

SOFT LITHOGRAPHY BASED PRINTED METHYL AMMONIUM IODIDE HYBRID ORGANO METAL PEROVSKITE SOLAR CELL WITHOUT HOLE TRANSPORTING LAYER

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Abstract- *Organo-metal halide perovskite (MAPbX₃; X=I, Cl, Br) solar cells are emerging as serious candidates for thin film photovoltaics with power conversion efficiencies 19% already exceed. For owing to higher power conversion efficiency by using various methodologies and materials aimed at producing low cost, efficient photovoltaic cells, inorganic-organic lead halide perovskite materials appear particularly promising for next-generation solar devices. To date the highest efficiencies reported for perovskite solar cells so far have been obtained mainly with methyl ammonium lead halide materials. Here, we report perovskite solar cell power conversion efficiency 7.91% achieved without hole transporting layer where the current density, open circuit voltage and fill factor are 17.39 mA/cm², 0.89 V and 51.1% respectively under a standard illumination of 100 milliwatts per square centimeter. This was enabled by the growth of a CH₃NH₃PbI₃ layer with a controlled morphology via a methyl ammonium Iodide solution printed procedure. Printing of a solution of CH₃NH₃I with different concentrations follows the spin-coating of PbI₂, and the morphology of CH₃NH₃PbI₃ is found to strongly depend on the concentration of temperature and solvent evaporation completely. The coverage, pore-filling, and morphology of the deposited perovskite are found to be critical in the photovoltaic performance of the mesoporous TiO₂ based perovskite solar cells. Further improvement is expected for this material by applying our method in terms of understanding charge accumulation and transport properties of our devices. Organo lead halide perovskite is now regarded as a fast raising, leading and promising solar cell material, opening new windows in solar cell research.*

Keywords: *Perovskite solar cell, Hybrid Energy, Solar Energy, Materials engineering, CH₃NH₃PbI₃.*

I. INTRODUCTION

Now a days perovskite are promising materials for organic-inorganic hybrid solar cell, however, recently its attracted much with a great attention for future solar cell. Whereas the materials are like children to the scientist though the perovskite type materials has been found in 1839 [1]. In recent study the perovskite type materials show remarkable performance of their power conversion efficiency. Perovskite organic lead halide (CH₃NH₃PbI₃) has attracted much attention in the past two years [2]. Where the halide ion and metal part of perovskite structure playing major role for research because of it has some limitation at atmospheric condition [3]. As a sensitized solar cell, the perovskite structure of CH₃NH₃PbI₃, CH₃NH₃PbBr₃ and iodide liquid electrolyte were first employed to fabricate for solar cell [15-16] on TiO₂ surface. Though the power conversion efficiency was less than 6% [4-7]. After introducing polymer hole transporting materials to substitute for the liquid electrolyte and then the PCE exceed 9% [8]. After that it was found, the perovskite itself able to transfer photo excited electron to the TiO₂ layer by applying scaffold for confirmation [9][14-16]. More recently PCE

improved more than 20% with two step deposition fabrication method of perovskite absorber. Also vacuum deposition methods achieved impressive power conversion efficiency of over 15% [5].

The sequential deposition method has been proposed to obtain higher power conversion efficiency where the perovskite pores to inside the mesoporous TiO₂ film where PbI₂ solution coated first on mesoporous layer and then immersed the thin film of PbI₂ in a MAI (CH₃NH₃I) solution [10]. The power conversion efficiency showed 15% [5][12] and the vacuum deposited mixed halide perovskite (CH₃NH₃PbI_{3-x}Cl_x) solar cell showed 15.4% [5][17-19].

The bilayer architecture of perovskite (MAPbI₃) formed by printing procedure technology. The composition of perovskite PbI₂ 1M concentration with DMF and 10 mg of MAI with IPA was used because of it greatly improved the overall performance of devices. PbI₂ was deposited using a DMF while spinning the layer was dense and uniform were formed. The DMF is used for lead halides as effective solvent. However, the spin casting of PbI₂ gives uniform layer having uniform thickness of a small area. Though the uniformity of perovskite layer depends on the thickness of compact TiO₂ blocking layer.

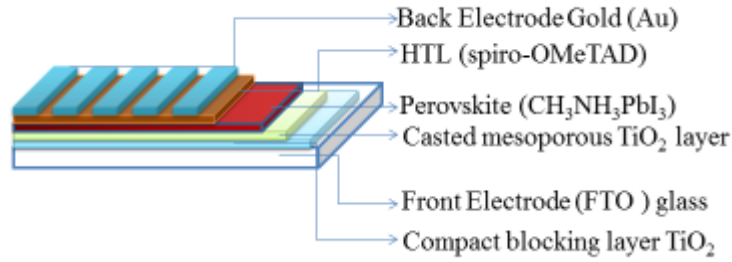


Fig. 1: Device architecture of printed cell Glass/ FTO/ bl-TiO₂/ ms-TiO₂-perovskite nanocomposite layer/ perovskite upper layer/ spiro-OMeTAD/Au.

Figure 1 represents the schematic diagram of the cell architecture and the perovskite layer deposition by printing technology.

In the figure 1 reveals that the active layer comprising mesoscopic and printed structure which is effective for sufficient absorbing the photons and properly collecting the charges, whereas the highly uniform perovskite layer lies in mesoporous TiO₂ layer. The highly work function Au materials were deposited next to the printed active layer as hole transporting and photo cathode, respectively.

II. METHODOLOGY OF THIN FILM FABRICATION

The formation perovskite active layer is extremely important and we developed our printing technology as fruitful tools for creating such active layer. The process involves several steps as depicted in figure 2.

The two-step method where CH₃NH₃I printed procedure is described schematically in Figure 2. Firstly, the mixture of lead iodide and DMF solvent with appropriately and spread over the surface of substrate and spin coater is accelerated to the desired RPM speed. Then evaporate the solvent by heat for a few minutes on the hot plate. Secondly dropping the CH₃NH₃I solution of IPA on the lead iodide layer for a few minutes, after cooling down the film. Thirdly, the layer color changes immediately to dark brown, formed crystal and then printed it with PDMS stamp. Fourthly, after that heated the printed film for 20 minutes at 100 C on a hot plate. After leaving the hot plate that was molded for several hours. Finally, converting into crystal and highly uniform layer after evaporating all solvent after several hours, we were able to get the desired CH₃NH₃I printed perovskite active layer. The morphology of perovskite film is comparable to others model, in figure 2 which has highly covered the whole area of the film with perovskite cuboids.

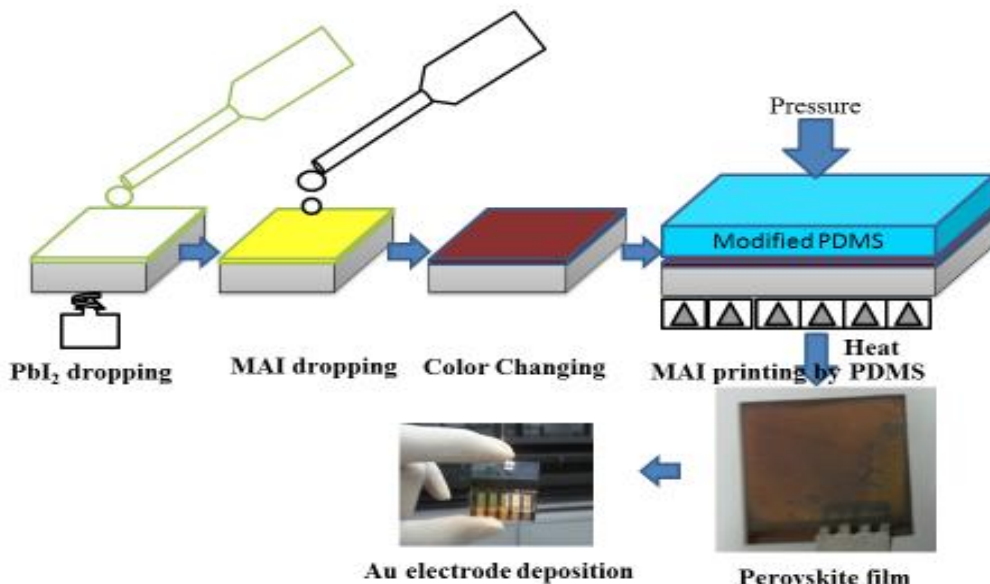


Fig 2: Printing procedure of perovskite active layer.

III. RESULTS AND DISCUSSION

We found that the two-step method follows of MAI printing procedure leads to the formation of MAPbI₃ cuboids and that the size and shape of these cuboids are greatly influenced by CH₃NH₃I concentration, keeping duration of MAI and temperature for solvent evaporation. As confirmed by the scanning electron microscopy (SEM) images in Figure 3, the size of the MAPbI₃ cuboids increases with higher temperature at 100 C. The average cuboid size is determined to be ~90 nm for 0.063M Methyl Ammonium Iodide. From the cross-sectional SEM images, the thickness of the cuboids is ~300–400 nm.

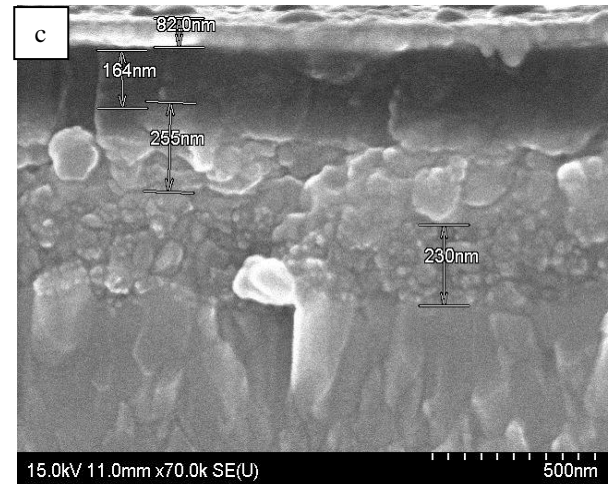
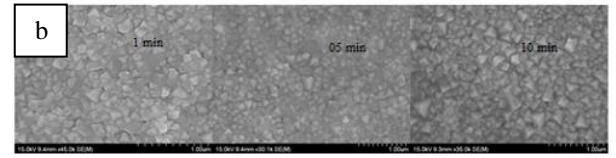
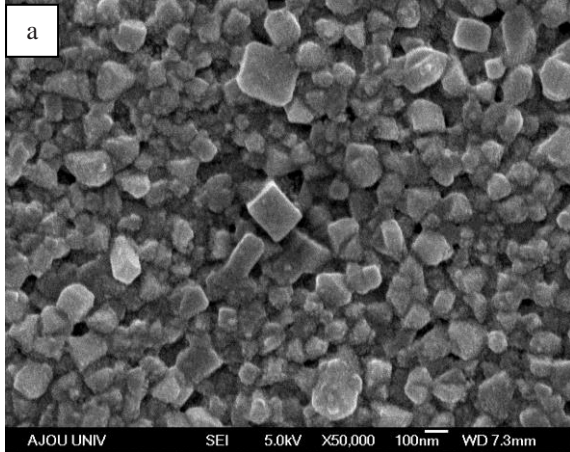


Fig.3: SEM image at different temperature and time duration; a-c; a. surface image at 100 C, b. SEM image at 100 C for different loading times for the 10 mg MAI concentration. c. Surface scanning electron microscopy (SEM) cross section of full devices.

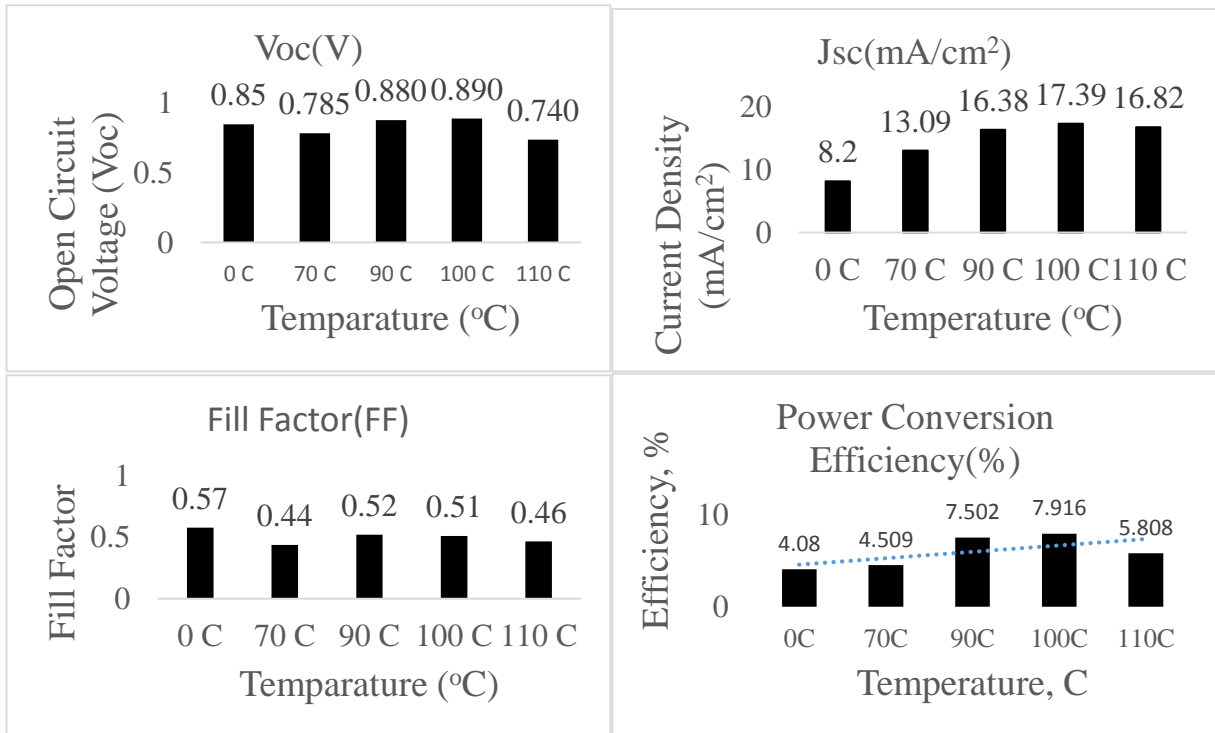


Fig.4: Effects of temperature on photovoltaic parameters and light-harvesting efficiency. a–d left to right clockwise, Short-circuit current density Jsc, open-circuit voltage Voc, fill factor (FF) and power conversion efficiency (PCE) versus applied temperature.

Table 1: Power conversion efficiency at different temperature of printed devices.

Temperature	V _{oc} (V)	J _{sc} (mA/cm ²)	FF	PCE(%)
0C	0.85	8.2	57.8	4.08
70C	0.785	13.096	0.439	4.509
90C	0.880	16.383	0.520	7.502
100C	0.890	17.392	0.511	7.916
110C	0.740	16.825	0.466	5.808

As we can see that the perovskite cuboids are much larger than TiO₂ nanoparticles (~50 nm), so perovskite is not a thin conformal layer covering the TiO₂ particles sandwiched with gold electrode. Also in Figure 3c, the TiO₂ pores are filled with PbI₂, with a capping layer of PbI₂ is also formed during the first coating step. All the PbI₂ is converted to perovskite during the second step of the printing procedure, as confirmed by X-ray diffraction (XRD) (data not shown). The perovskite therefore forms not only inside the TiO₂ pores, but also on top of the TiO₂ layer. Due to the pore size of the TiO₂ film, the growth of perovskite is limited inside the pores, whereas larger crystal growth is possible on top of the TiO₂ film. Finally the perovskite morphology is eventually found to play a more important role in a given cell structure although the layer structure is expected to influence the PCE.

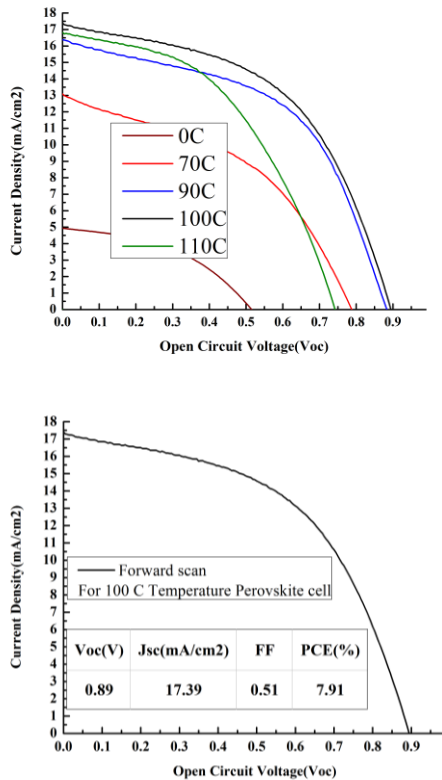


Fig.5: Current density and Voltage curve at different temperature and final I-V curve of devices.

As mentioned in the table 1 and figure 4b the higher current density 17.39 mA/cm² achieved from applied 100 °C temperature where higher open circuit voltage 0.89 V got also from 100 °C temperature scale. Overall

higher power conversion efficiency 7.91 % performed from 100 °C temperature. Over 100 °C, the devices burned and decreased the size of cuboids and overall fall the performance of the devices. Confirming that an intermediate cuboid size and optimal temperature for obtaining high photovoltaic performance as a result of excellent light harvesting and charge carrier extraction.

In the figure 6, as we can see that the absorption is about 90% of printed cell whereas one step method solution based reference film absorption capacity is so lower. However the photo transmittance of printed cell is comparatively lower than reference film case.

In the figure 5, the higher power conversion efficiency of 7.91% was achieved from printed MAI photovoltaic devices where the current density 17.39 mA/cm², open circuit voltage 0.89v and the fill factor are 51%.

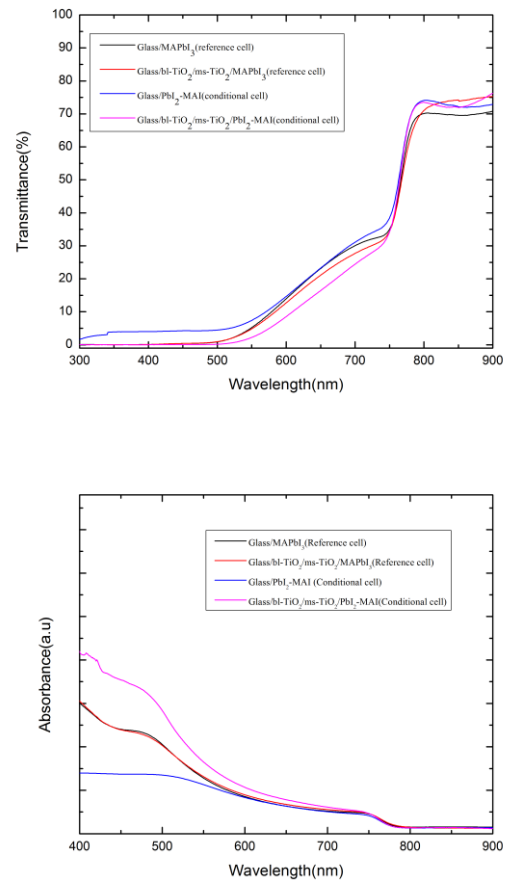


Fig.6: Incident light transmittance and photon absorption capacity of printed devices over solution casted one step method reference devices.

I. CONCLUSION

By applying soft lithography based two step method of CH₃NH₃I print follows of PbI₂ spin coated with proper solvent evaporation procedure, we have developed this reproducible for higher efficiency perovskite photovoltaic cell which without hole transporting layer. And the average power conversion efficiency as high as about 8%. That was very strongly dependent of solvent evaporation by applying proper temperature controlled to the fabricated devices.

Methods

Synthesis of CH₃NH₃I. Methylamine (27.86 ml, 40% in methanol, TCI) and hydroiodic acid (30 ml, 57 wt% in water, Aldrich) were mixed at 0 °C and stirred for 2 h. The precipitate was recovered by evaporation at 50 °C for 1 h. The product was washed with diethyl ether three times and finally dried at 60 °C in a vacuum oven for 24h.

Solar cell fabrication. After etched the FTO glasses were cleaned in an ultrasonic bath containing acetone, 2-isopropanol and DI water each for 30 min respectively and treated in a UV Ozone (UVO) cleaner for 30 min. The TiO₂ blocking layer (BL) was spin-coated on an FTO substrate at 3,000 r.p.m. for 30 s using 0.2 M titanium diisopropoxide bis (acetylacetonate) (75 wt% in isopropanol, Aldrich) in 2-isopropanol (99.8%, Aldrich) solution, which was heated at 125 °C for 10 min on the hot plate to remove organic compound and then annealed at 500 °C for 30 min in the furnace to prevent direct contact between FTO and hole conducting layer. After cooling to room temperature, the TiO₂ paste was spin-coated on the BL layer at 5,000 r.p.m. for 40 s, where the pristine paste was diluted in ethanol (1:3.5 wt%). After drying at 125 °C for 5 min, the film was annealed at 500 °C for 30 min, providing a thickness of about 300nm. CH₃NH₃PbI₃ was formed using two-step procedure where PbI₂ solution (1 M) was prepared by dissolving 462 mg PbI₂ (99%, Aldrich) in 1 ml N,N-dimethylformamide (DMF, 99.8%, Sigma-Aldrich) under stirring at 70 °C. PbI₂ solution (200µl) was spin-coated on the mesoporous TiO₂ film at 4,000 r.p.m. for 40 s. After spinning, the film was dried at 70 °C for 5 min and after cooling to room temperature, 500 µl of 0.063 M (10 mg ml⁻¹ CH₃NH₃I solution in 2-propanol was loaded on the PbI₂-coated substrate for 01 to 10 min (loading time) and printed by PDMS stamp and annealed at 100 °C for 20 min on hot plate for solvent evaporation and after leaving hot plate keeping about 7 hours with keeping molded. Finally, 80 nm of gold was deposited on the perovskite film by e-beam evaporator to form the back contact in the devices. The devices fabrication was carried out under controlled atmospheric condition.

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