropanol inside fume hood. The resulting mixture has a yellow color. The compact-TiO₂ layers were deposited onto three different cleaned and dried substrates by spin-coating at 3000, 4000, and 5000 rpm for 30 seconds respectively and annealed at 120°C for 10 minutes each. Immediately after spin coating before annealing on hot plate, small portion of the coated TiO₂ layers was removed by cotton wool rinsed in isopropanol to prevent the TiO₂ from covering the whole substrate.

The procedure was repeated twice to make pin hole free dense TiO₂ layers. After which the substrates were heated inside furnace at 500°C for 30 minutes to form compact-TiO₂ layers. Then the substrates were removed from the furnace after cooling down to room temperature. The mesoporous TiO₂ layer was prepared by diluting 0.5 g of TiO₂ (P-25) powder with 4.5 ml of absolute ethanol (the resulting solution was sonicated for 30 minutes to make a homogeneous solution) and then spin coated on top of the c-TiO₂ at 3000, 4000, and 5000 rpm for 30 seconds and then followed by annealing at 120°C for 10 minutes each. Similarly some portion of the coated mp-TiO₂ was wiped out with cotton wool rinsed in ethanol. The substrates were also heated in the furnace at 500°C for 30 minutes. Then the substrates were removed from the furnace after cooling down to room temperature and transferred to glove box (O₂ and H₂O concentration kept below 1 and 0.02 ppm respectively) to avoid hydrolysis and oxidation of the perovskite solution in contact with the air.

The sintered TiO₂ were coated with precursor of the perovskite solution prepared in equimolar ratio of CH₃NH₃I and SnI₂ in 1 ml *N,N* dimethyl-formamide DMF (99 %, Aldrich) with 35 wt concentration deposited by spin coating the precursor solution on top of the mp-TiO₂ at 3000 rpm for 30 minutes. The perovskite layer formed during the spin coating. Before spin coating the active layer, the same portions of the substrates were covered with adhesive tape to prevent the substrates from being covered by the perovskite layer. After formation of the perovskite layer, the hole transporting layer (HTL) spiro-OMeTAD is deposited on the active layer. The HTL solution was prepared by dissolving 250 mg of spiro-OMeTAD in 1 ml chlorobenzene (250mg/ml

¹) and stirred at 100°C for 30 minutes. The stirred solution was mixed with 9.615 μL *tert*-butylpyridine (tBP) and 20.83 μL bis(trifluoromethane) sulfonamide lithium salt (LiTFSI) (170 mg) in 1 ml acetonitrile (170 mgml^{-1}). LiTFSI and tBP are important dopants. The later is used to provide better interface between the HTL and the perovskite layer while the former increase the hole mobility [16]. The prepared HTL was spin-coated at 1500 rpm for 45 s. This stage requires no annealing. The device was characterized using X-ray diffraction (X-RD), Field Emission Scanning Electron Microscope (FESEM), Energy Dispersive X-ray (EDX) and photoluminescence spectrometer (PL).

IV. RESULTS AND DISCUSSION

X-Ray Diffraction Measurement

X-ray diffraction measurement on perovskite film was performed with X'Pert PRO PANalytical diffractometer operating at 40 kV and 30 mA employing Cu – $K\alpha$ radiation ($\lambda = 1.54060 \text{ \AA}$) to investigate if the desired perovskite layer ($\text{CH}_3\text{NH}_3\text{SnI}_3$) is formed. The measurement started from 20° (2θ) to 79° (2θ).

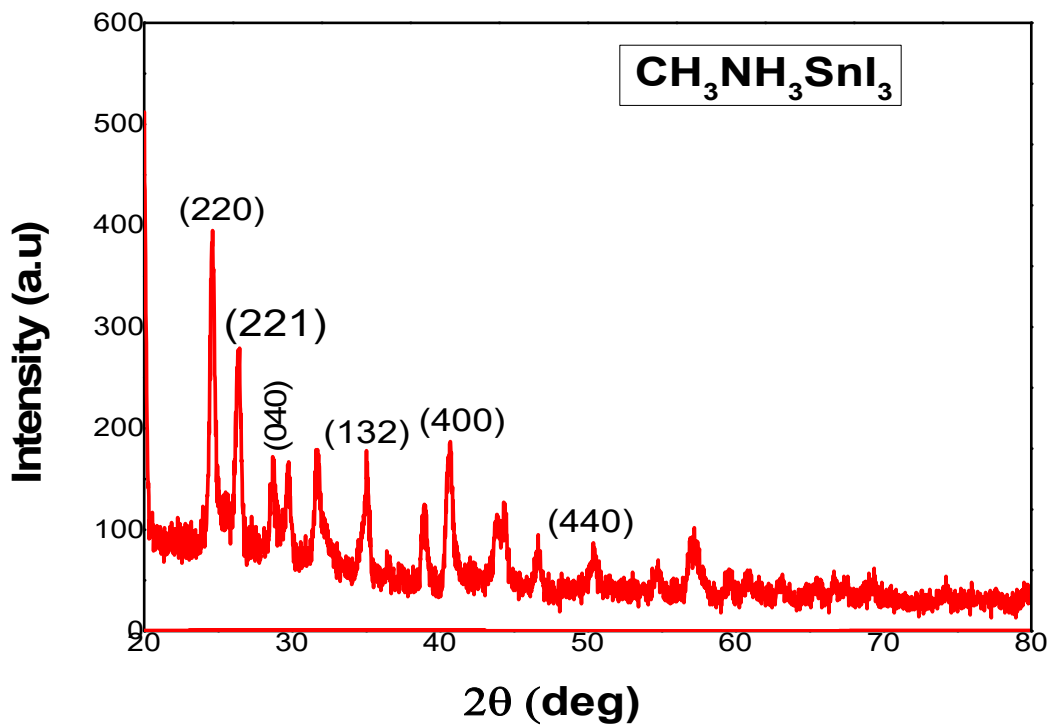


Figure 1.1. X-ray Diffraction of the Perovskite Layer ($\text{CH}_3\text{NH}_3\text{SnI}_3$)

The sharp diffraction peaks observed in figure 1.1, show the signals recorded from the synthesized $\text{CH}_3\text{NH}_3\text{SnI}_3$ structure. The signals; 24.6° , 26.4° , 28.7° , 31.6° , 40.6° , 50.48° , 54.7° which are ascribed to (220), (221), (040), (132), (400), and (440) planes respectively belong to the orthorhombic perovskite structure. The structure is similar to that of lead-based perovskite [17]. This indicates that substituting the B-site has no effect to the general crystal structure of a perovskite material.

Photoluminescence Spectroscopy Measurements

The electronic structure of the various components of the tin-based perovskite solar cells have been examined by observing the intensity and the spectral content of the emitted photoluminescence (PL) using Perkin Elmer LS 55 Fluorescence Spectrometer. The PL spectra were obtained with spectrometer with an excitation wavelength 380 nm. The PL intensity act as the qualitative measure of the emission intensity associated to the excitonic transition energy of the perovskite materials.

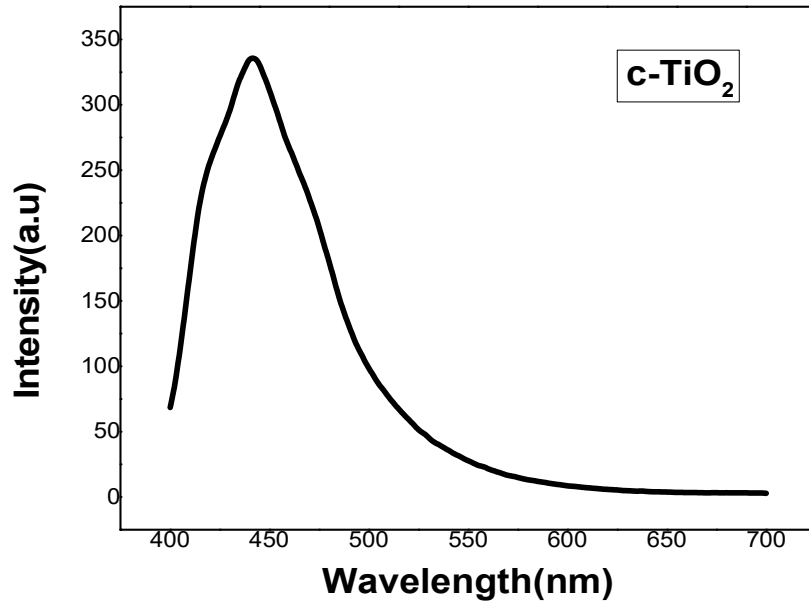


Figure 1.2. Photoluminescence Spectra of c-TiO₂ Layer

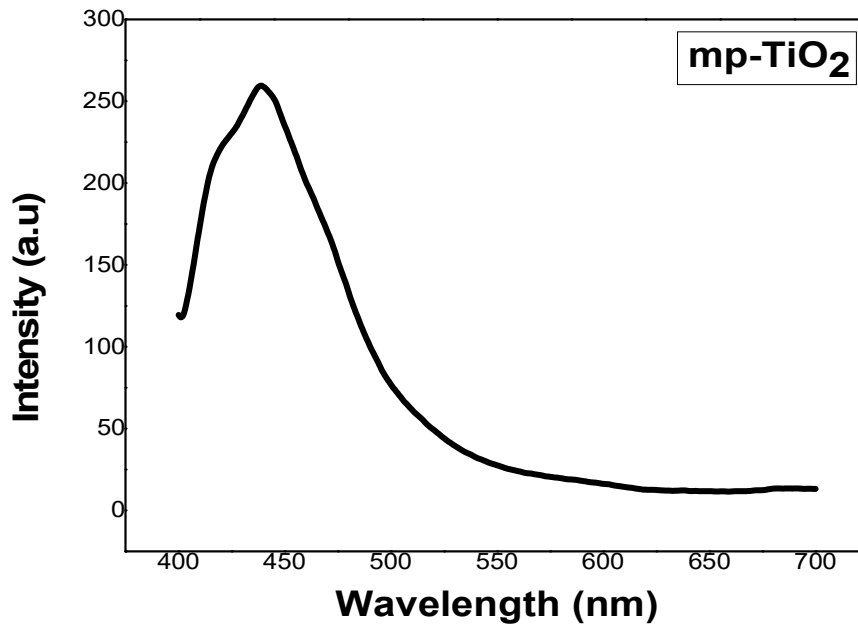


Figure 1.3. Photoluminescence Spectra of mp-TiO₂ Layer

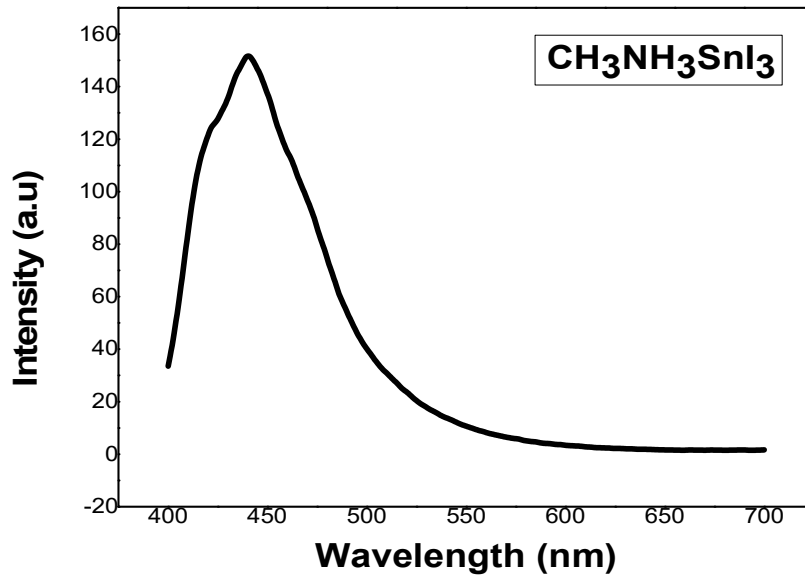


Figure 1.4. Photoluminescence Spectra of $\text{CH}_3\text{NH}_3\text{SnI}_3$ Layer

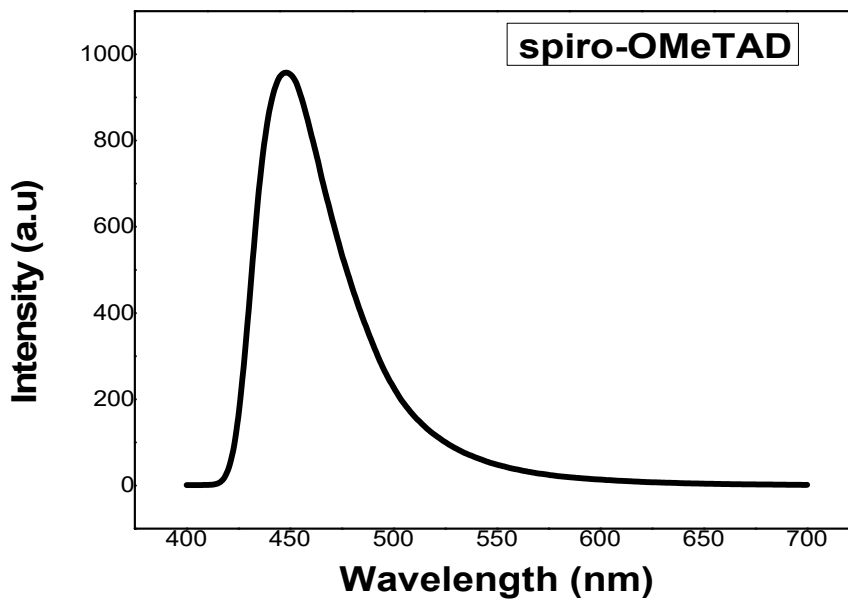


Figure 1.5. Photoluminescence Spectra of spiro-OMeTAD Layer

The PL results in figures 1.2, 1.3, 1.4 and 1.5 indicate the absorption peaks intensities of the c-TiO₂, mp-TiO₂, spiro-OMeTAD and $\text{CH}_3\text{NH}_3\text{SnI}_3$ around 340, 260, 150 and 900 respectively. The PL intensity of the film is dependent on the quality of the film. The high intense peak observed in spiro-

OMeTAD in figure 1.5 exhibited good quality. The low intensity peak observed in $\text{CH}_3\text{NH}_3\text{SnI}_3$ implying more defects within the $\text{CH}_3\text{NH}_3\text{SnI}_3$ layer. The defects can be minimized by varying the spin speed and the perovskite precursor solutions.

Field Emission Scanning Electron Microscope (FESEM) Measurement

The morphology analysis was carried out using ultra high resolution scanning electron microscope, NOVA NANOSEM

230 model. The sample coated with dense blocking layer, mesoporous layer, perovskite active layer and the hole transporting layer on an etched FTO glass was loaded in the FESEM vacuum chamber and the images were obtained with different magnifications.

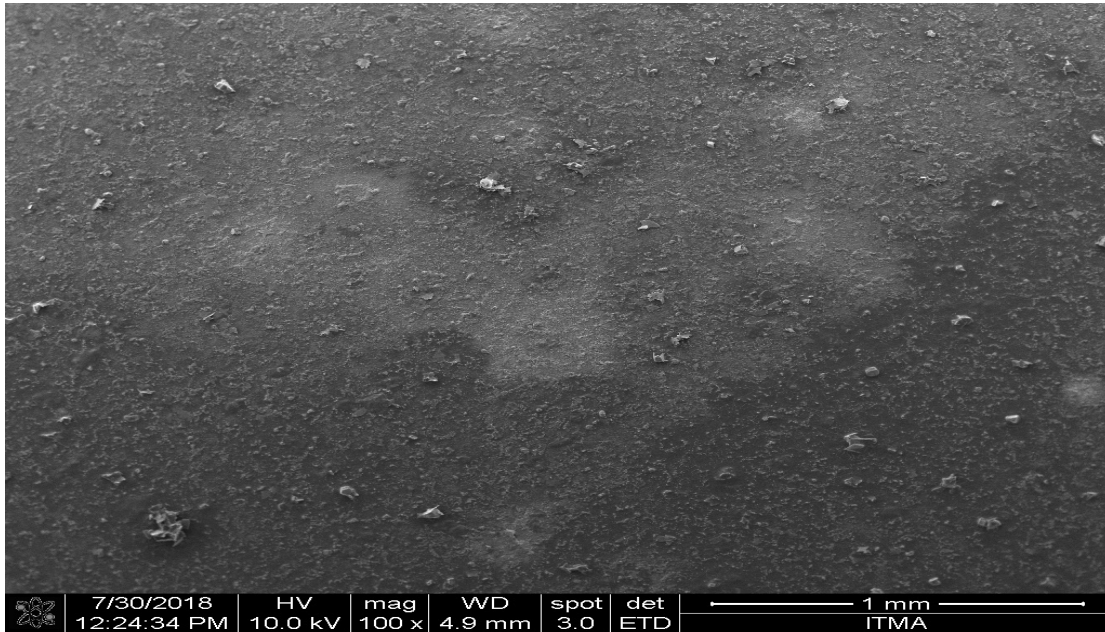


Figure 1.6. FESEM Micrograph of MASnI_3 Fabricated by One-step Deposition Method at 1 mm

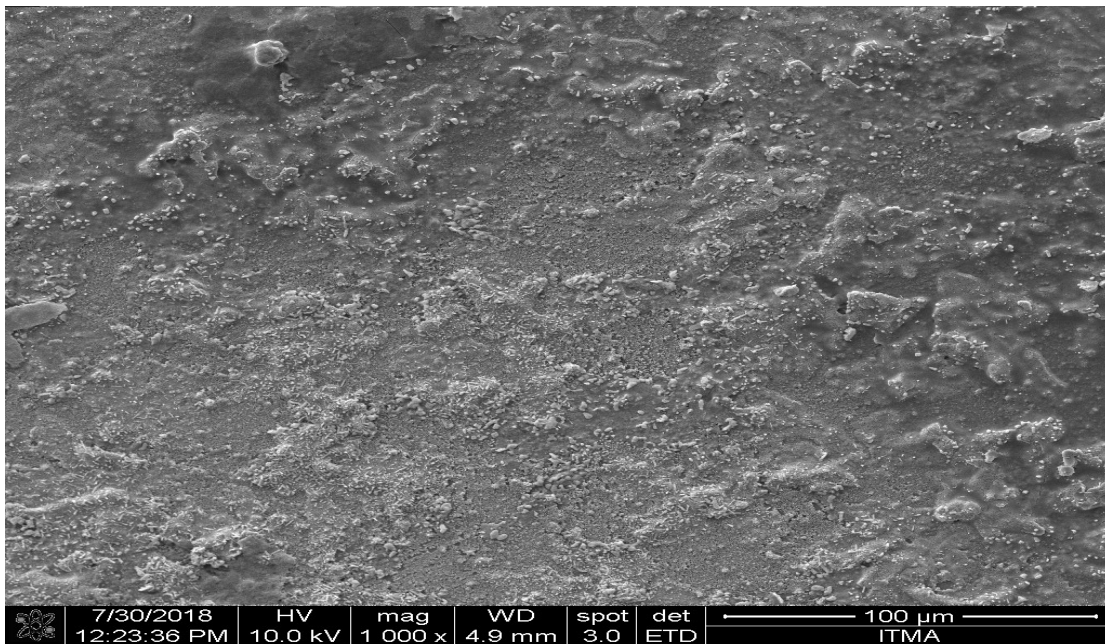


Figure 1.7. FESEM Micrograph of MASnI_3 Fabricated by One-step Deposition Method at 100 μm

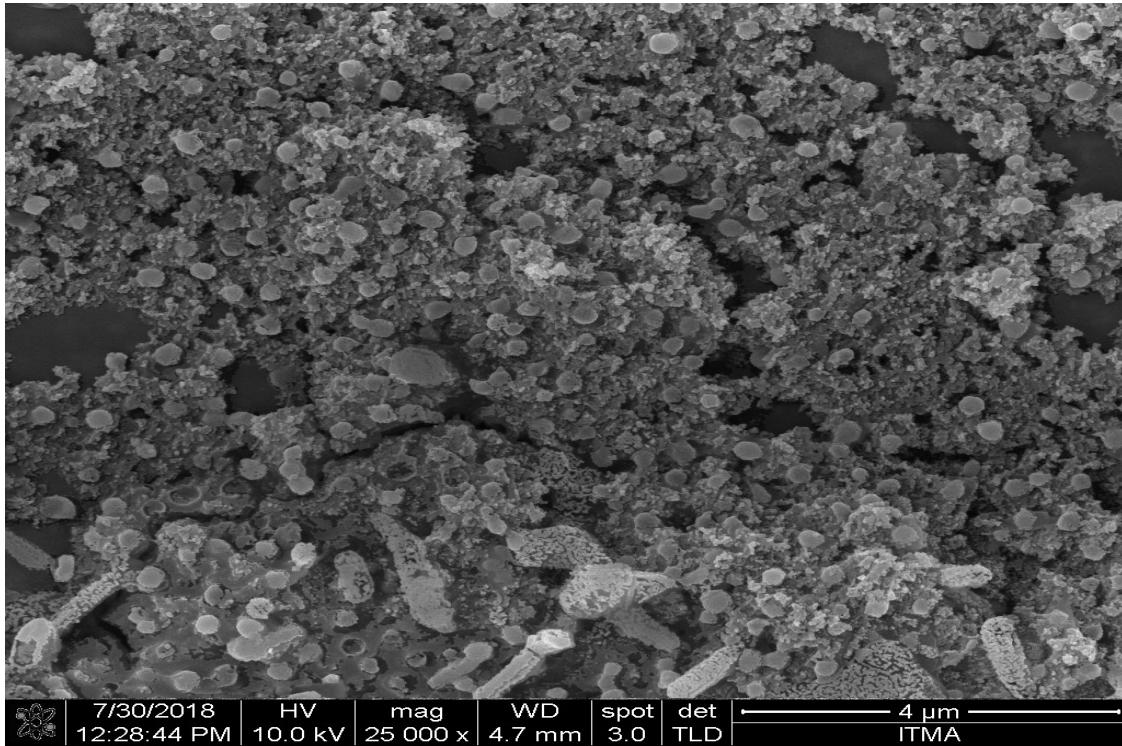


Figure 1.8. FESEM Micrograph of MASnI₃ Fabricated by One-step Deposition Method at 4 μm

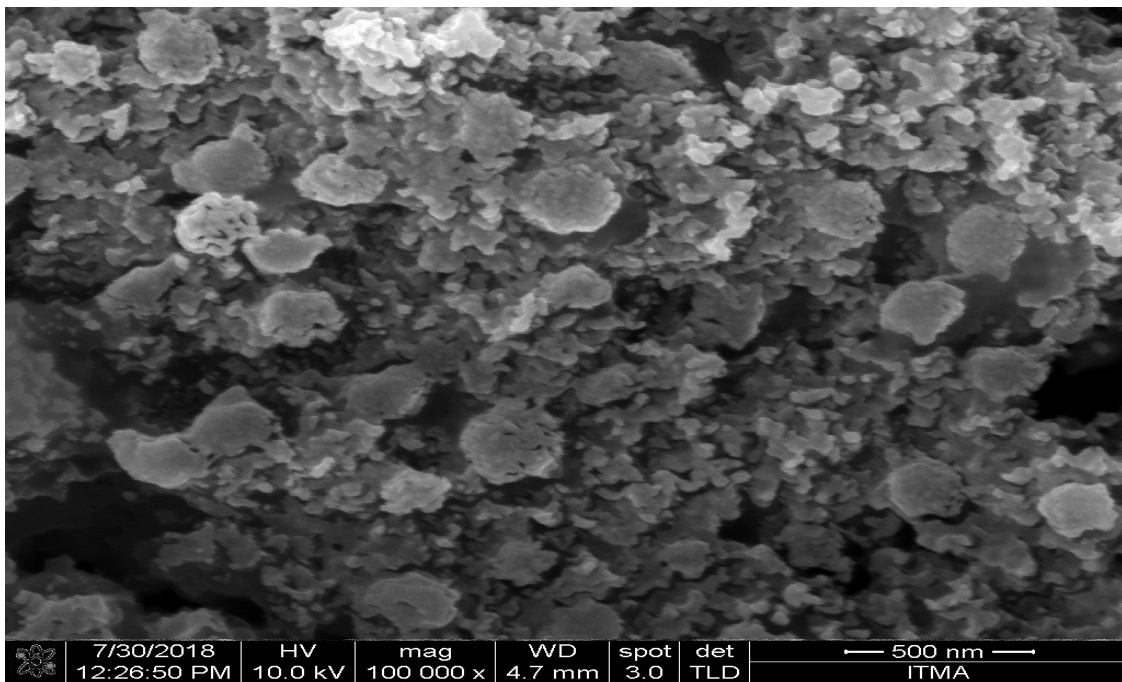


Figure 1.9. FESEM Micrograph of MASnI₃ Fabricated by One-step Deposition Method at 500 nm

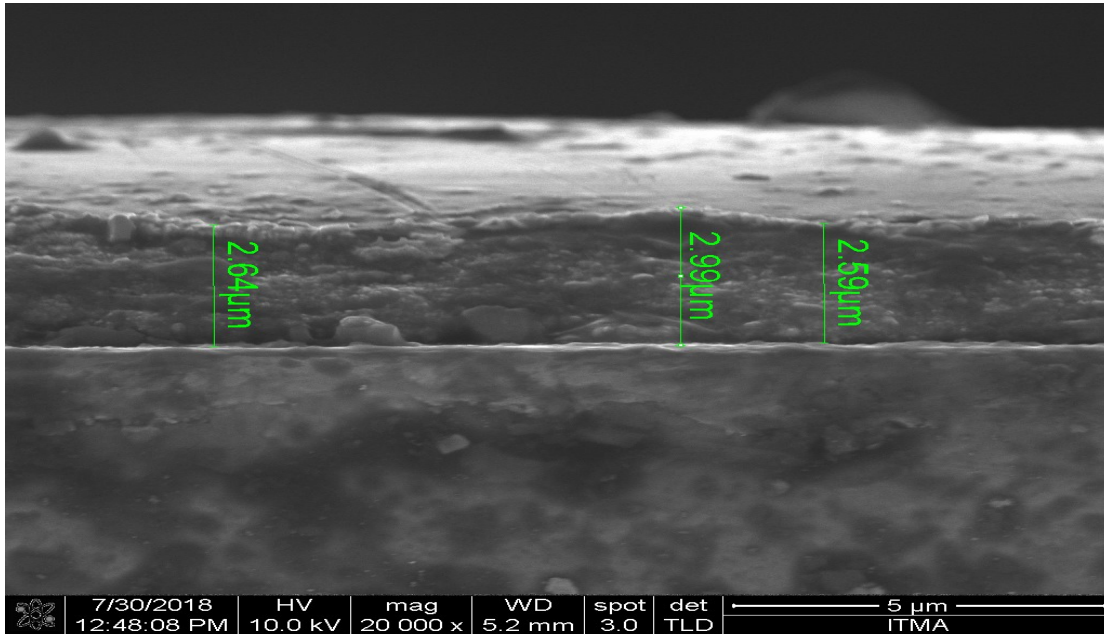


Figure 1.10. FESEM cross-sectional Micrograph of mp-TiO₂/MASnI₃ Fabricated by One-Step Deposition Method at 5 μm

Energy Dispersive X-ray (EDX) Measurement

The elemental compositions consist in different layers of the tin-based perovskite device measurement was carried out

using Energy Dispersive X-ray to confirm the presence and percentage compositions of various elements

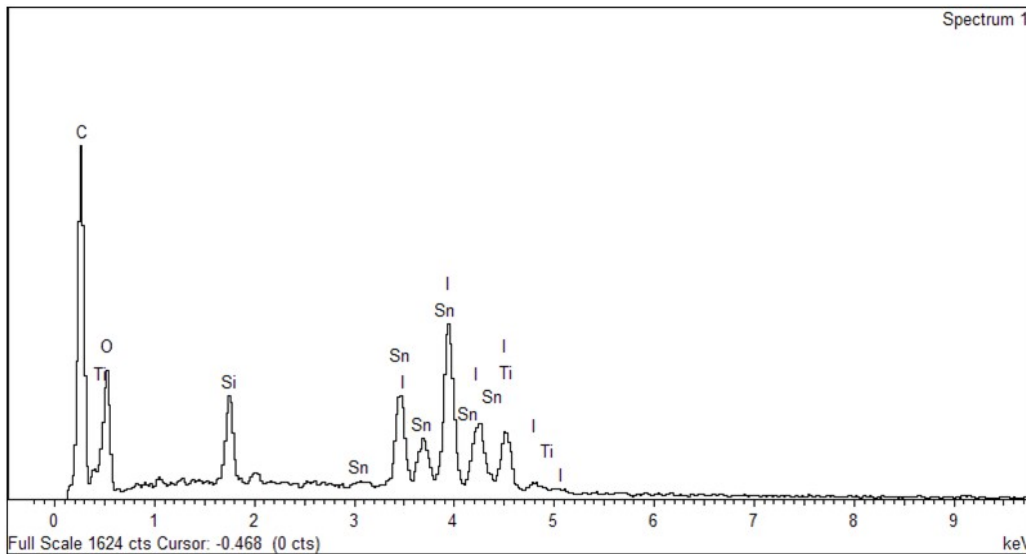


Figure 1.11. EDX Spectrum Obtained from the Mesoporous Sn-based Perovskite device.

To study the morphology of the device, Top view images at 1 mm, 100 μm 4 μm and 500 nm were recorded as obtained in figures 1.6, 1.7, 1.8 and 1.9 respectively. The figures show inhomogeneous coverage. Jelly like structure with large voids was observed in figure 1.8. The cross-sectional image in figure 1.10 shows infiltration of the mesoscopic layer into the

active layer with non-uniform film thickness averagely 2.74 μm. The presence of void observed in the top-view micrographs may results in either light to pass through the region uncovered by the perovskite without absorption leading to reduction of photocurrent allowing direct contact

between c-TiO₂ and the spiro-OMeTAD leading poor photovoltaic performance.

The uncontrolled film morphology in tin –based perovskite solar cells was a result of faster reaction between tin II iodide (SnI₂) with ammonium iodide (CH₃NH₃I) [18]. Film coverage has been reported as an important factor determining efficiency of organometal perovskite solar cells [19]. EDX results from figure 1.11 indicate the presence of the elemental compositions of the perovskite precursor solutions.

V. CONCLUSION

Tin-based hybrid perovskite with a chemical formula CH₃NH₃SnI₃ as an active layer was fabricated using solution based processing technique and characterized. Toxicity issue in perovskite solar cells could be solved using organo-tin-based perovskite material. The device based on MASnI₃ exhibited poor film coverage as observed from the FESEM micrographs. The uncontrolled film morphology in the tin-based perovskite solar cells was a result of faster reaction between tin II iodide (SnI₂) with ammonium iodide (CH₃NH₃I). Better film coverage can be attained by smoothing and optimizing the layer thickness by varying the precursor concentrations and spin coating parameters. It is concluded that the divalent tin (Sn) metal could be a better option to eliminate lead (Pb) in perovskite solar cells.

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