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15.76% Efficiency Perovskite Solar Cell Prepared under High Relative Humidity: Importance of PbI$_2$ Morphology in Two-Step Deposition of CH$_3$NH$_3$PbI$_3$

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Perovskite solar cell prepared at RH = 50%

- $J_{sc} = 21.27 \text{ mA/cm}^2$
- $V_{oc} = 1.033 \text{ V}$
- FF = 0.718
- PCE = 15.76%
Abstract

We report here an efficient method for preparing high efficiency CH$_3$NH$_3$PbI$_3$ perovskite solar cell under high relative humidity, where morphology of PbI$_2$ was found to be of crucial importance. CH$_3$NH$_3$PbI$_3$ was formed on mesoporous TiO$_2$ layer by two-step spin coating method. During the first-step spin-coating procedure to form PbI$_2$ layer, FTO glass substrate was pre-heated at temperature ranging from room temperature (without pre-heating) to 60°C. An average power conversion efficiency (PCE) showed 11.16% without pre-heating, which was improved to 15.31% as the temperature of substrate ($T_{\text{sub}}$) was raised to 50°C. Pre-heated substrate led to higher photocurrent and voltage than non-pre-heated one. When $T_{\text{sub}}$ increased to 60°C, a PCE was declined to 10.49% due to large portion of unreacted PbI$_2$. Compared to the non-pre-heated substrate, unreacted PbI$_2$ was presented on the pre-heated substrates after the second-step spin-coating of CH$_3$NH$_3$I as confirmed by X-ray diffraction and time-of-flight secondary ion mass spectroscopy (TOF-SIMS) depth profile analyses. Improved crystallinity of PbI$_2$ induced by substrate pre-heating was responsible for incomplete conversion of PbI$_2$ to CH$_3$NH$_3$PbI$_3$. Nevertheless, increases in photocurrent and voltage by pre-heating was attributed to better pore filling and surface coverage of perovskite layer, as observed by focused ion beam assisted scanning electron microscopy (FIB-SEM) images, which was associated with morphology of PbI$_2$ layer. According to the study on effect of CH$_3$NH$_3$PbI$_3$ thickness controlled by concentration of PbI$_2$, substrate temperature was found to play predominant role in determining photovoltaic performance rather than thickness. A best PCE of 15.76% was achieved along with photocurrent density of 21.27 mA/cm$^2$, voltage of 1.033 V and fill factor of 0.718 from the perovskite solar cell prepared in 50% relative humidity.
**Keywords:** Perovskite, CH$_3$NH$_3$PbI$_3$, Relative humidity, PbI$_2$ morphology, Substrate temperature
Introduction

Since the first report on long-term durable solid state perovskite solar cell in 2012 [1] following the reports on organo lead halides as sensitizer in liquid electrolyte based solar cell in 2009 [2] and 2011 [3], enormous attention has been focused on perovskite solar cell due to high power conversion efficiency (PCE) attained by low-cost and facile fabrication process. As a result, a PCE of 20.1% was certified in 2014 [4]. Solution-processed and vapor deposition methods have been proposed to achieve high quality perovskite layer and thereby high efficiency. Deposition from PbCl$_2$ and CH$_3$NH$_3$I vapors led to CH$_3$NH$_3$PbI$_3$ (MAPbI$_3$) phase with preferred orientation and flat surface morphology [5], which demonstrated a PCE of 15.4%. One-step spin coating using PbCl$_2$ and CH$_3$NH$_3$I could also result in highly oriented MAPbI$_3$ phase, leading to a PCE of 19.3% [6]. Solvent-engineering techniques were developed in one-step spin coating of PbI$_2$ and CH$_3$NH$_3$I, which produced large crystal domains with flat surface of MAPbI$_3$ [7,8]. One-step solvent engineering method gave recently rise to a PCE approaching 20% [9]. Apart from one-step solution process, a two-step sequential deposition has alternatively been proposed, in which reaction of CH$_3$NH$_3$I with the spin-coated PbI$_2$ layer readily formed MAPbI$_3$ [10]. Crystal size was found to be controlled by varying CH$_3$NH$_3$I concentration in two-step deposition procedure and a PCE of 17.01% was achieved from large MAPbI$_3$ cuboids [11]. Regardless of preparation methods, MAPbI$_3$ has been prepared under negligible or extremely low humidity in glove box. However, preparation in the glove box may be limited to mass production from the industrial point of view. We have been thus motivated to fabricate perovskite solar cell in ambient condition even under high humidity condition. To achieve high photovoltaic performance of perovskite solar cell prepared under relative humidity higher than $>$30%, modified two-step coating
method has been designed and carefully conducted. While we were investigating and developing fabrication of high efficiency perovskite solar cell under high relative humidity condition, a method for 12.73% perovskite solar cell prepared under high relative humidity was reported using a low-pressure chemical vapor deposition technology [12].

Here we report an effective way for preparing high efficiency MAPbI$_3$ perovskite solar cell under high relative humidity. In two-step coating procedure, morphology of the PbI$_2$ layer deposited on the mesoporous TiO$_2$ coated FTO glass substrate is crucial in determining the final morphology of MAPbI$_3$ and photovoltaic performance, which is found to depend significantly on the substrate temperature while preparing the PbI$_2$ layer under indoor humidity. Dependence of photovoltaic performance on the substrate pre-heating temperature has been investigated. Perovskite solar cell prepared under relative humidity of around 50% demonstrated a PCE of 15.76%.

**Methods**

**Materials synthesis.** CH$_3$NH$_3$I was synthesized by reaction of 27.8 mL of CH$_3$NH$_2$ (40 wt.% in methanol, TCI) with 30 mL of HI (57 wt.% in water, Aldrich) in a round bottomed flask under vigorous stirring for 2 h in ice bath [1,3]. The precipitated CH$_3$NH$_3$I was collected using rotary evaporator at 50 °C for 1 h, washed with diethyl ether several times and finally dried in vacuum for 24 h. TiO$_2$ nanoparticles with average diameter of about 50 nm were synthesized hydrothermally according to the method reported elsewhere [13]. The seed particles with diameter of about 20 nm were first synthesized using titanium isopropoxide (97%, Aldrich) in acidic condition at 230 °C for 12 h. Hydrothermal procedure
was repeated to grow the seed particles. A TiO$_2$ paste was prepared by mixing nanocrystalline TiO$_2$, terpineol, ethyl cellulose and lauric acid with nominal ratio of 1.25 : 6 : 0.9 : 0.1. For controlling thickness of mesoporous TiO$_2$ film, the paste was further diluted with ethanol (99.9%, Samchun).

**Solar cell fabrication.** Solar cells were fabricated under indoor humidity, usually higher than 40%. FTO glass (Pilkington, TEC-8, 8 ohms/sq) was cleaned in a UV-Ozone cleaner for 15 min, followed by washing with detergent solution and acetone. The substrate was further cleaned by sonication in an ethanol. 60 nm-thick compact TiO$_2$ was formed on the cleaned FTO glass by spin-coating the 0.15 M solution of titanium diisopropoxide bis(acetylacetonate) (75 wt% in isopropanol, Aldrich) in 1-butanol (99.8%, Aldrich) at 700 rpm for 8 s, 1000 rpm for 10 s and 2000 rpm for 40 s, which was dried at 125 °C for 5 min. A 150 nm-thick mesoporous TiO$_2$ layer was formed on the compact TiO$_2$ layer by spin-coating the diluted TiO$_2$ paste (0.14 g/ml) at 2000 rpm for 20s. After the coating, the substrate was dried at 125 °C for 5 min and annealed at 550 °C for 1 h. The mesoporous TiO$_2$ film was post-treated with 0.02 M aqueous TiCl$_4$ (>98%, Aldrich) solution at 70 °C for 10 min, followed by annealing at 500 °C for 30 min. PbI$_2$ solutions were prepared by dissolving 498 (1.0 M), 392 (0.8 M) and 290 (0.6 M) mg PbI$_2$ (99%, Aldrich) in 1 ml N,N-dimethylformamide (DMF, 99.8%, Aldrich) at 60 °C. 20 µl of PbI$_2$ solution was spin-coated on the mesoporous TiO$_2$ film at 7000 rpm for 20 s. The solution temperature was kept at 60 °C while spin-coating. Before PbI$_2$ coating, the substrates were pre-heated at 40 °C, 50 °C, and 60 °C on hot plate respectively. After the coating, the film was dried at 40 °C for 3 min, followed by 100 °C for 5 min. To convert the PbI$_2$ layer to MAPbI$_3$, 300 µl of 0.044 M (7 mg/ml) CH$_3$NH$_3$I dissolved in 2-propanol was spin-coated on top of the PbI$_2$ layer at 0 rpm
for 45 s (loading time) followed by 4000 rpm for 20 s, which was dried at 100 ºC for 5 min. A spiro-MeOTAD solution was prepared by dissolving 72.3 mg of spiro-MeOTAD in 1 ml chlorobenzene, in which 28.8 µl of 4-tert-butyl pyridine and 17.5 µl of lithium bis(trifluromethanesulfonyl)imide (LiTFSI) solution (520 mg/1 ml acetonitrile (99.8%, Aldrich)) was added. The spiro-MeOTAD solution was spin-coated on the MAPbI₃ film at 4000 rpm for 20 s. Finally, gold was thermally evaporated at 1Å/s.

Characterization. Photocurrent density and voltage curves were recorded using a Keithley 2400 source meter under AM 1.5G one-sun illumination (100 mW/cm²) provided by a solar simulator (Oriel Sol 3A class AAA). A 450 W Xenon lamp (Newport 6279NS) was used as a light source. The light intensity was adjusted using a NREL-calibrated Si solar cell equipped with KG-2 filter. During the measurement the device was covered with a metal mask with aperture area of 0.10 cm². Morphologies were investigated using a high-resolution field emission scanning electron microscopy (HR FE-SEM, JSM-7600F, JEOL) and a focused ion beam assisted SEM (FIB-SEM, Zeiss Auriga). The crystal structure of the PbI₂ and MAPbI₃ formed on the mesoporous-TiO₂ film was investigated using an X-ray diffraction measurement (XRD, D8 ADVANCE, Bruker Corporation) with Cu Kα radiation at scan rate of 4 ºC/min under operation condition of 40 kV and 40 mA. The absorption spectra of PbI₂ and MAPbI₃ films were analyzed using an UV/VIS spectrometer (Lambda 35, Perkinelmer) in the wavelength ranging from 300 to 900 nm. Photoluminescence (PL) spectra were measured by Cary Eclipse Fluorescence Spectrophotometer (Agilent Technologies), where the excited wavelength was 530 nm and detected in the wavelength ranging from 600 to 900 nm with 10 nm increment. Depth profile of the MAPbI₃ films were recorded using time-of-flight secondary ion mass spectrometry (TOF-SIMS, Model-TOF-SIMS 5 of ION-
TOF GmbH, Germany), where the pulsed primary ions from a 25 keV Bi$^+$ liquid-metal ion gun were used to pelt down the sample surface to produce secondary ions, and 1 keV O$_2$ source was used to sputter out the layers from the sample surface in order to investigate the depth. The sputtering was processed on $150 \times 150$ µm$^2$, whereas the analysis was done on $40 \times 40$ µm$^2$ area for all samples. The layer thickness was measured by an alpha-step IQ surface profiler (KLA Tencor).

Results and discussion

Two-step spin coating was performed outside glove box and under indoor humidity condition. In two-step spin coating procedure in the glove box, the DMF solution of PbI$_2$ has been normally spin-coated on the FTO glass substrate without pre-heating the substrate. However, we found that a turbid yellow PbI$_2$ film was formed at indoor humidity condition, which was serious as relative humidity increased. For the case of pre-heating the substrate, the deposited PbI$_2$ layers become more transparent. This indicates that morphology of the deposited PbI$_2$ film is likely to be influenced by the substrate pre-heating. Figure 1 shows plane-view and cross-sectional SEM images of the PbI$_2$ films depending on the pre-heating temperature. Imperfect coverage of PbI$_2$ on the substrate with porous nature is observed without pre-heating, whereas the substrate is fully covered with PbI$_2$ when the substrate is pre-heated. It is also found that perovskite is well infiltrated in mesopores of TiO$_2$ film upon pre-heating the substrate compared to non-pre-heated substrate. The PbI$_2$ layer thickness increases with increasing the pre-heating temperature from 40 °C to 60 °C. Average thickness of the PbI$_2$ film is estimated to be 300 nm, 350 nm, 400 nm and 540 nm without pre-heating.
and with pre-heating at 40 °C, 50 °C and 60 °C, respectively. This increase seems to be related to competition between solvent evaporation rate and PbI₂ crystallization rate, that is, PbI₂ crystallization rate becomes higher than the solvent evaporation rate as the pre-heating temperature increases.

![Fig. 1 Plane-view SEM images of PbI₂ layer deposited on the mesoporous TiO₂ coated FTO substrate, where the substrate was preheated at (a) room temperature (without pre-heating), (b) 40 °C, (c) 50 °C and (d) 60 °C and (e-h) corresponding cross-sectional SEM images. Scale bars in (a-d) represent 1 um and 300 nm in (e-h).](image)

**Figure 1** shows SEM images of MAPbI₃ formed by spin-coating of CH₃NH₃I solution on the PbI₂ coated substrate prepared at different substrate temperature. Cuboid MAPbI₃ crystals formed with gaps between crystals while depositing CH₃NH₃I on the PbI₂ prepared without pre-heating (Figure 2(a)). On the other hand, cuboids are closely packed when the substrates are pre-heated (Figures 2(b)-(d)). It is noted that MAPbI₃ size is bigger as the pre-heating temperature increase (~ 200 nm without pre-heating, ~400 nm at 40 °C and 50 °C and ~800 nm at 60 °C), which is associated with conversion rate of PbI₂ to MAPbI₃. If the conversion reaction requires longer time, crystal is expected to grow bigger. It was reported that it took very long time (several days) to get large sized single crystal MAPbI₃ [14-17],
which means that slow reaction leads to large crystal. Thus, an increase in MAPbI₃ crystal with pre-heating temperature is probably ascribed to slower reaction due to the increased crystallinity and in part thickness of PbI₂.

![SEM images](image)

**Fig. 2** Cross-sectional and plane-view (insets) SEM images of CH₃NH₃PbI₃ (MAPbI₃) formed by deposition of CH₃NH₃I on the PbI₂ layer formed at substrate temperature of (a) room temperature (without pre-heating), (b) 40 °C, (c) 50 °C and (d) 60 °C. Scale bars represent 100 nm (1 µm in insets).

X-ray diffraction was performed to investigate any change in crystallinity depending on the substrate pre-heating temperature. **Figure 3(a)** shows XRD patterns of the PbI₂ films on the mesoporous TiO₂ coated FTO glass at different pre-heating temperature. The (001) peak at 2 theta = 12.6° becomes intense and its full width at half maximum (FWHM) is narrowed after pre-heating and as the pre-heating temperature increases, which indicates that
crystallinity and X-ray crystallite size increase simultaneously. Such an improved crystallinity of PbI₂ is expected to retard the conversion of PbI₂ into MAPbI₃. **Figure 3(b)** shows XRD patterns of MAPbI₃. Compared to full conversion of PbI₂ into MAPbI₃ without pre-heating, unreacted PbI₂ peak appears upon pre-heating the substrate and its intensity increases as the pre-heating temperature increase. As expected, large portion of the unreacted PbI₂ at high substrate pre-heating temperature is attributed to the improved crystallinity of the deposited PbI₂, associated with longer reaction period. We have tried to convert fully the PbI₂ prepared at pre-heating temperature of 60 °C into MAPbI₃ by prolonged the loading time of CH₃NH₃I, it was however hard to be successful because PbI₂ would start to dissolve partially at long exposure to 2-propanol. Although some unreacted PbI₂ is presented in the film, the residual PbI₂ was reported to bring about a passivation effect in perovskite solar cells [18].
**Fig. 3** X-ray diffraction patterns of (a) PbI$_2$ and (b) MAPbI$_3$ films depending on the substrate temperature. Inset in (a) shows full width at half maximum (FWHM) of (001) peak of PbI$_2$. The data were collected using PbI$_2$ and MAPbI$_3$ film formed on mesoporous TiO$_2$ deposited FTO glass substrates.

TOF-SIMS depth profiling was carried out for elemental analysis in the film. **Figure 4** displays the depth profile of the MAPbI$_3$ layer formed on the mesoporous TiO$_2$ coated FTO glass substrate depending on the substrate pre-heating temperature. Elements of C, N, H, Pb, I, Ti, O, Sn and F were detected, where H, N, Pb, I, Ti, O and Sn are displayed in the figure. As can be seen in **Figure 4**, Pb decreases in parallel with I and then their intensities are not changed with time. Large cuboid of perovskite results in inhomogeneous perovskite capping
layer, and both parts with thin and thick perovskite capping layer are etched simultaneously during the TOF-SIMS measurement. As a result, the Pb and I profiles appear to decrease when crossing the perovskite capping layer. This indicates that Pb and I are in the same compound such as MAPbI$_3$ and/or PbI$_2$. Ti and O increase simultaneously and then their intensities are saturated, which is due to mesoporous TiO$_2$ film. For the case of without pre-heating the substrate, the intensities of Pb and I decrease gradually up to about 100 s (Figure 4(a)), while those decreases up to 180 s for the case of 60 °C-pre-heated case (Figure 4(d)). This indicates that the latter case has thicker MAPbI$_3$ layer. Since no PbI$_2$ peak is detected for the non-pre-heated case, depth profiling of Pb and I comes from pure MAPbI$_3$. There is difference in depth profile when comparing depth profile of Pb and I for the 60 °C-pre-heated sample with that for the non-pre-heated one in Figure 4(a) and (d), which may be due to the presence of PbI$_2$ as detected by XRD. Pb content in PbI$_2$ is 50% with respect to iodide, while Pb is 33% in MAPbI$_3$. The decreasing rate of Pb from 0 s to 100 s in the 60 °C-pre-heated sample is slower than that in the non-pre-heated one, which is indicative of higher Pb content. The unreacted PbI$_2$ is probably to be presented in bulk of perovskite capping layer, because the conversion of PbI$_2$ in bulk of thin film into MAPbI$_3$ takes much longer time compared to the conversion rate of PbI$_2$ in the pores of mesoporous TiO$_2$ film. It has been reported that CH$_3$NH$_3$I insertion hardly proceeds beyond the surface of thin PbI$_2$ films, and that the complete transformation of the crystal structure requires several hours while the conversion of PbI$_2$ in mesoporous TiO$_2$ into MAPbI$_3$ is completed within one minute [10]. If the wide band gap insulating PbI$_2$ layer is presented near the FTO, charge collection at FTO may be significantly hindered by the unreacted PbI$_2$ layer. However, all the samples prepared by pre-heating the substrate shows higher photocurrent despite the presence of PbI$_2$ (see Figure 5), supporting the unreacted PbI$_2$ exists in the bulk of MAPbI$_3$ capping layer.
**Fig. 4.** Time-of-flight secondary ion mass spectroscopy (TOF-SIMS) profile for the MAPbI$_3$ layer formed on the mesoporous TiO$_2$ deposited FTO glass substrate by reacting CH$_3$NH$_3$I with the PbI$_2$ deposited at substrate temperature of (a) without pre-heating, (b) 40 °C, (c) 50 °C and (d) 60 °C. Depth profiling was performed from perovskite layer to FTO substrate.

**Figure 5** shows short-circuit photocurrent density ($J_{sc}$), open-circuit voltage ($V_{oc}$), fill factor (FF) and power conversion efficiency (PCE) depending on the pre-heating temperature. The average photovoltaic parameters are listed in **Table 1**. $J_{sc}$ and $V_{oc}$ are significantly higher for the 40 °C- and 50 °C-pre-heated cases than for the non-pre-heated one. In addition, FF is slightly higher for the pre-heated cases. $J_{sc}$ is improved from 16.94 mA/cm$^2$ for the non-pre-heated case to 19.63 and to 20.71 mA/cm$^2$ upon deposition of PbI$_2$ on the 40 °C- and 50 °C-pre-heated substrates, respectively. $V_{oc}$ is also enhanced from 937 mV to 1012 and 1017 mV. As a result, average PCE is improved from 11.16% to 14.53 and 15.31%. On the other hand,
the device prepared based on 60 °C-pre-heating procedure deteriorates PCE to 10.49% along with large standard deviation. Compared to the non-pre-heated case, the lower PCE of the 60 °C-pre-heated case is mainly due to lower FF in spite of slightly higher $J_{sc}$ and $V_{oc}$. The superior performance obtained by pre-heating procedure (40 °C and 50 °C) is due to morphology of MAPbI$_3$ determined by the deposited PbI$_2$ morphology, as investigated previously. To understand property-structure relation, FIB-assisted SEM images are obtained for the full cell.

![Fig. 5](image)

**Fig. 5** Effect of substrate pre-heating temperature on (a) short-circuit photocurrent density ($J_{sc}$), (b) open-circuit voltage ($V_{oc}$), (c) fill factor (FF) and (d) power conversion efficiency (PCE).

**Table 1.** Short-circuit current density ($J_{sc}$), open-circuit voltage ($V_{oc}$), fill factor (FF) and power conversion efficiency (PCE) of MAPbI$_3$ solar cells by pre-heating conditions at AM 1.5G one-sun illumination (100 mW/cm$^2$). Relative humidity was about 44%.
<table>
<thead>
<tr>
<th>Pre-heating temperature</th>
<th>J&lt;sub&gt;sc&lt;/sub&gt; (mA/cm&lt;sup&gt;2&lt;/sup&gt;)</th>
<th>V&lt;sub&gt;oc&lt;/sub&gt; (V)</th>
<th>FF</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>w/o</td>
<td>16.94±0.47</td>
<td>0.937±0.010</td>
<td>0.70±0.01</td>
<td>11.16±0.43</td>
</tr>
<tr>
<td>40 °C</td>
<td>19.63±0.33</td>
<td>1.012±0.007</td>
<td>0.73±0.01</td>
<td>14.53±0.17</td>
</tr>
<tr>
<td>50 °C</td>
<td>20.71±0.35</td>
<td>1.017±0.018</td>
<td>0.73±0.01</td>
<td>15.31±0.35</td>
</tr>
<tr>
<td>60 °C</td>
<td>17.34±1.62</td>
<td>0.970±0.030</td>
<td>0.61±0.06</td>
<td>10.49±2.31</td>
</tr>
</tbody>
</table>

FIB-SEM images for the full cell in Figure 6 shows clearly each layer. The mesoporous TiO<sub>2</sub> film is not fully covered by the MAPbI<sub>3</sub> crystals when processing without pre-heating as can be seen in Figure 6(a). The uncovered TiO<sub>2</sub> is directly contacted with spiro-MeOTAD, which is likely to be responsible for low V<sub>oc</sub> due to recombination [19]. The relatively low J<sub>sc</sub> may be attributed to low MAPbI<sub>3</sub> coverage. The coverage of the TiO<sub>2</sub> layer with MAPbI<sub>3</sub> becomes better by substrate pre-heating and fully covered upon pre-heating the substrate at 50 °C (Figure 6(c)). Thus higher V<sub>oc</sub> along with higher J<sub>sc</sub> can be explained by morphology and coverage of MAPbI<sub>3</sub> for 40 °C- and 50 °C-pre-heating cases. It is noted that large MAPbI<sub>3</sub> crystals does not fully cover the TiO<sub>2</sub> film upon pre-heating at 60 °C (Figure 6(d)), which deteriorates J<sub>sc</sub> and V<sub>oc</sub> being close to those obtained without pre-heating. Moreover the increased capping layer thickness of MAPbI<sub>3</sub> for 60 °C-pre-heating is in part responsible for low FF due to increase in resistance [20,21]. From the cross-sectional SEM study on full cell structure, the highest performance obtained by the 50 °C-pre-heating procedure can be explained.
Fig. 6 Focused ion beam (FIB) assisted SEM images of full cells with MAPbI$_3$ perovskite layer formed by reacting CH$_3$NH$_3$I with the PbI$_2$ layer deposited at substrate temperature of (a) without pre-heating, (b) 40 °C, (c) 50 °C and (d) 60 °C. Scale bars represent 1 µm.

Figure 7 compares PL intensity of MAPbI$_3$ film depending on the pre-heating temperature. The sample for PL measurement is composed of MAPbI$_3$ film deposited on mesoporous TiO$_2$ coated FTO substrate (see the inset in Figure 7). The emission peaks appeared in 750 nm – 800 nm range are resulted from PL of MAPbI$_3$ because the emissive photon energy is corresponding to band gap of about 1.6 eV [22]. The PL peaks shift to longer wavelength as the pre-heating temperature increases. Since PL of perovskites is
expected to occur due to recombination of localized excitons, the bathochromic shift of both absorption (not shown here) and PL spectra can be attributed to less localized exciton states in large crystals. In addition, compared to the non-pre-heating case, the PL intensity decreases significantly upon pre-heating. When considering higher coverage of MAPbI₃ for the pre-heated cases than the non-preheated one, the reduced PL intensity is due to better electron injection into mesoporous TiO₂. This is well consistent with interfacial morphology as confirmed by FIB-SEM. The improved $J_{sc}$ is related to better charge separation and thereby charge collection. The lowest PL intensity observed for the 60 °C-pre-heating case is indicative of more effective charge separation occurred at TiO₂/perovskite interface. However, despite such an effective charge separation, the increased capping layer thickness and partially uncovered TiO₂ film are responsible for low $J_{sc}$ and $V_{oc}$.

**Fig. 7** Photoluminescence (PL) spectra of the MAPbI₃ layers deposited on FTO substrate showing effect of substrate temperature. Inset shows incident light on FTO side.
We investigated effect of preparation condition on I-V hysteresis. Figure 8 compares I-V hysteresis, where no significant I-V hysteresis in terms of scan direction is observed for the device prepared without pre-heating condition. On the other hand, I-V hysteresis is pronounced as pre-heating temperature increase and serious at 60 °C-pre-heating condition. It was reported that I-V hysteresis was dependent on MAPbI$_3$ crystal size and presence and absence of mesoporous TiO$_2$ layer [23], where serious I-V hysteresis was observed from planar structure (without mesoporous TiO$_2$ layer) and smaller crystal. Compared to the less I-V hysteresis from the non-pre-heating condition, the pronounced I-V hysteresis for the pre-heating condition is due to the increased capping layer at the same thickness of TiO$_2$. 
Since the thickness and crystallinity of PbI$_2$ and MAPbI$_3$ could be changed by not only substrate temperature but also concentration of PbI$_2$, it is required to investigate effect of concentration of PbI$_2$ (1.0, 0.8 and 0.6 M) on photovoltaic performance at different substrate temperature (50 °C and 60 °C). Figure 9 shows J-V curves, XRD and SEM images depending on the PbI$_2$ concentration at 50 °C and 60 °C. Photovoltaic parameters along with PbI$_2$ and MAPbI$_3$ film thickness are summarized in Table 2. As expected, the thickness of MAPbI$_3$ decreases with increasing the concentration of PbI$_2$ solution from 1.0 M to 0.6 M. On the other hand, the MAPbI$_3$ thickness increases as the substrate temperature increases from 50 °C to 60 °C. It is noted that $J_{sc}$, $V_{oc}$ and FF decrease simultaneously as the concentration of PbI$_2$ decreases regardless of the substrate temperature. Consequently PCEs decrease from 15.01% to 11.03% at 50 °C and from 14.53% to 11.24% at 60 °C. In addition, when comparing the photovoltaic performance for the similar MAPbI$_3$ thickness (~665 nm for the 1.0 M PbI$_2$ at 50 °C and ~602 nm for the 0.8 M at 60 °C), the device prepared at 50 °C with 1.0 M PbI$_2$ shows better photovoltaic performance. This indicates that substrate temperature plays more important role in determining the performance rather than film thickness. The basis for the difference in the performance is due to the fact that higher amount of unreacted PbI$_2$ originated from higher crystallinity of PbI$_2$ at higher temperature, as confirmed by XRD in Figures 9(c) and (d), leads to lower $J_{sc}$ and FF. The lower $V_{oc}$ at higher substrate temperature is probably due to direct contact of hole transporting layer with mesoporous TiO$_2$ as can be seen in Figure 9 (f), which might result from larger cuboid formed by higher crystallinity of
PbI$_2$. For the case of devices prepared at 60 °C, the photovoltaic performance was found to be sensitive to humidity compared to other temperatures. PCE was reproducibly observed to be relatively low at high humidity (see Table 1) but improved at low humidity (Table 2). We can draw conclusion that the photovoltaic performance of perovskite solar cell prepared at ambient environment is mainly influenced by substrate temperature.

Fig. 9 J-V curves of perovskite solar cells as a function of the concentration of PbI$_2$ solution (1.0, 0.8 and 0.6 M) at substrate temperature ($T_{\text{sub}}$) of (a) 50 °C and (b) 60 °C, measured at
AM 1.5 G one sun illumination. XRD patterns of (c) PbI$_2$ and (d) MAPbI$_3$ films formed from 1.0 M-50 °C and 0.8 M-60 °C conditions, where insets show FWHM of (001) peak for PbI$_2$ and peak intensity ratio of (001) peak of PbI$_2$ to (110) peak of MAPbI$_3$. SEM images of MAPbI$_3$ formed from (e) 1.0 M-50 °C and (f) 0.8 M-60 °C conditions, where insets show cross-sectional images. The J-V data and SEM images shown here were obtained from the devices prepared at relative humidity of less than 20%.

Table 2. Photovoltaic parameters and thicknesses depending on the PbI$_2$ concentration and substrate temperature. Photovoltaic parameters were measured at AM 1.5 G one sun illumination. Average values were obtained from 9 cells. Relative humidity was <20%.

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<thead>
<tr>
<th>$T_{\text{sub}}$ (°C)</th>
<th>[PbI$_2$] (M)</th>
<th>Thickness (nm) PbI$_2$(MAPbI$_3$)</th>
<th>$J_{\text{sc}}$ (mA/cm$^2$)</th>
<th>$V_{\text{oc}}$ (V)</th>
<th>FF</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 °C</td>
<td>1.0</td>
<td>414.2 (665.6)</td>
<td>19.84±0.30</td>
<td>1.042±0.004</td>
<td>0.73±0.01</td>
<td>15.01±0.35</td>
</tr>
<tr>
<td></td>
<td>0.8</td>
<td>252.7 (513.6)</td>
<td>18.32±0.83</td>
<td>0.953±0.013</td>
<td>0.71±0.01</td>
<td>12.36±0.54</td>
</tr>
<tr>
<td></td>
<td>0.6</td>
<td>231.5 (510.2)</td>
<td>17.11±0.70</td>
<td>0.935±0.013</td>
<td>0.69±0.01</td>
<td>11.03±0.46</td>
</tr>
<tr>
<td>60 °C</td>
<td>1.0</td>
<td>545.2 (742.6)</td>
<td>19.09±0.29</td>
<td>1.051±0.009</td>
<td>0.72±0.01</td>
<td>14.53±0.32</td>
</tr>
<tr>
<td></td>
<td>0.8</td>
<td>461.8 (602.3)</td>
<td>18.90±0.37</td>
<td>0.986±0.022</td>
<td>0.70±0.01</td>
<td>12.97±0.43</td>
</tr>
<tr>
<td></td>
<td>0.6</td>
<td>311.1 (459.3)</td>
<td>18.25±0.61</td>
<td>0.926±0.027</td>
<td>0.66±0.03</td>
<td>11.24±0.97</td>
</tr>
</tbody>
</table>

The best performing device with a PCE of 15.76% is obtained by two-step deposition procedure based on the 50 °C-pre-heating condition under relative humidity of 50% (Figure 10). Under high relative humidity condition, the procedure of pre-heating the substrate for the PbI$_2$ deposition is crucial and important to achieve high efficiency because the PbI$_2$ deposition process is sensitive to humidity.
Fig. 10 J-V curve of the best performing perovskite solar cell prepared in the relative humidity of 50%. MAPbI$_3$ was formed by reacting CH$_3$NH$_3$I with the PbI$_2$ layer deposited at substrate temperature of 50 °C. Data was collected by reverse scan at AM 1.5 G one sun illumination.

Conclusions

We developed an effective way to fabricate perovskite solar cell with high photovoltaic performance exceeding 15% under high relative humidity condition, in which the substrate pre-heating process for PbI$_2$ deposition in two-step coating procedure was important. While spin-coating of the PbI$_2$ solution, the pre-heated substrate led to infiltration of PbI$_2$ in the mesopores of TiO$_2$ film full coverage of the TiO$_2$ film with PbI$_2$. Optimal pre-heating temperature was around 50 °C at least in our experimental procedure. We also tried to investigate effect of pre-heating on photovoltaic performance for the one-step deposition condition, where preliminary results showed that pre-heating method did not work well for
one-step deposition under high relative humidity, more than 40%. This indicates that the PbI$_2$
coting process is most critical in producing high quality MAPbI$_3$ under high relative humidity
condition. Without pre-heating condition, average PCE of 10-11% is observed, while PCE
over 15% is reproducibly achieved by the substrate pre-heating process.

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