Gas-solid reaction based over one-micrometer thick stable perovskite films for efficient solar cells and modules

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Besides high efficiency, the stability and reproducibility of perovskite solar cells (PSCs) are also key for their commercialization. Herein, we report a simple perovskite formation method to fabricate perovskite films with thickness over 1 μm in ambient condition on the basis of the fast gas−solid reaction of chlorine-incorporated hydrogen lead triiodide and methylamine gas. The resultant thick and smooth chlorine-incorporated perovskite films exhibit full coverage, improved crystallinity, low surface roughness and low thickness variation. The resultant PSCs achieve an average power conversion efficiency of 19.1 ± 0.4% with good reproducibility. Meanwhile, this method enables an active area efficiency of 15.3% for 5 cm × 5 cm solar modules. The un-encapsulated PSCs exhibit an excellent T80 lifetime exceeding 1600 h under continuous operation conditions in dry nitrogen environment.

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Organic—inorganic lead halide perovskite solar cells (PSCs) have drawn a great deal of attention in the photovoltaic research community due to their high efficiency and simple manufacturing process. The power conversion efficiency (PCE) of PSCs has reached over 22% and is similar to other kinds of thin film photovoltaics, film qualities of perovskite layers can heavily influence device performance of PSCs. Thus, a delicate control of film quality of perovskite layers is key to achieving both superior performance and high reproducibility. Many solution processable perovskite formation methods have been developed to fabricate high-quality perovskite films, such as one-step method and two-step method. These methods usually involve a transformation of 2D lead halide inorganic framework to the 3D perovskite structure. This structure transformation is often accompanied with the formation of morphological defects and crystallographic structure dislocation within the grain and at grain boundaries, where defects are present as trap states causing serious charge recombination and limiting the charge carrier diffusion length (less than 1 μm). To ensure efficient charge collection in the presence of defects, perovskite films are usually made sufficiently thin. So far, high efficiency PSCs mainly adopt perovskite films with thickness ranging from 400 to 800 nm (Supplementary Table 1). The low thickness fluctuation tolerance and morphological defects of thin perovskite films decrease reproducibility of the fabrication process. Moreover, thin films are prone to thickness variations and pinhole defects, which increase significantly with the area.

It is obvious that thicker perovskite films are likely to reduce the risk of forming voids and pinholes due to the larger thickness fluctuation tolerance. A high-quality thick perovskite film is desirable to achieve a high device yield and reproducibility in making large-area solar modules. Besides, thicker perovskite films can not only improve the light harvesting but also broaden light response region by utilizing the below-band absorption. As such, it is advantageous to construct a high-quality thick perovskite film with enough carrier diffusion length in PSCs to endorse both higher efficiency and manufacturing viability. However, thick perovskite films over 1 μm have been found to be generally less efficient than thin-films devices due to the poor mobility, limited carrier diffusion length and are seldom explored (Supplementary Table 1). Moreover, conventional perovskite formation methods are usually not suitable for fabricating large-area high-quality thick perovskite films. Thus, improving the quality of thick perovskite films is critical to balance the thickness and efficiency. Also, the development of new perovskite formation techniques is desirable to construct high-quality and thick perovskite films.

Recently, a perovskite formation process based on methylvamine (CH$_3$NH$_3$) gas—solid reaction has been developed to prepare high-quality CH$_3$NH$_3$PbX$_3$ (X = I, Br, Cl), mixed halides CH$_3$NH$_3$I$_{1-x}$Cl$_x$-based perovskite and Cesium/CH$_3$NH$_3$I$_{1-x}$ mixed cations perovskite films. This gas—solid reaction-based method introduces a liquid intermediate, which leads to induced morphology reconstruction, defects healing, and also elimination of I$_2$. Meanwhile, CH$_3$NH$_3$I gas treatment can help reduce the defect density in perovskite films and reported to passivate trap states to improve device performance. Moreover, excess solvent is absent during this perovskite formation process, which avoids the possible detrimental effect-related residue solvent. Therefore, CH$_3$NH$_3$I gas-based processes are promising for depositing high-quality perovskite films across large area for PSC device fabrication.

In terms of the synthetic techniques developed for perovskite, using chloride containing raw materials to prepare perovskite is a commonly used method. Although the chloride content in resultant perovskite films is usually much lower than the nominal ratio of chloride added in the precursor solution and in some cases the chloride content in fully annealed perovskite films is below detection limit, both the optoelectronic properties and morphology can be tuned by appropriate chloride incorporation. The resultant carrier diffusion length improvement, defects density reduction, and charge transport make this method effective in obtaining high-quality perovskite films. In particular, CH$_3$NH$_3$PbI$_3$–Cl$_x$ (i.e., CH$_3$NH$_3$PbI$_3$ incorporated with a small amount of Cl) has been reported to exhibit a longer carrier diffusion length over 1 μm compared with pure CH$_3$NH$_3$PbI$_3$ and as a result device performance improved dramatically.

These earlier works have inspired us to combine the CH$_3$NH$_3$I gas-based perovskite formation method and partial substitution of iodine ions by chlorine ions to fabricate high quality over 1-μm-thick perovskite films with a sufficient charge diffusion length, which is not only beneficial for better light absorbing but also desirable for fabricating large-area solar modules with high yield and reproducibility via low-cost printing techniques.

Here we report a simple perovskite formation method to fabricate over 1-μm-thick perovskite films based on the fast gas—solid reaction of chloride-incorporated hydrogen lead triiodide (HPbI$_3$(Cl)) and CH$_3$NH$_3$I gas. The comprehensive characterization results reveal that with the synergistic effect of CH$_3$NH$_3$I gas and partial substitution of iodine ions by chlorine ions, the resultant CH$_3$NH$_3$PbI$_3$(Cl) (MAPbI$_3$(Cl)) films with a thickness over 1 μm and low thickness variation exhibit excellent film quality. The resultant PSCs gave an average PCE of 19.1% and low PCE standard deviation (±0.4%), which indicates the excellent reproducibility of this method. Meanwhile, this method enables an active area PCE of 15.3% for 5 cm × 5 cm solar modules. Besides, the un-encapsulated PSCs exhibit an excellent T$_{80}$ lifetime exceeding 1600 h under continuous operation conditions in dry N$_2$ environment. Our film stability study also offers the in-depth understanding for the underlying mechanisms responsible for device stability improvement.

**Results**

**Perovskite formation.** Conventional perovskite formation methods are usually not suitable for fabricating high-quality thick perovskite thin films (Supplementary Fig. 1). Here, we developed a fast gas—solid reaction of HPbI$_3$(Cl) and CH$_3$NH$_3$I gas to prepare high-quality thick perovskite films. In this method, hydrogen lead triiodide (HPbI$_3$) was used as the starting material aiming at taking advantage of its fully coordinated [PbI$_6$]$^{2-}$ structure to reduce iodide-vacancy and improve film quality (Supplementary Figs. 2, 3, 33). Firstly, we tuned the thickness of perovskite films based on the HPbI$_3$–CH$_3$NH$_3$I reaction by varying the substrate temperature (Supplementary Figs. 4, 5, 6, Supplementary Table 2 and Supplementary Note 1). As a result, perovskite films with thickness about 1.1 μm are used as our benchmark for further studies. Partial substitution of iodine ions by chlorine ions step depicted in Fig. 1a was achieved by reacting CH$_3$NH$_3$I(Cl) with HPbI$_3$ to form HPbI$_3$(Cl). Considering that MACl exists in the solid state at room temperature but sublimes at elevated temperatures (higher than 100 °C), the introduction of MACl can not only achieve a small amount of substitution of iodine ions by chlorine ions, but also tune the morphology of HPbI$_3$(Cl) films. Top set in Fig. 1b shows the top-view scanning electron microscope (SEM) images of HPbI$_3$(Cl) films prepared using HPbI$_3$/MACl precursor solution with different MACl contents. It is found that upon increasing the MACl content, the size of voids between islands-like crystals in the HPbI$_3$(Cl) films gradually decreases, and the crystals gradually turn from the hexagonal...
shape to the square shape and then to crystals with round edges (Supplementary Fig. 7). The enhanced coverage of HPbI₃(Cl) films is expected to be beneficial for the subsequent CH₃NH₂ gas-based perovskite formation process.

To further investigate the incorporation of chlorine into the HPbI₃, we used X-ray diffraction (XRD) spectroscopy to characterize the obtained HPbI₃(Cl) films. It is reported that the HPbI₃ films show a hexagonal structure. Upon increasing MACl content from 0 to 0.20, the low-angle peak around 11.7° shifts to a higher two theta value and the peak intensity increases significantly (Supplementary Fig. 8). This result suggests that the substitution of I⁻ ion with smaller Cl⁻ ion can shrink the crystal lattice, and HPbI₃(Cl) still preserves the pseudo-hexagonal phase in the case of MACl content lower than 0.4. When the MACl content is increased to 0.40, the XRD peak intensity of the HPbI₃(Cl) film at around 11.7° reduced substantially. This observation suggests that when the MACl content is too high, the crystal structure of HPbI₃(Cl) cannot maintain the previous structure, which is also supported by the observed shape difference of crystal islands by SEM (Supplementary Fig. 7). This is because the large difference between the ionic radii of I⁻ and Cl⁻ makes the crystal structure unstable when the content of chlorine is too high. Such a phenomenon has also been observed in MAPbI₃₋ₓClₓ. When a small amount of Cl was incorporated, MAPbI₃₋ₓClₓ can still maintain the pseudo-cubic phase. However, a continuous solid phase of MAPbI₃₋ₓClₓ theoretically cannot form at a high chlorine content due to the large size mismatch between chloride and iodide. Besides, a slight splitting of the XRD peaks around 11.7° and the formation of MAPbI₃ are observed for high MACl content of 0.70 and 1.00 cases. The former observation may be due to the incomplete removal of MACl or phase separation of HPbI₃(Cl), and the latter observation suggests that the reaction of MACl with HPbI₃ can form MAPbI₃. The nonvisible perovskite peaks in HPbI₃(Cl) films at low MACl content from 0.05 to 0.40 may be due to the low amount of MAPbI₃ seeds and detection limit of XRD. Here, we can deduce that the possible reaction for the formation of HPbI₃(Cl) at low MACl content up to 0.40 is as follows:

\[
\text{HPbI}_3 + (x + y)\text{MACl} \rightarrow \text{H}_1\text{–}_{x}\text{Pb}_{1\text{–}x}\text{I}_{3\text{–}4x}\text{Cl}_x
\]

\[+x\text{MAPbI}_3 + x\text{HI} (g) + y\text{MACl} (g), \]

where the chlorine-incorporated HPbI₃, i.e., H₁–ₓPb₁–ₓI₃–₄ₓClₓ is termed as HPbI₃(Cl) hereafter; for MACl, x + y represents the initial amount of MACl in the HPbI₃/MACl precursor solution, x represents the amount of MACl used for chlorine incorporation, and y represents the amount of MACl that sublimes during thermal annealing.

The as-prepared HPbI₃(Cl) films were then exposed to CH₃NH₂ gas atmosphere to form perovskite via the reaction, CH₃NH₂ + H⁺ → CH₃NH₃⁺. As shown in Fig. 1b bottom set, the apparent grain size of the MAPbI₃(Cl) films gradually increases upon the increase of MACl content. However, too much MACl is found to cause significant deterioration of the film morphology, especially for the MACl content of 1.00 case (Supplementary Fig. 9). The structural properties of MAPbI₃(Cl) films were further examined by XRD (Fig. 2a, b and Supplementary Fig. 10). All the samples show a preferred orientation along the (110) crystallographic plane, and the corresponding peak intensity becomes stronger with consecutive substitution of iodine ions by chlorine ions. This preferable (110) crystal orientation is induced by the CH₃NH₂-based perovskite formation process. The gradually increased peak intensity is ascribed to the effect of chlorine on perovskite film growth. Furthermore, it was found that the low-angle XRD peak around 14.1° shifts to a higher two theta value and the peak intensity also increases upon increasing the MACl content. The same as the aforementioned discussion about the HPbI₃(Cl), substitution of I⁻...
by smaller-size Cl\(^{-}\) can also lead to the shrinkage of the crystal lattice of perovskite, which is consistent with the cell parameters variation (Supplementary Fig. 11). A slight splitting of the XRD peaks is also observed in the case of the MACI content of 1.00, in which the large size mismatch between chloride and iodide precludes the formation of a continuous solid phase. The large size mismatch between chloride and iodide is also observed in the case of the MACI content of 1.00, variation (Supplementary Fig. 11). The observed additional peak around 28.2 ° is likely associated with the hydrate phase of perovskite\(^{38}\).

Although MACI is introduced into precursor with nominal ratios of MACI/HPbI\(_3\) from 0.1 to 1, the remaining contents of chlorine in HPbI\(_3\)(Cl) and MAPbI\(_3\)(Cl) can be significantly lower than the nominal content of chlorine in precursor solution. This is due to the fact that MACI tends to sublime at elevated temperatures. Furthermore, chlorine tends to form volatile chlorine-containing species, which also tends to gradually diffuse and sublimate from the film, especially in the presence of water\(^{25,27}\). Thus, after thermal annealing in open air (relative humidity of about 40–60%) the remaining chlorine content in the resultant MAPbI\(_3\)(Cl) films is much lower than the chlorine content in the precursor solution. The low content of chlorine in the MAPbI\(_3\)(Cl) films is proven by the tiny change in absorption edge (Fig. 2c)\(^{39}\). It should be noted that the fluctuation of absorption for the case of MACI content of 0.70 and 1.00 may be due to the observed slight phase segregation and large roughness (Supplementary Fig. 12)\(^{25,27,35,39}\). Similar to chlorine inclusion, phase segregation is also observed in the bromine inclusion case with high content, i.e., (MAPb(I\(_{1-x}\)Br\(_x\))\(_3\)) (0.1 < x < 0.8)\(^{40}\), in which perovskite undergo phase separation into iodide-rich and bromide-rich regions under light illumination\(^{41}\). In the case of bromine inclusion with low content, the existence of bromine is found to assist grain growth, improve stability, and device performance\(^{40–42}\).

To further confirm the existence of chlorine in MAPbI\(_3\)(Cl) films, we employed secondary-ion mass spectrometry (SIMS) to characterize the depth profile of chlorine in the perovskite film with MACI content of 0.1 (which gives the best device performance as discussed in the device performance section). As shown in Fig. 2d, the Cl depth profile exhibits a continuous and gradual increase, and then shows a significant spatial overlap on the Ti profile. This observation is consistent with other reports revealing that the distribution of chlorine within MAPbI\(_3\)(Cl) is often inhomogeneous\(^{25,43,45}\). One possible cause responsible for the inhomogeneous distribution of chlorine is due to the tendency of chlorine to form volatile chlorine-containing species gradually diffusing and sublimating from the top surface of the film, especially in ambient air, resulting in a gradient increase of the Cl content from the film surface to bottom\(^{25}\). Although the XRD results of the MAPbI\(_3\)(Cl) films do not show obvious peaks of PbCl\(_2\) or MAPbCl\(_3\), it is worth noting that in addition to incorporation into perovskite, the chlorine may form some chloride compounds that are nondetectable by XRD due to the detection limit or the amorphous nature of these compounds.

Here, we can complete the second step of MAPbI\(_3\)(Cl) formation reaction depicted in Fig. 1a as follows:

\[
\text{H}_1-x\text{Pb}_1-x\text{I}_x+4x\text{Cl}_x + x\text{MAPbI}_3 + (1-x)\text{CH}_3\text{NH}_2 \rightarrow \text{MAPbI}_{3-x}\text{Cl}_x, \tag{2}
\]

where the chlorine-incorporated perovskite, i.e., MAPbI\(_{3-x}\)Cl\(_x\) is termed as MAPbI\(_3\)(Cl) hereafter.

**Device performance.** To study the device performance, we implemented our smooth 1.1-μm-thick MAPbI\(_3\)(Cl) films in the
device configuration of fluorine-doped tin oxide (FTO) /compact TiO$_2$/meso-TiO$_2$/perovskite/spiro-OMeTAD/Au. Supplementary Fig. 13 and Supplementary Table 3 show the device performance results. The MACI content of 0.10 case delivers the best device performance (Supplementary Note 2) with an average current density ($J_{SC}$) of 22.9 ± 0.3 mA cm$^{-2}$, open-circuit voltage ($V_{OC}$) of 1.09 ± 0.02 V, fill factor (FF) of 0.793 ± 0.015, and PCE of 19.1 ± 0.4%. As shown in Fig. 3a, a best PCE of 20.0% was achieved. The integrated $J_{SC}$ from external quantum efficiency (EQE) is in excellent agreement with current density–voltage ($J$–$V$) measurements, with a discrepancy below 2% (Fig. 3b). The representative $J$–$V$ curves under different scan directions indicate the negligible hysteresis effect (Supplementary Fig. 14). In addition, a stabilized PCE approaching 19% for device (with efficiency of 19.2% from $J$–$V$ measurements) is also achieved by holding the voltage at the maximum power point for 500 s (Fig. 3c), which further confirms the negligible hysteresis effect. When compared with reports listed in Supplementary Table 1, the MAPbI$_3$(Cl)-based devices in this work can also deliver a comparable high efficiency with perovskite film thickness over 1.1 μm as shown in Fig. 3d. This suggests that at least the 1.1-μm-thick MAPbI$_3$(Cl) layer deposited here does not show a detrimental effect in carrier transport. To further inspect the devices, we performed the cross-sectional-view SEM (Fig. 4a). It is found that the grains extend across the entire absorber layer minimizing grain boundaries and providing facile pathways for efficient charge transport. All these results prove that we obtained high-quality thick perovskite films, and high efficiency PSCs can be fabricated based on these films.

Reproducibility is crucial for mass production of low-cost optoelectronic device applications. When compared with PSCs based on perovskite films fabricated using the antisolvent method, our 1.1-μm-thick MAPbI$_3$(Cl) film-based devices show significantly improved reproducibility represented by a much smaller PCE standard deviation (decreasing from ±1.2% to ±0.4%, Supplementary Fig. 15 and Supplementary Table 4). The high reproducibility of device performance is attributed to the high reproducibility of 1.1-μm-thick MAPbI$_3$(Cl) films. To confirm this point, we measured the thickness and roughness of 16 samples of the 1.1-μm-thick MAPbI$_3$(Cl) films (Fig. 4b, c and Supplementary Figs. 16, 17). The average thickness and roughness together with their standard deviations are determined to be 1.13 ± 0.03 μm and 5.4 ± 0.4 nm, respectively. In addition, the device performance of 1.1-μm-thick MAPbI$_3$(Cl) devices is higher than that of the devices based on 450-nm-thick perovskite film deposited by the antisolvent method. The higher efficiency for the former case is mainly due to the improved $J_{SC}$ and FF, which is also supported by the EQE results in Supplementary Fig. 15. This improvement is not only due to the thicker film but also its improved film quality. Moreover, a slightly wider spectral response is observed for the 1.1-μm-thick MAPbI$_3$(Cl) film-based devices. These results suggest that high-quality, thick perovskite films can benefit the enhancement of light harvesting capability, especially at the near-infrared region, towards better device performance.

Development of scalable fabrication processes is key to further industrialization of the PSC technology. We demonstrate that our new perovskite formation method is scalable and can be used to fabricate large-area solar modules. Figure 4d shows the optical photograph of 1.1-μm-thick MAPbI$_3$(Cl) film on 5 cm × 5 cm substrates with the mirror-like smooth surface. It is also found that the film is much more uniform over the entire 5 cm × 5 cm substrate than that of antisolvent case (Supplementary Figs. 18,
We then fabricated six-cell modules (active area = 12.0 cm², geometric fill factor = 48%) as shown in Fig. 4e. A best active area PCE of 15.3% under reverse scan was achieved with a J_SC of 3.66 mA cm⁻², V_OC of 6.65 V, and FF of 0.630 (Fig. 4f), which is among the top PCE values obtained for perovskite solar modules with an active area greater than 10 cm². Furthermore, our new method shows good reproducibility in the large-area device fabrication with an average module PCE and standard deviation of 13.6 ± 0.8% (Supplementary Table 5), which is much better than that of the antisolvent case (8.6 ± 1.6%, Supplementary Fig. 20 and Supplementary Table 6). These results further confirm the excellent reproducibility of our 1.1-μm-thick MAPbI₃(Cl) films on large scale, which is a key advantage for manufacturing in the realistic industrial large-scale setting. Note that small J-V hysteresis was observed for solar modules (Supplementary Fig. 21).

**Charge carrier transport behavior.** As shown in Fig. 3d, we obtained high efficiencies with 1.1-μm-thick perovskite films. The promising device performance inspired us to conduct systematical investigations of charge transport properties of our PSC devices to find out what factors lead to the high device performance. We first performed conductive atomic force microscopy (c-AFM) measurements on the 1.1-μm-thick MAPbI₃(Cl) film and perovskite film prepared by the antisolvent method (denoted as MAPbI₃(AS)). It was found that the former shows lower roughness (Supplementary Note 3) and rounded large grains with almost four times larger grain size, and its corresponding fewer grain boundaries are expected to reduce the defects density (Supplementary Fig. 22). Moreover, the 1.1-μm-thick MAPbI₃(Cl) film also shows nearly an order of magnitude higher light-induced current (Fig. 5a), which indicates its good electrical conductivity. This observation can be ascribed to the improved crystallinity of the MAPbI₃(Cl) films with preferential (110) orientation (Fig. 5b), as a result of synergistic effect of CH₃NH₂ gas¹⁹,⁵⁷ and partial substitution of I⁻ by Cl⁻¹¹,¹².

In addition to the improvement in terms of the film morphology and conductivity, the defect nature in perovskite
films may also play a role in influencing charge carrier transport properties. To investigate radiative and nonradiative charge carrier recombination channels within perovskite films, we carried out time-resolved photoluminescence (TRPL) measurements on glass/perovskite/poly(methyl methacrylate) (PMMA) samples (Supplementary Fig. 23). Figure 5c shows the TRPL decay curves obtained from both the glass side and PMMA side for the 1.1-μm-thick perovskite films with (MAPbI₃(Cl)) and without (denoted as MAPbI₃) chlorine incorporation. Considering the limited penetration depth (tens of nanometers) of the light source, the PL emission signal only contains the charge carrier information on the surface layer that is facing the light source. The time constants (τ) are calculated to be 54 ns for the MAPbI₃ film no matter whether the laser light incidents from the PMMA side or the glass side, which indicates that perovskite on the bottom and top of film has nearly the same charge carrier properties. In the MAPbI₃(Cl) case, the PL lifetime obtained from the glass side is longer than that obtained from the PMMA side. This observation suggests that perovskite on the bottom has better charge carrier properties than the perovskite on the top in MAPbI₃(Cl) film. This observation may be correlated with the inhomogeneous distribution of chlorine within MAPbI₃(Cl) film, where chlorine within a certain range of concentrations can benefit charge carrier properties. Besides, the MAPbI₃(Cl) film shows longer PL lifetimes than that of the MAPbI₃ film. This improvement can be ascribed to the better crystallinity and a lower defect density of the MAPbI₃(Cl) film.

To quantitatively evaluate the defect density, we fabricated sandwich devices by inserting the perovskite films between FTO and gold, and characterized the evolution of the space-charge-limited current (SCLC) for different biases, as shown in Fig. 5d-i. In general, the presence of mobile species in perovskite can lead to complication in interpreting the SCLC measurement results, and often precludes a robust quantitative analysis based on such measurements. On the other hand, we observed low hysteresis on the basis of J–V measurements, which indicates a negligible effect of mobile species. Thus, in this case we can safely deduce defects density (N₁) within perovskite films based on the SCLC measurements according to the equation 13.61:

\[ N_1 = \frac{2e\xi_0 V_{\text{TTL}}}{\epsilon L^2} \]
where $\varepsilon$ and $\varepsilon_0$ are the dielectric constants of perovskite and the vacuum permittivity, respectively, $V_{TFL}$ is trap-filled limit voltage, $L$ is the thickness of the perovskite films, and $e$ is the elementary charge. We estimated the defect density to be $2.13 \times 10^{15}$ and $2.51 \times 10^{15} \text{cm}^{-3}$ for the 1.1-$\mu$m-thick MAPbI$_3$(Cl) film and MAPbI$_3$ film, respectively, prepared by the HPbI$_3$(Cl)/CH$_3$NH$_2$ method (Table 1). These defect density values are significantly lower than antisolvent case ($1.48 \times 10^{17} \text{cm}^{-3}$). The similar magnitude in terms of defects densities derived from the SCLC measurements in contrast with the clear difference in terms of lifetime derived from PL measurements is possibly due to the fact that the former measurement gives the defect information in the entire film, and the latter measurements only provides the defect information for perovskite on the top or bottom of the film. When the bias voltage further increases in the SCLC curves, the current shows a linear relationship with the square of the voltage, where we can deduce the mobility ($\mu$) from the Mott–Gurney law:

$$J_D = \frac{9\varepsilon_0\varepsilon\mu V^2}{8L^3}.$$  

The mobility are estimated to be 1.12 and 0.83 cm$^2$ V$^{-1}$ s$^{-1}$ for the 1.1-$\mu$m-thick MAPbI$_3$(Cl) film and MAPbI$_3$ film, respectively. The much higher carrier conductivity is consistent with the higher device performance of the MAPbI$_3$(Cl) case, which again verifies the positive effect of small content chlorine incorporation on the optoelectronic properties of perovskite films. In addition, these mobility values around 1 cm$^2$ V$^{-1}$ s$^{-1}$ are two orders of magnitude higher than that in antisolvent case (0.014 cm$^2$ V$^{-1}$ s$^{-1}$), which further confirms the excellent charge carrier transport properties of CH$_3$NH$_2$ gas-based perovskite films. The improved carrier properties of the 1.1-$\mu$m-thick MAPbI$_3$(Cl) films when implemented into PSCs is also verified by impedance spectroscopy characterization of devices under light illumination (Table 1 Supplementary Fig. 24 and Supplementary Note 4).

Device stability and perovskite film stability. Operational stability is another key aspect of PSCs. We studied the stability of the small size devices under the operation conditions (Fig. 6a). It was found that the 1.1-$\mu$m-thick MAPbI$_3$(Cl)-based devices showed much better stability than the MAPbI$_3$(AS) devices. Especially, the MAPbI$_3$(Cl) devices maintained over 90% of their initial performance for 800 h under continuous light illumination with

![Fig. 6](https://example.com/fig6.png)
maximum power point tracking (MPPT). While the PCEs of the MAPbI₃(AS) devices decreased to 90% of their initial performance after approximately 300 h. An initial increase of PCEs for the MAPbI₃(Cl) devices suggests the excellent long-term stability of these four devices. Note that the thickness differences between MAPbI₃(Cl) devices and MAPbI₃(AS) devices is most likely caused by the quality of the perovskite films such as crystallinity, grain size and/or defects, etc. 13,22,34.

To reveal the underlying mechanism responsible for the improved stability, we prepared four kinds of films, i.e., film A: 1.1 μm MAPbI₃(Cl) film prepared by the HPbI₃(AS)/CH₃NH₂ method; film B: 1.1 μm MAPbI₃ film by the HPbI₃/CH₃NH₂ method; film C: 0.5 μm MAPbI₃(Cl) films prepared by the HPbI₃(Cl)/CH₃NH₂ method; film D: 0.45 μm MAPbI₃(AS) films prepared by the antisolvent method. We tested the stability of these films under light illumination, a high relative humidity of about 100% and gentle thermal environment of 50 °C (denoted as LHT) as shown in Supplementary Fig. 25. It is found that the stability of these four films is in the order film A > film B > film C > film D (Supplementary Figs. 25 to 28). The improved stability of film A is firstly attributed to its improved grain crystallinity and larger grain size, which can be clearly seen by comparing the XRD peak intensity and full width half maximum of fresh film A with fresh film D (Supplementary Fig. 28b, c and Supplementary Note 5). This is because the ions in highly crystalline perovskite films have higher chemical binding energies to prevent themselves from migrating, which benefit light and thermal stability. 65 This is confirmed by SEM results shown in Supplementary Fig. 29. We found that the decomposition of perovskite mainly started from grain boundaries for all films after 1 h of LHT testing, where H₂O and O₂ can easily react with perovskite films due to the facts that (1) chemical binding at grain boundaries with low crystallinity is much weaker than that within crystals and (2) the severe ion migration in low crystallinity region especially at grain boundaries facilitates degradation (Fig. 6b)65. When further comparing film A with film B, film A shows better crystallinity, larger grain size, and also better stability (Supplementary Figs. 26 to 30). In addition, better stability of films A and B than thinner films C and D also verifies that thicker films are more advantageous in achieving better stability because the extra top layer of the compact high-quality film in the thicker films naturally helps as a protection layer to protect the film underlying the top layer. Besides, previous reports have demonstrated that often a tiny amount of I₂ existing in perovskite films can cause severe degradation of perovskite. 13,66 While, CH₃NH₂ used here provides an alkaline condition to suppress the formation of I₂ during the perovskite formation process and/or reduce the I₂ amount during the initial degradation of iodine containing perovskite films (Fig. 6b and Supplementary Fig. 28f), which may contribute to the better stability of films A, B and C than film D 13,66.

Discussion

A simple perovskite formation method based on fast reaction of chlorine-incorporated HPbI₃ and CH₃NH₂ has been developed to fabricate high-quality, over 1 μm thick and stable CH₃NH₃PbI₃(Cl) perovskite films in ambient condition. The resultant films can not only enable high efficiencies of 19.1 ± 0.4% (champion PCE = 20.0%) for small size PSCs and 13.6 ± 0.8% (champion active area PCE = 15.3%) for 5 cm × 5 cm perovskite solar modules, but also deliver excellent device reproducibility. In addition, the resultant un-encapsulated small size PSCs exhibit an excellent Tₘ₀ lifetime exceeding 1600 h under continuous light illumination with MPPT in dry N₂ environment. The excellent device stability is mainly a result of the excellent films stability. Our study not only provides a highly reproducible method to fabricate PSCs and modules with enhanced efficiency and stability, but also offers the in-depth understanding for the underlying mechanisms responsible for device stability improvement. The encouraging device performance and excellent stability in this work points out to a promising direction, i.e., use of thick absorber films to realize PSCs and modules with high efficiency, reproducibility, and stability.

Methods

Materials. All reagents were used as received without further purification, including PbI₂ (99.99%, TCI), hydroiodic acid (57 wt% in H₂O, distilled, stabilized, 99.95%, Sigma-Aldrich), chlorobenzene (99.8%, Wako), methylamine (40% in methanol, TCI), 2,2′,7′,7′-tetakis(N,N-di-p-methoxyphenylamine)-9′-spirobifluorene (spiro-MeOTAD, Merck), N,N-dimethylformamide (DMF, 99.99%, Sigma-Aldrich), methylammonium chloride (Wako), ethanol (Wako), HI (57%, Alfa Aesar), 4-tert-butylpyridine, acetonitrile (99.9%, Sigma-Aldrich), titanium disopropoxide bis(acetylacetonate) (75 wt% in isopropanol, Sigma-Aldrich), n-butyl alcohol (Sigma-Aldrich), FTO glasses (7–8 Ω sq⁻¹, Optevtech.), TiO₂ (DySelol, 30 NR-D).

Synthesis of HPbI₃: The HPbI₃ crystals were prepared using an antisolvent vapor-assisted crystallization method as shown in Supplementary Fig. 2. Briefly, 11 g PbI₂ and 7 g of HI were mixed and dissolved in 17 g of DMF to form an HPbI₃ coating HPbI₃ precursor (60 wt% HPbI₃ in DMF) at 5000 rpm for 30 s on substrates under different temperatures (room temperature, 60, 70, 80, 90, 100 °C) in ambient air condition. For chlorine-incorporated perovskite deposition, the precursor solutions containing different molar ratios of MACI:HPbI₃ (0.05, 0.10, 0.15, 0.20, 0.40, 0.70, 1.00) are deposited on substrates preheated at 90 °C at 5000 rpm for 30 s. After thermal annealing at 100 °C for 5 min to remove the solvent, part of the MACI and also part or all of the formed HI during this process, the obtained films react with CH₃NH₂ gas to form perovskite. 20,22 Then the obtained perovskite films are annealed at 100 °C for 5 min in ambient air condition before device fabrication or other characterization. A 30 μL of spiro-OmeTAD was spin coated on the perovskite film at 3000 rpm for 30 s, whereas a spiro-OmeTAD/ chlorobenzene (72.3 mg mL⁻¹) solution was employed with the addition of 17.5 μL Li-TFSI/acetonitrile (520 mg mL⁻¹) and 28.8 μL 4-tert-butylpyridine. Finally, a gold layer with a thickness of 100 nm was deposited as the counter electrode on the top of spiro-OmeTAD layer through shadow masks via thermal evaporation vacuum (5×10⁻5 Torr).

Fabrication of perovskite films and solar cells. To study the dependence of the film thickness on preparation conditions, the HPbI₃ films are obtained by spin-coating HPbI₃ precursor (60 wt% HPbI₃, DMF) at 5000 rpm for 30 s on substrates under different temperatures (room temperature, 60, 70, 80, 90, 100 °C) in ambient air condition. For chlorine-incorporated perovskite deposition, the precursor solutions containing different molar ratios of MACI:HPbI₃ (0.05, 0.10, 0.15, 0.20, 0.40, 0.70, 1.00) are deposited on substrates preheated at 90 °C at 5000 rpm for 30 s. After thermal annealing at 100 °C for 5 min to remove the solvent, part of the MACI and also part or all of the formed HI during this process, the obtained films react with CH₃NH₂ gas to form perovskite. Then the obtained perovskite films are annealed at 100 °C for 5 min in ambient air condition before device fabrication or other characterization. A 30 μL of spiro-OmeTAD was spin coated on the perovskite film at 3000 rpm for 30 s, whereas a spiro-OmeTAD/ chlorobenzene (72.3 mg mL⁻¹) solution was employed with the addition of 17.5 μL Li-TFSI/acetonitrile (520 mg mL⁻¹) and 28.8 μL 4-tert-butylpyridine. Finally, a gold layer with a thickness of 100 nm was deposited as the counter electrode on the top of spiro-OmeTAD layer through shadow masks via thermal evaporation vacuum (5×10⁻5 Torr).
Characterization. Current–voltage (J–V) characteristics of PSCs are measured under one sun illumination (AM 1.5 G, 100 mW cm⁻², calibrated using a Newport reference cell, Oriel Instruments Model Number 90025564, 2 × 2 cm²) using a solar simulator (Newport Oriel Sol 1A, Xenon-lamp, USHIO, UXL-150ISO) and a Keithley 2400 source meter in ambient air at about 25 °C and a relative humidity of about 40–60%. The small size PSCs were measured using a 0.1 cm² metal mask. No mask is used for measurement of perovskite modules. The active area of perovskite modules is 12.0 cm², determined by the overlap areas of top and bottom electrodes described in our previous publication. All the J–V curves are measured under reverse scan with a scan rate of 0.25 V s⁻¹ without preconditioning unless otherwise specified. For stability measurements, the cells were subsequently loaded in our home-designed environmental chamber coupled with a solar simulator (Pecell PEC-L01, AM1.5G) and source meter (Keithley 2401) controlled by a LabView program allowing automatic sequential measurements on the devices with adjustable acquisition time intervals. To simulate continuous solar cell operation an active bias voltage was applied to the cells maintaining the solar cell operation at the maximum power point. The devices were kept at the maximum power output voltage during the intervals between consecutive measurements. No UV-filters were used, i.e., the UV component is included in illumination. The stability measurement was performed under nitrogen box with a relative humidity below 5%. EQE measurements were performed on an Oriel IQE 200 in DC mode. SEM measurements was carried out in scanning electron microscope (Hitachi NanoLab G3 UC, FEI). XRD measurements were carried out in a Bruker D8 below 5%. EQE measurements were performed on an Oriel IQE 200 in DC mode. Impedance Spectroscopy measurements had a quadrupole mass spectrometer (HAL 7, Hiden Analytical) was used to collect the mixture from H2O and O2. SEM measurements was carried out in scanning electron microscope (Helios NanoLab G3 UC, FEI). XRD measurements were carried out in a Bruker D8 below 5%. EQE measurements were performed on an Oriel IQE 200 in DC mode. Impedance Spectroscopy measurements had a quadrupole mass spectrometer (HAL 7, Hiden Analytical) was used to collect the mixture from H2O and O2. SEM measurements was carried out in scanning electron microscope (Helios NanoLab G3 UC, FEI). XRD measurements were carried out in a Bruker D8 below 5%. EQE measurements were performed on an Oriel IQE 200 in DC mode. Impedance Spectroscopy measurements had a quadrupole mass spectrometer (HAL 7, Hiden Analytical) was used to collect the mixture from H2O and O2.

Data availability

The data that support the findings of this study are available from the corresponding author on reasonable request.

Received: 29 April 2018 Accepted: 24 August 2018

Published online: 24 September 2018

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Acknowledgements
This work was supported by funding from the Energy Materials and Surface Sciences Unit of the Okinawa Institute of Science and Technology Graduate University, the OIST Open Innovation Program, the OIST R&D Cluster Research Program, and JSPS KAKENHI Grant Number JP18K05266. S.L. acknowledges the funding support from the NII Project (B14041). The authors thank Dr. Mikas Remeika for writing the software for steady-state power measurements, Mr. Toshihiko Sasaki, Mr. Laszlo Szikszai and the Nanofab team for SEM characterization, Dr. Zhanhao Hu and Dr. Qing Wang for insightful discussion for SCLC characterization.

Author contributions
Y.Q. supervised the project. Y.Q. and Z.L. conceived the ideas and designed the experiments. Z.L. conducted the corresponding device fabrication and basic characterization. L.Q. helped with TiO₂ fabrication and stability study. E.J.-P. helped with ELS characterization, performed XRD cell parameter calibration, and TRPL fitting. Z.H. performed the conductive AFM characterization. T.K. and Z.H. performed SIMS characterization. Y.J. helped with module fabrication. Z.W. helped with mesoporous TiO₂ fabrication. S.R.R. and L.K.O. helped with CH₃NH₂ gas reaction system setup. S.L. provided valuable suggestions for this work. Z.L. and Y.Q. participated in all the data analysis. All authors contributed to writing the paper.

Additional information
Supplementary Information accompanies this paper at https://doi.org/10.1038/s41467-018-06317-8.

Competing interests: The authors declare no competing interests.

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