Controlled reaction for improved CH$_3$NH$_3$PbI$_3$ transition in perovskite solar cells


Hybrid halide perovskites represent one of the most promising solutions toward the fabrication of all solid nanostructured solar cells, with improved efficiency and long-term stability. This article aims at investigating the properties of CH$_3$NH$_3$PbI$_3$ with controlled loading time in CH$_3$NH$_3$I solution via a two-step sequential deposition and correlating them with their photovoltaic performances. It is found that the optimum PCE of the loading time in the CH$_3$NH$_3$I solution is possible only at a relatively short time (10 min). Prolonging the loading time will degrade the perovskite film, and deteriorate the device performance by introducing a large amount of excessive defects and recombination. However, even if the material band gap remains substantially unchanged, a suitable loading time can dramatically improve the charge transport within the perovskite layer, exhibiting the outstanding performances of meso-superstructured solar cells.

Introduction

Organic–inorganic hybrid all-solid-state solar cells based on methylammonium lead halide perovskite absorbers have been attracting increasing interest because of their ease of fabrication and performances rivaling the best thin-film photovoltaic devices. Introduced by Miyasaka et al., the devices exhibited a starting point power conversion efficiency (PCE) of 3.8% and further improved to reach over 6% in liquid electrolyte systems. The reported perovskite-based solar cells in solid-state forms have reached an efficiency of 19.3%, owing to the advantageous characteristics of perovskite materials: an appropriate direct band gap, a high absorption coefficient, and a propensity to form thin films with excellent carrier-transport properties and an apparent tolerance of defects. The design versatility of perovskite solar cells has allowed both a mesoporous metal-oxide scaffold, donor–acceptor conjugated polymer or simply a thin film structure to be adopted, both with high efficiency. Some of the key advantages for this material system over other competing device concepts are that they are compatible with solution-processing techniques and can be fully processed at low temperatures, thus enabling their use in flexible device applications. So far, the perovskite pigment has been deposited in a single step, by co-evaporation of two precursors (PbCl$_2$ and CH$_3$NH$_3$I), vapor assisted solution process, two-step sequential deposition, etc. Hereinto, the two-step sequential deposition of perovskite provides an efficient low-cost route to high performance perovskite solar cells, and is better for tolerating I–V hysteresis. In this method, the transformation process from PbI$_2$ to CH$_3$NH$_3$PbI$_3$ is the most important section which seriously affects the photovoltaic performance. Different PbI$_2$ concentrations, the spin coating step of PbI$_2$, and different solvents for different crystallizing processes of PbI$_2$ were studied. In addition, different CH$_3$NH$_3$I concentrations, pre-wetting process control, and reaction temperature control were used for investigations of the conversion process and morphology control, which are closely related to the photovoltaic performance. However, the loading/dipping time in CH$_3$NH$_3$I solution for perovskite conversion process was reported differently in previous investigations. The loading time of PbI$_2$ in CH$_3$NH$_3$I solution directly affects the perovskite crystallite size, the defects, interfacial roughness and charge recombination, whereas, it is hardly found to affect the systematic investigation of the perovskite fabrication.

Herein, a detailed investigation of the controlled loading time of a PbI$_2$ film in CH$_3$NH$_3$I solution via a two-step sequential...
deposition procedure has been conducted. Loading in a solution of CH$_3$NH$_3$I for different times follows the spin-coating of PbI$_2$, and the size of CH$_3$NH$_3$PbI$_3$ crystals, the surface roughness and the PCE of the perovskite device are found to strongly depend on the loading time of CH$_3$NH$_3$I.

**Experimental**

**Materials**

PbI$_2$ and N,N-dimethylformamide (DMF) were purchased from Sigma-Aldrich and Alfa Aesar, respectively. Spiro-MeOTAD was purchased from Shenzhen Feiming Science and Technology Co., Ltd. All other materials were purchased from J&K Scientific Ltd and used as received. Substrates of the cells are fluoride-doped tin oxide conducting glass (FTO, Pilkington, thickness: 2.2 mm, sheet resistance 14 Ω per square). CH$_3$NH$_3$I was synthesized according to the literature.$^{7,1}$ CH$_3$NH$_3$I was synthesized by reacting 30 ml of methylamine and 32.3 ml of hydroiodic acid in a 250 ml round-bottom flask at 0 °C for 2 h with stirring. The precipitate was recovered by putting the solution on a rotary evaporator and carefully removing the solvents at 50 °C. The yellowish raw product, methylammonium iodide (CH$_3$NH$_3$I), was washed with diethyl ether by stirring the solution for 30 min, a step which was repeated three times, and then finally recrystallized from a mixed solvent of diethyl ether and ethanol. After filtration, the solid was collected and dried at 60 °C in a vacuum oven for 24 h.

**Device fabrication**

**Substrate preparation.** First, laser-patterned, FTO-coated glass substrates were cleaned by ultrasonication in an alkaline, aqueous washing solution, rinsed with deionized water, ethanol, acetone and 2-propanol, respectively. A hole-blocking layer of compact TiO$_2$ with a thickness of about 50 nm was deposited by a dip-coating method with a TiO$_2$ organic solution,$^{3,2}$ followed by a sintering process at 500 °C for 30 min. After cooling to room temperature, the substrates were treated in a 40 mM aqueous solution of TiCl$_4$ at 70 °C for 30 min, rinsed with deionized water and dried at 500 °C for 30 min. The mesoporous TiO$_2$ layer with a thickness of ~200 nm was prepared as previously reported.$^1$ The mesoporous TiO$_2$ film was immersed in 20 mM aqueous TiCl$_4$ (>98%, Aldrich) solution at 70 °C for 30 min and sintered at 500 °C for 30 min.

**Perovskite solar cell fabrication.** PbI$_2$ was dissolved in DMF at a concentration of 462 mg ml$^{-1}$ (~1 M) under a low stirring speed of 200 rpm at 70 °C, to obtain a homogeneous CH$_3$NH$_3$I solution around the FTO substrate. The solution was maintained at 70 °C during the whole procedure. The mesoporous TiO$_2$ films were then infiltrated with PbI$_2$ by spin coating at 6500 rpm for 5 s and dried. The films were then dipped in a solution of CH$_3$NH$_3$I in 2-propanol (10 mg ml$^{-1}$) for 20 s, 1 min, 2 min, 5 min, 10 min, 30 min, 60 min and 120 min, respectively, rinsed with 2-propanol and dried at 70 °C for 30 min.

The HTM was then deposited by spin coating at 4000 rpm for 30 s. The spin-coating formulation was prepared by dissolving 72.3 mg (2,2',7,7'-tetrakis(N,N-di-p-methoxyphenylamine)-9,9-spirobifluorene) (spiro-MeOTAD), 28.8 μl 4-tert-butylpyridine, 17.5 μl of a stock solution of 520 mg ml$^{-1}$ lithium bis(trifluoromethylsulphonimide) imide in acetonitrile in 1 ml chlorobenzene. For fabrication, the perovskite film and HTM were prepared in a glove box. Finally, 150 nm Ag was thermally evaporated onto the HTM layer under vacuum to act as the cathode. The cell area is 0.07065 cm$^2$. While moving, our samples were placed in special boxes filled with nitrogen, and the device was stored in a cabinet with flowing N$_2$ gas. The core device fabrication was carried out under controlled atmospheric conditions and a humidity of <1%.

**Characterization**

UV-Vis absorption and TRPL spectra were recorded with a Shimadzu UV-2550 (300–600 nm: xenon lamp, 300 W; 600–900 nm: tungsten–halogen lamp, 150 W) and Fls-800 spectrometers, respectively. XRD patterns were obtained using D8 Advance (Germany) diffractometer with Cu Kα radiation (40 kV and 40 mA) with the scanning rate of 4° min$^{-1}$ for wide angle test increment over the Bragg angle range of 10–70°. SEM (Scanning Electron Microscopy) analysis was performed using a Hitachi-S-4800 electron microscope. Atomic force microscopy (AFM) was performed using a Bruker Multimode 8 Scanning Probe Microscope (SPM) in “tapping” mode. The photocurrent-voltage (I–V) characteristics of the solar cells were measured using a Keithley 2400 source under illumination of a simulated sunlight (AM1.5, 100 mW cm$^{-2}$) provided by a solar simulator (Newport 69907) with an AM1.5 filter. The light intensity was adjusted with an NREL-calibrated Si solar cell with a KG-2 filter for approximating 1 sunlight intensity. While measuring current and voltage, the cell was covered with a black mask with an aperture (aperture area is close to the active device area). The incident photon-to-current efficiency (IPCE) was measured in DC mode with a 1/4 m double monochromator (Crowntech DK242), a multi-meter (Keithley 2000), and two light sources depending on the wavelength range required (300–600 nm: xenon lamp, 300 W; 600–900 nm: tungsten–halogen lamp, 150 W). The monochromatic light intensity for IPCE efficiency was calibrated with a reference silicon photodiode. All the measurements of the solar cells were performed under an ambient atmosphere at room temperature without encapsulation.

**Results and discussion**

The two-step sequential deposition on mesoporous TiO$_2$ is described schematically in Scheme 1. The mesoporous TiO$_2$ film (the thickness of ~200 nm) was deposited on a thin compact TiO$_2$ blocking layer, followed by spin-coating PbI$_2$ in N,N-dimethylformamide (DMF). In the second step, the naturally dried PbI$_2$ film was dipped into the CH$_3$NH$_3$I solution for different times (20 s, 1 min, 2 min, 5 min, 10 min, 10 min, 30 min,
60 min, 120 min), while the CH$_3$NH$_3$I solution was magnetically simultaneously stirred for uniform reaction and then dried at 70 °C to form CH$_3$NH$_3$PbI$_3$. After the HTM layer was spin-coated and Ag film evaporated, the cross-sectional structure of a representative device was investigated by scanning electron microscopy (Fig. 1). The present two-step sequential deposition method is expected to be more precise than the two-step dipping method, thanks to its uniform reaction procedure.

Typical curves of photocurrent density ($J$) versus voltage ($V$) for solar cells with different loading times in CH$_3$NH$_3$I solution are shown in Fig. 2, and the parameters for photovoltaic performance are summarized in Table 1. The champion turned out to be the perovskite solar cell with a loading time of 10 min in Fig. 2b, and this solar cell exhibits the highest power-conversion efficiency (PCE) of 14.51%, with a short-circuit current ($J_{sc}$) of 21.14 mA cm$^{-2}$, an open-circuit voltage ($V_{oc}$) of 0.939 V and a fill factor (FF) of 0.73. The perovskite solar cell with different loading times of 20 s, 1 min, 2 min, 5 min, 30 min, 60 min, and 120 min showed a maximum PCE value of 8.90%, 11.65%, 12.83%, 13.34%, 13.21%, 13.42%, and 12.76%, respectively. Little $I$–$V$ hysteresis is observed for the CH$_3$NH$_3$PbI$_3$ grown at different loading times, which indicates that the two-step deposition method is better for tolerating $I$–$V$ hysteresis. The performance of devices with different loading times is also plotted in Fig. 3. The increase of $J_{sc}$ with the loading time from 20 s to the 120 min is ascribed to the improved pure CH$_3$NH$_3$PbI$_3$ crystals, subsequent growth of the crystallite size for enhancing the light absorption and electron blocking of the leftover PbI$_2$ prevent charge recombination. On the other hand, with the loading time from 10 min to 120 min, the decrease in $V_{oc}$ and FF is most likely due to the increasing surface roughness and the

Table 1  Summary of the $J$–$V$ parameters of perovskite device, where the absorbers are prepared by reacting at different times

<table>
<thead>
<tr>
<th>Loading time</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF</th>
<th>PCE (%) (maximum)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 s</td>
<td>16.9 ± 1.6</td>
<td>0.86 ± 0.02</td>
<td>0.50 ± 0.04</td>
<td>7.20 (8.90)</td>
</tr>
<tr>
<td>1 min</td>
<td>19.0 ± 1.2</td>
<td>0.86 ± 0.03</td>
<td>0.62 ± 0.02</td>
<td>10.13 (11.65)</td>
</tr>
<tr>
<td>2 min</td>
<td>19.2 ± 1.2</td>
<td>0.89 ± 0.02</td>
<td>0.66 ± 0.03</td>
<td>11.28 (12.83)</td>
</tr>
<tr>
<td>5 min</td>
<td>19.6 ± 1.0</td>
<td>0.90 ± 0.02</td>
<td>0.68 ± 0.02</td>
<td>12.00 (13.34)</td>
</tr>
<tr>
<td>10 min</td>
<td>20.0 ± 1.2</td>
<td>0.93 ± 0.01</td>
<td>0.71 ± 0.02</td>
<td>13.2 (14.51)</td>
</tr>
<tr>
<td>30 min</td>
<td>20.3 ± 1.1</td>
<td>0.90 ± 0.02</td>
<td>0.62 ± 0.05</td>
<td>11.32 (13.21)</td>
</tr>
<tr>
<td>60 min</td>
<td>20.3 ± 0.8</td>
<td>0.87 ± 0.03</td>
<td>0.64 ± 0.03</td>
<td>11.30 (13.42)</td>
</tr>
<tr>
<td>120 min</td>
<td>20.1 ± 1.0</td>
<td>0.86 ± 0.03</td>
<td>0.63 ± 0.03</td>
<td>10.89 (12.76)</td>
</tr>
</tbody>
</table>
dissolution of perovskite with the increasing amount of defects (AFM images in Fig. 6) and the charge recombination at an enhanced loading time, and also the bigger perovskite crystals and interfacial roughness which prevent charge fluent transport through the perovskite particles and interfaces of mesoporous TiO₂/perovskite/HTM layers.³⁴–³⁶,³⁹

Fig. 4 presents a field emission scanning electron microscopy (FE-SEM) image of the synthesized PbI₂ film fully deposited on mesoporous TiO₂. Fig. 5 demonstrates the color variations of the CH₃NH₃PbI₃ film at different loading times in CH₃NH₃I solution. With increasing loading time, the film surface color gradually changes from yellow to dark. The SEM images in Fig. 7 showed the two dimensional morphology of the perovskite crystal at different loading times of 20 s, 1 min, 2 min, 5 min, 10 min, 30 min, 60 min and 120 min, respectively. It is noticeable that the perovskite crystallites not only filled the mesoporous TiO₂ film but also covered it as a continuous layer. With the increase of the loading time, perovskite crystallites with a maximum grain size of ~200 nm from 20 s to 30 min, enlarged to a maximum grain size of ~500 nm of 60 min in the capping layer, leading to a much rougher surface. The particle size of the perovskite gradually increased which is in agreement with the AFM images (Fig. 6). Accordingly the 3D topographic AFM images displayed increase in roughness on prolonging the loading time from 20 s to 120 min. The calculated rms roughnesses for films 20 s, 1 min, 2 min, 5 min, 10 min, 30 min, 60 min and 120 min, were 18.3 nm, 18.7 nm, 36.2 nm, 39.8 nm, 41.7 nm, 44.3 nm, 45.8 nm and 51.3 nm, respectively (Fig. 6I). However, the increase of roughness was the result of volume expansion occurring (~75%) due to the conversion of PbI₂ into CH₃NH₃PbI₃ with a prolonged loading time in CH₃NH₃I solution.¹³ Prolonging the loading time increased the surface roughness with the amount of defects (voids and pinholes). The defects of 30 min, 60 min and 120 min were not favorable to device performance, where Voc and FF decreased severely in Fig. 3. Light-harvesting efficiency and charge-carrier extraction are significantly affected by the perovskite crystals size and roughness.¹⁶ A cross-sectional SEM of the full cell (Fig. 1) shows that the increasing perovskite grain size improves the interfacial roughness and defects of the spiro-MeOTAD/perovskite/mesoporous TiO₂ film in a prolonged loading time, and then the PCE of the devices deteriorates at a prolonged loading time from 30 min.

X-ray diffraction measurements were carried out to study the transformation process, as shown in Fig. 8. When the PbI₂ film was treated in CH₃NH₃I solution for 20 s, very strong diffraction peaks indexed to tetragonal CH₃NH₃PbI₃ were observed,³⁸ whereas there were still some PbI₂ left unreacted, as evidenced by the strong 12.8° (001) and 39.6° (003) diffraction peaks.³⁹,⁴⁰,⁶⁴ Prolonged treatment to 120 min can greatly reduce the intensity of PbI₂ diffraction peaks to very small intensities, suggesting the reaction between PbI₂ and CH₃NH₃I was almost complete. Though the trace amount of leftover PbI₂ was also observed in the CH₃NH₃PbI₃ film produced
through alternative approaches, the residual PbI$_2$ would cause inefficient light absorption, whereas the leftover PbI$_2$ would not be very harmful because of its large band gap. A suitable amount of PbI$_2$ species in the CH$_3$NH$_3$PbI$_3$ film improves the carrier behavior possibly due to reduced charge recombination in the grain boundaries and the TiO$_2$/perovskite surface. The grain size estimated from the Scherrer equation was approximately 38.3 nm corresponding to the in-plane perovskite grain size in previous SEM observations.

To further investigate the perovskite conversion with different loading times in CH$_3$NH$_3$I solution, UV-vis spectra were recorded for the PbI$_2$ and CH$_3$NH$_3$PbI$_3$ as a function of the loading time (Fig. 9). The CH$_3$NH$_3$PbI$_3$ conversion exhibited clearly increased light absorption across the 450 nm into the band-edge 780–790 nm. The systematic rise in absorption should be a result of the increasing pure perovskite crystallinity and grain size processed with an additive loading time, which can also be observed in the reduced intensity of reflections at 12.8° and 39.6° in the XRD patterns of PbI$_2$ in Fig. 8. Although intensity decrease in XRD is possibly due to several factors, in this case, identical instrumental parameters, sample quantities, and compositions were used for analysis. The increased absorption of the 10 min loading time around 400–440 nm can be attributed to the improved surface coverage and a more uniform crystal formation in the perovskite thin film.

We further examined the incident-photon-to-current efficiency (IPCE, Fig. 10). The integrated photocurrent from the IPCE is consistent with the measured $J_{sc}$ value. A prolonged loading time at 10 min would deteriorate the photovoltaic performance. Since the perovskite film with increasing defects prevented charge carrier diffusion in perovskite grain and the interfaces, and enhancing the charge carrier recombination, the poor CH$_3$NH$_3$PbI$_3$ capping layer at 60 min and 120 min decreased the absorption of photons in the long wavelength region 600–800 nm.

The electron injection dynamics from the photoexcited perovskite layers to the neighboring film structures could be

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**Fig. 6** Tapping-mode AFM 5 × 5 μm height images (a–h) of perovskite films at different loading times, 20 s, 1 min, 2 min, 5 min, 10 min, 30 min, 60 min and 120 min, respectively. (Inset: the corresponding 3D topographic image.) (g) Surface roughness of the corresponding perovskite films (room mean square average of height deviations taken from the mean image data plane, expressed as $\sqrt{\frac{\sum Z_i^2}{N}}$).

**Fig. 7** Top view HR-SEM micrographs of perovskite crystals deposited on mesoporous TiO$_2$ surface at different loading times.
directly monitored via the transient bleaching dynamics of the perovskite and thus systematically studied as a function of the layer-by-layer architecture. To bridge the enhanced device performance to the CH$_3$NH$_3$PbI$_3$/TiO$_2$ layers with different loading time in CH$_3$NH$_3$I solution. We further employed time-resolved photoluminescence (TRPL) decay to measure the carrier lifetime in the representative perovskite film and study exciton diffusion. Fig. 11 shows the PL decay curves monitored at the wavelength of 770 nm, extracted from the perovskite films prepared on the mesoporous TiO$_2$/compact TiO$_2$/FTO film substrates. All the curves are fitted with a biexponential function in accordance with the reports [eqn (1)]$^{44,46,47}$ as summarized in Table 2.

$$I(t) = A_1 \exp \left( \frac{t}{\tau_1} \right) + A_2 \exp \left( -\frac{t}{\tau_2} \right)$$  \hspace{1cm} (1)

Typically, the initially photogenerated excitons diffuse into defects, and the large time constant $\tau_2$ reflects this early event and might come from bimolecular recombination.$^{42}$ $A_1$ and $A_2$ are the percentages of the component with the defined fluorescence lifetime, and $A_1 \gg A_2$, therefore the small time constant $\tau_1$ is associated with the exciton lifetime of CH$_3$NH$_3$PbI$_3$. These high electron-extraction and -transport rates contribute significantly to the high $J_{sc}$ value for the perovskite solar cell. We assume that the radiative and non-radiative decay process of CH$_3$NH$_3$PbI$_3$ associated with TiO$_2$.

Table 2 Summary of the parameters from fits to the TRPL measurement. The fitting functions of the double exponential equation.

<table>
<thead>
<tr>
<th>Loading time</th>
<th>$\tau_1$ (ns)</th>
<th>$A_1$</th>
<th>$\tau_2$ (ns)</th>
<th>$A_2$</th>
<th>$k_{et}$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 s</td>
<td>0.490</td>
<td>25.83465</td>
<td>3.896</td>
<td>2043.14</td>
<td>1.784 x 10$^5$</td>
</tr>
<tr>
<td>1 min</td>
<td>0.487</td>
<td>29.40117</td>
<td>3.469</td>
<td>1299.69</td>
<td>1.765 x 10$^5$</td>
</tr>
<tr>
<td>2 min</td>
<td>0.492</td>
<td>26.82870</td>
<td>3.525</td>
<td>1197.95</td>
<td>1.748 x 10$^5$</td>
</tr>
<tr>
<td>5 min</td>
<td>0.498</td>
<td>28.21269</td>
<td>3.692</td>
<td>1270.09</td>
<td>1.737 x 10$^5$</td>
</tr>
<tr>
<td>10 min</td>
<td>0.492</td>
<td>27.27322</td>
<td>3.457</td>
<td>1748.14</td>
<td>1.743 x 10$^5$</td>
</tr>
<tr>
<td>30 min</td>
<td>0.367</td>
<td>35.85723</td>
<td>2.878</td>
<td>1644.96</td>
<td>2.377 x 10$^5$</td>
</tr>
<tr>
<td>60 min</td>
<td>0.342</td>
<td>41.08029</td>
<td>2.971</td>
<td>782.40</td>
<td>2.587 x 10$^5$</td>
</tr>
<tr>
<td>120 min</td>
<td>0.521</td>
<td>29.33282</td>
<td>5.806</td>
<td>75.00</td>
<td>1.747 x 10$^5$</td>
</tr>
<tr>
<td>Contrast</td>
<td>1.180</td>
<td>6745.36</td>
<td>49.410</td>
<td>1347.87</td>
<td>0.827 x 10$^5$</td>
</tr>
</tbody>
</table>

Fig. 8 XRD patterns of CH$_3$NH$_3$PbI$_3$/TiO$_2$/FTO glass samples at different loading times.

Fig. 9 The absorbance spectra of PbI$_2$ and CH$_3$NH$_3$PbI$_3$ as a function of the loading time.

Fig. 10 Effect of loading time on the IPCE spectra of the perovskite devices.
occur at rates otherwise identical to those of CH$_3$NH$_3$Pbl$_3$ in a neat film in the absence of TiO$_2$. Under these conditions, the observed fast lifetime can be correlated to the rate for interfacial electron transfer by eqn (2),

$$k_{et} = 1/\tau_{ads} - 1/\tau_{un}$$

where $\tau_{ads}$ and $\tau_{un}$ denote the emission lifetimes for the CH$_3$NH$_3$Pbl$_3$/TiO$_2$ surface complex and for the neat CH$_3$NH$_3$Pbl$_3$, respectively, whereas $k_{et}$ is the specific rate constant for the charge injection process. On the interfaces of CH$_3$NH$_3$Pbl$_3$/mesoporous TiO$_2$, the electron injection rate of 2.587 $\times$ 10$^9$ s$^{-1}$, 2.377 $\times$ 10$^9$ s$^{-1}$ for 60 min and 30 min loading times, respectively, is faster than 10 min of 1.743 $\times$ 10$^9$ s$^{-1}$ in Table 2. Whereas the open-circuit voltage and fill factor of solid-state devices are deteriorated by increasing the crystallite size and defects of perovskite, and improving the interfacial roughness of mesoporous TiO$_2$/CH$_3$NH$_3$Pbl$_3$/HTM, which is mainly attributed to the increase in electron transport resistance and bi-molecular recombination.

Thus, a small $\tau_1$ value indicates a fast exciton- or electron-diffusion process. At the 10 min, 30 min and 60 min loading time, $\tau_1$ appears to be reaching 0.492 ns, 0.367 ns, and 0.342 ns, respectively, suggesting that a fast electron diffusion occurred that leads to the extremely high photocurrent from the photovoltaic device. While the loading time is prolonged from 10 to 60 min, the corresponding constant $\tau_2$ of the film drops from 3.457 ns to 2.971 ns. It means that an increased amount of defects in the film affects the carrier recombination behavior significantly, suggesting a distinctive mechanism of defect chemistry that leads to the decreased fill factor (FF) and open-circuit voltage ($V_{oc}$) from the photovoltaic device. These high electron-extraction and -transport rates contribute significantly to the high $J_{sc}$ value for the perovskite solar cell.

However, prolonging the loading time for hours will increase the interfacial roughness and deteriorate the device performance by introducing a large amount of excessive defects. Additionally, kinetic analysis reveals that perovskite films with less Pbl$_2$ show faster relaxation rates than those containing more Pbl$_2$. These fast dynamics are attributed to charge carrier trapping at perovskite grain boundaries, and the slower dynamics in samples containing Pbl$_2$ are due to a passivation effect, in line with other recently reported work.

Fig. 12 shows the reproducibility of the perovskite solar cell made using the optimum conditions describe above. More than 44% of cells show efficiency above 13%, and the average power conversion efficiency is 12.87%. The influence of the loading time in CH$_3$NH$_3$I on photovoltaic performance is observed. The optimum PCE was observed for the loading time of 10 min.

The AFM images in Fig. 6 present the three-dimensional morphology and roughness of the perovskite surface from 20 s to 120 min. It is noticeable that prolonging the loading time increases the crystallite CH$_3$NH$_3$Pbl$_3$ grain size, defects and surface roughness of the perovskite film. The AFM images and $J$–$V$ curves in Fig. 2 reveal that prolonging the loading time from 60 min increases the amount of defects and enhances the charge carrier recombination, deteriorating the parameters ($J_{sc}$, $V_{oc}$, FF, PCE) of perovskite devices. In series, loading times from 20 s to 60 min, improving pure CH$_3$NH$_3$Pbl$_3$ crystallinity, subsequent growth of the perovskite size and electron blocking of the leftover Pbl$_2$ play a crucial role in enhancing the $J_{sc}$, which is in accordance with XRD data in Fig. 8 and the UV-vis absorbance in Fig. 9. The prolonged contact of the liquid CH$_3$NH$_3$I solution with the as-formed CH$_3$NH$_3$Pbl$_3$ perovskite film appears to degrade its morphology making it defects with voids and pinholes. Extending the loading time from 30 min, the water content (or moisture) in regular IPA or accumulated overtime for anhydrous IPA can accelerate the degradation process.

The electrons and holes produced in the CH$_3$NH$_3$Pbl$_3$ perovskite exhibit a small effective mass resulting in high carrier mobility. Their recombination occurs on a timescale of hundreds of nanoseconds, and the average distance that can be covered by carriers before they recombine within 100 nm. Therefore on prolonging the loading time from 10 min, the increase of big perovskite crystal size prevents charge carrier diffusion through the perovskite particles, and prolonging the loading time increases the interfacial roughness and the defects of the perovskite film, and then the open circuit voltage ($V_{oc}$) and fill factors (FF) were decreased at 30 min, 60 min and 120 min.

Prof. Grätzel's group has reported that the best dipping time is 20 s, however, our group investigated the high conversion efficiency near 15% with 10 min dipping duration. The reasons for the variation in the loading time near 15% of PCE should be induced by the different experimental procedures, such as those in Prof. Grätzel's work, (1) the thickness of mesoporous TiO$_2$ film was approximately 300–350 nm, (2) the mesoporous TiO$_2$/Pbl$_2$ film was kept at 70 °C for drying, (3) the Pbl$_2$ films “were subjected to a 'pre-wetting' by dipping in 2-propanol for 1–2 s before being dipped in the solution of CH$_3$NH$_3$I and 2-propanol”. Whereas our mesoporous TiO$_2$ film was ~200 nm thick, and the mesoporous TiO$_2$/Pbl$_2$ film dried at room temperature, and we didn't pre-wet the Pbl$_2$ film before dipping in the CH$_3$NH$_3$I solution. The morphology and crystallinity of the Pbl$_2$ film and the incomplete conversion of Pbl$_2$ to CH$_3$NH$_3$Pbl$_3$ were induced by the subtle experimental
procedures such as the thickness of the mesoporous TiO₂ film, pre-heating procedure and so on, which were investigated by Prof. Nam-Gyu Park.⁶⁴

The XRD pattern of Prof. Grätzel’s results distinctly showed the incomplete conversion of PbI₂ to CH₃NH₃PbI₃ in 20 s. We found that a uniform and high coverage CH₃NH₃PbI₃ perovskite film with a thick layer with high coverage can hardly be deposited in 60 s, which is in accordance with the studies by Prof. Liyuan Han²⁰ and Prof. Qingbo Meng.²⁷ Additionally, our investigations are complementary to Prof. Grätzel’s work in more than 20 s dipping time of PbI₂ in the solution of CH₃NH₃I.

Conclusions

By using a two-step sequential deposition procedure, we have prepared MAPbI₃-based perovskite solar cells in CH₃NH₃I solution at different loading times from 20 s to 120 min. Optimizing the loading time of MAPbI₃, perovskite crystallite size and the surface roughness of the perovskite film play the crucial roles in obtaining high light harvesting and charge carrier extraction. The photovoltaic parameters were found to be significantly dependent on the loading time in CH₃NH₃I solution, since the loading time of CH₃NH₃I could affect the size of the perovskite, the leftover PbI₂, defects and the charge recombination.

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Notes and references


