Supporting information of

Void-free perovskite layers exceeding one micrometer in thickness enable highly efficient, fully printed solar cells

Shudi Qiu^{1,#}, Martin Majewski^{2,#}, Lirong Dong¹, Andreas Distler¹, Chaohui Li¹, Karen Forberich^{1,3}, Jingjing Tian¹, Naveen Harindu Hemasiri³, Chao Liu³, Jiyun Zhang^{1,3}, Fu Yang⁴, Vincent M. Le Corre¹, Max Bibrack³, Robin Basu¹, Anastasia Barabash¹, Jens Harting^{2,5}, Olivier Ronsin^{2,*}, Tian Du^{1,3,*}, Hans-Joachim Egelhaaf^{1,3} and Christoph J. Brabec^{1,3,6,7,8*}

¹Department of Material Science, Materials for Electronics and Energy Technology (i-MEET), Friedrich-Alexander-Universität Erlangen-Nürnberg, Martensstraße 7, 91058 Erlangen, Germany

²Helmholtz Institute Erlangen-Nürnberg for Renewable Energy (HIERN), Forschungszentrum Jülich, Fürther Straße 248, 90429 Nürnberg, Germany

³Forschungszentrum Jülich GmbH, Helmholtz-Institute Erlangen-Nürnberg (HI ERN), Immerwahrstraße 2, 91058 Erlangen, Germany

⁴Laboratory of Advanced Optoelectronic Materials, Suzhou Key Laboratory of Novel Semiconductoroptoelectronics Materials and Devices, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou, 215123 China

⁵Department of Chemical and Biological Engineering and Department of Physics, Friedrich-Alexander-Universität Erlangen-Nürnberg, Fürther Straße 248, 90429 Nürnberg, Germany

⁶Energy Campus Nürnberg (EnCN), Fürther Straße 250, 90429 Nürnberg, Germany

⁷FAU Solar, Friedrich-Alexander-Universität Erlangen-Nürnberg Profile Center Solar, Martensstraße 7,91058 Erlangen, Germany

⁸Lead contact

#These authors contributed equally: Shudi Qiu, Martin Majewski

*Correspondence:

o.ronsin@fz-juelich.de (Olivier Ronsin)

tian.du@fau.de (Tian Du)

christoph.brabec@fau.de (Christoph J. Brabec)

1. Phase field simulation details

This chapter presents a summary of the Phase Field (PF) model used in this work. The model was created to describe an evaporating and simultaneously crystallizing thin film.^{1,2}

1.1 Simulation method

Similar to our previous work, the system is described by three volume fraction fields. The first one is used to describe the solutes (perovskite material), the second one stands for the solvents, and the third one is a buffer material to replace the solvent escaping from the constant volume simulation box. Additionally, the state of the system is described by two order parameters. The first one tracks whether the solute is in an amorphous or in a crystalline state. The second one describes whether the solvents are in the liquid or vapor phase. Finally, there is a labeling field to distinguish the different perovskite crystallites. The evolution of the system is obtained by minimizing the whole system's Gibbs free energy according to the Allen-Cahn equation for both order parameters and the Cahn-Hilliard equation for the volume fractions. Within this framework, evaporation, crystal nucleation and growth, as well as advective and diffusive mass transport, can be taken into account. Compared to reality, this is a huge simplification, as all the complex chemical reactions, including intermediate phases, are neglected. However, as demonstrated in our previous work¹ as well as in the current paper, this is sufficient to investigate how the balance of the evaporation, nucleation and growth processes impacts the final film morphology. Beyond this, this also allows us to understand the general mechanisms that drive the morphology formation and identify generic process design rules, which are then expected to be valid for a wide range of perovskite compositions.

1.2 Simulation setup

A 2D cross-section of the drying film is simulated. Periodic boundary conditions are applied in the horizontal direction and Neumann boundary conditions in the vertical direction. The substrate is at the bottom of the simulation box and the vapor phase is within the simulation box, on top of the drying film. Initially, the wet film is composed of a fully liquid phase. Different scenarios corresponding to different processing conditions or internal parameters are simulated. These variations are detailed in the following for the seven different cases investigated:

Case 1: Fast evaporation of a thin film (Fig. 3A, main text)

The thin film setup is similar to that in our previous work.¹ The initial system composition is a mixed amorphous phase composed of 25 % perovskite precursor material and 75 % of solvent. The initial wet film height is 230 nm. Three cases are tested, corresponding to a low, a medium, and a high evaporation rate. Despite some parameter adjustments as compared to our previous studies, all the trends and mechanistic conclusions regarding the transition from a rough film

with pinholes to a smooth and fully closed film upon an increase in the drying rate are fully recovered. This shows their robustness versus parameter changes.

Case 2: Fast evaporation of a thick film (Fig. 3B, main text)

The film has a higher initial wet film thickness of 575 nm compared to 230 nm in our previous investigations.¹ The initial system is composed of 25% perovskite precursor material and 75% solvent. Since it was found that a high evaporation rate is beneficial for the morphology of thin films, the evaporation rate is set to a high value.

Case 3: Fast evaporation of a thick film with pre-existing crystals (Fig. 3C, main text)

The input parameters are the same as those in case 2. However, four crystals with an initial radius of 40 nm are placed equidistantly in the simulation box, directly on the substrate.

Case 4: Slow evaporation of a thick film with pre-existing crystals (Fig. 3D, main text)

The input parameters are identical to those in cases 1 and 2. The four crystals are placed in the same positions as before. Only the evaporation rate is reduced by a factor of six.

Case 5: Drying of thin films with varying evaporation rates (Extended Data Fig. 1, main text)

The input parameters are identical to those in case 1. Three cases are tested, corresponding to a high (1A), a medium (1B), and a low (1C) evaporation rate.

Case 6: Thick film with slow diffusion of the precursor (Extended Data Fig. 2, main text)

The input parameters are identical to those in case 2 (fast drying of a thick film without initial crystals), except that the perovskite precursor's diffusivity is decreased by a factor of 1,000. No pre-existing crystals are placed.

Case 7: Thick film with slow evaporation of the solvent (Extended Data Fig. 3, main text)

The input parameters are identical to those in case 2, except for a decrease in the evaporation rate of the solvent by a factor of 60. No pre-existing crystals are placed.

Case 8: Evolution of pre-existing crystals in nearly pure solvent (Extended Data Fig. 4, main text)

The input parameters are identical to those in cases 1 and 2. The four crystals are placed in the same position as in case 2. The initial perovskite precursor concentration is reduced to 1 % and the evaporation rate is lowered.

Evaluation of the number of crystals in the simulation

A labeling field is used to detect the number of crystals in simulations. To evaluate the number of crystals, the number of distinct labels is counted. To exclude fluctuations in the order

parameter resulting in an orientation on a few pixels, only domains with more than 300 pixels are counted as crystals.

1.3 Extended Data for the Phase-Field Simulations

Drying of thin films with various evaporation rates

The current scenarios are connected to the simulations performed in our previous work,³⁵ but with some adjustments in model parameters. As a first test, it has been checked that the trends on morphological transitions observed in this previous work are recovered with the new parameter set. This is tested visually by investigating the formation pathway processed with a high (**Extended Data Fig. 1A**), a medium (**Extended Data Fig. 1B**), and a small (**Extended Data Fig. 1C**) evaporation rate. The trend of decreasing pinhole density and decreasing roughness by increasing the evaporation rate on the dry film is still observable.



Extended Data Fig. 1. Final film morphologies for thin films with varying evaporation rates. The crystalline order parameter is shown, together with the perovskite precursor concentration (inset). (A): high, (B): medium, (C): slow solvent evaporation rate. For a high evaporation rate, crystallization takes place when the film is nearly dry. For a medium evaporation rate, the film is thick enough during the crystallization phase to create roughness. For a low evaporation rate, the film is still thick when the solute crystallizes. This leads to tower-like structures with pinholes.

Thick film with slow diffusion of the precursor

One potential solution one might think of to improve the film quality of thick films is to increase the evaporation rate further (as compared to the evaporation rate discussed in the main manuscript). However, even neglecting experimental constraints (e.g. the film should not be blown away), this approach is not feasible. The reason can be explained with the Péclet number, which is the ratio of advective transport to diffusive transport. For this setup, this can be approximated as the ratio of evaporation rate to diffusion rate. Therefore, the number is an indicator of whether diffusion is fast enough to redistribute the material in the liquid film.

If the evaporation rate increases, at some point, diffusion will be slow compared to evaporation, and a skin effect will occur (see **Extended Data Fig. 2**). This skin effect causes an overconcentration of perovskite precursor (non-crystalline material) at the condensed-vapor interface. As a result, nucleation is more pronounced at the interface, leading to the formation of a closed crystalline layer, blocking evaporation. Consequently, the remaining solvent becomes trapped in the voids within the film. This phenomenon provides a second possible explanation for the formation of voids in thick perovskite films.



Extended Data Fig. 2. Simulation of the drying process of a thick film with slow diffusion of the perovskite precursor. Time proceeds from left to right. The crystalline order parameter is shown, together with the perovskite precursor concentration (inset). (A) Initial setup: the film is homogeneous and amorphous. (B) Visible skin effect/overconcentration of perovskite precursor material at the condensed-vapor interface. The system is not in a crystalline phase at this stage. (C) Overconcentration leads to faster crystallization at the top of the film. (D) This results in a closed crystalline layer blocking evaporation.

Thick film with slow evaporation of the solvent

For a lower evaporation rate, a lower value of supersaturation is reached during the drying process, and therefore, less nucleation of new crystals takes place. These crystals grow to a larger size and may not form a complete blocking layer. This results in a very rough final morphology, as illustrated in **Extended Data Fig. 3**.



Extended Data Fig. 3. Simulation of the drying process of a thick film with a low evaporation rate. The crystalline order parameter is shown, together with the perovskite precursor concentration (inset). (A) Initial amorphous wet film. (B) First, nuclei appear randomly inside the liquid film. Note that the film is substantially thicker, and hence, the precursor concentration is lower at this nucleation stage compared to the thin film (see Extended Data Fig. 1). (C) Crystals are nearly fully grown in the wet film. (D) Final film morphology with a rough surface and (small) voids inside the film.

Evolution of pre-existing crystals in (nearly) pure solvent

The experiments performed to select a suitable pre-coated layer can be reproduced with the simulations. A further condition of primary importance is the initial precursor concentration. A crystal surrounded by a fluid with a precursor concentration lower than the saturation concentration will begin to dissolve. This scenario is illustrated in **Extended Data Fig. 4**. In this case, the pre-existing crystals dissolve into the liquid film. The remaining film would be, in principle, similar to a (thick) film without initial crystals.



Extended Data Fig. 4. Simulation of a film drying with pre-existing crystals, but at a low initial volume fraction. The crystalline order parameter is shown, together with the perovskite precursor concentration (inset). (A) Initial setup: The lower initial volume fraction as compared to the other cases can be observed in the inset. (B) The size of the crystals shrinks since the crystals dissolve in such a low-concentration solution. (C) The crystals are nearly fully

dissolved. (**D**) The crystals are fully dissolved. The film is entirely amorphous and will subsequently behave like a film without pre-coated crystals.

Parameters	Full Name	Value	Unit	
dx, dy	Grid Spacing	1	nm	
Т	Temperature	300	К	
ρ_i	Density	4000, 1000, 1000	kg/m ³	
<i>m</i> ₁ , <i>m</i> ₂ , <i>m</i> ₃	Molar Mass 0.6,0.1,0.03		kg/mol	
ν ₀	Molar Volume of the Flory $3\cdot 10^{-5}$ Huggins Lattice Site			
$\chi_{12,LL'}\chi_{13,LL'}\chi_{23,LL}$	Liquid – liquid interaction 0.48,1.6,0 parameter			
<i>X</i> _{12,SL} , <i>X</i> _{13,SL}	Liquid – solid interaction 0.075,0.25 parameter		-	
T _m	Melting Temperature	600	К	
L _{fus}	Heat of Fusion	9375	J/kg	
W	Energy barrier upon crystallization	17750	J/kg	
P ₀	Reference Pressure	10 ⁵	Ра	
$P_{sat,1}, P_{sat,2}, P_{sat,3}$	Vapor Pressure	10^2 ,1.5 \cdot 10^3 ,10 ⁸	Ра	
P_i^{∞}	Partial Vapor Pressure in the Environment	0	Ра	
E ₀	Solid-Vapor interaction energy	$5\cdot 10^8$	<i>J/m</i> ³	
β	Numerical Free Energy Coefficient	10 ⁻⁵	<i></i>	
κ ₁ ,κ ₂ ,κ ₃	Surface Tension Parameters for Volume Fraction Gradients	2 · 10 ⁻¹⁰ ,2 · 10 ⁻¹⁰ ,6 · 10 ⁻⁹	J/m	
$\epsilon_{c},\epsilon_{vap}$	Surface Tension Parameters for Order Parameter Gradients	1.5 · 10 ^{- 5} ,2 · 10 ^{- 4}	$(J/m)^{0.5}$	
ϵ_g	Surface Tension parameters for the grain boundaries	ce Tension parameters for 0.2 the grain boundaries		
<i>M_c</i> , <i>M_v</i>	Allen-Cahn mobility coefficients	5, 10 ⁶	s ⁻¹	
η_1, η_2, η_3	Material viscosities	$1 \cdot 10^{6}$, $1 \cdot 10^{3}$, $1 \cdot 10^{-2}$	Pa's	
D_{1}^{vap} , D_{2}^{vap} , D_{3}^{vap}	Diffusion Coefficients in the Vapor Phase	10 ⁻¹⁶ ,10 ⁻⁹ ,10 ⁻⁹	<i>m</i> ² / <i>s</i>	
$t_{\phi}, t_{\varphi}, t_{\phi}_{v}$	Thresholds for crystal detection	0.4,0.02,5 · 10 ⁻²	-	
$d_{\xi}, c_{\xi}, w_{\xi}$	Amplitude, center and width of	10 ⁻² ,0.85,15	-	

1.4 Simulation Parameters

	the penalty function for the order parameter fluctuations		
$d_{\eta'}c_{\eta'}w_{\eta}$	Amplitude, center and width of the penalty function for the viscosities	10 ⁻⁷ ,0.2,20	-
d _{sv} ,c _{sv} ,w _{sv}	Amplitude, center and width of the penalty function for the Allen- Cahn mobility and the solid- vapor interaction energy	10 ⁻⁹ ,0.3,15	-

1.4 Simulation Parameters varied between different cases

Parameters	Full Name	Case	Value	Unit
α	Evaporation-	1-3	$1.38 \cdot 10^{-4}$	-
	condensation	4,5c,7	$2.3 \cdot 10^{-5}$	
	coefficient	5b	9.2 · 10 ^{- 5}	
		5a,6	$2.07 \cdot 10^{-4}$	
		7,8	2.3 · 10 ⁻⁶	
$arphi_{1,ini}$	Initial precursor	1-7	25%	
	concentration	8	1%	
nx, ny	Grid Size	2-4,6-8	512x640	-
		1,5a-c	512x256	
$D_{s,i}^{\phi_j \to 1}$	Self-Diffusion	1-5,7-8	10 ⁻¹³ ,10 ⁻¹⁰ ,10 ⁻¹⁰ ,10 ⁻¹¹ ,	m^2/s
	Coefficients in		10 ⁻⁹ ,10 ⁻⁹ ,10 ⁻¹¹ ,10 ⁻⁹ ,10 ⁻⁹	
	pure materials			
		6	10 ⁻¹⁶ ,10 ⁻¹⁰ ,10 ⁻¹⁰ ,10 ⁻¹¹ ,	
			10 ⁻⁹ ,10 ⁻⁹ ,10 ⁻¹¹ ,10 ⁻⁹ ,10 ⁻⁹	
d_{sl}, c_{sl}, w_{sl}	Amplitude,	1-5,7-8	10 ⁻⁶ ,0.85,10	-
	center and width	6	10 ⁻⁶ ,0.93,20	
	of the penalty			
	function for the			
	diffusion			
	coefficients upon			
	liquid solid			
	transition			

2. Transfer matrix simulation

The original MATLAB code can be found from Armin's group³ for determining the optical constants and McGehee's group⁴ for forward simulations. The workflow can be found in **Fig. S1**. We first measured the transmission spectra of SnO₂ layers with 10 nm and 15 nm, perovskite layers with 20 nm and 50 nm, PEDOT:PSS layers with 10 nm and 60 nm, carbon electrode with 20 µm and 40 µm, respectively. Based on the transmittance, we calculated the optical constants, namely, the refractive index (*n*) and extinction coefficient (*k*) via a reverse matrix approach. The optical constants of vapor-deposited metal electrodes, e.g., silver and gold electrodes, were obtained from the website refractiveindex.info. All calculated values were compared to the values reported on the website of refractiveindex.info^{5,6} and match well with reported values except for the non-reflective carbon electrode. We, therefore, assumed the initial *n* and *k* values of the carbon electrode based on reported values within a reasonable range, e.g., *n* = 1.5 and *k* = 0.1. According to the simplified version of the Fresnel equations for normal incidence reflectance on a non-absorbing substrate, the theoretical reflectance (*R_t*) can be approximated for a surface with *n* and *k*:

$$R_t = \frac{(n-1)^2 + k^2}{(n-1)^2 + k^2}$$

Then, we calculated the difference between the theoretical reflectance (R_t) for a material's surface (given *n* and *k*) and the measured reflectance (*R*) via an iterative/fitting method (fminsearch function in MATLAB). When the deviation of $D = R_t - R$ is minimized, it finds values for *n* and *k* that best reproduce the measured reflectance. The calculated values are within the upper and lower bounds of the refractive index ($1 \le n \le 3$) and extinction coefficient (0.0001 $\le k \le 1$), which are reasonable to typical carbon-based materials.⁷

Now, we have all the required optical constants for transfer matrix simulations, shown in **Fig. S2**. We fixed the thickness of ITO, SnO₂, PEDOT:PSS with 110 nm, 30nm and 50 nm, respectively, while we varied the thickness of the perovskite layer from 200 nm to 1500 nm, and the type of the electrode, respectively. The distribution of normalized optical field intensity represents the optical intensity. Typically, the optical intensity (I(z)) at a position z is proportional to the square of the electric field magnitude ($E^2(z)$):

$$I_{(z)} \propto |E_{(z)}|^2$$

3. Experimental details

3.1 Solar cell fabrication

All materials used in this study were used as received, i.e., without further purification. The blade-coating of all layers in the solar cells was carried out on a commercial blade coater

(ZAA2300.H from ZEHNTNER) using a ZUA 2000.100 blade (from ZEHNTNER) at room temperature in air. ITO (Indium Tin Oxide) Coated Glass with 11 Ω/\Box (Liaoning Huite photoelectric Technology Co., Ltd.) substrates were ultrasonically cleaned sequentially for 15 min in acetone and isopropanol. Afterwards the substrates were treated under UV–Ozone box for 20 min to enable better wetting. An aqueous SnO₂ nanoparticle solution (Alfa Aesar) was used to prepare the ETL. The solution was diluted to 5.0 wt% SnO₂ and treated in the ultrasonic bath for 10 min followed by filtering using a 0.45 µm PTFE filter. A volume of 20 µL solution was then doctor bladed at 80 °C with 15 mm s⁻¹ and a gap height of 100 µm. Subsequently the film was annealed at 150 °C for 30 min to form a compact layer.

For the pre-coated layer preparation: 0.5 M PbI₂ (Tokyo Chemical Industry, 99%) was dissolved in anhydrous dimethylformamide (DMF, Aldrich, 99.8%), anhydrous 1-methyl-2-pyrrolidinone (NMP, Aldrich, 99.8%), (DMF:NMP, v:v=9:1) to prepare PbI₂ solution. 0.5 M perovskite precursor solution was diluted from 1.25 M stock solution. 0.5 M FABr and 0.5 PbBr₂ were dissolved in DMF:NMP=9:1 (v:v) to get 0.5 M FAPbBr₃ precursor solution. 0.5 M Phenethylammonium iodide (PEAI, Sigma) and 0.5 M PbI₂ were dissolved in DMF:NMP=9:1 (v:v) to get 0.5 M PEA₂(PbI)₄ precursor solution. All the precursor solutions were blade-coated onto the SnO₂ layer at a speed of 2 mm s⁻¹ and a gap of 100 µm. The annealing temperature for PbI₂ is at 80 °C for 5 mins. For a regular pre-coated perovskite layer it is at 150 °C for 10 mins, for FAPbBr₃ it is at 150 °C for 5 mins and for the PEA₂(PbI)₄ layer it is at 80 °C for 5 mins, respectively.

The regular MA-free perovskite precursor solution was prepared by dissolving 1.25 M of FAI (Sigma, 98%) and 1.35M PbI₂ (Tokyo Chemical Industry, 99%) in anhydrous dimethylformamide (DMF, Aldrich, 99.8%), anhydrous DMF:NMP = 9:1 (v:v) to prepare the FAPbI₃ stock solution and stirred at room temperature for 1 h. Cesium chloride (CsCl, Tokyo Chemical Industry, 99%) was used as additives into the perovskite precursor solution with 10% molar ratios.

The precursor solution was doctor-bladed onto the substrate at speeds of 1 mm s⁻¹ to 20 mm s⁻¹ and a gap height of 150 μ m. The coating temperature was set as low as 28 °C to prevent drying of the film before the gas flow step. The liquid film was then dried with continuous air flow for 30 seconds. The air flow was provided by a compressed air gun with a controllable pressure of 0 ~ 2.5 bar, and the air gun was approximately 15 cm above the substrate with the nozzle perpendicular to the substrate. The effective airflow area affected by the small jet nozzle is a circular area of about 10 cm in diameter. The optimal air flow is 1.0 bar for a 2D perovskite layer-assisted growth for a thick film. Then the film was annealed at 80 °C for 20 min and 150 °C for 5 min. For (4-[4-(trifluoromethyl)phenyl]phenyl)methylaminehydrochloride (TFMACl, Sigma) was dissolved in isopropanol to form a 0.25 mg/ml solution. The annealed perovskite film was placed in a petri dish with a lid, which was positioned on a hot plate set to 80 °C.

Subsequently, $10 \ \mu L$ of TFMACL solution was added to the lid, and heating was continued for 10 minutes.

For the hole transport layer, the toluene-dispersed PEDOT complex (Ossila, HTL Solar 3 PEDOT Complex) was used as received. A gap height of 150 μ m, a coating speed of 10 mm s⁻¹ and a volume of 40 μ L were used for doctor blading PEDOT dispersion. The coating temperatures and speeds for PEDOT were 60 °C as well as 10 mm s⁻¹, respectively. After coating the PEDOT, the film was annealed at 100 °C for 5 min.

3.2 Carbon-electrode fabrication

For the carbon electrode, the carbon paste (Liaoning Huite Photoelectric Technology Co. Ltd.) was stencil printed on the as-prepared film and annealed at 120 °C for 15 min. The electrodes pattern was cut out of adhesive tape with a laser. The tape with a thickness of around 160 μ m was then placed on the substrate with the sticky side down. The cutouts were filled with carbon paste by stencil printing method. The tape was then removed carefully, and the substrate annealed on a hot plate at 120 °C for 15 min. The thickness of the dry carbon electrode is around 45 μ m.

3.3 Flexible solar cell fabrication

The flexible substrates PET/IMI (purchased from OPVIUS GmbH) were ultrasonically cleaned sequentially for 10 minutes in acetone and isopropanol. Then, the substrates were treated under a UV-Ozone box for 10 minutes (flexible substrates for 5 mins) to remove organic residues and to enable better wetting. Both tin oxide layer and perovskite layer on a flexible PET substrate were annealed at 130 °C for 30 min. All the other coating parameters were conducted as mentioned before.

3.4 For inverted Ag-electrode solar cells fabrication

First, a NiO nanocrystal (10 mg ml⁻¹ in H₂O, Advanced ElectionTechnology Co., Ltd.) layer was spin-coated on as-cleaned ITO substrates at 5000 rpm for 30 s and then annealed at 150 °C for 10 min at ambient air. After cooling, the substrates were immediately transferred to the N2filled glovebox. Then, the hole transport layers of [4-(3,6-Dimethyl-9H-carbazol-9yl)butyl]phosphonic Acid (Me-4PACz, TCI Development Co.) and MPA (Methylphosphonic acid, Sigma-Aldrich) were sequentially deposited on the ITO substrate at 4000 rpm for 30 s and annealed at 100 °C for 10 min. The concentration of precursor was 0.5 mg/mL of Me-4PACz or MPA in alcohol solution. Subsequently, a diluted Al_2O_3 dispersion (v:v = 1:50 in IPA) was spin-coated on the SAM layer at 5000 rpm for 20 s and then heated at 100 °C for 5 min. After that, the perovskite layer was deposited by gas-quenching assisted blade coating as mentioned before. The PCBM (20 mg/mL in chlorobenzene, Nano-C.) solution was spin-coated on the perovskite layer at 2000 rpm for 30 s and then annealed for 10 min at 60 °C. Subsequently, BCP (0.25 mg/mL in chlorobenzene, Sigma-Aldrich) solution was deposited on the PCBM layer at 4000 rpm for 30 s. Finally, the Ag electrode (100 nm) was evaporated on the BCP layer using the thermal evaporation method. The deposition rate is between 0.1 Å s⁻¹ and 0.5 Å s⁻¹, and the whole deposition process takes around 1 h.

3.5 Mini solar module fabrication

Mini solar modules with seven cells monolithically interconnected in series were fabricated on 5×5 cm² ITO-coated glass substrates. The subcell width and length are 5.35 mm and 45 mm respectively, generating a total active area of 2.41 cm² for each subcell. The interconnect region with a width of 1.2625 mm and a length of 45 mm, generates a total dead of 3.41 cm² for the whole mini module. The P1 lines on ITO substrates were prepatterned by laser scribing. On the cleaned ITO substrates, the used volume of precursors increased 2 times compared with that on 2.5×2.5 cm² substrate, and all of the functional layers were blade-coated as detailed above. To complete the module fabrication, the carbon electrode was stencil printed using a shadow mask which is pre-patterned to define the P3 lines. For better electrical connection, conductive adhesive bus bars were pasted on the cathode and anode, respectively. The seriesinterconnection of the module is realized by the mechanically separated but electrically interconnected P1, P2, and P3 lines. The laser patterning of the solar modules, "P1", "P2", and "P3", was conducted by means of a femtosecond laser by InnoLas Photonics. For "P1" and "P3", a Spirit 1040-8 SHG laser from Spectra-Physics (Pmax =6W, 1 = 520 nm, Yb:KYW) with 350 fs femtosecond pulse width in combination with a galvanometer scanner with f-theta lens and a focal length of 506 mm was used. Laser powers of 1860 w and 1116 w were used for "P1" and "P2" respectively, which results in line widths of 250 and 230 µm.

3.6 Characterization

Solar cells were characterized by measuring their current–voltage (J–V)-characteristics with an AAA solar simulator, which provides AM1.5G illumination and source measurement system from LOT-Quantum Design, calibrated with a certified silicon solar module. The sweeping ranges for solar cells were -0.5 to 1.5 V in steps of 20 mV. The scan rate for mini modules is fixed at 100 mV s⁻¹ for both reverse scans (8.0 to -0.5 V) and forward scans (-0.5 to 8.0 V).

Scanning electron microscopy (SEM): JEOL JSM-7610F was used to acquire SEM images and to prepare FIB cross-sections. The final polishing with the ion beam was performed at $3 \sim 15$ kV and $60 \sim 80$ pA.

X-ray powder diffraction (XRD): X-ray diffraction analysis was performed by classical ex-situ Bragg–Brentano geometry using a Panalytical X'pert powder diffractometer with filtered Cu-K α radiation ($\lambda = 1.54056$ Å) and an X'Celerator solid-state stripe detector. All the perovskite film were prepared on the ITO substrates for XRD characterization. The XRD patterns were calibrated by the ITO substrate as background.

Transmittance and reflectance spectra of the samples were carried out using a UV-VIS-NIR spectrometer (Lambda 950, from Perkin Elmer). For the haze measurement, the diffuse transmittance and total transmittance were detected without or with a reflection standard placed, respectively. The detector with R955 PMT works at the wavelength of 160 nm to 900 nm.

Photoluminescence (Steady state PL) and the time-resolved photoluminescence (TRPL) spectra were performed with a Fluotime 300 system. The samples were excited by the PDL 820 picosecond diode laser with a wavelength of 402 nm at an average incident power of 4 μ W at a frequency of 20000 kHz. A cutting-off filter (415 nm) was adopted to block the excitation laser. The EasyTau software was used to control measurement. The TRPL decay curves were fitted using a bi-exponential decay function, as described below.

$$I_{PL}(t) = A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right) + I_0$$
(1)

$$t_{av} = (A_1 \tau_1^2 + A_2 \tau_2^2) / (A_1 \tau_1 + A_2 \tau_2)$$
⁽²⁾

Where t is the start time of the decay process, τ_1 and τ_2 represent the first- and second-order decay times, the fast decay (τ_1) component is attributed to the surface recombination, while the slow decay (τ_2) component is associated with the recombination occurring in the bulk of the perovskite structures. A_1 and A_2 are weighting coefficients of each decay channel, I_0 is a constant, τ_{av} is the Average lifetime.

In Situ PL: PL measurements were acquired on a home-built confocal setup using a 532 nm or 405 nm laser diode, a plano-convex lens above the substrate, a 500 nm or 550 nm long-pass filter, and a fiber-coupled spectrometer (AVANTES, ULS2048XL Sensline series) calibrated by the manufacturer. This house-made setup integrates excitation and detection within the same holder using a beamsplitter, allowing the entire setup to be mounted either above or below the sample. Laser of 532 nm penetration depth estimation. Intensity decay calculated using the Beer-Lambert law: $I_{(z)} = I_0 e^{-\alpha z}$. The absorption coefficient was assumed to be 1.8 x 10⁵ cm⁻¹ as was reported for α -FAPbI₃ thin films. The penetration depth of about 54 nm was defined as the depth by which the intensity decays to 1/e of its initial value. For a laser of 405 nm, the penetration depth could be less than 54 nm. The distance between the plano-convex lens and the substrate was optimized such that the PL intensity of a dry film was maximized. Both the laser light source and the optical fiber used as the detector can be flexibly fixed on the top and bottom surfaces of the sample. The working distance was not adjusted with the change of the wet film thickness during the drying process. The intensity of the laser diode can be controlled by Benchtop LD Current Controller (THORLABs, LDC205C). The measurement was turned on simultaneously with the gas quenching treatment, and signals were acquired every 0.5 s till the end of the gas quenching treatment.

In situ UV-vis: The *in-situ* absorption measurements were performed using a spectrometer (AVANTES, ULS2048XL Sensline series) equipped with a deuterium halogen source (Avantes, AvaLight-DH-S-BAL). The signal is detected with the same fiber-coupled spectrometer with a spectral range of 300 to 1000 nm. Both the light source (halogen lamp) and the optical fiber used as the detector can be flexibly fixed on the top and bottom surfaces of the sample. Most of the measurements were performed with an integration time of 0.5 s per transmission spectrum. The UV-vis absorption spectra were calculated from the transmission spectra, using the following equation: $A\lambda = -\log_{10}(T)$, where $A\lambda$ is the absorbance at a certain wavelength (λ) and T is the calibrated transmitted radiation. All the situ measurements were conducted in a dark fume hood.

4. Supporting Figures



Fig. S1. A general overview of the transmittance/transfer matrix procedure when modeling a single-layer or multilayer stack with unknown optical constants. Once the optical constants have been derived, the device model can be used to model useful properties such as distribution of optical field intensity, charge generation rate, current density (*Jsc*).



Fig. S2. Reported and extracted optical constants of functional layers by inverse transfer matrix.



Fig. S3. Distribution of normalized optical field intensity for four wavelengths (400, 500,600 and 700 nm) and the normalized charge generation rate in the (**A**) carbon-electrode (40 μ m) and (**B**) silver-electrode (100 nm) solar cells with various thicknesses of the perovskite layer (200, 500 and 800 nm).



Fig. S4. *Jsc* simulation output of MAPbI₃ perovskite with around 1.60 eV bandgap depending on different thickness of perovskite layer and type of electrode, under AM1.5 illumination assuming 100% internal quantum efficiency.



Fig. S5. The representative thickness measurement as a function of the coating speed provided by the profilometer.



Fig. S6. SEM top-view images of perovskite film printed with various coating speeds (wet film height), from 1 mm s⁻¹ to 20 mm s⁻¹, respectively.



Fig. S7. SEM cross-sectional images of perovskite film printed with various coating speeds (wet film height), from 1 mm s⁻¹ to 20 mm s⁻¹, respectively.



Fig. S8. Optical microscopy images of the 3D perovskite films after thermal annealing on different substrates coated at various speeds (3 mm s⁻¹, 7 mm s⁻¹, 10 mm s⁻¹, 15 mm s⁻¹). Aluminum oxide (Al₂O₃), tin oxide (SnO₂), 2D perovskite layer and self-assembled monolayer (Bis SAM: a fullerene bis(alkyl phosphonic acid)) with a thickness of approximately 20 nm are deposited on ITO substrates by blade coating. 3D perovskite solutions are deposited via blade coating at different wet film thicknesses. The hatched areas indicate the presence of voids at the bottom interface. It should be noted that thin Al₂O₃ and Bis SAM are commonly used with a very thin layer for high-efficiency solar cells due to the poor charge extraction. Thus, the thickness and microstructure of these pre-coating layers are rather limited in its use for thick film growth.



Fig. S9. In situ time-resolved UV-vis absorption spectra of the blade-coated solvents (DMF/NMP) on the seeds for 10 s: (**A**) PbI_2 ; (**B**) 3D-perovskite; (**C**) FAPbBr₃; (**D**) 2D-perovskite. Moreover, we blade-coated same perovskite solution with 1.25 M on the 3D-perovskite layer, as shown in (**E**). Unfortunately, the 3D perovskite layer is likely to dissolve completely after 1 s, suggesting it is not suitable as a seed layer.



Fig. S10. Dynamic light scattering (DLS) spectra of 2D PEA2PbI4 perovskite powder in DMF, NMP and DMF/NMP mixture, respectively. We measured the DLS spectra at about 2s, 5 min, and 1 h after adding the solvent to the 2D perovskite powder. 2D perovskite powder slowly dissolves in DMF and DMF/NMP mixed solvents within 5 min.



Fig. S11. The energy-dispersive spectroscopy (EDS) elemental line scans across two grains. The grain boundary region, indicated by the white arrow, shows a significant decrease in the amounts of Cs, I and Pb elements, while the C element increases markedly (Inset is the chemical structure of 2D ligand). This observation suggests that the carbon-rich 2D cations are primarily located at the grain boundary.



Fig. S12. Atomic force microscopy (AFM) images of perovskite dry thin film and thick film prepared by regular blade coating and seeding growth, respectively.



Fig. S13. (A) Cross-section SEM images of the 2D perovskite layer-assisted growth (2D-LAG) films with varying the air flow rate from 0.0 bar to 2.0 bar, (B) Top-view SEM image of the 2D-LAG film with 0 bar. Based on our previous study,⁸ we found that relying solely on natural drying represents an extreme case of a low evaporation rate. This insufficient evaporation cannot drive adequate α -phase nucleation, leading to the formation of a discontinuous film.



Fig. S14. (A) UV-vis absorption spectra of films prepared by regular one step blade coating (left) and 2D-SAG (right). The films prepared by one-step blade coating with the coating speed of over 7 mm s⁻¹ show a lot of voids at the bottom surface. (B) XRD patterns of the films prepared by one step blade coating with various coating speeds.



Fig. S15. The configuration and cross-section SEM image of fully printed C-PSCs on the rigid substrate.



Fig. S16. EQE spectra of different perovskites prepared with different coating speed (wet film thickness).



Fig. S17. The distribution of Jsc, Voc, FF and PCE values for different perovskite layers prepared with different coating speed (wet film thickness).



Fig. S18. The distribution of Jsc, Voc, FF and PCE values for perovskite solar cells prepared with 2D-LAG perovskite layers varying the air flow from 3.0 bar to 0.0 bar. The device structure is based on the stack of glass/ITO/SnO₂/perovskite/PEDOT/Carbon devices (C-PSCs). As the air flow gradually decreases to 1.0 bar, we obtain the optimal PCE with improved J_{SC} , V_{OC} and FF, which is consistent with the SEM observations (Fig. S13).



Fig. S19. Statistical data of photovoltaic parameters of the rigid C-PSCs with 1100 nm thick perovskite layers prepared by regular one-step blade coating thick film (control) and 2D perovskite layer-assisted growth (2D-LAG) with or without TFMACl passivation.



Fig. S20. Time-dependent PL evolution of perovskite thick film processed with CFMACl treatment in the stage of gas quenching after solution immersion.



Fig. S21. Statistic PCE, Voc, FF and Jsc of PSCs of thick layers with or without CFMACl treatment. As reference, Ag-electrode devices are fabricated with an architecture of ITO/NiO@SAM/Perovskite/PCBM/BCP/Ag. Only the thick perovskite layers are blade-coated via 2D-LAG, while the other layers are spin coated. Significantly, it is noticed that the efficiency increase mainly arises from the enhancement in $V_{\rm OC}$, while the current density ($J_{\rm SC}$) and fill factor (FF) of the devices only change slightly.



Fig. S22. Light intensity dependence of *Voc* of the devices prepared by conventional one-step blade-coating thick film (control), 2D perovskite layer-assisted growth (2D-LAG), 2D-LAG thick film with TFMACl treatment.



Fig. S23. The evolution of photovoltaic parameters normalized to the initial values of unencapsulated C-PSCs prepared by (A) regular one-step blade coating and (B) 2D-LAG strategy, aging under continuous illumination of 1 sun equivalent irradiation (metal halide lamps with ultra-violet filter) at 85 °C in a nitrogen atmosphere.

Table S1. Summary of the parameters from fitting to the TRPL decay.

Film		A_1	τ_1 (ns)	A_2	τ_2 (ns)	$\tau_{\rm ave}({\rm ns})$
Thin film	Тор	0.48	6.18	0.52	146.35	141.09
	Bottom	0.55	6.43	0.45	181.22	173.95
Thick film	Тор	0.79	18.78	0.21	265.62	213.76
	Bottom	0.87	48.4	0.13	187.12	99.19
2D-LAG thick film	Тор	0.89	12.73	0.11	261.07	190.81
	Bottom	0.85	17.45	0.15	277.43	209.11

Parameter	ΙΤΟ	SnO ₂	Perovskite	PEDOT:PSS	Carbon
Thickness		30 nm	1000 nm	50 nm	
VB (HOMO)		8.4 eV	5.5 eV	5.1 eV	
CB (LOMO)		4.2 eV	3.9 eV	3.0 eV	
Work function	4.25 eV				5.1 eV
Density of states		2.0×10 ²⁴ m ⁻³	5.0×10 ²⁴ m ⁻³	5.0×10 ²⁶ m ⁻³	
Carrier mobility		$5 \times 10^{-5} \text{ cm}^2 \text{V}^{-1} \text{S}^{-1}$		5×10 ⁻⁷ cm ² V ⁻¹ S ⁻¹	
Dielectric constant		10		3.5	

Table S2. Summary of input parameters for the Drift-diffusion simulations

Table S3. Summary of output parameters for the Drift-diffusion simulations

Parameter	Gehp (m ⁻³ s ⁻¹)	Rshunt (Ohms m ²)	Rseries (Ohms m²)	Bulk_tr (m ⁻³)	Tr_top (m ⁻²)	Tr_bottom (m ⁻²)
One-step						
blade-coated	1.38×10 ²⁷	67	2.1×10-4	1.3×10 ²¹	1.1×10 ¹³	1.5×10 ¹⁴
thick film						
2D-LAG	1.52×1027	205	1.0×10-4	9.5×10 ²⁰	2.9×1012	2.2×1012
thick film	1.53×10 ²⁷	305	1.0×10 ⁺	8.5×10 ²⁰	2.8×10 ¹²	3.2×10 ¹²
2D-LAG						
thick film with	1.56×10 ²⁷	128	1.0×10 ⁻⁵	5.5v×10 ²⁰	3.8×10 ¹²	3.5×10 ¹²
TFMACl						

Supplemental references

- 1. Martin Majewski, *et al.* "Simulation of perovskite thin layer crystallization with varying evaporation rates." *Materials Horizons*, 12,555 (2025), doi: 10.1039/D4MH00957F (2024).
- Olivier J. J. Ronsin, *et al.* "Phase-Field Simulations of the Morphology Formation in Evaporating Crystalline Multicomponent Films." *Advanced theory and simulations*, 5(10), 2200286 (2022).
- Robin Kerremans, *et al.* "The optical constants of solution-processed semiconductors new challenges with perovskites and non-fullerene acceptors." *Advanced Optical Materials* 8, 2000319 (2020).
- George F. Burkhard, *et al* "Accounting for interference, scattering, and electrode absorption to make accurate internal quantum efficiency measurements in organic and other thin solar cells." *Advanced Materials* 22.30: 3293-3297 (2010).
- Mikhail N. Polyanskiy, "Refractiveindex.info database of optical constants." *Scientific Data* 11, 94. <u>https://doi.org/10.1038/s41597-023-02898-2</u> (2024).
- Mikhail N. Polyanskiy, "Refractive index database," <u>https://refractiveindex.info.</u>" Accessed on 2024-10-11.
- Sai Kiran Hota, *et al.* "Influence of optical constants in carbon-based dispersions for enhanced solar evaporation." *Journal of Thermal Analysis and Calorimetry*, 144(3), 741-750 (2021).
- Shudi Qiu, *et al.* "Printing High-Quality Formanidinum Lead Triiodide Films: Understanding the Critical Role of α-Phase Nucleation Before Thermal Annealing." *Advanced Energy Materials*, 2402616 (2024).