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 efficiencies 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 immerged 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 (CH3NH3PbI3,Cl3) 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.
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 TiO$_2$ 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 CH$_3$NH$_3$I 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 CH$_3$NH$_3$I 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 CH$_3$NH$_3$I printed perovskite active layer. The morphology of perovskie 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.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>FF</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0°C</td>
<td>0.85</td>
<td>8.2</td>
<td>57.8</td>
<td>4.08</td>
</tr>
<tr>
<td>70°C</td>
<td>0.785</td>
<td>13.096</td>
<td>0.439</td>
<td>4.509</td>
</tr>
<tr>
<td>90°C</td>
<td>0.880</td>
<td>16.383</td>
<td>0.520</td>
<td>7.502</td>
</tr>
<tr>
<td>100°C</td>
<td>0.890</td>
<td>17.392</td>
<td>0.511</td>
<td>7.916</td>
</tr>
<tr>
<td>110°C</td>
<td>0.740</td>
<td>16.825</td>
<td>0.466</td>
<td>5.808</td>
</tr>
</tbody>
</table>

As we can see that the perovskite cuboids are much larger than TiO$_2$ nanoparticles (~50 nm), so perovskite is not a thin conformal layer covering the TiO$_2$ particles sandwiched with gold electrode. Also in Figure 3c, the TiO$_2$ pores are filled with PbI$_2$, with a capping layer of PbI$_2$ is also formed during the first coating step. All the PbI$_2$ 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 TiO$_2$ pores, but also on top of the TiO$_2$ layer. Due to the pore size of the TiO$_2$ film, the growth of perovskite is limited inside the pores, whereas larger crystal growth is possible on top of the TiO$_2$ 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.

![Graph 1](image1.png)

As mentioned in the table 1 and figure 4b the higher current density 17.39 mA/cm$^2$ 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 5, 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/cm$^2$, open circuit voltage 0.89v and the fill factor are 51%.

![Graph 2](image2.png)

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

![Graph 3](image3.png)

As we can see that the perovskite cuboids are much larger than TiO$_2$ nanoparticles (~50 nm), so perovskite is not a thin conformal layer covering the TiO$_2$ particles sandwiched with gold electrode. Also in Figure 3c, the TiO$_2$ pores are filled with PbI$_2$, with a capping layer of PbI$_2$ is also formed during the first coating step. All the PbI$_2$ 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 TiO$_2$ pores, but also on top of the TiO$_2$ layer. Due to the pore size of the TiO$_2$ film, the growth of perovskite is limited inside the pores, whereas larger crystal growth is possible on top of the TiO$_2$ 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.

![Graph 4](image4.png)

![Graph 5](image5.png)

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 CH$_3$NH$_3$I print follows of PbI$_2$ 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.

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Methods
Synthesis of CH$_3$NH$_3$I. 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 24 h.

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 TiO$_2$ 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 TiO$_2$ 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 100 °C for 20 min on hot plate (loading 0.063 M (10 mg ml$^{-1}$) CH$_3$NH$_3$PbI$_3$ solution (200 μl)) was formed using two-step procedure where PbI$_2$ solution (1 M) was prepared by dissolving 462 mg PbI$_2$ (99%, Aldrich) in 1 ml N,N-dimethylformamide (DMF, 99.8%, Sigma-Aldrich) under stirring at 70 °C. PbI$_2$ solution (200 μl) was spin-coated on the mesoporous TiO$_2$ 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$^{-1}$) CH$_3$NH$_3$I solution in 2-propanol was loaded on the PbI$_2$-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.

Reference