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Square-Centimeter Solution-Processed Planar CH₃NH₃Pbl₃ Perovskite Solar Cells with Efficiency Exceeding 15%

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Organolead trihalide perovskites (e.g., CH₃NH₃PbI₃ or MAPbI₂) have seen rapid development for solar cell applications since their first demonstration in sensitized solar cells in 2009.^[1-10] Within a short period of time, the power conversion efficiencies (PCEs) of perovskite solar cells (PSCs) have now topped 20%.^[11,12] The certified or reported efficiencies for PSCs are usually based on relatively small active areas; device areas of around 0.1 cm², and sometimes even as small as 0.03 cm², are often used.^[13-18] One of the reasons for choosing small active areas is presumably associated with the challenge of making continuous, pinhole-free, and uniform perovskite films over a large area, especially during the early stages of PSCs development.^[6,8] The nonuniformity of perovskite layers over a large area, in particular when solution routes are used, leads to significant variation in the device performance. Consequently, statistical analyses of the PSC characteristics are often required of most reports.^[19] To address this challenge, various groups have devoted significant effort in developing/improving synthetic methods to control the morphology of perovskite films. Many of these studies have led to significant efficiency enhancement in small-area solar cells with improved reproducibility.[13,20-24] Despite the remarkable progress in perovskite synthesis, there have been only a handful of studies attempting to fabricate large-area PSCs.^[25-28] This has prompted some critics to question the reported progress of the PSC field, in comparison with other established photovoltaic (PV) technologies (e.g., Si).^[29,30] In particular, the use of small-area devices has been criticized because the measurement errors tend to increase as the active cell area becomes smaller. Thus, the development of PSCs with active areas on the square-centimeter scale is recommended for the evaluation of a new PV technology.^[31] To that end, it is necessary to develop a high-quality perovskite absorber layer^[32] with large-area uniformity and high crystallinity. This has been a challenge as it requires control over several key steps during the perovskite film formation over a large device area. These steps include formation reaction, crystallization, grain growth, and decomposition, which are often intertwined in conventional one-step solution processing methods.^[33–35]

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Here, we demonstrate a solution-based synthetic route, as shown schematically in **Figure 1**, for the formation of uniform, large-grain, and high-crystallinity planar MAPbI3 perovskite films. This is achieved by controlling the nucleation/crystallization and the grain-growth processes, with a goal of allowing better decoupling of these processes. The first step in this route is the formation of crystalline perovskite film using our previously reported room-temperature (RT) solvent-solvent extraction (SSE) approach,^[36] but with excess methylammonium iodide (MAI) (e.g., MAI:PbI₂ = 1.2:1, molar ratio) embedded within the precursor film. In a typical SSE process with stoichiometric precursor (PbI₂:MAI = 1:1, molar ratio), a precursor solution film is immersed in a RT bath of a second (anti)solvent (also referred to as solvent bathing). The miscible behavior of the precursor solvent with the antisolvent bath (with apparent extraction of the precursor solvent into the large-volume antisolvent bath) allows rapid nucleation/crystallization before significant growth of perovskite grains, leading to controlled formation of a dense, uniform, fine-grained, and ultrasmooth perovskite film.^[36] In the route we demonstrated here the excess MAI plays a key role in promoting the growth of perovskite grains up to $1-2 \mu m$ during a second grain-growth step, where the as-deposited perovskite thin film is air-annealed at an elevated temperature (e.g., 150 °C). When excess MAI is absent, the grain size is typically limited to a few hundred nanometers. But when excess MAI is present, it compensates for the loss of any MAI, and suppresses (or delays) the formation of a PbI₂ phase during annealing. This in turn facilitates the growth of fine, native grains into larger, more-textured micrometer-sized grains with high aspect ratio. Using this crystallization-coarsening two-step approach with the nonstoichiometric MAPbI₃ precursor solution, the best PCE of 16.3% is achieved for a planar PSC with 1.2 cm² active area (stabilized PCE output of \approx 15.6%). When the device area is reduced to 0.12 cm², a maximum PCE of 18.3% is achieved (stabilized output of $\approx 17.5\%$). The effect of cell area (0.12, 0.3, 0.6, and 1.2 cm²) on the device characteristics is further investigated.

Figure 2a shows a top-view scanning electron microscope (SEM) image of the MAPbI₃ perovskite film prepared using the nonstoichiometric precursor (MAI:PbI₂ = 1.2:1, molar ratio) solution after the solvent-bathing step but without airannealing. The resulting film consists of fine grains with relatively nonuniform sizes (roughly from 30 to 150 nm). Figure 2b shows the morphology of the perovskite film after the subsequent air-annealing (grain-growth) step at 150 °C for 15 min, where large grains of sizes of up to 1–2 µm (in plane) are seen. (Note that some grain boundaries appear to crack (Figure 2b) during SEM observation under the electron beam.) While the film thickness is around 350 nm, the in-plane grains are three







Figure 1. Schematic illustration of perovskite film nucleation/crystallization from solvent bathing, followed by grain growth under thermal annealing in air, using nonstoichiometric MAPbI₃ precursor (with excess MAI; e.g., MAI:PbI₂ = 1.2:1, molar ratio).

to six times that of the size along the thickness direction of the film. Such high-aspect-ratio growth of the MAPbI₂ grains in these films is somewhat atypical compared to general polycrystalline thin film growth.^[37] UV-vis absorption spectra of the film before and after air annealing are compared in Figure 2c. The absorption edges for both spectra are close to 800 nm, which is in agreement with literature reports.^[38,39] Note that the baselines for both UV-vis spectra at long wavelengths are very low, which is due to the low light scattering associated with a smooth perovskite film. As compared to as-deposited film (without the grain-coarsening step), the absorption for the air-annealed film is much stronger, especially at the absorption edge. Figure 2d compares X-ray diffraction (XRD) patterns from as-deposited and air-annealed MAPbI3 perovskite films. Although the XRD patterns of both films can be indexed to the tetragonal phase (space group I4/mcm), the air-annealed MAPbI₃ perovskite film shows 110 texture. The ratio of the intensities of 110 to 310 peaks increases from ≈3 for the as-

deposited film to ≈23 for the air-annealed film. Furthermore, as seen in Figure 2d and Figure S1 (Supporting Information). while the intensity of the 110 peak increases, its full-width at half-maximum decreases significantly, from 0.42° to 0.08° after air-annealing. This is indicative of simultaneous enhancement of the crystallinity and the grain size after the air-annealing step. Taken together, the quantitative XRD and the SEM results indicate that the solvent-bathing step results in fine-grained, lower-crystallinity MAPbI3 perovskite thin films, which is followed by grain growth and significant improvement in the crystallinity during the air-annealing step. It is interesting that the excess MAI is not detected in the XRD pattern in the asdeposited film, which is presumably because of the low crystallinity of MAI in the film. In order to confirm the presence of excess MAI in the film after the solvent-bathing step using nonstoichiometric MAPbI3 precursor, Fourier-transform infrared spectra (FTIR) from samples removed from the two perovskite films (before and after air-annealing), as well as a control MAI



Figure 2. SEM images (top view) of a) as-deposited and b) air-annealed MAPbI₃ perovskite films. c) Absorption spectra and d) XRD patterns of as-deposited and air-annealed MAPbI₃ perovskite films. e) FTIR spectra of as-deposited, air-annealed MAPbI₃ perovskite films, and pure MAI film. Non-stoichiometric MAPbI₃ precursor (MAI:PbI₂ = 1.2:1, molar ratio) is used in all cases and air-annealing is performed at 150 °C for 15 min.

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film, were collected. The FTIR spectra in Figure 2e show three weak transmittance peaks between 1020 and 1200 cm⁻¹ in the as-deposited film, which agree with those in the MAI control film. In contrast, those three FTIR peaks are absent in the air-annealed film, which is consistent with previous reports of well-crystallized stoichiometric MAPbI₃ perovskite.^[13,36] Energy-dispersive spectroscopy analysis was also performed to verify the excess MAI in the nonstoichiometric MAPbI₃ films. The I/ Pb ratio in the film was found to increase systematically with increasing I/Pb ratio in the precursor (Figure S2, Supporting Information). These results indicate the existence of MAI phase in the as-deposited perovskite film and the consumption of the excess MAI during air annealing.

To gain further understanding of the influence of excess MAI on the film microstructure, SEM image (Figure S3a, Supporting Information) of the perovskite film prepared from stoichiometric MAPbI₃ precursor (MAI:PbI₂ = 1:1, molar ratio) and air annealed at 150 °C for 15 min was obtained. In contrast to the nonstoichiometric precursor film with the same treatment (Figure 2b or Figure S3b in the Supporting Information), the grain size of the stoichiometric-precursor film after airannealing is substantially smaller. The XRD patterns from both the stoichiometric- and nonstoichiometric-precursor films as a function of air-annealing duration are compared in Figure S4 (Supporting Information). It is clear that air-annealing greatly enhances the crystallinity of the perovskite film in both cases, as evinced by the increase in the intensity of the perovskite 110 peak. However, when excess MAI is absent, there is a clear indication of PbI₂ formation (peak at $2\theta \approx 12.6^{\circ}$) after airannealing for 5 min (Figure S4a Supporting Information). The PbI₂ peak-intensity increases significantly with a 10-min airannealing, and it is further enhanced for 15-min air-annealing. These results indicate that for the stoichiometric MAPbI₃ precursor, an air-annealing temperature of 150 °C is sufficient to enhance perovskite crystallinity, but significant decomposition of MAPbI₃ via release of MAI and formation of PbI₂ occurs after 5-10 min of air-annealing. In contrast, when excess MAI $(MAI:PbI_2 = 1.2:1, molar ratio)$ is used in the precursor, PbI_2 starts to form at around 15 min, with much weaker intensity of the PbI₂ peak at $2\theta \approx 12.6^{\circ}$ under the same annealing condition (Figure S4b, Supporting Information), suggesting that the excess MAI compensates for the loss of MAI, suppressing (or delaying) the formation of PbI₂ during air-annealing. It is also noteworthy that with excess MAI, the intensity of the perovskite 110 peak is about three to four times higher compared to that for stoichiometric-precursor case after air-annealing for 15 min. The comparison of XRD patterns over a wider range (10°-45°) for the as-deposited or air-annealed (150 °C, 15 min) MAPbI₃ perovskite films using stoichiometric (MAI:PbI₂ = 1:1, molar ratio) or 20% excess MAI (MAI:PbI₂ = 1.2:1, molar ratio) precursors is given in Figure S5 (Supporting Information). It is also worth noting that annealing at 150 °C does not appear to generate defects to enhance nonradiative recombination (Figure S6, Supporting Information).

Based on the above results, it is clear that the excess MAI plays a critical role in facilitating the enhancement of perovskite crystallinity and grain size. It is known that the organic component MAI can be released from MAPbI₃ under thermal annealing, leading to the formation of PbI₂, primarily at grain boundaries.^[40] While a small amount of PbI₂ seems to be beneficial for device operation, a large amount of $\ensuremath{\text{PbI}}_2$ could be detrimental to device performance.^[33,40] In this study, the excess MAI is mixed uniformly in the precursor and thus it is expected to be distributed across the entire film, presumably at grain surfaces. Regardless of its exact location, the as-formed excess MAI phase after the solvent-bathing step serves as a reservoir of MA⁺ and I⁻. This reservoir allows ready diffusion of MA⁺ and I⁻ into the thermally created MA⁺ and I⁻ vacancies in the MAPbI₃ perovskite; this diffusion leads to the reformation of MAPbI₃ perovskite.^[41,42] This dynamic perovskite-formation process, as depicted schematically in Figure 1, appears to be responsible for the textured growth of high-crystallinity large grains with high aspect ratio. It is worth noting that further increase in excess MAI (e.g., MAI:PbI₂ = 1.4:1 or 1.8:1, molar ratio) results in perovskite films with rougher surfaces and noticeable pinholes, as seen in the optical microscope images in Figure S7 (Supporting Information). This observation is also supported by comparing SEM images (Figure S3, Supporting Information) of perovskites prepared from precursors with different MAI/PbI₂ ratios.

In addition to the full coverage, high crystallinity, highaspect-ratio grain-structure, and strong 110 texture, the final MAPbI₃ perovskite film also retains its uniformity at multiple length scales over a square-inch area. This is demonstrated using a combination of microscopy techniques, as described next. Figure 3a is a cross-sectional transmission electron microscope (TEM) image showing the MAPbI₃ perovskite film sandwiched between a compact layer of TiO₂ on fluorine-doped tin oxide (FTO) and a hole-transporting material (HTM)/Ag layer. The perovskite layer (dark contrast) is dense and of uniform thickness of ≈350 nm, with grains spanning the entire thickness of the film. Also, pinholes and voids are absent. The highresolution transmission electron microscope (HRTEM) image in Figure 3b shows clear lattice fringes with an inter-planar spacing of 0.32 nm, which can be assigned to (220) or (004) planes. This further supports the notion of high crystallinity in the final perovskite film. The selected-area electron diffraction (SAED) pattern in Figure 3c shows spots confirming the tetragonal structure of the perovskite grains within the film. Note that only the brightest diffraction spots are indexed, whereas other weak diffraction spots may be associated with planar faults and/or possible electron-beam damage in the film.^[43] The optical image in Figure 3d shows that the perovskite film is uniform and smooth without obvious macroscale defects. For comparison, an optical image of a control sample of an MAPbI₃ perovskite film made using the conventional one-step method (stoichiometric dimethylformamide (DMF) solution of MAI and PbI₂ mixture) is also shown in the inset of Figure 3d (same magnification). That control film is considerable rough and it is replete with macroscale defects, which is consistent with previous reports.^[23,44] To further demonstrate the uniformity over a large area, atomic force microscope (AFM) was used to measure the surface roughness of 16 areas ($20 \times 20 \ \mu m^2$) distributed over a square-inch area sample (optical image in Figure 3e). All of these areas show about the same surface roughness of 15 ± 1 nm. A typical AFM image of one such area is shown in Figure 3e. Also, the apparent grain size observed in the AFM image is consistent with that seen in the SEM



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Figure 3. a) Cross-sectional TEM image of MAPbl₃ perovskite film (air-annealed) sandwiched between a compact-TiO₂-coated FTO layer and an HTM/ Ag layer. b) High-resolution TEM image of the MAPbl₃ perovskite layer. c) SAED pattern from the green spot indicated in (a). The zone axis is denoted by B and the transmission beam is denoted by T. d) Optical image of air-annealed MAPbl₃ perovskite film (inset: control perovskite film made using the conventional one-step method using stoichiometric MAI:Pbl₂ (1:1, molar ratio) DMF solution). e) Typical AFM image of air-annealed MAPbl₃ perovskite film from one of the 16 squares ($20 \times 20 \ \mu$ m²) shown in the square-inch-size MAPbl₃ perovskite film shown in the right bottom corner. Nonstoichiometric MAPbl₃ (MAI:Pbl₂ = 1.2:1, molar ratio) precursor is used unless stated otherwise, and the air-annealing is performed at 150 °C for 15 min.

image in Figure 2b. Additional Kelvin probe force microscopy (KPFM) experiments were conducted to further examine the grain properties, results from which are presented in Figure S8 (Supporting Information). There is one-to-one correspondence between the grain-boundary topography in the AFM image (Figure S8a, Supporting Information) and the potential in the KPFM image (Figure S8b, Supporting Information), indicating that the grains observed in the SEM and AFM images are not aggregates of smaller crystallites.

Using these uniform, large-grained MAPbI₃ perovskite thin films, planar PSCs were fabricated. To understand the effect of active cell area on the device characteristics, the areas are varied systematically in the range of 0.12–1.2 cm² (specifically: 0.12, 0.3, 0.6, and 1.2 cm²). **Figure 4**a shows typical current density–voltage (*J*–*V*) curves for planar PSCs with these different cell areas. For the 0.12 cm² area, the PSC shows a short-circuit photocurrent density (*J*_{sc}) of 21.9 mA cm⁻², open-circuit voltage (*V*_{oc}) of 1.10 V, fill factor (FF) of 0.741, and overall PCE of 17.8%. Note that the MAI:PbI₂ = 1.2:1 molar ratio in the precursor was found to be optimum for device performance (see Table S1, Supporting Information). The PCE decreases to 15.3% for the PSC with an increase in the active cell area to 1.2 cm². This decrease is primarily the result of reduced FF. The details of PV parameters for

these typical *I-V* curves are also tabulated in Figure 4a. To further confirm the uniformity of photoresponse within the large-area device, external quantum efficiency (EQE) was measured at five different areas (four corners and center), as shown in Figure 4b. These five EQE curves are almost identical, attesting to the uniformity of the perovskite film at the square-centimeter scale. The average integrated current density is 21.1 mA cm⁻², which compares with the I_{sc} from the *I–V* curve (Figure 4a). (Note that there is a dimple at \approx 650 nm in the EQE spectra, which is presumably caused by the optical interference effect. This interference effect in the planar PSCs has been shown and discussed in detail in ref.^[45]) A group of devices, with 10-15 devices for each area category (i.e., 0.12, 0.3, 0.6, and 1.2 cm²), were fabricated in order to further elucidate the relationship between device performance and active cell area. Figure 4c shows the statistics (mean values and standard deviations) of the dependence of each photovoltaic parameter on the cell area from 0.12 to 1.2 cm². Values of both I_{sc} and V_{oc} show very small variations when the cell area is changed, which further confirms the uniformity of the perovskite film and device over large area. In contrast, FF decreases significantly with increasing cell area; average FF decreases from 0.75 at 0.12 cm², to 0.71 at 0.3 cm², to 0.68 at 0.6 cm^2 , and finally to $0.66 \text{ at } 1.2 \text{ cm}^2$. As mentioned earlier,

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Figure 4. a) Typical *J*–V curves and extracted PV parameters for planar MAPbI₃ PSCs with different active areas (0.12, 0.3, 0.6, and 1.2 cm²). b) EQE spectra from five different spots in the large-area (1.2 cm²) PSC. c) Statistics (mean values and standard deviations) of PV parameters and d) series resistances for PSCs with different active areas. Nonstoichiometric MAPbI₃ (MAI:PbI₂ = 1.2:1, molar ratio) precursor is used in all cases, and air-annealing is performed at 150 °C for 15 min.

this decrease in FF is primarily responsible for the loss in PCE with increasing area.

To determine further the underlying mechanism for the lower PCE and FF with increasing active area, the series resistances $R_{\rm s}$ of these PSCs were analyzed from their *J*–V curves using an approach described previously.^[46,47] Briefly, using standard single-heterojunction *J*–V characteristic equations,^[48] and with the assumption that the shunt resistance is much larger than the series resistance, the value of $R_{\rm s}$ can be determined by

$$-\frac{\mathrm{d}V}{\mathrm{d}J} = \frac{AK_{\mathrm{B}}T}{e} \left(J_{\mathrm{sc}} - J\right)^{-1} + R_{\mathrm{s}} \tag{1}$$

where *V* is the bias voltage applied to the cell, *J* is the current density under the applied bias, *A* is the diode ideality factor, *K*_B is the Boltzmann constant, *T* is the absolute temperature, and *e* is the elementary charge. The value of *R*_s can be obtained from a linear fitting of -dV/dJ versus $(J_{sc} - J)^{-1}$, especially at biases near the *V*_{oc} region. A typical fitting curve is illustrated in Figure S9 (Supporting Information). Figure 4d shows the average and standard deviation of *R*_s values for devices with different cell areas. *R*_s increases monotonically with larger active cell area, changing from about 1.4 Ω cm² for 0.12 cm² to 5.7 Ω cm² for

1.2 cm² active cell area. FF has a similar but opposite trend with increasing cell area, implying that R_s is the primary factor determining the device performance for large-area (square centimeter) PSCs in this study. This is expected only when the properties of the active (absorber) layer and other contact layers are not affected by the fabrication methods for different film/ device areas. It is worth noting that the shunt resistance ($R_{\rm sh}$) decreases slightly (<15%) from about 5000 to 4300 Ω cm² when the active area is increased from 0.12 to 1.2 cm². Such small change of $R_{\rm sh}$ is expected to have a minimum impact on FF of PSCs. One of the main factors determining the $R_{\rm s}$ value is the resistance of the transparent-conducting oxide (TCO) anode (FTO in this study).^[49] It is expected that further improvement for large-area PSCs would benefit from TCOs with higher conductivities, without sacrificing optical transmittance.

Figure 5a shows the *J*–*V* curves for a "champion" device with 1.2 cm² active area, under forward (from J_{sc} to V_{oc}) and reverse (from V_{oc} to J_{sc}) scan directions. The reverse scan shows a PCE of 16.3% with J_{sc} of 21.9 mA cm⁻², V_{oc} of 1.10 V, and FF of 0.677. However, this PSC displays hysteresis, with a PCE of 12.6% under forward scan. This type of *J*–*V* hysteretic behavior has been often observed for PSCs, especially for PSCs with TiO₂-based normal planar device structure,^[50–52] although the exact cause of the hysteresis is still being debated. To verify

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Figure 5. a) J-V characteristics with both forward and reverse scans for the "champion" cell with 1.2 cm² active area. b) Stabilized output of PCE and J at maximum power point as a function of time for the same cell in (a) under simulated one-sun illumination.

the performance of the PSC, stabilized power output was monitored over time near the maximum power output point. Figure 5b shows that a 15.6% stabilized PCE output is achieved for the same large-area device in Figure 5a. We attribute this high efficiency level (>15%) for >1 cm² area PSC to the high crystallinity and uniformity at multiple length scales of the MAPbI₃ perovskite thin films. Note that for small-area active area (0.12 cm²), which is close to a cell area often reported in literature, a PCE of 18.3% has been achieved (reverse scan), with a stabilized power output at PCE of 17.5% (Figure S10, Supporting Information). This stabilized efficiency output is amongst the best reported in the literature^[23,28,53] for planar PSCs.

In summary, we report a solution route for the deposition of uniform, large-grain, textured, and high-crystallinity planar MAPbI₃ perovskite films with high-aspect-ratio grain structure. This is achieved by gaining better control over the decoupling of the nucleation/crystallization and the grain-growth processes through the use of a nonstoichiometric MAPbI₃ precursor (specifically, MAI:PbI₂ = 1.2:1, molar ratio). The room-temperature solvent-bathing process is used to promote rapid nucleation/ crystallization of MAPbI₃ perovskite from this precursor film, while suppressing grain growth. This results in the uniform



formation of a dense, fine-grained perovskite film over a large area (square-inch scale). It is shown that the excess MAI plays a critical role during the subsequent air-annealing that facilitates significant grain growth, development of strong 110 texture, and mitigation of MAPbI₃ decomposition. Planar PSCs with active area ranging from 0.12 to 1.2 cm² are fabricated and their characteristics analyzed. Over 15% stabilized PCE has been achieved for large-area (1.2 cm²) PSCs, while a smallarea "champion" PSC (0.12 cm²) has a PCE of 18.3%, with a stabilized PCE output at ~17.5%. The performance of large-area PSCs is limited by the lower FF associated with larger series resistance for the large-area devices. The solution-processing route demonstrated here paves the way for further development of the much needed large-area PSCs.

Experimental Section

Perovskite Film Synthesis: MAI was purchased from Dyesol, PbI₂ was obtained from Alfa Aesar, and all the solvents were purchased from Sigma-Aldrich unless stated otherwise. A nonstoichiometric mixture of MAI and PbI₂ (MAI:PbI₂ = 1.2:1, molar ratio) was dissolved in a solvent comprising a mixture of *N*-methyl-2-pyrrolidinone/ γ -butyrolactone (7:3, weight ratio) solvent to form an \approx 50 wt% precursor solution. Precursors with other MAI:PbI₂ ratios (1.1:1, 1.4:1, and 1.8:1) were also prepared for related experiments. The precursor was cast onto a substrate by spincoating at 4500 rpm for 25 s. The substrate was then transferred into a diethyl ether (DEE, Fisher Chemical) bath for about 90 s. After taking it out of the DEE bath, the substrate was dried in air, followed by air-annealing covered under a petri dish on a hotplate at 150 °C for 15 min.

Device Fabrication: FTO substrate (TEC 15, Hartford Glass Co) was patterned using zinc powder and HCl solution, as reported previously.[44] Prepatterned FTO was cleaned and then deposited with a thin compact TiO₂ layer by spray pyrolysis using 0.2 м titanium diisopropoxide bis(acetylacetonate) in a 1-butanol solution at 450 °C. The TiO₂ layer was annealed at 450 °C for 1 h. The perovskite film was deposited using the aforementioned method. A hole transport layer (HTL) was spin coated at 4000 rpm for 30 s with a HTL solution consisting of . 80 2,2',7,7'-tetrakis (N,N-dip-methoxyphenylamine)-9,9'mg spirobifluorene (Spiro-MeOTAD; Merck), 30 µL bis(trifluoromethane) sulfonimide lithium salt stock solution (500 mg Li-TFSI in 1 mL acetonitrile), and 30 µL 4-tert-butylpyridine, and 1 mL chlorobenzene solvent. Finally, a 150 nm Ag layer was deposited on the HTL layer by thermal evaporation using different patterns for different cell areas.

Characterization: XRD of the perovskite thin films was performed using a X-ray diffractometer (Rigaku D/Max 2200) with Cu K α radiation. Absorption spectra were carried out using an UV-vis spectrometer (Cary-6000i). Atomic force microscopy (AFM) images were obtained in tapping mode (Veeco 5000 and Nanoscope V) using a probe with tip radius of ≈10 nm and a resonance frequency of ≈300 kHz (AC160TS, Olympus). The AFM system is setup in an Ar glovebox with H₂O and O2 concentrations of less than 0.1 ppm. Based on the noncontact mode AFM (Veeco D5100 and Nanoscope V), the KPFM measures contact potential difference (CPD) between the probe (Nanosenser PPP-EFM) and surface of a solid-state sample by constantly probing and nullifying the Coulomb force between the probe and the sample. The AFM topography and the CPD are measured simultaneously at the first harmonic frequency (≈50 kHz) and the second harmonic frequency (≈300 kHz) of the probe cantilever, respectively. In this setup, KPFM maps the electrostatic potential of a sample surface with the spatial and energy resolutions of 30-50 nm and ≈10 meV, respectively. The morphologies of the films were examined by field emission scanning electron microscopy (FE-SEM, JEOL JSM-7000F). Transmission electron microscopy (TEM) was conducted using TEM (2100F, JEOL) operated at a 200 kV accelerating voltage. Cross-sectional TEM specimens from



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as-fabricated PSCs were prepared using focused ion beam (FIB; Helios 600, FEI) equipped with C and Pt gas injectors and micromanipulator (Omniprobe). A Pt layer 2-3 µm thick was deposited on the surface of the sample prior to the FIB cross-section preparation. The crosssections measuring about 8 \times 5 μm^2 in area and 0.5 μm in thickness were cut by 30 kV Ga⁺ ions with ion beam current of 28 nA, removed from the bulk sample, and then attached to the Omniprobe semiring. Final thinning was performed with 30 kV Ga+ ions with ion beam current 2.8 nA followed by cleaning with 2 keV Ga⁺ ions with a beam current as low as 10 pA.^[43] Optical images of the films were taken using an optical microscope (Eclipse LV100, Nikon). The material scratched from the film samples was characterized using FTIR spectroscopy (4100, Jasco Instruments). Time-resolved photoluminescence decays were measured with a time-correlated single-photon counting system, where light source is a Fianium Supercontinuum high power broadband fiber filter (SC400-2-PP). The excitation wavelength was 500 nm with a power of \approx 25 µW on a spot size of 0.02 mm². The decay curve was fitted using a double exponential model. The *I-V* characteristics of the cells were obtained using a 2400 SourceMeter (Keithley) under simulated one-sun AM 1.5G illumination (100 mW cm⁻²) (Oriel Sol3A Class AAA Solar Simulator, Newport Corporation). A set of shadow masks (nonreflective metal apertures) with areas 0.12, 0.3, 0.6, and 1.2 cm² were used to define the active areas during the measurements. EQE was measured using a solar cell quantum efficiency measurement system (QEX10, PV Measurements). Stabilized power output was monitored by a potentiostat (VersaSTAT MC, Princeton Applied Research) near the maximum power output point.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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