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In-depth Investigation of Methylamine Gas Post-treatment for MAPbI₃ Films and its Potential for Upscaling Perovskite Solar Cells

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Broader context

Scaling up perovskite solar cells (PSCs) for commercial applications requires maintaining high film quality over large areas, a challenge hindered by morphological defects and chemical inconsistencies. Most existing approaches to large-area fabrication involve modifying the drying process - such as using co-solvents or alternative techniques - to improve film uniformity. While these methods enhance film, quality compared to small-area antisolvent processes, they still result in performance losses during scale-up, indicating that a truly lossless transition to large-area devices has not yet been achieved. We propose that a more practical and effective solution lies in post-treatment strategies that repair or modify films after deposition to homogenize morphology and composition. Among these, methylamine gas treatment (MATM), which induces film liquefaction and recrystallization, shows particular promise. This method offers the potential to enhance film uniformity and preserve device efficiency during scaling. In our earlier research, we demonstrated control of MATM through adsorption kinetics and developed a prototype reactor capable of uniformly treating substrates as large as 10 cm × 10 cm, laying the groundwork for scalable, efficiency-retaining fabrication of perovskite films.



ARTICLE

In-depth Investigation of Methylamine Gas Post-treatment for MAPbI₃ Films and its Potential for Upscaling Perovskite Solar CellsDuc-Anh Le,^a Tzu-Chien Wei^{*a,b}Received 00th January 20xx,
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Scaling up perovskite solar cells (PSCs) for commercial applications requires maintaining film quality across large areas, a challenge often compounded by morphological defects and chemical heterogeneity. Methylamine gas treatment (MATM) offers a promising post-processing strategy by inducing liquefaction and recrystallization of Methylammonium-based perovskite films, thereby enhancing their uniformity and chemical homogeneity. However, how to properly conduct the MATM—particularly the influence of environmental humidity on its outcome has rarely been investigated. In this study, we report that environmental moisture critically undermines MATM efficacy by triggering side reactions that generate PbO, PbIOH, and MAPbI₂OH impurities. Through systematic comparison of MAPbI₃ films treated under dry and humid conditions, we elucidate the degradation mechanisms using various analyses and conclude moisture exposure during MATM drastically increases trap densities and non-radiative recombination, leading to reduced carrier lifetimes and photovoltaic performance. A PSC with an initial power conversion efficiency (PCE) of 16.67% exhibits a significant improvement to 19.48% after undergoing MATM in a dry environment. In contrast, when MATM is performed under humid conditions, although the surface smoothness of the MAPbI₃ film is greatly improved, the PCE of the device declines instead of increasing. This outcome highlights the detrimental effects of side reactions induced by moisture during the MATM process. These findings underscore the importance of moisture isolation in MATM to enable the reliable upscaling of high-efficiency and stable perovskite solar modules.

Introduction

Organic lead halide perovskites (PVSKs) have garnered significant attention in recent years as absorbers for photovoltaic devices due to their low exciton binding energy, high extinction coefficient and exceptional defect tolerance¹⁻⁵. Since Miyasaka's group first reported perovskite solar cells (PSCs) based on these materials in 2009, their power conversion efficiency (PCE) has sharply increased to 27.0%, rivalling that of crystalline silicon photovoltaic technology, which has been developed for over half a century^{6, 7}. Despite this impressive progress, such high PCE PSCs were achieved primarily on very small active areas (mostly <0.1 cm²). However, in practical applications, the performance of photovoltaic devices is evaluated by power output rather than efficiency alone. Thus, the ability to maintain high PCE over large-area substrates has become a critical challenge in the commercialization of PSCs. An ideal PVSK layer should exhibit a homogeneous chemical composition, a compact and smooth morphology, and low impurity content. After more than a decade of effort, these properties can now be reliably achieved in small-area devices.

Despite the promising results achieved with small-area devices, the application of these techniques to large-area substrates remains technically challenging, particularly in terms of uniform film formation, defect control, and process reproducibility. Various methods for fabricating large-area perovskite absorber layers have been reported, among which solution-based, wet-coating processes remain the most mature and widely applied. These approaches involve dissolving perovskite precursors in highly polar organic solvents, coating them onto substrates to form wet films, and then inducing crystallization by removing the solvent. Based on a literature survey on large-area PVSK thin film fabrication, the process can be generally divided into three steps:

Step-1: deposition of the wet precursor film, using methods such as spin coating⁸, slot-die coating⁹, spray coating^{10, 11}, screen printing¹², and inkjet printing¹³;

Step-2: drying and crystallization to form a primary PVSK film, using techniques such as anti-solvent treatment^{14, 15}, thermal annealing¹⁶, vacuum-assisted drying^{17, 18}, or hot wind drying^{19, 20};

Step-3: post-treatment to further improve PVSK film quality, such as passivation, solvent annealing²¹⁻²³ or liquefaction–recrystallization strategies^{24, 25}.

It is worth noting that in many reports on large-area PSCs, the precursor solution used in Step-1 is often supplemented with a secondary solvent or specific additives to modulate the

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crystallization behaviour and improve the morphology and quality of the resulting PVSK films²⁶⁻²⁹. Among these three steps, we believe that Step-3, the post-treatment stage, is particularly critical for future large-scale production, as it possibly provides a “healing” mechanism to fix the quality of the primary PVSK film formed in Step-2, if it is properly designed. This, in turn, reduces the precision demands and investment on both the coating equipment and the solvent removal systems, which can have a positive impact on lowering manufacturing costs and improving production yield.

The liquefaction-recrystallization strategy is one typical example for Step-3, it involves reacting the primary PVSK film (formed after Step-2) with amine compounds to produce a chemically adsorbed intermediate in a liquid phase. This liquid intermediate allows for self-levelling of the film, and upon removal of the amine species, a recrystallized PVSK film (hereafter named as secondary PVSK) with enhanced uniformity and compactness can be obtained. A representative showcase of this strategy is the methylamine gas treatment (MATM) for MA-based perovskites. Methylamine (MA⁰) is a volatile chemical (boiling point -6 °C) that can rapidly react with MAPbI₃, inducing liquefaction of the perovskite layer within less than one second. Subsequent removal of MA⁰ leads to recrystallization, enhancing crystal quality and reducing defect density, thereby improving PSC performance^{24, 25, 30-33}.

MATM was first proposed by Pang et al. in 2015, who attributed the liquefaction-recrystallization mechanism to interactions between the lone electron pair on the nitrogen atom of MA⁰ and the PbI₆ octahedra in MAPbI₃, disrupting the 3D crystal structure and resulting in liquefaction. Other studies have shown that PbI₂, a common precursor in perovskite formation, can also transit into a molten state upon exposure to MA⁰ or other amines, suggesting that the liquefaction is driven by coordination between Pb²⁺ ions and amines^{24, 25, 30, 34-37}. Kerner et al. further reported that the formation of Pb-amide bonds via proton transfer plays a critical role in triggering the liquefaction³⁸.

As noted above, the adsorption and desorption kinetics in MATM are extremely rapid, with the liquefaction occurring within ~1 second³². This narrow process window poses a major challenge for implementing MATM in scalable manufacturing systems. To address this issue, we have developed a controllable MATM technique in which the partial pressure of MA⁰ is finely tuned to control the liquefaction kinetics. We have found that the amount of MA⁰ adsorbed onto the primary MAPbI₃ film significantly influences the morphology and crystallinity of the resulting secondary film. Moderately reducing the MA⁰ concentration during MATM facilitates the formation of high-quality films. Using our home-made MATM chamber, we successfully scaled up the process from small-area devices to 5 cm × 5 cm mini-modules without PCE loss³¹.

To further evaluate the industrial feasibility of MATM, this study investigates the influence of environmental moisture during treatment, as humidity content is an important factor in PSC fabrication. In 2020, Bogachuk et al. reported that MA⁰ reacted with MAPbI₃ powders in humid environments to form photo-inactive by-products such as PbIOH, demonstrating that

moisture can significantly hinder successful recrystallization during MATM³⁹. Controlling humidity during production is closely tied to manufacturing cost. Therefore, humidity not only affects the outcome of MATM but also represents a critical consideration in the design of future PSC production lines. Based on this background, this study systematically examines the effect of ambient humidity on the crystallinity, morphology, and optoelectronic properties of secondary MAPbI₃ films treated with MA⁰. We further correlate these findings with device performance, stability, and reproducibility, in order to strengthen the feasibility of this method for future large-scale PSC manufacturing.

Experimental section

Substrate cleaning

The fluorine doped tin oxide glass (FTO, 2.2 mm thick, 8 Ωsq⁻¹, Dyesol) was dried etching by laser machine (LMF-020F, Laser Life Company, Taiwan). The etching FTO was cleaned by detergent solution (PK-LCG46, Parker International Co. Ltd., Taiwan) and reverse osmosis (RO), then rinsed with deionized water (DI), ethanol 95% (ECHO, Taiwan), and dried by hot-air blow gun. Before compact layer TiO₂ (cTiO₂) deposition, the cleaned FTO substrate was treated by UV/Ozone for 30 min.

Electron transport layer (ETL)

The cTiO₂ precursor solution was prepared by mixing 6% v/v of titanium diisopropoxide bis(acetylacetonate) solution, 4% v/v of acetylacetonate and ethanol. The cTiO₂ precursor was sprayed on hot reheated FTO for 8 circles. In which, the flow of O₂ was controlled at 0.4 L/min, and 1 min resting time for each circle. After spraying process, the substrates were annealed at 500 °C for 30 min.

A commercial paste TiO₂ (30 NR-D, GreatcellSolar) was diluted in ethanol absolute 99.8% (Honeywell) with ratio 1:7 (weight). Then it was coated onto the cTiO₂ substrate at 6000 rpm for 30 s. Mesoporous TiO₂ (mTiO₂) coated substrate was dried on the 120 °C hotplate for 5 min, then the mTiO₂ films were gradually to 500 °C and cooled to room temperature. After cooling down to 150 °C, the mTiO₂ substrate was treated by UV-Ozone for 20 min, then transferred to humidity-controlled room (10-20% humidity) for preparation of perovskite films.

PVSK fabrication

A PVSK precursor solution contains 1.5 M PbI₂ (99.0%, Xian Polymer Chemicals) 1.5 M MAI (GreatcellSolar) and 0.35 M MACI (99.9%, GreatcellSolar) in DMF:DMSO (99.9%, Sigma-Aldrich) mix solvent (volume ratio = 9:1). **Primary-MAPbI₃** films were prepared by coating the precursor solution onto mTiO₂ substrate at 3000 rpm for 10 s, then the wet PVSK film was transferred to a vacuum chamber with continuous N₂ flow. The pressure of chamber was controlled at 150 torr, and the PVSK film was in vacuum for 30 seconds. After that, the dried PVSK film was heated at 150 °C for 10 min.

MATM under various moisture conditions

A MA⁰ induced liquefaction and recrystallization reactor (MALCR) was used to prepare MA⁰-treated MAPbI₃ films (**2nd-**



MAPbI₃/dry). MA⁰ gas was generated from a 33 wt% MA⁰ ethanol solution (Sigma-Aldrich). The effective MA⁰ concentration was determined using Raoult's law, and the measured vapor pressure (149 kPa) corresponded to ~45% MA⁰ concentration during MATM. The Primary-MAPbI₃ films were moved into the MALCR system and vacuum for 5 min to remove moisture absorption on PVSK films. Then MA⁰ gas was exposed into the reaction chamber. At the point during exposure where the PVSK completely changes to transparent (a few seconds), the MALCR chamber was vacuum to remove MA⁰ gas. The transparent film was changed back to the dark brown film. Then the pressure was released and the **2nd-MAPbI₃/dry** films were moved onto the 100 °C hotplate for 10 min to completely remove remaining MA⁰ gas on the PVSK films.

For the MATM in the presence of moisture, the MA⁰ gas was premixed with air from a controlled dry room (25 °C, 20% RH) before injection into the MALCR. Thus, the chamber humidity was maintained consistently at 20% RH throughout the treatment for 5 minutes. **2nd-MAPbI₃/wet** films were then obtained after evacuating the chamber to complete the desorption process. **2nd-MAPbI₃/wet/heat** films were prepared by heating the **2nd-MAPbI₃/wet** films at 100 °C for 5 min.

After cooling down to room temperature, the **2nd-MAPbI₃** films were moved back to the humidity-control room to be deposited hole transporting material (HTM).

Hole transporting layer (HTL) deposition

The HTM precursor containing 32 mM Lithium bis(trifluoromethanesulfonyl)imide (Li-TFSI, >99.9%, Sigma-Aldrich), and 195 mM 4-tert-Butylpyridine (4-tBP, 96%, Sigma-Aldrich) in CB was kept stirring in room temperature for 1 day. The 2,2',7,7'-Tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene (Spiro-OMeTAD, 99.5%, Lumtec) powder was added into the HTM precursor (75 mM) as the HTM solution. The HTM solution was spin-coated onto the FTO/ETL/Perovskite substrate at 4000 rpm for 25 s. Then, the pre-mature devices (FTO/ETL/PVSK/HTL) were stored at a dark and dry box (RH = 10%) overnight.

Electrode deposition

An ~100 nm thickness gold electrode was thermally evaporated onto the HTL at 1 × 10⁻⁶ mbar.

Module fabrication

The FTO glass was cut as 4 cm × 4 cm or 5 cm × 5 cm then was scribed P1 by laser machine with 532 nm Laser (Lifelasar Co. Ltd). The laser speed, power ratio and frequency were 300 mm/s, 40% and 20 kHz, respectively. The etching FTO was cleaned by following the substrate cleaning process. Before spraying cTiO₂, the clean FTO was cleaned under UV-O₃ for 30 min then reheated at 500 °C for 30 min and kept at 500 °C during spraying process.

The cTiO₂ and mTiO₂ coating were following the spray-coating compact layer and spin-coating mesoporous layer above. After annealing mTiO₂ and cooling down to 150 °C, the TiO₂ substrate was treated by UV-Ozone for 30 min, then transferred to humidity-controlled room (10-15% humidity) for preparation of PVSK films. The PVSK precursor was prepared 1.5 M MAPbI₃

as above. The PVSK coating followed the coating process using vacuum method.

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The MATM was operated by using the home-made MALCR as the **2nd-MAPbI₃/dry** film preparation. The MA solution (33 wt.% in absolute ethanol) was stored in MA⁰ source chamber. Another chamber was used as reacting chamber. The reacting chamber was vacuum drawn to reach around 8 torr on sensor. Then the valve, which connected the MA⁰ source chamber and reacting chamber, was slowly opened until the pressure value on sensor reached 150 Torr. The N₂ flow and vacuum pump were used to purge MA⁰ gas out of the MATM chamber. Then PVSK films were heated at 100 °C for 10 min.

The pre-solution containing 16 mM Li-TFSI, and 85 mM 4-tBP in CB was kept stirring in room temperature for 1 day. The Spiro-OMeTAD powder was added into the pre-solution (35.5 mM) as the HTM solution. The HTM solution was spin-coated onto the perovskite film at 2000 rpm for 25 s.

Then, the pre-mature devices (FTO/ETL/Perovskite/HTL) were scribed P2 by laser with 100% power ratio, 70 kHz in frequency and 1800 mm/s speed of laser. Then the pre-mature devices stored at a dark and dry box (RH = 10%) overnight.

An ~100 nm thickness gold electrode was thermally evaporated onto the HTL at 1 × 10⁻⁶ mbar. Finally, P3 etching used at the same laser with P2 with laser power ratio of 100%, frequency of 80 kHz and 1800 mm/s.

Characterization

The surface morphology of the samples was examined using field-emission scanning electron microscopy (FESEM, HITACHI, Japan), while atomic force microscopy (AFM, C3000 Nanosurf, Switzerland) was employed to assess surface roughness. The optical properties were characterized through ultraviolet-visible (UV-Vis) spectroscopy using a spectrometer (UV-vis HP8453, USA). Steady-state and time-resolved photoluminescence (PL and TRPL) measurements were conducted with a photoluminescence spectrometer (FS5 EDINBURGH Instrument, England). Structural analysis of the thin-film samples was performed via X-ray diffraction (XRD) using a Bruker 8D X-ray diffractometer, equipped with a ceramic tube (Cu K α , λ = 1.5418 Å). X-ray photoelectron spectroscopy (XPS, PHI 5000 Versa Probe II, USA) was applied to investigate the chemical state of different types of PVSK and PbI₂ films. The photovoltaic performance of was evaluated using a computer-controlled digital source meter (Keithley 2401, USA) under simulated sunlight provided by a commercial solar simulator (PEC-L15, Percell Technologies, Japan) at 1 sun, AM1.5G, with light intensity calibrated by a monocrystalline silicon photodiode (KG3, Oriel, USA). A 0.056 cm² photomask was affixed to the front of the PSC to ensure precise control over the illuminated area for small-scale devices. Additionally, the trap-filled limit voltage (V_{TFL}) was determined through space charge limited current (SCLC) measurements using a digital source meter (Keithley 2401, USA), employing a scanning rate of 10 mV/s within a voltage range of 0 to 4 V

Results and discussion



Chemical reaction of MAPbI₃/PbI₂ and MA⁰ in moisture.

Four types of MAPbI₃ films were investigated in this study, including the primary MAPbI₃ film (**Primary-MAPbI₃**) used as a control and three secondary MAPbI₃ films subjected to different MATM conditions. All MATM processes were carried out in a home-made, custom-designed methylamine liquefaction and crystallization reactor (MALCR, shown in **Figure S1**), which features a dual-function chamber that allows for either vacuum evacuation or methylamine treatment to be conducted independently. The first secondary MAPbI₃ sample (**2nd-MAPbI₃/dry**) was prepared by placing the primary MAPbI₃ film into the MALCR chamber, followed by a 10-minute vacuum treatment to remove moisture from both the film surface and the chamber interior. Afterward, MATM was performed to

ensure that the reaction occurred in a moisture-free environment. Following this, the chamber was evacuated to complete the desorption process. This sample is hereafter named as the **2nd-MAPbI₃/wet**. For the third secondary MAPbI₃ sample, after undergoing the same MATM process as the previous sample, the film was further heated on a 100 °C hotplate for 10 minutes after removal from the chamber, this sample is hereafter named as **2nd-MAPbI₃/wet/heat**. The sample preparation flowchart is illustrated in **Figure 1**.

Firstly, crystallinity and phase composition of the investigated MAPbI₃ films was analysed using XRD. The XRD patterns are collected and shown in **Figure 2a**. Crystallographic reference data were obtained from the following databases: tetragonal MAPbI₃ (COD-4518042)⁴⁰, PbO.PbIOH (COD-9017630), PbIOH

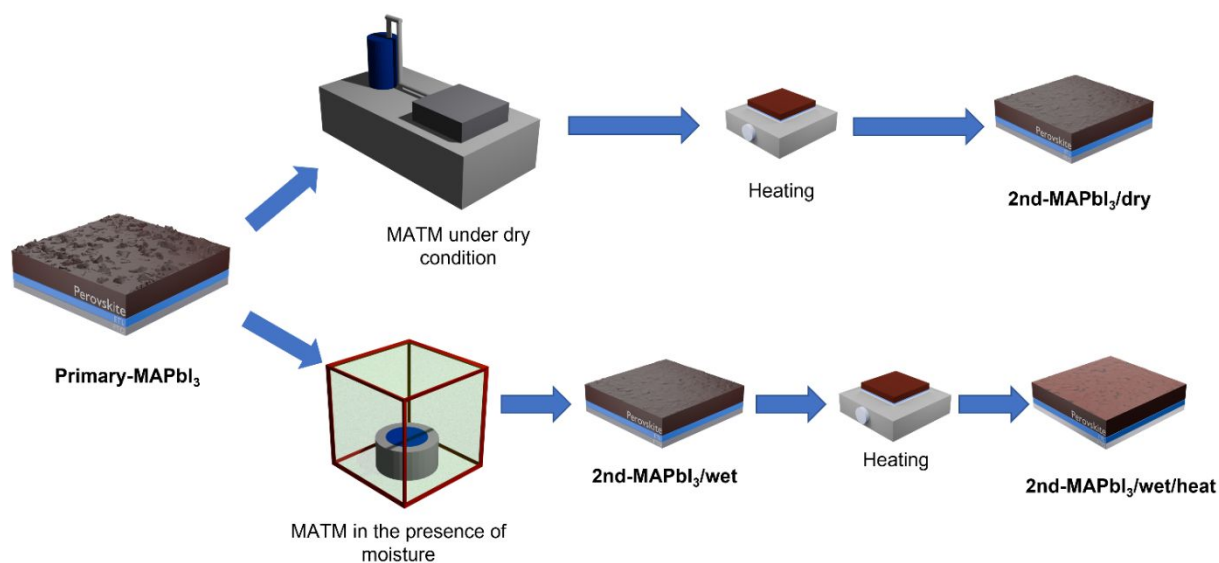


Figure 1: Schematic diagram of sample preparation

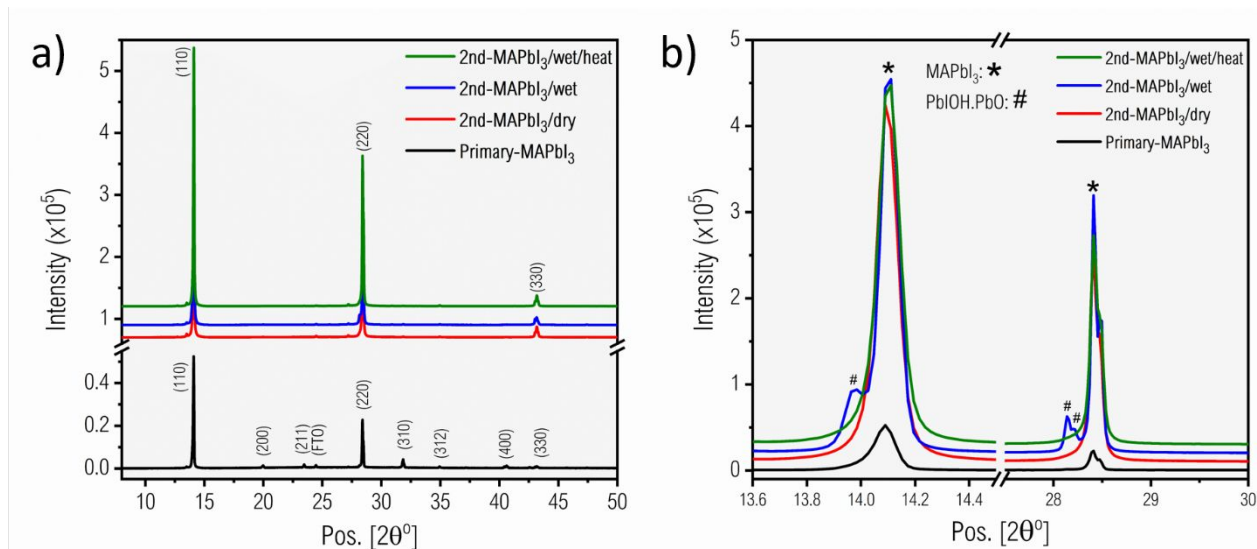


Figure 2: a) XRD pattern and b) zoom-in peak at 14.0° and 28.5° of Primary-MAPbI₃, 2nd-MAPbI₃/dry, 2nd-MAPbI₃/wet and 2nd-MAPbI₃/heat films



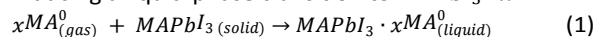
(COD-9017629)⁴¹, PbO (COD-9012703)⁴², and PbI₂ (COD-9009141)⁴³, which were used to identify the formation of the main perovskite phase and possible impurity phases. **Primary-MAPbI₃** exhibits characteristic diffraction peaks at 2θ values of 14.09°, 19.98°, 23.47°, and 28.43°, corresponding to the (110), (200), (211), and (220) planes of polycrystalline MAPbI₃, respectively. In contrast, the three secondary MAPbI₃ samples display three prominent diffraction peaks at 14.10°, 28.39°, and 43.23°. Notably, the peak corresponding to the (110) plane (2θ = 14°) is significantly enhanced – by approximately one order of magnitude – consistent with previous reports^{25, 31, 35, 44}. Zoom-in XRD pattern of the **2nd-MAPbI₃/wet** (Figure 2b) shows extra diffraction peaks at 2θ = 13.94°, 28.13°, and 28.33°, which are attributed to PbO, PbOH, clearly indicating that the presence of moisture during the MATM process can lead to the formation of impurity. This observation is in agreement with the findings reported by Bogachuk et al.³⁹. Although these impurity-related diffraction peaks disappeared **2nd-MAPbI₃/wet/heat**, further investigation is necessary to confirm whether the impurities have been eliminated.

The XPS survey spectrum (Figure S2) of a MAPbI₃ perovskite film reveals peaks at binding energies of 532 eV, 402.5 eV, and 285 eV, corresponding to O 1s, N 1s, and C 1s orbitals, respectively. The characteristic doublet peaks of Pb 4f and I 3d are observed at approximately 138 eV/143 eV and 619 eV/631 eV, respectively, with their expected spin-orbit splitting. To study the chemical modifications in MAPbI₃ films under moisture exposure, XPS elemental spectra were analysed. The spectra were calibrated to 285.0 eV, referencing the C 1s binding energy associated with adventitious (aliphatic) carbon or surface-adsorbed hydrocarbon species from the atmosphere⁴⁵. The core-level spectra were fitted using Gaussian line shapes with a Shirley background to ensure accurate peak deconvolution. **Figure S3a** displays the XPS spectra of the C 1s core level of investigated samples. All of them exhibit five peaks at 285.0 eV, 286.4 eV, and 286.7 eV. The peak at 285.0 eV is used for calibration and is attributed to adventitious carbon or surface-adsorbed hydrocarbon species. The peak at 286.4 eV can be assigned to C–O or C–OH, which is also associated with surface-adsorbed species. The peak at 286.5 eV can be attributed to C–N bond of ammonium species in the MAPbI₃ film. **Figure S3b** shows the XPS of N 1s core level of MAPbI₃ films. All samples contain a single peak at 402.5 eV, corresponding to the C–N bond in MAPbI₃ films. The XPS spectra for core level I 3d (**Figure S3c**) exhibit two peaks at 619.4 eV and 630.8 eV, corresponding to doublets I 3d_{5/2} and I 3d_{3/2}, which are assigned to Pb–I bonding in MAPbI₃ film.

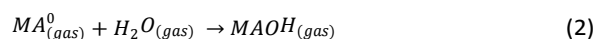
Figure 3 shows Pb 4f core level spectra of investigated MAPbI₃ films. **Primary-MAPbI₃** (**Figure 3a**) and **2nd-MAPbI₃/dry** (**Figure 3b**) exhibit nearly identical spectra, in which the Pb 4f_{7/2} peaks can be further deconvoluted to two contributions at 138.5 eV and 136.8 eV, corresponding to Pb–I, and metallic lead (Pb⁰), respectively. For **2nd-MAPbI₃/wet** (**Figure 3c**) and **2nd-MAPbI₃/wet/heat** (**Figure 3d**), the Pb 4f_{7/2} spectra exhibit a positive shift, allowing for the fitting of an additional peak at

approximately 138.7 eV, which is attributed to Pb–OH.⁴⁶ A zoom-in observation (**Figure S4**) of 136.0 to 138.0 eV region of Pb 4f_{7/2} spectra reveals the existence of an additional peak at 137.1 eV for **2nd-MAPbI₃/wet** and **2nd-MAPbI₃/wet/heat**, which is attributed to Pb–O.⁴⁷ **Figure 4** depicts the binding ratios from deconvoluted Pb 4f_{7/2} spectra. In **Primary MAPbI₃**, Pb–I bonding characteristic of MAPbI₃ accounts for as much as 95.3% of the total lead signal, with the remaining 4.7% consisting of Pb⁰. Notably, contributions from Pb–OH and Pb–O species are not detectable. The result for **2nd-MAPbI₃/dry** is similar to those of **Primary-MAPbI₃**, with contributions from Pb–I, Pb⁰ accounting for 96.7%, and 3.3% respectively. This strongly supports the conclusion that MATM conducted in a dry condition, specifically repairs film morphology without altering the chemical composition of the MAPbI₃ layer. On the contrary, in **2nd-MAPbI₃/wet**, the proportion of Pb–I bonds decrease sharply to 56.6%, accompanied by a significant increase in Pb–OH and Pb–O signals to 41.6% and 1.4%, respectively. This clearly confirms the catastrophic chemical transformation that occurs when MATM is conducted in a humid environment: nearly one-third of the MAPbI₃ is converted into photoinactive by-products. For **2nd-MAPbI₃/wet/heat**, the contributions of Pb–I, Pb–OH, and Pb–O are 60.6%, 36.6%, and 2.8%, respectively. These results indicate that post-heating fails to remove the degradation products formed during the moisture-involved MATM. In fact, the Pb–O signal slightly increases, suggesting further chemical transformation during the heat treatment. This strongly implies that the Pb–OH species in the **2nd-MAPbI₃/wet** are not merely in the form of Pb(OH)₂, but rather exist as photoinactive MAPbI_{3-y}(OH)_y-type pseudo-perovskites.

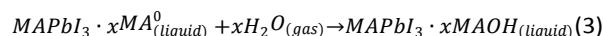
Based on the XPS analysis, we propose the following reaction mechanism when MATM undergoes in the presence of moisture. Ideally, MA⁰ gas is absorbed onto the MAPbI₃ film, inducing a liquid-phase transition to MAPbI₃ · xMA⁰:



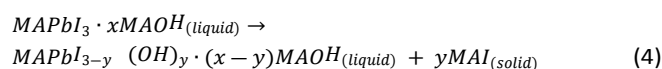
When moisture exists, the unpaired electron on the nitrogen atom of MA⁰ readily interacts with H₂O, leading to the formation of MAOH:



Water can also react with adsorbed MA⁰ to form MAOH-related intermediates:



The OH[−] then exchanges with the I[−] in the liquid intermediate, leading to the formation of MAPbI_{3-y}(OH)_y intermediate:



This intermediate can further degrade into PbOH and PbO:



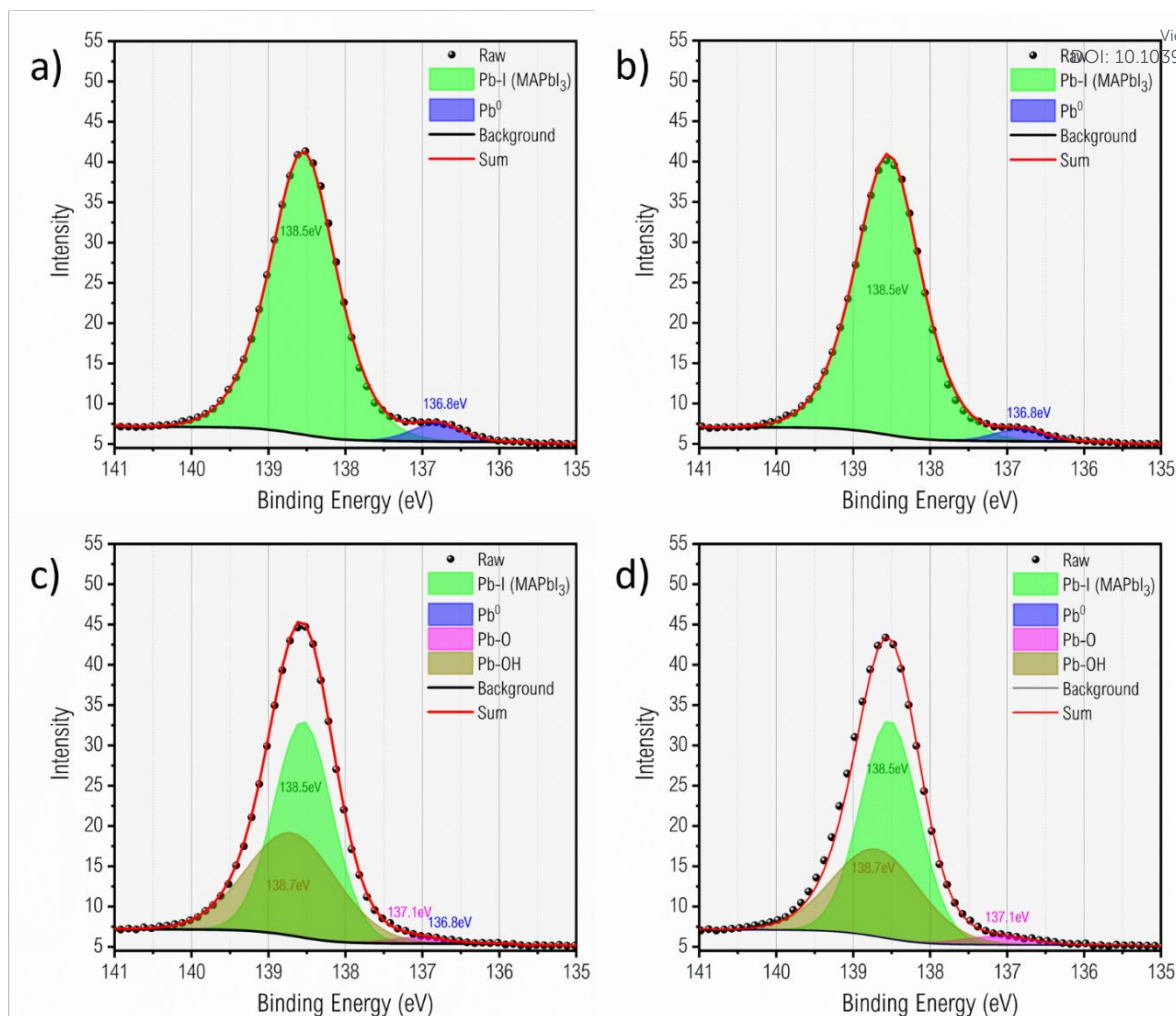
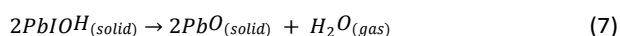
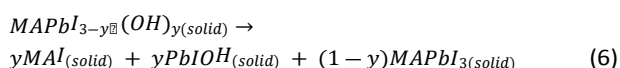
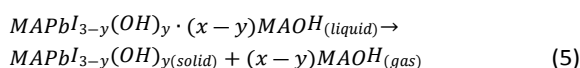


Figure 3: XPS Pb 4f_{7/2} region of a) Primary-MAPbI₃, b) 2nd-MAPbI₃/dry, c) 2nd-MAPbI₃/wet and d) 2nd-MAPbI₃/heat films



Since solution-processed MAPbI₃ films typically contain unreacted PbI₂⁴⁸⁻⁵⁰, we then shifted our focus on the effect of PbI₂ during moisture-involved MATM. Whether and how this residual PbI₂ undergoes transformation during the MATM process remains an intriguing yet explored question. Following the same analytical approach used for MAPbI₃, we prepared three types of PbI₂ film samples: **Raw-PbI₂**, **PbI₂/wet**, and **PbI₂/wet/heat**. These correspond to PbI₂ films spin-coated onto glass substrates, films subjected to moisture-involved MATM, and those further treated by post-annealing, respectively. **Figure 5** presents the XRD patterns of the investigated PbI₂ samples, in which the diffraction pattern of **Raw-PbI₂** displays characteristic peaks at 12.68°, 22.99°, 25.45°, 33.66°, 39.54°, and 41.70°, corresponding to (001), (010), (002), (120), (121)

orientations of PbI₂ polycrystals. For **PbI₂/wet**, additional peaks emerge at 14.11°, 28.39°, 31.87°, 40.80°, and 43.26°. Notably, the peak at 14.11° closely aligns with the (110) characteristic diffraction of MAPbI₃, strongly implying the formation of

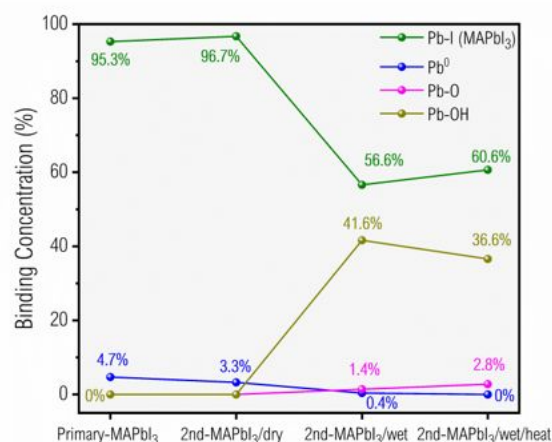


Figure 4: Pb binding ratios of four types MAPbI₃ films from deconvoluted Pb 4f_{7/2} spectra.



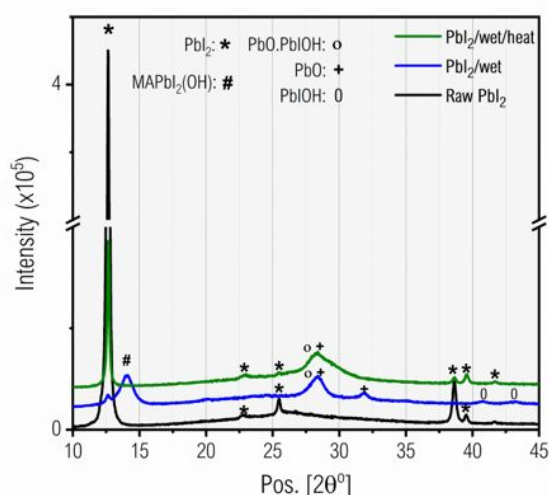


Figure 5: XRD patterns of Raw-PbI₂, PbI₂/wet and PbI₂/wet/heat films

MAPbI₂OH pseudo-perovskite⁵¹. Other additional peaks of **PbI₂/wet** at 28.39°, 31.87°, 40.80°, and 43.26° are associated with lead oxide and hydroxide compounds, specifically PbO.PbIOH, PbO, and PbIOH. Upon heating (**PbI₂/wet/heat**), the

peak at 14.11° disappears, whereas the peak at corresponding to PbO.PbIOH (28.2°) persists.

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XPS survey spectra of investigated PbI₂ films is shown in **Figure S5**. Similarly, C 1s, O 1s, Pb 4f and I 3d orbitals are clearly identified, in which Pb 4f elemental spectra are deconvoluted for discussion. As shown in **Figure 6a**, **Raw-PbI₂** exhibits a dominant peak at 138.9 eV, attributed to the Pb–I in PbI₂, along with a minor peak at 137.1 eV (shown in **Figure S6**), corresponding to Pb–O in the PbI₂(DMSO)_x complex, respectively^{52–54}. For **PbI₂/wet** (**Figure 6b**), a shift in binding energy to 138.76 eV is observed, enabling the fitting of an additional peak at 138.7 eV, which corresponds to Pb–OH bonding. Upon heating (**PbI₂/wet/heat**), the removal of MAOH reduces the Pb–OH contribution, causing the main peak to revert to 138.84 eV (**Figure 6c**). **Figure 6d** summarizes the bonding ratio of lead species in the PbI₂ film, which is normalized by the area of Pb 4f_{7/2} peak. In the **Raw-PbI₂** films, the Pb–I bonds dominate, accounting for 96.3%, with a small fraction of Pb–O bonds as 3.7%. In contrast, the **PbI₂/wet** film shows a dramatic decrease in Pb–I bonding to 53.4%, accompanied by a significant increase in Pb–OH bonding to 40%, and a slight rise in Pb–O bonding to 6.6%, indicating the

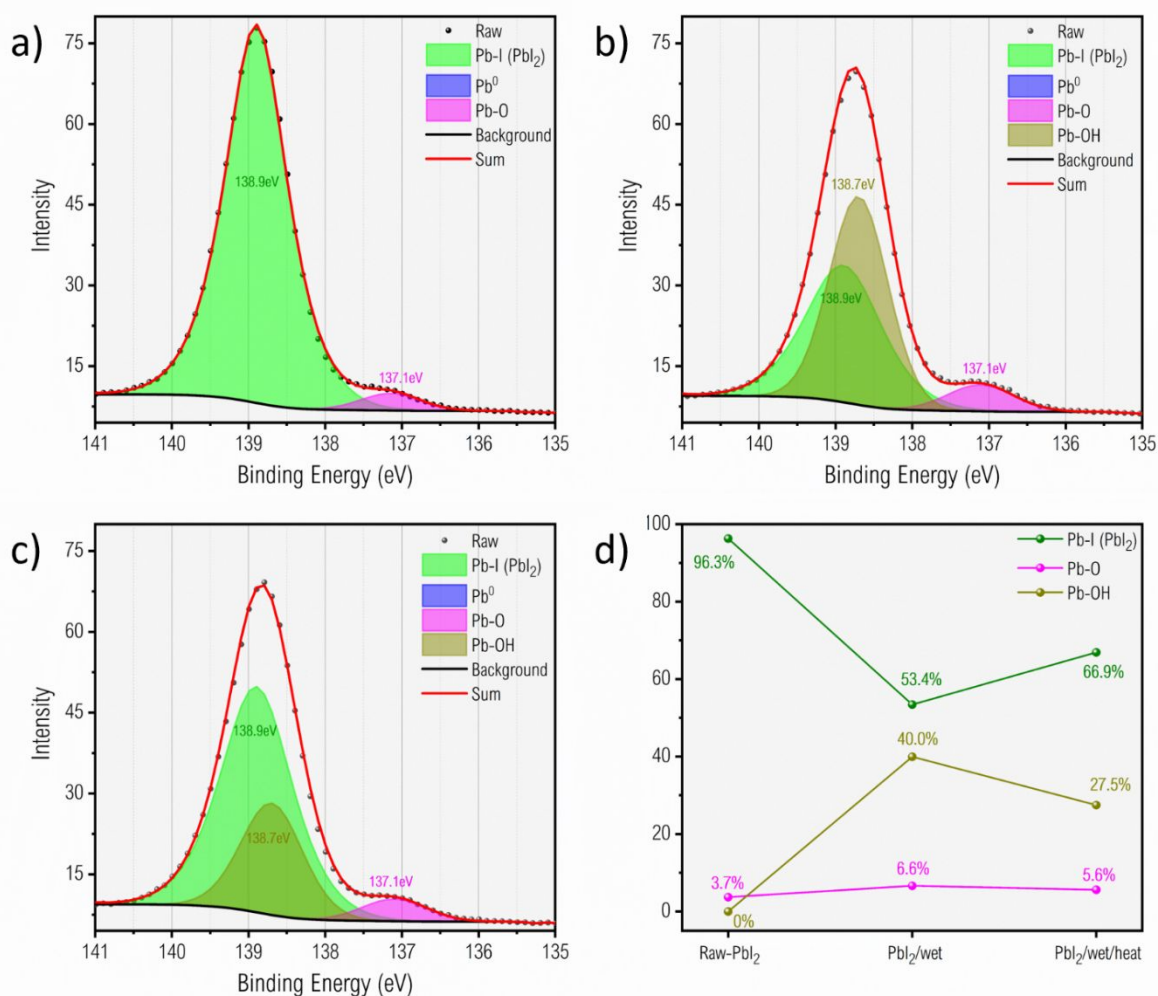
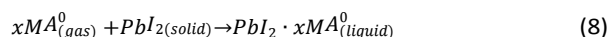


Figure 6: a, b, c) XPS Pb 4f_{7/2} regions and d) binding ratios of Raw-PbI₂, PbI₂/wet, PbI₂/wet/heat films

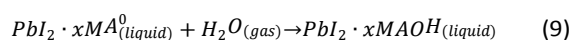


formation of lead hydroxide and lead oxide in the **PbI₂/wet** film. Upon annealing (the **PbI₂/wet/heat**), the Pb–I bond ratio increases moderately to 66.9%, while Pb–OH and Pb–O decrease modestly to 27.5% and 5.6%, respectively. These results indicate that the interaction of PbI₂ film and MA⁰ under humid conditions leads to the formation of Pb–OH and Pb–O, both will remain in the resultant film, even with a post-heating treatment.

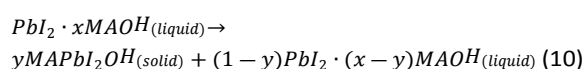
Similarly, possible reactions involved in MATM on PbI₂ film in the presence of moisture are proposed below. Ideally, PbI₂ chemisorbs MA⁰ to form a liquid-phase PbI₂ · xMA⁰ complex:



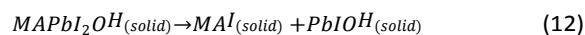
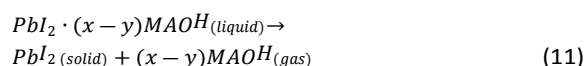
However, water can also react with MA⁰, as mentioned previously in reaction (2). Or with adsorbed MA⁰ intermediate, eventually forming PbI₂ · xMAOH:



The OH[−] can exchange with I[−] to produce pseudo perovskite MAPbI₂OH and PbI₂ · MAOH intermediate:



The pseudo perovskite and intermediate can further decompose into PbIOH and PbO:



PbIOH further decomposes into PbO and H₂O as mentioned above in reaction (7).

Morphology analysis

Figure 7 illustrates the SEM and AFM topographies of the investigated MAPbI₃ films. **Primary-MAPbI₃** film (**Figure 7a**), consists of large MAPbI₃ grains ranging from 500 to 2000 nm, rendering to a rough surface with a surface roughness (Sa) of 66.7 nm. All MA⁰-treated samples reveal significantly reduced surface roughness. Sa of **2nd-MAPbI₃/dry**, **2nd-MAPbI₃/wet** and **2nd-MAPbI₃/wet/heat** are 13.96 nm, 12.58 nm and 14.16 nm, respectively. Due to the inherent dissolution–recrystallization behaviour of MATM, the significant reduction in Sa values observed in the three MATM-treated samples is expected, as this mechanism naturally smoothens the MAPbI₃ film surface. The top-view images of **2nd-MAPbI₃/dry** (**Figure 7b**) and **2nd-MAPbI₃/wet** (**Figure 7c**) show almost no discernible differences, either in SEM morphology or Sa values.

In

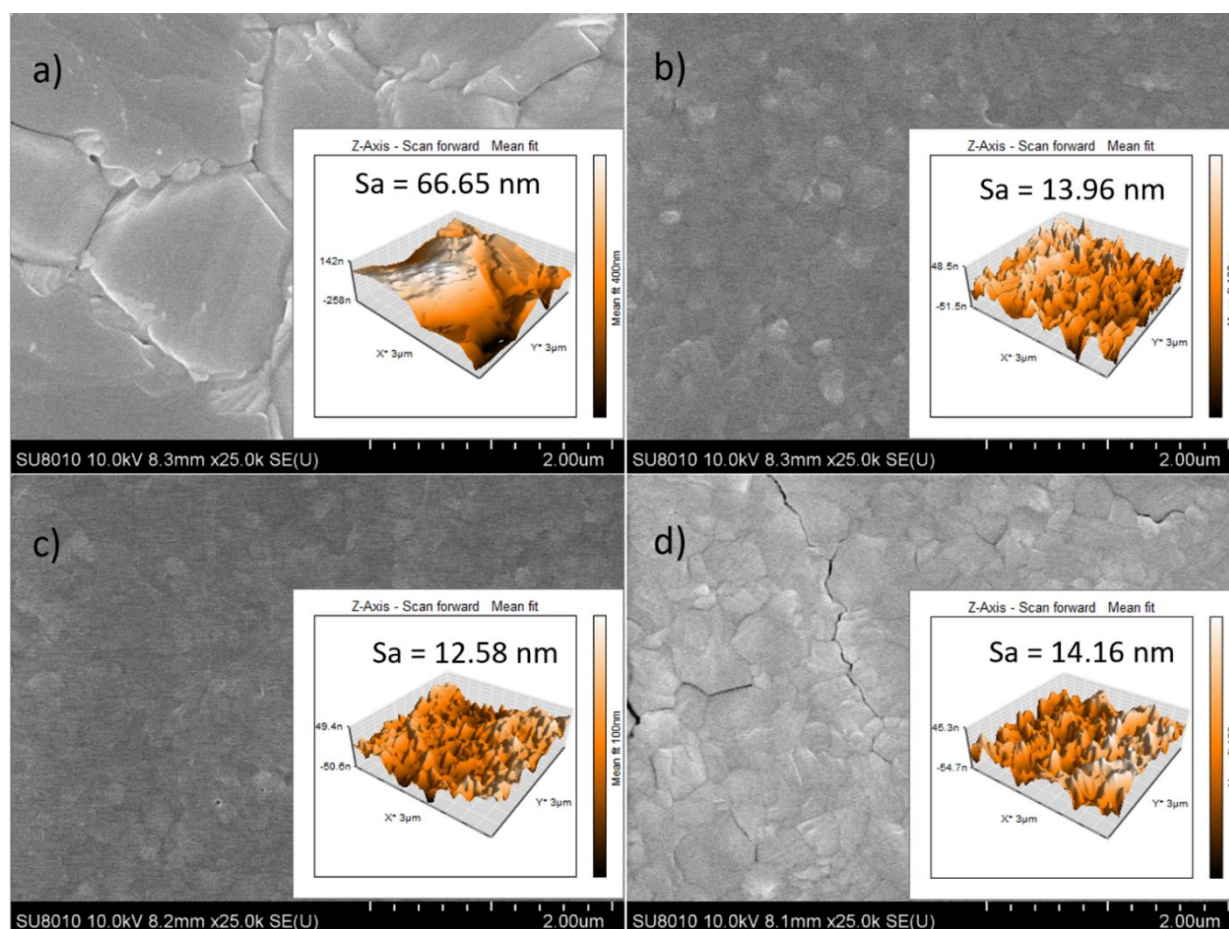


Figure 7: SEM topographic view and AFM of PVSK films: a) Primary-MAPbI₃, b) 2nd-MAPbI₃/dry, c) 2nd-MAPbI₃/wet and d) 2nd-MAPbI₃/wet/heat films



fact, this is not favourable for the practical operation of MATM, as the chemical composition of **2nd-MAPbI₃/wet** has already deteriorated, as discussed above. Its seemingly smooth and uniform surface morphology may lead to a misleading assessment of film quality. On the other hand, a closer inspection of the **2nd-MAPbI₃/wet/heat** sample (Figure 7d) reveals the presence of prominent cracks, indicating that the moisture content during MATM may still affect the integrity of the resultant film. Based on the preceding discussion, we have reason to believe that the outgassing of MAOH during the post-heating process of the **2nd-MAPbI₃/wet** sample is the primary cause of the observed cracking.

Optoelectrical properties

Figure 8a presents the UV-vis absorption spectra of **Primary-MAPbI₃** and **2nd-MAPbI₃** films. The three **2nd-MAPbI₃** films exhibit similar absorbance in the 650–900 nm range, whereas the **Primary-MAPbI₃** film demonstrates a higher overall absorbance. The reduced absorbance observed in the **2nd-MAPbI₃** films is attributed to their lower surface roughness (Sa),

which reduces light scattering. The Tauc-plot derived from the absorption spectra, shown in Figure 8b, indicates that the optical bandgap (E_g) of the **Primary-MAPbI₃** film is 1.591 eV. In contrast, the **2nd-MAPbI₃** films exhibit a slightly higher E_g of approximately 1.600 eV. The change is small and is likely due to the preferred (110) crystallographic orientation in the MAPbI₃ PVSK structure^{24, 31}.

Space-charge-limited current (SCLC) measurements were conducted to quantitatively assess the impact on trap-filling limited voltage (V_{TFL}) and trap density (N_t). The corresponding SCLC curves are presented in Figure 8c. The V_{TFL} value is identified at the transition point between the Ohmic and trap-filled limit (TFL) regions, while N_t is determined using the following equation:

$$Nt = 2\epsilon\epsilon_0 \frac{V_{TFL}}{eL^2}$$

In this equation, e represents the elementary charge (1.602×10^{-19} C), ϵ_0 denotes the vacuum permittivity (8.854×10^{-12} F/m), ϵ corresponds to the relative dielectric constant of MAPbI₃ (32),

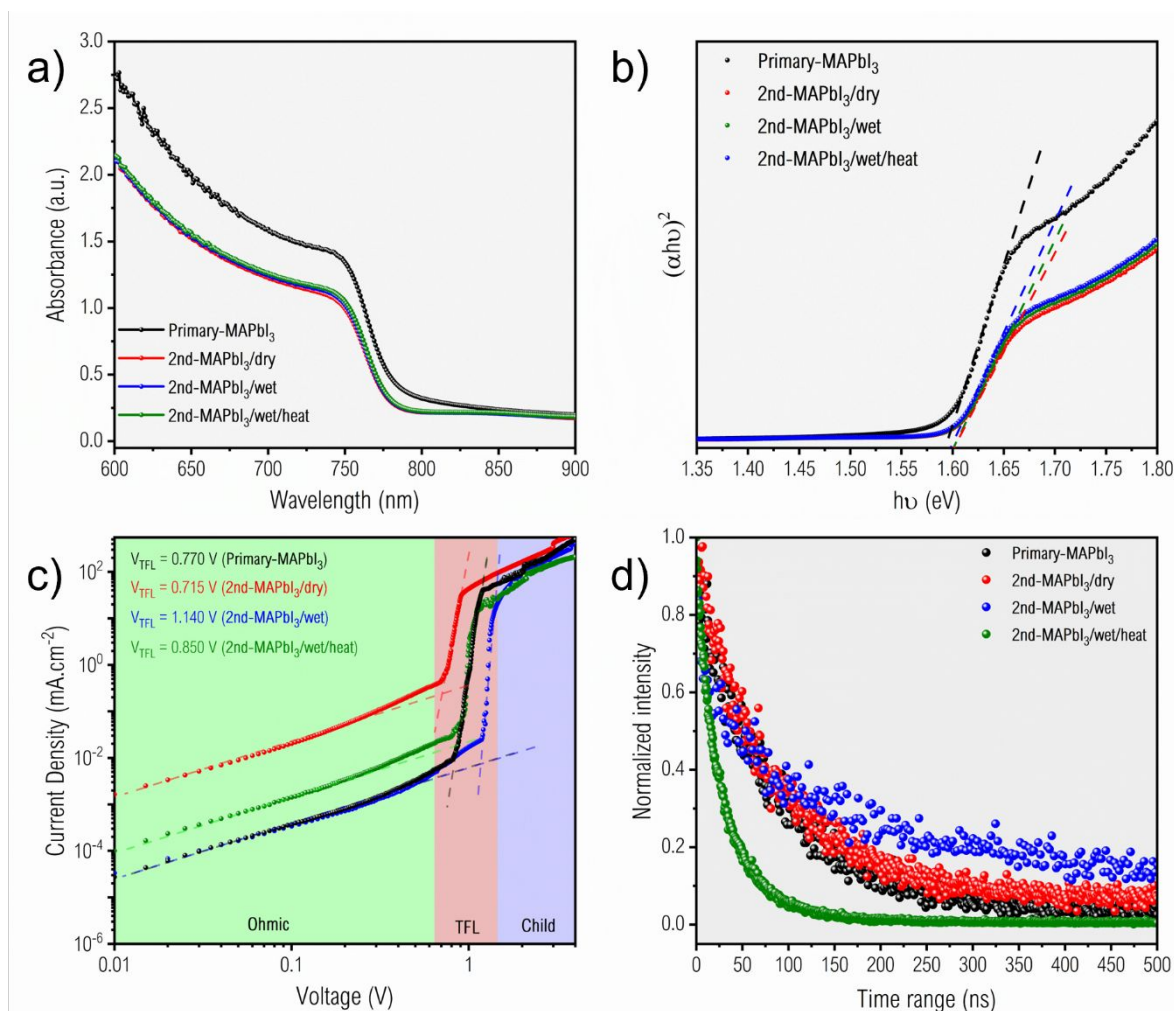


Figure 8: a) UV-vis absorption spectra, b) Tauc-plot, c) the SCLC curves and d) the TRPL spectra of Glass/Al₂O₃/PVSK film of Primary-MAPbI₃, 2nd-MAPbI₃/dry, 2nd-MAPbI₃/wet and 2nd-MAPbI₃/wet/heat films



Table 1: Optoelectronic parameters of various MAPbI₃ filmsView Article Online
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	Primary-MAPbI ₃	2nd-MAPbI ₃ /dry	2nd-MAPbI ₃ /wet	2nd-MAPbI ₃ /wet /heat
V_{TFL} (V)	0.770	0.715	1.14	0.850
N_t ($\times 10^{16} \text{ cm}^{-3}$)	1.421	1.250	1.993	1.486
τ_1 (ns)	8.69	31.08	3.55	12.15
A1 (%)	11.19	26.05	43.33	36.52
τ_2 (ns)	93.19	108.46	120.71	39.23
A2 (%)	88.81	73.95	56.67	63.48
τ_{avg} (ns)	83.74	88.30	69.95	29.34

and L signifies the thickness of the perovskite film. A summary of the V_{TFL} and N_t values for the examined samples is provided in **Table 1**. The **Primary-MAPbI₃** exhibits a V_{TFL} of 0.770 V and a N_t of $1.42 \times 10^{16} \text{ cm}^{-3}$. **2nd-MAPbI₃/dry** demonstrates a reduced V_{TFL} (0.715 V) and N_t ($1.25 \times 10^{16} \text{ cm}^{-3}$), suggesting that the quality of the film is enhanced by the MATM process, which is consistent with previous studies³¹. However, at **2nd-MAPbI₃/wet**, both V_{TFL} and N_t exhibit a significant increase, reaching 1.14 V and $1.99 \times 10^{16} \text{ cm}^{-3}$, respectively. This indicates that impurities such as MAPbI₂OH, PbO, and PbOH introduce a higher density of defect-trap states within the crystal lattice. Following post-heating treatment (**2nd-MAPbI₃/wet/heat**), a substantial portion of MAOH is removed; however, residual PbO and PbOH persist in the perovskite film, contributing to an elevated defect density, measured at $1.486 \times 10^{16} \text{ cm}^{-3}$.

The carrier lifetime of the investigated samples was probed using time-resolved photoluminescence (TRPL). The TRPL data shown in **Figure 8d** were fitted with the following bi-exponential function:

$$I(t) = A_1 e^{-\frac{t}{\tau_1}} + A_2 e^{-\frac{t}{\tau_2}} + I_0$$

where A_1 and A_2 represent the pre-exponential factors, while I_0 is a constant accounting for the background signal. The short lifetime (τ_1) is primarily associated with non-radiative surface recombination, whereas the long lifetime (τ_2) corresponds to bulk radiative recombination within the PVSK film.

We subsequently calculated the average carrier lifetime using the amplitude-weighted method⁵⁵:

$$\tau_{\text{avg}} = \frac{\sum(A_i \tau_i)}{\sum(A_i)}$$

The results are summarized in **Table 1**. The **Primary-MAPbI₃** film shows a τ_1 of 8.69 ns and a τ_2 of 93.19 ns, with an average lifetime (τ_{avg}) of 83.74 ns. For the **2nd-MAPbI₃/dry** sample, both τ_1 , τ_2 and τ_{avg} increase to 31.08 ns, 108.46 ns, and 88.30 ns, respectively, indicating that when the MATM process proceeds without moisture interference, both film integrity and trap density are improved.

For the moisture-affected samples (**2nd-MAPbI₃/wet** and **2nd-MAPbI₃/wet/heat**), a shorter τ_{avg} is observed, suggesting that the moisture-induced photovoltaic-inactive hydrated byproducts adversely influence carrier lifetime and consequently degrade photovoltaic properties. Interestingly, the **2nd-MAPbI₃/wet** film exhibits the longest τ_2 (120.71 ns) but simultaneously the shortest τ_1 (3.55 ns) among all samples. We attribute this phenomenon to moisture-induced, photovoltaic-inactive phases forming electrically isolated high-quality domains, which artificially inflate the average PL lifetime – resulting in a pseudo-long lifetime – while the majority of photogenerated carriers still undergo rapid non-radiative interfacial recombination before reaching the charge-transport layers, as evidenced by the shortest τ_1 . Combining TRPL and SCLC analysis, it is evident that the existence of impurities such as MAPbI₂OH, PbO, and PbOH formed during moisture-involved MATM lead to the reduction in electron lifetime. As for **2nd-MAPbI₃/wet/heat**, both τ_1 and τ_2 became shorter even compared with **Primary-MAPbI₃**, saying that even with a post-heating treatment, the damage of MAPbI₃ due to improper MATM is difficultly reverted. We attribute this is because although post-heating removes certain OH-species, the post-heating itself also induces fast diffusion of impurities from surface to bulk film. Such effect increases trap density and eventually shortens the electron lifetime of the entire PVSK film.

Photovoltaic performance

Table 2 and Figure S7 illustrates the photovoltaic statistics of the PSC made with the investigated MAPbI₃ films. J-V curves of the best-performing devices is plotted in **Figure 9a**, in which the best **Primary-MAPbI₃**-based device exhibited a PCE of 16.55%, with a short-circuit current density (J_{sc}) of 21.41 mA/cm², an open-circuit voltage (V_{oc}) of 1.01 V, and a fill factor (FF) of 76.30%. For **2nd-MAPbI₃/dry**-based devices, improved PVSK film quality led to an increase in all photovoltaic parameters. The best-performing PSC employed with **2nd-MAPbI₃/dry** showed J_{sc} , V_{oc} , and FF of 23.78 mA/cm², 1.04 V, and 78.71%, respectively, resulting in an improved PCE of 19.48%. If the MATM underwent with moisture interference, PCEs of the devices declined considerably to 16.11% and 18.74%, for the case of **2nd-MAPbI₃/wet** and **2nd-MAPbI₃/wet/heat**, respectively. This result once again highlights the critical importance of environmental conditions during MATM of



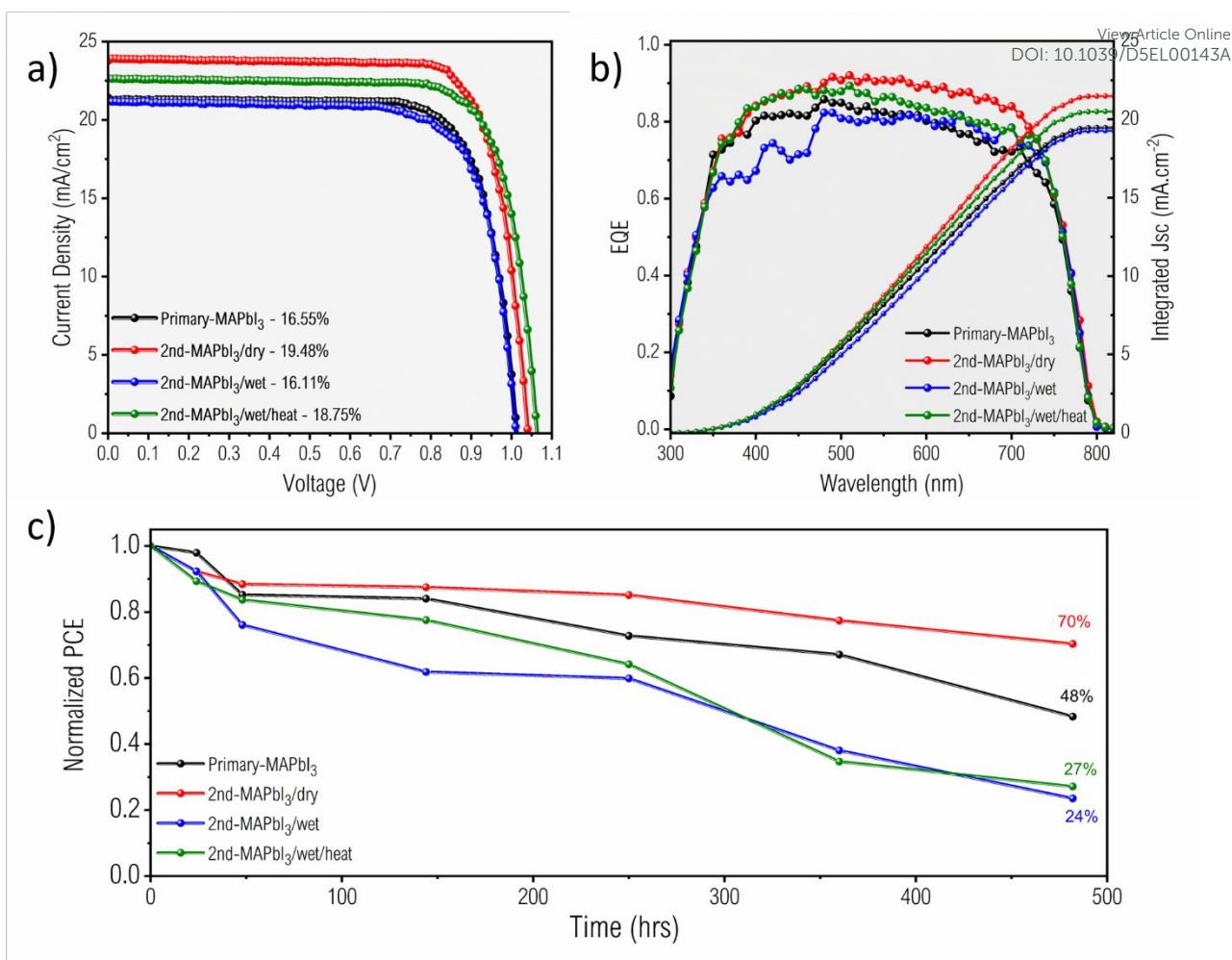


Figure 9: a) The best performance J-V curves of perovskite MAPbI₃ devices with Primary-MAPbI₃ and 2nd-MAPbI₃ (backward scan); b) EQE and integrated J_{sc} of perovskite MAPbI₃ devices and c) Stability of devices made from Primary-MAPbI₃ and 2nd-MAPbI₃ films

Table 2: Photovoltaic parameters of various MAPbI₃ films (based on 15 Cells)

Device	$EQE\text{-}J_{sc}$ (mA/cm ²)		J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)	PCE (%)	HI
Primary-MAPbI ₃	19.47	Champion	21.41	1.01	76.30	16.55	0.30
		Average	22.36 ± 0.68	0.99 ± 0.02	72.03 ± 3.55	15.91 ± 0.63	
2nd-MAPbI ₃ /dry	21.50	Champion	23.78	1.04	78.71	19.48	0.07
		Average	22.97 ± 0.55	1.04 ± 0.02	77.63 ± 1.52	18.67 ± 0.56	
2nd-MAPbI ₃ /wet	19.28	Champion	21.19	1.01	75.81	16.11	0.09
		Average	20.98 ± 0.86	1.00 ± 0.01	67.04 ± 4.43	14.10 ± 0.79	
2 nd -MAPbI ₃ /wet/heat	20.50	Champion	22.64	1.06	77.86	18.74	0.08
		Average	22.49 ± 0.31	1.05 ± 0.02	73.27 ± 2.74	17.26 ± 0.80	

MAPbI₃ films. In particular, in the presence of moisture, although surface morphology can still be effectively smoothed, the formation of undesirable by-products significantly deteriorates the optoelectronic properties of the

resultant MAPbI₃ films, ultimately leading to decreased device performance rather than improvement.

The hysteresis index (HI), which is defined as:



$$HI = \frac{(PCE_{reverse\ scan} - PCE_{forward\ scan})}{PCE_{reverse\ scan}}$$

is a key indicator for evaluating trap-assisted recombination, surface charge recombination, and ion migration in PSCs. As can be seen in **Figure S8** and **Table S1**, **Primary-MAPbI₃** exhibited a relatively large HI of 0.30, confirming its significant hysteresis behavior. In contrast, all three types of **2nd-MAPbI₃** devices demonstrated substantially reduced HI values (0.07–0.09), highlighting that the liquefaction-recrystallization mechanism of MATM effectively improves film uniformity and compactness, leading to suppressed hysteresis. Among the three 2nd-MAPbI₃ devices, the **2nd-MAPbI₃/dry** film showed the lowest HI compared to the **2nd-MAPbI₃/wet** and **2nd-MAPbI₃/wet/heat** films. This increase in hysteresis for the latter two devices is primarily attributed to the presence of photovoltaic-inactive impurities introduced by moisture during MATM, which results in higher defect density within the perovskite film.

Overall, based on the current results, improved film compactness appears to be the dominant factor in hysteresis suppression, which is a fundamental benefit provided by the MATM process. With further refinement of MATM operation—particularly by eliminating moisture interference—the enhancement in film quality and corresponding hysteresis reduction can be further strengthened.

Figure 9b shows the incident photon-to-electron conversion efficiency (IPCE) spectra of the four investigated devices. The integrated J_{SC} values are 19.47 mA/cm² for **Primary-MAPbI₃**, 21.50 mA/cm² for **2nd-MAPbI₃/dry**, 19.28 mA/cm² for **2nd-MAPbI₃/wet**, and 20.50 mA/cm² for **2nd-MAPbI₃/wet/heat**, which are consistent with the trend observed in the J–V characteristics.

For **2nd-MAPbI₃/wet** device, the reduced integrated J_{SC} can be attributed to two major factors. First, the EQE is significantly suppressed in the 300–450 nm region, suggesting enhanced surface recombination or parasitic absorption at the transport-layer/perovskite interface (e.g., TiO₂/PVSK)⁵⁶. This is supported by the shortened TRPL lifetime ($\tau_1 \approx 3.55$ ns) and pronounced SSPL quenching in the **2nd-MAPbI₃/wet** films. A slight suppression in this region is also found for **Primary-MAPbI₃**, indicating the presence of residual surface recombination. Second, the suppressed EQE in the 500–750 nm region indicates an increase in bulk recombination due to the presence of intrinsic defects in the perovskite film. This interpretation is further validated by the results from SSPL, SCLC, and TRPL characterizations.

Overall, MATM performed under dry conditions effectively improves perovskite film morphology, heals defects, and reduces trap density, thereby contributing to the enhancement of photovoltaic performance.

Notably, although the **2nd-MAPbI₃** films exhibit a reduced average grain size compared with the **Primary-MAPbI₃** films, their device performance is significantly improved. This observation contrasts with the widely accepted understanding that larger perovskite grains are beneficial for reducing defect density and enhancing optoelectronic properties. Such a counter-intuitive result highlights

that grain size is not the sole dominant factor determining device performance. Instead, the MATM improves crystallographic quality, film compactness and suppressed defect formation through a liquefaction–recrystallization mechanism. These improvements collectively facilitate enhanced charge extraction and reduced non-radiative recombination losses, ultimately leading to superior photovoltaic performance despite the smaller grain size. Our results therefore reinforce that structural coherence, defect passivation, and film continuity can outweigh grain-size effects in governing PSC efficiency.

To evaluate the impact of moisture during MATM on the stability of PSC, we fabricated both **Primary-MAPbI₃** and **2nd-MAPbI₃** films, storing them under controlled humidity conditions (15–25%) without encapsulation. As shown in **Figure 9c**, the long-term stability of PSCs fabricated from **Primary-MAPbI₃**, **2nd-MAPbI₃/dry**, **2nd-MAPbI₃/wet**, and **2nd-MAPbI₃/wet/heat** was systematically compared. After more than 480 hours of ambient storage, PSCs based on **2nd-MAPbI₃/dry** films retained 70% of their initial power conversion efficiency (PCE), while devices based on **Primary-MAPbI₃** retained only 48%. In contrast, devices that underwent MA⁰ treatment in the presence of moisture and those subjected to subsequent heating exhibited markedly accelerated degradation, retaining only 24% and 27% of their initial PCE, respectively.

These results indicate that the incorporation of impurities during the moisture-influenced MATM process significantly accelerates device degradation. Furthermore, the MATM process conducted within the MALCR system, which functions as a moisture-isolated environment, yields enhanced device stability compared to PSCs fabricated using untreated **Primary-MAPbI₃** films.

Upscaling PSC using moisture-free MATM

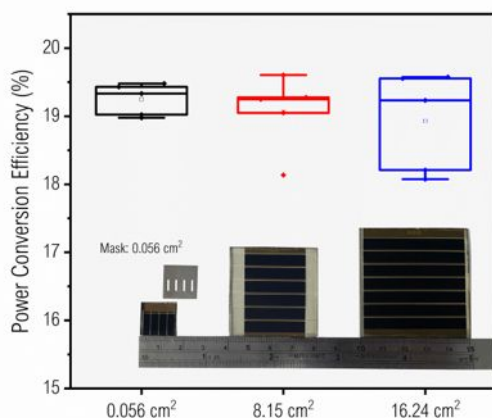
After confirming that proper implementation of MATM can simultaneously enhance both the efficiency and stability of PSCs, we further investigated another critical advantage of this technique: its applicability in the fabrication of large-area perovskite solar modules. In addition to the laboratory-scale small-area devices (0.056 cm²), we progressively scaled up the active area to 8.15 cm² (a 4.0 cm × 4.0 cm module consisting of six sub-cells in series) and 16.24 cm² (a 5.0 cm × 5.0 cm module comprising seven sub-cells in series).

Figure 10 and **Table 3** summarize the performance statistics of PSCs with various active areas. Remarkably, under identical device architecture, material composition, and processing conditions, the PCE remained essentially unchanged across different device scales. The laboratory-scale small-area cell exhibited a PCE of 19.68%, while the 8.15 cm² and 16.24 cm² modules achieved PCEs of 19.60% and 19.57%, respectively. This demonstrates a truly lossless scaling process and represents a significant milestone in the upscaling of high-performance PSC modules.



Table 3: Photovoltaic parameters of 2nd-MAPbI₃/dry devices at different active area (based on 5 devices)View Article Online
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	PSC	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)	PCE (%)
Cell with active area of 0.056 cm ²	Champion	23.78	1.04	78.71	19.48
	Average	23.43 ± 0.38	1.04 ± 0.02	78.57 ± 1.05	19.25 ± 0.21
Module with active area of 8.15 cm ²	Champion	3.85	6.73	75.66	19.60
	Average	3.81 ± 0.11	6.69 ± 0.09	74.77 ± 1.48	19.06 ± 0.50
Module with active area of 16.24 cm ²	Champion	3.23	7.87	77.00	19.57
	Average	3.22 ± 0.06	7.47 ± 0.30	78.78 ± 1.61	18.93 ± 0.66

**Figure 10:** Performance of small devices and module devices

Conclusions

This study systematically elucidates the impact of environmental moisture on the MATM of MA-based perovskite films and its implications for scalable PSC manufacturing. We demonstrate that uncontrolled humidity during MATM induces the formation of photoinactive by-products such as PbO, PbIOH, and MAPbI₂OH, which significantly deteriorate the film's crystallinity, increase trap-state density, and shorten carrier lifetimes. More importantly, the formation of these by-products is uncontrollable, which significantly undermines the feasibility and yield of large-area MATM processing. These defects not only compromise photovoltaic performance but also severely accelerate device degradation. In contrast, performing MATM in a dry condition effectively preserves the liquefaction–recrystallization benefits while preventing deleterious side reactions. Devices treated under dry conditions exhibit superior PCE of 19.48% and improved long-term stability from a control device with an initial 16.67% PCE. We further demonstrated the scalability of the moisture-free MATM protocol by successfully increasing the device area from 0.056 cm² to 16.24 cm² without statistical loss in PCE. This clearly highlights the tremendous potential of properly implemented MATM for the fabrication of large-area perovskite films.

Author contributions

Tzu-Chien Wei supervised the study. Duc-Anh Le conceived the idea, designed the experiments, and wrote the first manuscript draft. Both authors contributed to the writing and revision.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the ESI.† More raw data are available from the corresponding author on reasonable request.

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Data availability statement

The data supporting this article have been included as part of the ESI.† More raw data are available from the corresponding author on reasonable request.

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