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# Sequential slot-die coating of perovskite solar cell modules under ambient conditions with precise phase-transition control

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# ABSTRACT

The commercialization of perovskite solar modules (PSMs) requires scalable fabrication processes that enable uniform, large-area film formation with precise control over perovskite crystallization. In this study, an airprocessable perovskite fabrication process using sequential slot-die coating was developed, enabling scalable and uniform film formation. This process integrates near-infrared (NIR) heating to facilitate rapid solvent removal and minimize prolonged exposure to ambient air, while incorporating methylammonium thiocyanate (MASCN) to promote controlled crystallization, reduce trap density, and improve optoelectronic properties of perovskite crystals. As a result, large-area perovskite films with enhanced grain growth, fewer defects, and improved phase stability were obtained. Using this approach, slot-die-coated perovskite solar cells (PSCs) achieved a maximum power conversion efficiency (PCE) of 17.37 %, while a  $10 \times 10$  cm<sup>2</sup> PSM reached a PCE of 11.08 %. These findings demonstrate an air-processable, scalable fabrication strategy for high-performance and reproducible perovskite solar cells and modules, addressing key challenges in large-area film fabrication and improving the manufacturability of perovskite photovoltaics.

#### 1. Introduction

Over the past decade, perovskite solar cells (PSCs) have emerged as leading candidates for next-generation photovoltaics owing to their excellent properties, such as a tunable bandgap, high carrier mobility, and solution-processability. The impressive power conversion efficiency (PCE) of PSCs has reached 27.0 % [1], demonstrating their potential for commercialization [2]. However, in high-performance PSCs, perovskite films are predominately fabricated using a spin-coating process under a nitrogen atmosphere. These processing conditions pose scalability challenges, limiting the commercial viability of PSCs. To overcome these limitations, many research groups have explored various techniques for manufacturing large-area PSCs [3–10]. Among them, the slot-die coating process has emerged as a promising, cost-effective and scalable deposition technique, gaining significant attention for large-scale perovskite film production [11-17].

The performance of PSCs is highly dependent on the quality of perovskite films [18]. For large-area films, controlling the drying rate and widening the crystallization process window are critical factors for achieving a scalable fabrication process. To address this challenge, additive engineering is frequently employed to enhance the stability and PCE of large-area PSCs [19–21]. It is well known that chloride additives significantly enhance the performance of PSCs by influencing the crystallization process and altering the surface morphology of perovskite films [22]. Alex K.-Y. Jen et al. demonstrated that volatile methylammonium chloride (MACl) plays a crucial role in facilitating secondary crystallization during the annealing process, enabling PSCs to achieve a PCE of 23.1 % [23]. Similarly, A.W.Y. Ho-Baillie et al. reported that

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chlorine significantly enhances film coverage by reducing pinholes and improving crystallinity, favoring a (100) crystallographic orientation. These improvements contribute to higher current density and voltage outputs in PSCs [24]. G. Fang et al. observed that perovskite films treated with MACl exhibit larger grain sizes, longer carrier lifetimes, and lower trap densities, all of which are critical for enhancing device performance [25]. MACl has been widely utilized in the fabrication of highefficiency PSCs under an N<sub>2</sub> atmosphere. However, under ambient air conditions, moisture can promote the deprotonation of MACl, triggering its reaction with formamidinium (FA<sup>+</sup>) and leading to the formation of non-volatile byproducts such as N-methylformamidinium (MFA<sup>+</sup>) and N,N'-dimethylformamidinium (DMFA<sup>+</sup>) [26–28]. These byproducts can disrupt the stoichiometry of the perovskite material, potentially degrading its structural integrity and optoelectronic performance. Therefore, for air-processable perovskites, moisture-sensitive additives should be replaced with more stable alternatives.

In air-processable perovskites, factors such as humidity, oxygen exposure, and temperature critically influence the morphology of perovskite films. Nevertheless, fabrication of perovskite films under ambient conditions offers practical advantages for industrial-scale production, including reduced equipment costs, simplified processing steps, and elimination of the need for inert gas environments such as gloveboxes. However, the ambient atmosphere, including humidity and oxygen exposure, significantly influences the crystallization dynamics, morphology, and stability of the resulting perovskite films. Moisture, in particular, poses a significant challenge by affecting both crystal formation and stability during deposition [29-31]. Since perovskite precursor solutions are generally dissolved in polar solvents, they readily interact with water molecules, forming intermediate complexes that hinder the transition to the desired perovskite phase. Additionally, water molecules disrupt the bonding between lead halide octahedra and A-site cations, promoting the formation of hydrated perovskite compounds through hydrogen bonding [32]. Our previous research demonstrated that rapid heating strategies effectively counteract moisture-related challenges by accelerating solidification and crystallization in air, thus achieving high film uniformity [3]. However, while this approach improves film coverage, it often results in small-grained perovskite films with pronounced grain boundary defects, ultimately undermining both device PCE and stability. A viable alternative for perovskite fabrication is sequential deposition, which separates solidification from crystallization, ensuring efficient crystallization. This technique involves depositing an inorganic laver, such as lead iodide (PbI<sub>2</sub>), followed by its reaction with an organic solution. Several approaches have been explored to mitigate moisture interference during sequential deposition under ambient conditions. Our previous work demonstrated that incorporating diamine additives into the PbI2 precursor effectively passivates Pb sites, shielding against moisture and ensuring complete conversion to the α-phase FAPbI<sub>3</sub> without residual PbI<sub>2</sub> in the perovskite film. The results yielded PSCs with a champion PCE of 18.73 % [33]. In addition, pseudo-halide anion engineering has attracted attention for enhancing crystallinity and reducing defects related to ion vacancies in perovskite films [34,35]. The incorporation of thiocyanate anions (SCN<sup>-</sup>) has been explored to modify surface morphology and improve crystallinity under ambient conditions [36-38]. Q. Tai et al. used SCN<sup>-</sup> as a co-additive to facilitate crystallization and protect against water-induced degradation during annealing. Pb(SCN)<sub>2</sub> suppressed unwanted coordination complexes, yielding highquality films with fewer defects, longer carrier lifetimes, and improved stability across a relative humidity range of 0 %-80 % [39]. These improvements stem from pseudo-halide anions that promote uniform crystal growth, reducing defect densities, and improving film coverage, all of which are essential for high-performance PSCs in ambient conditions.

In this study, we fabricated large-area perovskite films using a sequential slot-die coating process in air. We combined near-infrared (NIR) heating with partial MACl substitution by pseudo-halides, particularly SCN<sup>-</sup>, to enhance the uniformity of the perovskite layer. Incorporating n-butanol as a low water-soluble solvent in the second deposition step facilitated interactions between MACl and methyl-ammonium thiocyanate (MASCN), improving perovskite film formation. The introduction of SCN<sup>-</sup> effectively passivated defects, promoted uniform crystal growth, and reduced charge recombination, leading to enhanced device performance. As a result, the highest PCE of PSCs reached 17.37 %, while the T<sub>80</sub> lifetime of unencapsulated PSCs exceeded 600 h under ambient storage conditions. To the best of our knowledge, this is the first report of a sequentially deposited perovskite film fabricated via a slot-die coating process conducted entirely under ambient conditions, rather than under an inert environment. Additionally, a 10 cm × 10 cm perovskite solar module (PSM) achieved a PCE 11.08 %, highlighting the effectiveness of SCN<sup>-</sup> in engineering and NIR heating advancing air-processable perovskite solar technology.

## 2. Experimentals

# 2.1. Materials

Nickel acetate tetrahydrate (Ni(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O, 99.0 %) was purchased from Showa Chemical. Poly[3-(6-carboxyhexyl) thiophene-2,5diyl] (P3HT-COOH,  $M_W \sim 90$  K) was purchased from Rieke Metals. Ethanolamine (EA, 99 %) was obtained from Acros Organics. Formamidinium Iodide (FAI, 99.99 %), methylammonium chloride (MACl, 99.99 %) and methylammonium thiocyanate (MASCN, 99.5 %) were purchased from Greatcell solar materials. Cesium iodide (CsI, 99.99 %), dimethyl sulfoxide (DMSO, 99.9 %), dimethylformamide (DMF,  $\geq$ 99.9 %), chlorobenzene (CB, 99.9 %), isopropanol (IPA, 99.5 %), 1-butanol (99.9 %) were purchased from Sigma-Aldrich. Lead iodide (PbI<sub>2</sub>, 99.99 %) and bathocuproine (BCP, >99 %) were purchased from TCI. Fullerene (C<sub>60</sub>) was purchased from Nano-C. All the chemicals were used without further purification. 2-Thiopheneethylamine, hydrochloride (TEACI) solution was purchased from FMPV.

#### 2.2. Preparation of precursor solutions for slot-die coating

For the sol–gel NiO<sub>X</sub> precursor solution, 0.062 mg nickel acetate tetrahydrate was dissolved in 1 mL of ethanol and stirred at 60 °C until clear. After adding 15  $\mu$ L of ethanolamine, the solution was filtered through a 0.22  $\mu$ m poly(1,1,2,2-tetrafluoroethylene) (PTFE) filter before use. For the P3HT-COOH solution, 0.125 mg P3HT-COOH was dissolved in 1 mL of DMF. The 0.4 M inorganic solution, consisting of 0.4 mmol PbI<sub>2</sub> doped with 5 mol% CsI, was dissolved in a 1 mL DMF:DMSO solvent mixture (9:1 vol%). The solution was stirred at 70 °C overnight. The organic salt solution, containing 0.37 M FAI and 0.1 M of the MACl and MASCN mixture with different molar ratios, was dissolved into n-butanol and stirred for 3 h.

## 2.3. Device fabrication

The structure of the PSCs was FTO/NiO<sub>X</sub>/P3HT-COOH/Perovskite/ TEACl/C<sub>60</sub>/BCP/Ag. The slot-die-coated PSCs were fabricated using an automated slot-die equipment (Coatema, Easy coater). Firstly, the FTO substrates were treated with UV-ozone for 30 min. The sol–gel NiO<sub>X</sub> was prepared following our previous work [14]. The wet film of NiO<sub>X</sub>, acting as the hole transport layer (HTL), was processed at 55 °C, with a coating speed of 0.5 m min<sup>-1</sup> and a feeding rate of 2.5 ml min<sup>-1</sup>. The crystalline NiO<sub>X</sub> film was then obtained by annealing at 310 °C for 30 min. For P3HT-COOH deposition, the slot-die head was positioned 200–220 µm above the substrate. The P3HT-COOH solution was processed at 105 °C, with a coating speed of 1.5 m min<sup>-1</sup> and a feeding rate of 1.5 ml min<sup>-1</sup>. The resulting P3HT-COOH film was annealed at 150 °C for 10 min. The perovskite layer was prepared using a sequential deposition method. The inorganic layer was firstly slot-die coated with a slot-die head spacing of 200–250 µm. The coating parameters were set at 40 °C, a coating speed of 1.5 m min<sup>-1</sup> and a feeding rate of 2.0 ml min<sup>-1</sup>. The wet film was dried using a 1.5 kW NIR lamp with a lamp movement rate of 1.9 m/min. The organic solution was subsequently slot-die coated onto the inorganic layer at a substrate temperature is 90 °C, a coating speed of 0.5 m min<sup>-1</sup> and a feeding rate of 3.0 ml min<sup>-1</sup>. The as-prepared perovskite films were then annealed 100 °C for 15 min. Next, a TEACl solution was slot-die coated onto the perovskite layer at a coating speed of 0.5 m min<sup>-1</sup> and a feeding rate of 2.5 ml min<sup>-1</sup>. The electron transport layer (ETL) and work function modified layer (WFL), consisting of 20 nm  $C_{60}$  and 5 nm BCP, were deposited by thermal evaporation. Finally, a 120 nm Ag electrode was thermally evaporated under a vacuum of 2 × 10<sup>-6</sup> torr.

## 2.4. Module fabrication

For the fabrication of modules with different substrate sizes (4 cm  $\times$  4 cm and 10 cm  $\times$  10 cm), the module design included 4 and 11 sub-cells connected in series via P1, P2 and P3 interconnections. FTO substrates were initially patterned into sub-cells using a 532 nm laser (E-sun Co., Ltd), with an interval distance of 0.75 cm between P1 lines. After depositing the HTL, perovskite layer, ETL and WFL, P2 lines were formed by mechanical scribing. A 100 nm silver electrode was then thermally evaporated, followed by the mechanical scribing of the P3 line. The sub-cell width of the module was 0.3 cm, limited by the movement range of the stage.

# 2.5. Device characterization

Steady-state photoluminescence (PL) and time-resolved photoluminescence (TRPL) spectra were recorded using a fluorescence spectrophotometer (FLS1000, Edinburgh Instrument). Crystal structures of perovskite films were characterized using an X-ray diffractometer (XRD, D2 PHASER, Bruker). PL mapping of perovskite films was characterized using a JadeMat-Material Inspection system (Southport Corporation). Surface morphology was studied via field emission scanning electron microscope (SEM) (JSM-IT700HR, JEOL). Transient photovoltage (TPV) and transient photocurrent (TPC) measurements were performed using a system (PAIOS, Fluxim). Current-voltage curves were measured using a source meter (Keithley 2410) under air-mass 1.5 global (AM 1.5 G) illumination from a solar simulator (SS-X100R AAA, Enlitech). In situ grazing incidence wide-angle X-ray scattering (GIWAXS) measurements were performed at beamline 23A1 (BL 23A1) of the National Synchrotron Radiation Research Center (NSRRC) in Taiwan. A monochromatic X-ray beam ( $\lambda = 1.2398$  Å) was delivered at a fixed incident angle of 2.0° relative to the sample surface. Wide-angle scattering patterns were collected using a flat-panel detector (model C10158DK, 2352  $\times$  2352 pixels) positioned 18.2 cm from the sample. X-ray photoelectron spectroscopy (XPS) analysis were performed using a system (PHI 5000 VersaProbe III, ULVAC-PHI Inc.) equipped with a monochromatic Al Ka X-ray source. Depth profiling employed 2 keV Ar ions sputtering with 2 min etching cycles between analysis intervals.

## 3. Results and discussion

To prepare large-area perovskite films in air, a sequential slot-die coating process was employed. This method involves first coating the inorganic precursors to form a structural scaffold, followed by coating the solution-phase organic precursors to enable perovskite formation via a solid–liquid phase reaction. For the inorganic layer, many studies have demonstrated that a solvent mixture of DMSO and DMF produces higher-quality PbI<sub>2</sub> films compared to DMF alone in the spin-coating process. The highly polar solvent DMSO readily reacts with PbI<sub>2</sub> to facilitate the subsequent organic salt ion-exchange. However, the drying process is critical in slot-die coating compared to spin-coating. To achieve high-quality perovskite films via slot-die coating, NIR heating has been demonstrated as an effective approach for scalable perovskite solar

cell fabrication [3,40]. To investigate the effect of different drying processes on the inorganic films and their influence on the perovskite films, surface morphology and crystal structure of the films were analyzed using SEM and XRD, respectively. Samples prepared using different drying and coating processes were named as spin coating with hot-plate heating (SP-HP), slot-die coating with hot-plate heating (SD-HP), and slot-die coating with NIR heating (SD-NIR). The SEM images of inorganic films are illustrated in Fig. 1a. The SP-HP inorganic film exhibited relatively dense morphology with well-defined grains. In contrast, the SD-HP film displayed poor coverage with needle-like PbI<sub>2</sub> crystals and large voids, likely due to the slow drying rate of hot-plate heating in slot-die coating. Notably, the SD-NIR inorganic film exhibited dense morphology with circular crystals. The XRD patterns in Fig. 1b reveal the crystallization of the inorganic films. The SD-NIR inorganic film exhibited strong PbI<sub>2</sub>·DMSO complex peaks and a weak PbI<sub>2</sub> peak. In contrast, the SD-HP inorganic film showed weak PbI<sub>2</sub>·DMSO peaks and a strong PbI<sub>2</sub> peak. Furthermore, as shown in Fig. 1c, the SD-NIR perovskite film exhibited the strongest perovskite peaks compared to SD-HP and SP-HP films. These results suggest that the formation of a strong PbI<sub>2</sub>·DMSO complex enhances the following perovskite conversion in air, leading to improved film quality.

The drying rate and temperature significantly impact the morphology of films [41,42]. To elucidate the role of PbI2:DMSO complex formation in perovskite phase transition, the effect of NIR power on the crystallographic and morphological features of both inorganic and perovskite films was systematically investigated. SEM images (Fig. S1) reveal that the variations in NIR power greatly alter the morphology of inorganic films, which in turn affects their transition into perovskite films. At a low NIR power of 10 %, the inorganic film exhibits a needlelike surface morphology, indicative of a lower degree of densification. However, when the NIR power exceeds 30 %, rapid solvent evaporation induces a more compact and continuous morphology, characterized by a densely packed grain structure. Despite the improved uniformity of the inorganic film, the perovskite layer formed from this denser inorganic film appears rough, exhibiting distinct circular grains. In contrast, the perovskite film derived from the 10 % NIR power-treated inorganic layer is comparatively smoother. This phenomenon suggests that excessive densification of the inorganic film at higher NIR power levels hinders the diffusion of organic salts, such as FAI, into the PbI<sub>2</sub> layer. The limited ion diffusion results in non-uniform crystallization, excessive organic salt accumulation on the surface, and poor interfacial contact between the perovskite layer and the ETL. These findings highlight the necessity of optimizing the NIR heating conditions to balance solvent evaporation and inorganic film porosity, ensuring efficient ion diffusion and defectfree perovskite formation. Fig. S2 presents the XRD patterns of inorganic films with varying NIR power levels and their subsequent transition into perovskite films. The inorganic film exhibits a significant reduction in the DMSO:PbI2 complex peak with the increasing NIR power, which corresponds to a decreased intensity of (0 0 1) perovskite phase after the transition. This reduction suggests that the inorganic film may not fully react with the organic salt when complex formation is insufficient. Therefore, precise control of the inorganic layer is essential for fabricating efficient sequentially deposited PSCs. Based on the results for surface morphology and crystallinity, an NIR power of 10 % is optimal for the slot-die coating process, as it yields a predominantly (001)-oriented perovskite with uniform surface morphology and minimal defect formation.

A key challenge in slot-die coating under ambient conditions for the organic solution is the use of common additives, such as MACl, which lower the crystallization activation energy required for the perovskite phase transition. The chloride salt of MACl dissociated into  $MA^0$  and HCl, facilitated by the deprotonation of  $MA^+$  through  $MA\cdots H^+-Cl^-$  interactions with PbI<sub>2</sub>, thereby promoting controlled perovskite formation [43]. However, the  $MA^0$  molecule can undergo an addition–elimination reaction with FA<sup>+</sup>, leading to the formation of non-volatile reaction products such as  $MFA^+$  [44]. This side reaction depletes FA<sup>+</sup> in the



Fig. 1. (a) Top-view SEM images of inorganic films prepared using different coating processes and dry methods. XRD patterns of (b) inorganic films prepared using different coating processes and dry methods, and (c) after transition into perovskite films.



Fig. 2. (a) Chemical structures of MACl and MASCN. (b) XRD patterns of the inorganic film after reacting with MACl and MASCN, respectively. (c) TGA and DTG analysis of MACl and MASCN.

precursor solution, resulting in non-optimal and less reproducible perovskite compositions, which pose challenges for the fabrication of air-processable perovskite layers. To further accelerate the reaction between organic salts and inorganic layers in air, we introduced the SCN<sup>-</sup> ion during the second deposition step. This substitution partially replaces I<sup>-</sup> with SCN<sup>-</sup> at halogenated sites, modifying the crystallization dynamics and defect formation within the perovskite lattice [45]. Moreover, MASCN facilitates solvent removal, thereby reducing the formation of Pb-DMSO intermediates, which can otherwise hinder complete perovskite conversion [46]. The chemical structures of MACl and MASCN are shown in Fig. 2a., highlighting their respective functional groups. To investigate their interactions with the inorganic precursor, organic precursor solutions without A-site cations were drop-cast onto pre-deposited inorganic films. This setup allowed us to study the evolution of intermediate phases without initiating complete perovskite formation. The resulting XRD patterns presented in Fig. 2b, reveal that the film treated with MASCN exhibits the strongest diffraction signal for the DMSO:PbI<sub>2</sub> complex among the three samples. This enhancement is attributed to MASCN's ability to promote partial DMSO evaporation while suppressing premature perovskite crystallization in the absence of cations. Consequently, the DMSO-PbI<sub>2</sub> complex is retained in a more concentrated form, leading to a stronger diffraction signal. These observations confirm that MASCN plays a critical role in modulating solvent-solute interactions and the crystallization kinetics of the perovskite layer. The MASCN-treated inorganic film exhibited a stronger perovskite peak while maintaining the DMSO:PbI<sub>2</sub> complex. In contrast, the DMSO: PbI<sub>2</sub> peak was significantly diminished in the MACl-treated film, leading to the formation of PbI2 and MAPbCl3. These results indicate that MASCN promotes a more controlled crystallization process, preserving key intermediates that facilitate uniform perovskite formation. Consequently, we demonstrate that MASCN enhances preferential orientation in perovskite films when processed via sequential deposition under ambient conditions. To further investigate their molecular decomposition behavior, thermogravimetric analysis (TGA) was performed, as shown in Fig. 2c. In derivative thermogravimetry (DTG), MACl exhibits a single decomposition peak, whereas MASCN shows two distinct peaks, indicating that the C-S bonds decompose first. This behavior is consistent with the bond dissociation energies: 272 kJ/mol for C-S, 305 kJ/ mol for C-N [47]. The presence of sulfur atoms may enable bonding with uncoordinated Pb<sup>2+</sup> ions [48], thereby facilitating the perovskite transition by promoting defect passivation and enhanced crystallization. Fig. S3 shows the in situ GIWAXS measurements showing the phase evolution from inorganic films to perovskite during sequential coating. This analysis supports the hypothesis that MASCN actively interacts with the PbI<sub>2</sub>, facilitating perovskite transition and improving the overall film formation process, making it a promising additive for airprocessable PSCs.

The organic solution commonly contained 10 mol% MACl as an additive. To further evaluate the effect of MASCN on the perovskite transition, we systematically investigated the impact of different MACI: MASCN molar mixing ratios in the organic solution on the formation of slot-die coated perovskite films and the performance of PSCs. The performance distribution of PSCs fabricated using perovskite films with varying MACI:MASCN molar ratios is presented in Table 1 and Fig. 3. With increasing MASCN content, the average short-circuit current density (J<sub>SC</sub>) and fill factor (FF) of PSCs improved significantly, resulting in an overall enhancement in PCE of PSCs. This improvement suggests that the MASCN facilitates perovskite formation by accelerating its reaction with PbI<sub>2</sub> in air. However, at high MASCN concentrations, the phase transition to the hexagonal  $\delta$  phase is accelerated, which is known to be detrimental to device performance [49]. Consequently, an optimal MACI:MASCN molar ratio of 5:5 was identified, yielding the highest PCE of 17.37 % in the air-processable slot-die coated PSCs. Fig. S4 shows the PCE distribution across multiple batches, confirming the reproducibility of our fabrication approach. These results demonstrate that the incorporation of SCN<sup>-</sup> ions greatly enhances the interaction between organic

#### Table 1

Photovoltaic characteristics of PSCs fabricated using perovskite films with varying MACI:MASCN molar ratios.

Molar ratios of MACl: MASCN	V <sub>OC</sub> (V)	J <sub>SC</sub> (mA/cm <sup>2</sup> )	FF (%)	PCE (%)
10:0	1.04	21.77	65.46	14.75
	$0.95 \pm$	20.43 $\pm$	$62.59~\pm$	$12.12~\pm$
	0.05	1.66	4.28	1.42
7:3	1.04	21.37	71.64	15.89
	0.98 $\pm$	$20.89~\pm$	$61.83~\pm$	12.73 $\pm$
	0.06	1.40	5.03	1.91
5:5	1.05	22.56	73.64	17.37
	1.00 $\pm$	22.54 $\pm$	$68.72 \pm$	15.47 $\pm$
	0.03	0.46	3.23	1.04
3:7	1.00	21.99	69.95	15.34
	1.00 $\pm$	$\textbf{21.18} \pm$	$61.86~\pm$	13.14 $\pm$
	0.02	0.98	4.62	1.39
0:10	0.98	20.48	69.34	13.88
	1.01 $\pm$	$20.42~\pm$	57.21 $\pm$	11.81 $\pm$
	0.02	0.65	6.57	1.12

and inorganic components, promotes improved film quality, and thereby improving device performance in scalable ambient processing.

To investigate the effect of MASCN in the organic solutions on perovskite films, the optical properties and carrier dynamics of perovskite films were conducted by using photoluminescence (PL) and timeresolved photoluminescence (TRPL) measurements. Samples labeled as "Without MASCN" contain only MACl in the organic solution, whereas those labeled as "With MASCN" had a MACI:MASCN molar ratio of 5:5. The PL spectra of perovskite films with and without MASCN are shown in Fig. 4a. The perovskite film with MASCN exhibits a higher PL intensity than the film without MASCN, suggesting improved film quality. The TRPL spectra of these films are presented in Fig. 4b, with fitting results summarized in Table S1. Upon the addition of MASCN, the average carrier lifetime of perovskite films increases from 156.57 ns to 525.43 ns. The extended carrier lifetime further indicates reduced carrier recombination, demonstrating a lower non-radiative recombination rate, likely due to minimized bulk or surface trap states [34]. This improvement can be attributed to the strong coordination interaction between SCN<sup>-</sup> and Pb<sup>2+</sup> ions, which effectively passivates deep-level defects and stabilizes the perovskite lattice. We conducted X-ray photoelectron spectroscopy (XPS) on perovskite films with and without MASCN. As shown in Fig. S5, XPS measurements revealed that in MASCN-treated films, the Pb  $4f_{5/2}$  and Pb  $4f_{7/2}$  peaks shifted from 138.14 eV and 143.01 eV to lower binding energies of 137.80 eV and 142.65 eV, respectively. Similarly, the I 3d<sub>5/2</sub> and I 3d<sub>3/2</sub> peaks shifted from 618.80 eV and 630.33 eV to 618.45 eV and 629.90 eV. These shifts confirm the formation of chemical interactions between MASCN and the inorganic layer. Such coordination modulates the local electronic structure, suppresses defect states, and reduces trap-assisted recombination, thereby enhancing film quality and device performance. Additionally, the surface morphology of perovskite films with and without MASCN was examined using top-view SEM images, as shown in Fig. S6. The perovskite film with MASCN exhibits larger grains and denser surface morphology compared to the film without MASCN. This improvement is attributed to the lower energy barrier of MASCN compared to MACl during the perovskite transition. MASCN reacts with  $PbI_2$  to form a perovskite intermediate phase, thereby regulating the crystallization process and resulting in high-quality films with larger grain sizes and fewer grain boundaries. Furthermore, PL mapping was performed to assess the uniformity of large-area perovskite films, as shown in Fig. 4c. The PL mapping results reveal significant spatial variation in PL emission intensity for large-area perovskite films without MASCN, indicating that while MACl is essential in the sequential deposition, environmental moisture and temperature fluctuations during fabrication adversely impact perovskite quality in air. In contrast, the incorporation of MASCN significantly enhances overall film uniformity, corroborating



Fig. 3. Photovoltaic characteristic distributions of PSCs fabricated using perovskite films with varying MACI:MASCN molar ratios.

the improved morphological and optical properties observed in perovskite films with MASCN. Table S2 provides a detailed comparison of our approach with previously reported sequential deposition-based PSCs. Notably, our study represents the first demonstration of sequentially deposited perovskite films fabricated via a scalable slot-die coating technique entirely under ambient conditions, rather than in an inert atmosphere. This work contributes to the advancement of highperformance PSCs by integrating an industrially viable two-step deposition method with precise crystallization control, offering a promising approach for scalable PSCs. To investigate the effect of MASCN on carrier dynamics, we conducted transient photovoltage (TPV) and transient photocurrent (TPC) measurements (Fig. S7), with corresponding values summarized in Table S3. The results show that devices incorporating MASCN exhibit an extended carrier recombination lifetime and a reduced carrier extraction time, indicating more efficient charge transport and reduced recombination losses. These improvements are attributed to enhanced crystallinity and defect passivation in the perovskite layer induced by MASCN treatment. In addition, lightintensity-dependent measurements of  $V_{\text{OC}}$  and  $J_{\text{SC}}$  were performed. As shown in Fig. S8, the ideality factor (n<sub>id</sub>) decreased from 1.72 (without MASCN) to 1.59 (with MASCN), further confirming the suppression of non-radiative recombination due to defect passivation. These results demonstrate that MASCN not only improves the morphological quality of the perovskite film but also significantly reduces trap-assisted recombination, thereby enhancing overall device performance.

To evaluate the stability of PSCs with and without MASCN, a stability test was conducted on unencapsulated PSCs stored in the dry box, which condition is relative humidity (RH) of 25 % and 25 °C, as shown in Fig. S9. For PSCs without MASCN, the  $T_{80}$  lifetime was below 200 h, whereas those with MASCN retained 80 % of their initial PCE over 600 h. Moreover, an additional stability test was performed on unencapsulated PSCs stored in a dry box with a relative humidity (RH) of 57 % at

25 °C, as shown in Fig. S10, further confirming the role of MASCN in enhancing the long-term stability of perovskite devices. This enhanced stability is attributed to the ability of MASCN to reduce bulk defects within the perovskite film and suppress anion migration, thereby mitigating degradation pathways. Additionally, we evaluated the device operation stability under ambient conditions (RH 57 %/22 °C) by periodically recording PCEs of devices using a light-emitting diode (LED) solar simulator (LSH-7320), as shown in Fig. S11. To further verify the suppression of anion migration in PSCs, we performed XPS depth profiling analyses on devices both before and after storage under ambient conditions. Fig. S12a and b present the element depth profiles of PSCs without MASCN, measured immediately after fabrication and following ambient exposure, respectively. After aging, pronounced I<sup>-</sup> and Pb<sup>2+</sup> signals were detected within the PCBM region (highlighted in yellow), indicating significant ion migration. In contrast, Figures Fig. S12c and d show the depth profiles for PSCs with MASCN. Notably, even after extended exposure to ambient conditions, no discernible I<sup>-</sup> or Pb<sup>2+</sup> signals were observed in the PCBM layer of the MASCN-treated devices. These results confirm that the incorporation of MASCN effectively inhibits anion migration within the perovskite films, even under prolonged ambient exposure, thereby enhancing device stability under practical operating conditions.

We have further extended our process to accommodate the fabrication of PSMs. Prior to fabricating the large-area modules, fully slot-die-coated PSCs (from the HTL to perovskite layer) were developed. The all-slot-die-coated PSCs exhibited an average PCE of 10.78 %, with a  $J_{SC}$  of 20.00 mA/cm<sup>2</sup>,  $V_{OC}$  of 0.92 V, and an FF of 58.39 %. Finally, PSMs were fabricated using slot-die processes, producing 4 cm  $\times$  4 cm and 10 cm  $\times$  10 cm PSMs. Fig. 5a and 5b presents the J–V curves and photograph (10 cm  $\times$  10 cm) of PSMs, respectively, with photovoltaic parameters summarized in Table 2. The 4 cm  $\times$  4 cm PSMs, with an active area of 5.5 cm<sup>2</sup> based on the optimal MACI:MASCN ratio (5:5), achieved a PCE



Fig. 4. Effect of MASCN in the organic solutions on perovskite films with and without MASCN: (a) PL spectra, (b) TRPL spectra, (c) PL mapping.



Fig. 5. (a) J-V curves of typical PSMs with dimensions of 4 cm  $\times$  4 cm and 10 cm  $\times$  10 cm. (b) The photograph of 10 cm  $\times$  10 cm PSM.

of 11.02 %, with a  $V_{OC}$  = 3.89 V,  $J_{SC}$  = 5.05 mA/cm<sup>2</sup>, and FF = 56.79 %. The 10 cm × 10 cm PSMs with an active area of 34.16 cm<sup>2</sup> exhibited a PCE of 11.08 %, with a  $V_{OC}$  = 10.15 V,  $J_{SC}$  = 1.96 mA/cm<sup>2</sup>, and FF = 55.52 %. The consistent PCE between the two module sizes suggests that the optimized slot-die coating process, combined with MASCN incorporation, effectively mitigates typical efficiency losses associated with scale-up. The high film uniformity, controlled crystallization dynamics, and minimized defect density across large-area deposition played a critical role in preserving efficiency. Unlike conventional large-area fabrication challenges where film thickness variation and

crystallization inhomogeneity often lead to efficiency loss, the enhanced solvent removal and PbI<sub>2</sub>–SCN<sup>-</sup> intermediate phase formation facilitated by MASCN contributed to uniform perovskite grain growth and charge transport properties across the entire active area. The improved process reproducibility and stability in larger modules underscore the viability of this scalable, air-processable perovskite fabrication technique for industrial applications. The increased reaction rate in large-area processing facilitated preferred crystal growth orientation and enlarged perovskite grain size, leading to an extended carrier lifetime and reduced carrier recombination. Consequently, our approach ensures

#### Table 2

Device performance of slot-die coated PSCs and PSMs.

Device	Active area (cm <sup>2</sup> )	V <sub>OC</sub> (V)	J <sub>SC</sub> (mA/cm <sup>2</sup> )	FF (%)	PCE (%)
Standard cell	0.09	$\begin{array}{c} 0.98 \\ 0.92 \pm \\ 0.07 \end{array}$	$23.08 \\ 20.00 \pm \\ 2.25$	$62.56 \\ 58.39 \pm \\ 4.68$	$14.15 \\ 10.78 \pm \\ 1.67$
$4 \text{ cm} \times 4 \text{ cm}$ Module	5.5	3.89	5.05	56.79	11.02
10 cm × 10 cm Module	34.16	10.15	1.96	55.52	11.08

high reproducibility in slot-die-coated large-area PSM fabrication under ambient conditions, demonstrating its potential for high-efficiency, large-area PSCs.

# 4. Conclusions

We have developed an air-processable perovskite fabrication method based on sequential deposition and slot-die coating. The integration of NIR heating into the slot-die coating process enables the formation of smooth and uniform inorganic layers, ensuring high film quality. To control the reaction kinetics of perovskite phase transition in air, optimizing the MACI:MASCN molar ratio in the organic solution facilitates the interdiffusion of organic components and promotes favourable grain orientation. This approach effectively reduces deep level defects and improves the optoelectronic properties of perovskite films. As a result, the highest PCE of PSCs reached 17.37 %, while a 10 cm  $\times$  10 cm PSM achieved a PCE of 11.08 %. Additionally, unencapsulated PSCs incorporating MASCN retained 80 % of their initial PCE after 600 h under controlled ambient conditions (RH 25 %, 25 °C), demonstrating superior stability compared to devices without MASCN. This study demonstrates a scalable, air-processable fabrication strategy for high-performance and reproducible PSCs and large-area PSMs using a fully slot-die coated process, advancing the industrial feasibility of PSCs.

#### CRediT authorship contribution statement

Chia-Feng Li: Writing – original draft, Validation, Methodology, Investigation, Formal analysis, Data curation. Shih-Han Huang: Writing – review & editing, Methodology, Formal analysis. You-Ren Chen: Investigation, Formal analysis, Data curation. Hou-Chin Cha: Investigation, Formal analysis. Ssu-Yung Chung: Validation, Investigation, Data curation. Yu-Hung Hsiao: Validation, Investigation, Data curation. Feng-Yu Tsai: Supervision, Resources. Yu-Ching Huang: Writing – review & editing, Supervision, Resources, Project administration, Funding acquisition, Conceptualization.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cej.2025.164194.

## Data availability

The datasets generated during and/or analyzed during the current study are available from the corresponding author upon reasonable request.

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