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Highly Reproducible Sn-Based Hybrid Perovskite Solar Cells with 9% Efficiency

Shuyan Shao, Jian Liu, Giuseppe Portale, Hong-Hua Fang, Graeme R. Blake, Gert H. ten Brink, L. Jan Anton Koster, and Maria Antonietta Loi*

The low power conversion efficiency (PCE) of tin-based hybrid perovskite solar cells (HPSCs) is mainly attributed to the high background carrier density due to a high density of intrinsic defects such as Sn vacancies and oxidized species (Sn²⁺) that characterize Sn-based HPSCs. Herein, this study reports on the successful reduction of the background carrier density by more than one order of magnitude by depositing near-single-crystalline formamidinium tin iodide (FASnI₃) films with the orthorhombic a-axis in the out-of-plane direction. Using these highly crystalline films, obtained by mixing a very small amount (0.08 m) of layered (2D) Sn perovskite with 0.92 m (3D) FASnI₃, for the first time a PCE as high as 9.0% in a planar p–i–n device structure is achieved. These devices display negligible hysteresis and light soaking, as they benefit from very low trap-assisted recombination, low shunt losses, and more efficient charge collection. This represents a 50% improvement in PCE compared to the best reference cell based on a pure FASnI₃ film using SnF₂ as a reducing agent. Moreover, the 2D/3D-based HPSCs show considerable improved stability due to the enhanced robustness of the perovskite film compared to the reference cell.
n–i–p device structure (with the n-type layer being mesoscopic) and demonstrated a PCE of ~2% using tin fluoride (SnF₂) as a reducing agent.¹⁴ Later, Seok and co-workers demonstrated a PCE of 4.8% by improving the FASnI₃ film morphology using pyrazine to form a complex with SnF₂ and slowing down the thin film crystallization.¹⁵ More recently, Yan and co-workers reported a PCE of 6.22% in an inverted p–i–n planar device structure.¹⁶

However, an excess of SnF₂ deteriorates the perovskite film morphology and the device performance,¹⁴–¹⁶ implying that the SnF₂ concentration must be kept low with the consequence that the background carrier density in these HPSCs is still too high to achieve equivalent performance to the lead-based perovskites. Therefore, it is necessary to develop new and more effective strategies to further reduce the background carrier density and improve the device performance of tin-based HPSCs.

Such alternative strategies have been explored by only a handful of research groups. Kanatzidis and co-workers showed that processing the perovskite film containing SnF₂ under a reducing vapor atmosphere helps to reduce the hole carrier density in MAPSnI₃ films.¹⁹ Unlike SnF₂, the reducing vapor protects the tin-perovskite film from oxidation during the film-forming process but is absent in the HPSCs themselves. The best device created using this method, however, displayed a PCE of around 3.8%, i.e., inferior to previously reported devices processed without a reducing atmosphere. Hatton and co-workers reported that adding an excess of tin chloride (SnCl₂) and tin iodide (SnI₂) to CsSnI₃ films improves both the stability and PCE of the corresponding solar cells, which displayed a PCE of ~3%.²⁰,²¹ Just before the submission of this manuscript, Zhao et al. reported tin-based HPSCs with a PCE of 8.12% by using mixed cation tin perovskite (FA₀.₇₅MA₀.₂₅SnI₃) as light harvesting layer.²² Despite the relatively high efficiency, the resistance to moisture and the device performance,²³–²⁵ implying that the hydrophilic FA⁺ and MA⁺ cations.

A lesson learned from lead-based perovskite is that low-dimensional perovskite formed by replacing the small hydrophilic cations with much bulkier organic ones can help to improve the stability of the HPSCs upon exposure to moisture.²³–²⁵ Unlike the comprehensive studies on lead-based perovskite, only two papers about tin-based HPSCs using low-dimensional perovskite such as (CH₃(CH₂)₃NH₃)₂(CH₃NH₃)SnI₃₊₁ and PEA₂FAₓSnₓI₃₊₁ (n is the number of the inorganic SnI₆ octahedra layers encapsulated by the PEA⁺ (PEA = C₆H₅(CH2)₂NH₃) double layer, the increase (decrease) in n value means increase (decrease) in the dimension; n = ∞ 3D perovskite, n = 1 2D perovskite) were published during the preparation of this manuscript.²⁶,²⁷ In both papers, the PCE of the tin-based HPSCs are still lower than 6%. Cao et al. reported a PCE of 2.5% by using (CH₃(CH₂)₃NH₃)₂(CH₃NH₃)SnI₃ (n = 4) as light harvesting layer.²⁶ Ning and co-workers reported a PCE of 5.9% using PEA₂FAₓSnₓI₂₈ (n = 9) as light harvesting layer.²⁷ For the low-dimensional tin-based perovskite family (CH₃(CH₂)₃NH₃)₂(CH₃NH₃)SnI₃₊₁ and PEA₂FAₓSnₓI₃₊₁, how the device using tin perovskite with lower content of bulkier organic cations (∞ > x > 5 for (CH₃(CH₂)₃NH₃)₂(CH₃NH₃)SnI₃₊₁, ∞ > n > 9 for PEA₂FAₓSnₓI₃₊₁) as light harvesting layer behaves, remains an open question.

Herein, for the first time, we report a PCE as high as 9% for tin-based HPSCs in a p–i–n planar device structure. These devices show negligible hysteresis and light soaking, with the background carrier density lowered by more than one order of magnitude compared to a reference cell incorporating an SnF₂ reducing agent. We demonstrate that addition of a very small amount (0.08 m) of layered (2D) tin perovskite in 0.92 m 3D tin perovskite induces superior crystallinity and a well-defined orientation of the 3D FASnI₃ grains (hereafter referred to as 2D/3D mixture perovskite). The extended ordering and packing of crystal planes improves the robustness and integrity of the perovskite structure and helps to suppress the formation of tin vacancies and therefore the background carrier density. The high degree of crystallinity and the preferential crystal orientation are fundamental for the improved solar cell performance. The champion reference solar cell gives a PCE of about 6%, i.e., 50% inferior to the record device fabricated with 2D/3D perovskite, due to the high leakage current and severe trap-assisted recombination caused by the high p-doping (10¹⁷ cm⁻³) level. Moreover, the 2D/3D-based HPSCs have much higher stability upon exposure to light and ambient conditions due to the enhanced robustness of the perovskite film.

We prepared the tin-based perovskite films via a single-step spin-coating method with antisolvent dripping.¹⁰ The films were subsequently annealed at 65 °C for 20 min. We obtained pristine 3D FASnI₃ perovskite films, acting in this work as the reference, from a precursor solution comprising formamidinium iodide (FAI), SnI₂, and SnF₂ with a 1:1:0.1 molar ratio, in a mixture of dimethyl sulfoxide (DMSO) and N,N-dimethylformamide (DMF).

Our 2D/3D samples were made from a precursor solution containing mixtures of stoichiometric 2-phenylethylammonium iodide (PEAI) xM, FAI (1 – x) m and 1 m SnI₂ and 0.1 m SnF₂, where x = 0, 0.04, 0.08, 0.12, and 0.16, corresponding to stoichiometric FASnI₃, PEAI₂FA₄Sn₅₀I₁₅₁ (n = 50), PEAI₂FA₄Sn₅₁I₁₅₆ (n = 25), PEAI₂FA₄Sn₅₁I₄₉ (n = 16), and PEAI₂FA₄Sn₅₁I₁₇ (n = 12). In our case, the PEAI⁺ content in the perovskite film is much lower than what reported in previous works. In the following section, we show that the 2D/3D samples are most probably the mixtures of 2D materials and 3D materials rather than a stoichiometric pure phase as shown here.

Figure S1a (Supporting Information) shows X-ray diffraction (XRD) patterns of the different films. The reference FASnI₃ film shows five dominant diffraction peaks at angles of 14.0°, 24.4°, 28.2°, 31.6°, 40.37° assigned to the crystallographic planes (100), (120)/(102), (200), (122), (222), respectively. This diffraction pattern is in agreement with previous reports and is consistent with the orthorhombic (Ainn2) crystal structure of FASnI₃, the presence of all the above peaks indicating that the reference film is composed of grains with random orientations. The 2D/3D perovskite films all exhibit the (100) and (200) peaks at angles of 14.0° and 28.2°, as well as a weaker peak at 42.9° assigned to the (300) plane, indicating the same orthorhombic 3D crystal structure as the reference film (see Figure 1a). However, the suppression of the 120/102, 122 and 222 peaks together with the enhanced h00 peak intensities suggests preferential crystallization with h00 planes parallel to the film surface. This observation is further confirmed by the grazing incidence X-ray scattering data discussed below. The 100 peak
of the FASnI₃ film with 2D/3D perovskite (0.08 m) is about 40 times more intense than for the reference film (Figure S1b, Supporting Information), with a decreased full-width at half-maximum (FWHM). These data indicate significantly improved crystallinity and more perfect packing of the (100) and (200) planes upon incorporation of PEAI into the FASnI₃ film.

In addition, several very weak peaks (magnified 100 times in Figure S1a in the Supporting Information) appear at lower 2θ values (<12°). These new peaks do not belong to either SnI₂ or SnF₂ (see Figure S1c in the Supporting Information). Instead, they may indicate formation of a layered tin perovskite (for the probable structure, see Figure 1b). The low diffraction intensity indicates a limited proportion of 2D tin perovskite in the 3D matrix of FASnI₃. Figure S1d (Supporting Information) shows the XRD pattern of the pure 2D material (PEA₂SnI₄), which shows strongly preferential crystallization with (h00) planes parallel to the film surface. The a-axis periodicity of ~32 Å is in agreement with the monoclinic structure (space group C2/m) reported by Papavassiliou et al.[28] However, the first peak in the XRD pattern of the 2D/3D sample (0.08 m) at 2θ = 3.8° indicates an a-axis of ~23 Å. In the reported PEA₂SnI₄ structure, a double layer of PEA molecules occupies approximately 10.0 Å in the a-direction, whereas a single layer of SnI₆ octahedra in both PEA₂SnI₄ and FASnI₃ occupies

Figure 1. Crystal structure and morphology. Schematic crystal structure of a) 3D reference FASnI₃, b) 2D/3D mixture (2D 0.08 m), with the unit cells of each component outlined in red, and c) 2D PEA₂SnI₄. Respective GIWAXS images of samples annealed at 65 °C recorded at an incident angle of 0.25°: d) 3D reference, e) 2D/3D mixture, and f) 2D film. g–j) SEM images of FASnI₃ films with different 2D Sn perovskite concentrations (0, 0.08; 0.012, 0.16 m).
firming that the crystal structure of the FASnI₃ perovskite in orthorhombic structure in agreement with the XRD data, con-
to the substrate. All the Bragg spots can be indexed using an
phology with preferential orientation of the grains with respect
around the same rings, indicating a strongly textured film mor-
qz
contrast, the 2D/3D film (0.08 C) exhibits Debye–Scherrer-like rings whose positions
were observed. This implies that the alignment of the SnI₆ (Figure S3, Supporting
information); no significant changes
for the same set of samples without any thermal annealing
2D/3D mixture and pure 2D perovskite films (annealed at 65 °C) recorded using an incident angle of 0.25°. The refer-
ce 3D film exhibits Debye–Scherrer-like rings whose positions
has compact morphology with very few pinholes. The FASnI₃
grains range from 0.5 to 2 μm and pack together irregularly
(28) We speculate that the organic PEA⁺
cations are oriented perpendicularly to the substrate, and
the van der Waals interactions of the benzene ring between
the interdigitate PEA⁺ cations may facilitate self-assembly of
the inorganic SnI₆ layers parallel to the substrate, inducing strong
orientation and crystallization of the 2D PEA₂SnI₄.
Figure 1g–j shows scanning electron microscopy (SEM)
images of the different perovskite films. The reference film
compact morphology with very few pinholes. The FASnI₃
films (annealed at 65 °C) recorded using an incident angle of 0.25° (low X-ray penetra-
dent angle of 2° and shown in Figure S2a–c in the Supporting
information). This is because the excess SnF₂ forms
interdigitate PEA⁺ layers which the tin vacancies are the dominant defects due to their
higher annealing temperatures, most probably due to the for-
mation of tin vacancies.
We further assessed the effects of adding a small amount of
2D perovskite and of thermal annealing on the structure and
orientation of the FASnI₃ crystals with respect to the substrate
using grazing incidence wide-angle X-ray scattering (GIWAXS).
Figure 1d–f shows the GIWAXS patterns of the pure 3D,
2D/3D mixture and pure 2D perovskite films (annealed at 65 °C) recorded using an incident angle of 0.25°. The refer-
ence 3D film exhibits Debye–Scherrer-like rings whose positions
are in agreement with the two lowest angle peaks in the XRD
pattern. The rings actually consist of many isotropically distrib-
uted spots, indicating significant randomness in the orienta-
tions of the grains within the polycrystalline FASnI₃ film. In
contrast, the 2D/3D film (0.08 C) exhibits Bragg spots located
around the same rings, indicating a strongly textured film mor-
phology with preferential orientation of the grains with respect
to the substrate. All the Bragg spots can be indexed using an
orthorhombic structure in agreement with the XRD data, con-
firming that the crystal structure of the FASnI₃ perovskite in
the 2D/3D mixed film is the same as that of the reference 3D
material. The location of the 100 and 200 Bragg spots along the
q₃ direction indicates that the grains orient preferentially with
(h00) planes parallel to the substrate, i.e., the a-axis is oriented
perpendicular to the substrate. The structure and orientation
of the FASnI₃ grains is homogeneous throughout the entire
film thickness, as GIWAXS patterns recorded using an inci-
dent angle of 2° and shown in Figure S2a–c in the Supporting
Information (full X-ray penetration of the film) are similar to
those recorded at an incident angle of 0.25° (low X-ray penetra-
dent depth). Note that two weak diffraction peaks originating
from the 2D material become visible only when full penetration
of the film by the X-rays is achieved (Figure S2b, Supporting
Information), suggesting that the 2D material is mostly located
in the proximity of the substrate. The positions of these peaks
are in agreement with the two lowest angle peaks in the XRD
data. In order to understand whether the thermal treatment at
65 °C affects the structure, GIWAXS images were also recorded
for the same set of samples without any thermal annealing
(Figure S3, Supporting Information); no significant changes
were observed. This implies that the alignment of the SnI₆
octahedra parallel to the substrate is thermodynamically stable.
This is an important result as low-temperature processing is
fundamental to reduce trap states in the FASnI₃ films, es-
specially if one considers the low formation energy of tin vacancies
and Sn⁺⁴.
The Pb-based 2D perovskite BA₂MA₂PbI₄½, which contains
another large organic cation n-butylammonium, forms ran-
domly oriented grains at room temperature and hot casting
of the film is necessary to obtain high crystallinity and grains
oriented with the layer stacking direction parallel to the film
surface.[25] The host casting method is unfavorable for tin-
based HPSCs because the high temperature may induce a high
density of tin vacancies in the perovskite film. Therefore, our
finding is very important as it demonstrates that a very small
amount of 2D perovskite inserted into the 3D material is able to
induce a highly uniform orientation of the 3D FASnI₃ grains at
room temperature.
In summary, the 2D tin perovskite functions as a seed layer
to induce large-scale crystallization and orientation of the 3D
FASnI₃ grains (see Figure 1b). The strong tendency of the
2D perovskite to form highly ordered, aligned structures is
confirmed by GIWAXS patterns of the pure PEA₂SnI₄ films
(Figure 1f; Figure S3c,f in the Supporting Information). The
2D structure could be indexed according to the reported mono-
clinic unit cell with an a-axis of 32 Å, highly oriented perpen-
dicular to the substrate.[28] We speculate that the organic PEA⁺
cations are oriented perpendicularly to the substrate, and
the van der Waals interactions of the benzene ring between
the interdigitate PEA⁺ cations may facilitate self-assembly of
the inorganic SnI₆ layers parallel to the substrate, inducing strong
orientation and crystallization of the 2D PEA₂SnI₄.
We further investigated the effect of thermal annealing on
2D perovskite increases up to 0.16 μm, many pinholes
appear in the FASnI₃ film, making the morphology far from
ideal for the fabrication of solar cells.
To test the effects of the morphological and crystallographic
changes in our FASnI₃ films on solar cell performance, we
implemented them in devices using structures of the type ITO/
poly(3,4-ethylendioxythiophene):polystyrene sulfonate (PEDOT:
PSS)/FASnI₃/C₆₀ + 2,9-dimethyl-4,7-diphenyl-1,10-phenan-
throline (BCP)/Al as depicted in Figure 2.[16] We chose C₆₀ as it pro-
duces not only a more uniform and dense electron transport layer
but also avoids the need for solvents.
For the fabrication of the reference cell based on 3D FASnI₃,
we used SnF₂ as a reducing agent to reduce the background
carrier density. The reference device has an optimum PCE
when the concentration of SnF₂ is 0.1 m and beyond this con-
centration the device performance deteriorates (Figure S4, Sup-
porting Information). This is because the excess SnF₂ forms
aggregates in the FASnI₃ film as indicated by previous studies.
We further investigated the effect of thermal annealing on
the device performance. Optimum performance was obtained
when the active layer was annealed at 65 °C (Figure S5, Sup-
porting Information). The performance dropped significantly at
higher annealing temperatures, most probably due to the for-
mation of tin vacancies. This again highlights the importance
of depositing high-quality FASnI₃ films at low temperature for
efficient tin-based HPSCs.
Figure 2a shows the current density ($J$)–voltage ($V$) characteristics under one sun illumination of the best performing reference cell, displaying a $V_{OC}$ of 0.458, a $J_{SC}$ of 22.5 mA cm$^{-2}$, fill factor (FF) of 0.58 and PCE of 6.0%. We list all the device parameters in Table 1. Figure 2c shows the distribution of PCE for the reference cells; the broad variation indicates poor reproducibility over the 20 fabricated devices.

We used the same experimental conditions to fabricate devices with 2D/3D films where PEAI was added to the active layer with different concentrations (Figure S6 in the Supporting Information shows the corresponding $J$–$V$ curves). We obtained the best performing devices with a 0.08 m concentration of 2D perovskite in the FASnI$_3$ film, and we observed a significant drop in performance for higher concentrations of 2D perovskite. This is because the pin holes in the perovskite active layer (see Figure 1j) give rise to shunt paths and direct contact between the cathode and anode, with consequent high leakage current (see Figure S7 in the Supporting Information).

Figure 2a shows the $J$–$V$ characteristics of the best performing device with the 2D/3D film and a comparison with the best reference cell. The 2D/3D device shows a $V_{OC}$ of 0.525 V, a $J_{SC}$ of 24.1 mA cm$^{-2}$ and an FF of 0.71 resulting in a PCE of 9.0%. It is important to note that this is the highest FF and PCE reported so far for all-tin-based perovskite solar cells. Moreover, the $J$–$V$ curves of these solar cells are identical for forward and reverse scans and different sweeping rates (negligible $J$V hysteresis), as shown in Figure 2b. We also point out that this device shows no obvious light-soaking effect, which is confirmed by the fast saturation of the steady state photoluminescence (PL) upon photoexcitation with a 400 nm laser (Figure S8, Supporting Information). The absence of hysteresis and light-soaking effects in these devices is very important, as it represents a sign of their reliability. These phenomena often affect Pb-based HPSCs and render the device performance unreliable.[5,35,36] To further confirm our observations, we independently tested the steady state PCE of the device using 2D/3D mixture (see Figure S9 in the Supporting Information). The 2D/3D-based device from a different batch with a PCE of 8.8% (from $J$–$V$ measurement) has a very similar steady state PCE of 8.5%, confirming the reliable device performance. The PCE statistics (Figure 2d) of more than 20 devices demonstrates the small variation and good reproducibility of our 2D/3D devices compared to the reference devices.

The device containing the 2D/3D film shows substantially improved performance parameters with respect to the 3D
reference: 15% higher $V_{OC}$, 7% higher $J_{SC}$, 20% higher FF and 50% higher PCE. The integrated $J_{SC}$ values (23.8 mA cm$^{-2}$ for 2D/3D-based device and 22.2 mA cm$^{-2}$ for 3D-based device) from the external quantum efficiency of incident photons to electrons (EQE) measurement confirm the value of the photocurrent density measured using the $J$–$V$ characteristics (Figure S10, Supporting Information).

The 2D/3D film (0.08 m) has the same absorption onset as the 3D film (see Figure S11a in the Supporting Information), but it has higher optical constants (extinction coefficient and refractive index) than the 3D film due to its superior crystallinity (Figure S11b, Supporting Information). Optical simulations performed using transfer matrix formalism provide photocurrent generation profiles for both devices, showing similar theoretical photocurrent densities and excluding optical absorption as the dominant factor for the improvement in the experimental $J_{SC}$ of the device with the 2D/3D film (Figure S11c, Supporting Information).

In order to gain deeper insight into the 50% improvement in device performance with the 2D/3D film, we performed steady-state and time-resolved PL measurements on the different FASnI$_3$ films. In Figure 3a, we observe that all the FASnI$_3$ films have emission peaks around 895 nm. The reference sample displays the lowest emission intensity, implying higher nonradiative trap-assisted recombination losses of charge carriers. Due to the capture of free carriers by the defect sites, the photogenerated carriers decay rather fast and the emission lifetime is as short as 4.1 ns. A consequence of this short lifetime is that the charge carriers can only diffuse a short distance and have a high probability of recombination with the opposite charge carriers before they reach the respective electrodes. Therefore, the inefficient charge collection efficiency leads to lower $J_{SC}$ and FF in the reference device. The reference FASnI$_3$ films are affected by large fluctuations in the number of defects due to the randomly packed grains or sensitivity to the atmosphere in the N$_2$-filled glove box. As a result, the reference cell shows a broad distribution of PCEs.

The 2D/3D film (0.08 m) has significantly improved emission intensity and lifetime (up to 9.47 ns), indicating much lower trap density than the pure 3D film. These results confirm that the extended ordering of the crystal planes and the reduced number of grain boundaries help to reduce the trap density in the perovskite film. As mentioned earlier, the highly ordered and oriented crystal planes parallel to the substrate may form fast transport pathways for the charge carriers in the device. In this case, the long-lived charge carriers can be transported efficiently to the respective electrodes before recombination occurs, which leads to the improved FF and $J_{SC}$ in the device.

Because of the negligible hysteresis and light soaking, we further performed the $J$–$V$ measurements under various light intensities with an interval of 5–10 s between the $J$–$V$ sweeps. Figure 3c shows that the device containing the 2D/3D film exhibits a lower slope of $V_{OC}$ versus semilogarithmic light intensity, further confirming that trap-assisted recombination losses are suppressed compared to the reference device. Previous studies indicate that the severe trap-assisted recombination loss of charge carriers is one of the main reasons for the loss in $V_{OC}$ of the HPSCs.$^{[5,28,29]}$ Therefore, the device based on the 2D/3D tin perovskite exhibits higher $V_{OC}$ than the reference device.
Figure 4 shows the thermal voltage versus temperature gradient for the 3D and 2D/3D perovskite films, which demonstrate a positive Seebeck coefficient (p-type) of 504 and 796 µV K⁻¹ confirming that holes are the dominant carriers. The Seebeck coefficient of 2D/3D sample is a signature of lower charge carrier density compared to the pure 3D sample. To further probe how the 2D perovskite influences the p-doping level in FASnI₃ films, we carried out electrical conductivity measurements. Figure 4b shows that the reference film has the highest conductivity (1.72 × 10⁻² S cm⁻¹) of all the samples. This is a further indication of self-doping by the large density of background holes generated by tin vacancies and oxidized species (Sn⁴⁺) and highlights the limitation of SnF₂ as a reducing agent in suppressing these defects. As discussed earlier, the high p-doping level leads to high leakage current and device shorts. The 2D/3D perovskite films have much lower electrical conductivity, indicating de-doping of the FASnI₃ film and reduction of the background charge carrier density. We believe that this is related to the increased crystallinity and smaller number of grain boundaries in the 2D/3D perovskite film, which lowers the possibility of forming tin vacancies and Sn⁴⁺. The 2D/3D perovskite film (0.08 µ) exhibits a hole conductivity of 2.1 × 10⁻⁴ S cm⁻¹, which is more than two orders of magnitude lower than the reference sample.

Figure 4c shows the variation of the background charge carrier density in the devices containing 3D and 2D/3D perovskite layers obtained from capacitance (C)-voltage (V) measurements under dark conditions. Using Mott–Schottky analysis the background charge carrier density can be obtained from the slope of C⁻² versus the applied voltage V in the depletion region. The hole carrier density (2.76 × 10¹⁶ cm⁻³) in solar cells with layered tin perovskite is reduced by more than 20 times compared to the reference cell (5.83 × 10¹⁷ cm⁻³), in agreement with the conductivity measurements.

Figure 4d shows the dark J-V curves of the devices containing 3D and 2D/3D tin perovskite layers, from which we extracted the shunt resistances (Rsh). The reference solar cell has a small Rsh (9.7 kΩ cm²) and suffers significantly from a high leakage current due to the high p-doping level. In contrast, the device with the 2D/3D perovskite layer has a much higher shunt resistance (175 kΩ cm²) and very good diode behavior, which originates from the low background carrier density. In addition, the improved crystallinity and the highly oriented packing of the crystal planes in the out-of-plane direction favor charge transport and collection in the device. This provides more evidence that the high device performance is correlated with the crystallographic and morphological characteristics of the 2D/3D film. In addition, the highly crystalline and oriented structure of the 2D/3D film is also the reason for the good reproducibility of the device performance.

Beside the efficiency, the stability is equally important for practical applications of perovskite solar cells. We firstly tested the device stability under one sun illumination in an N₂-filled glove box (Figure S12, Supporting Information). During
2 h exposure to the solar light, both the reference and 2D/3D devices show relatively constant $V_{OC}$. However, the reference device shows considerable degradation of both $J_{SC}$ and FF with time. In contrast, the 2D/3D perovskite device has relatively stable $J_{SC}$ and FF. As a consequence, the efficiency of the reference cell is reduced to 75% of its initial efficiency after 2 h whereas the 2D/3D device does not show any obvious degradation. The improved crystallinity of the perovskite film may enable higher resistance to light illumination and reduce the possibility for formation of the defects in the 2D/3D-based device, leading to enhanced stability.

Furthermore, we tested the stability of the devices ($C_{40}$ 70 nm) without any encapsulation in ambient condition with humidity about 20% (temperature about 20°C) as shown in Figure S1 in the Supporting Information. Between the intervals of the test, the devices were stored in dark condition. The device based on 2D/3D sample shows much higher stability compared to the device using pure 3D sample. After 76 h exposure to ambient air the device using pure 3D perovskite completely failed, whereas the device using 2D/3D mixture retained 59% of the original PCE. In order to understand the discrepancy in the stability of the devices, we further performed XRD measurements for the perovskite samples stored in nitrogen filled glove box ($H_2O < 0.1$ ppm, $O_2 < 0.1$ ppm) and in air (humidity about 70%, temperature 22 °C). Both the 3D and 2D/3D samples do not show obvious decomposition after 6 h in inert atmosphere, whereas the 3D sample undergoes faster chemical degradation than the 2D/3D sample when stored in ambient conditions (Figure S14, Supporting Information). The improved ambient stability of the 2D/3D-based device is probably due to higher resistance to oxygen and moisture as a result of the improved crystallinity and the higher hydrophobicity of the perovskite film.

In conclusion, we have demonstrated all-tin-based HPSCs with efficiencies of up to 9%. The addition of a trace amount of 2D tin perovskite initiates the homogenous growth of highly crystalline and oriented FASnI$_3$ grains at low temperature. The high degree of order has three positive consequences: (i) a reduced number of grain boundaries; (ii) the suppression of tin vacancies or Sn$^{4+}$ and a consequent reduction in background carrier density by more than one order of magnitude compared to pristine FASnI$_3$ films; (iii) a longer lifetime of the charge carriers. Therefore, devices based on a 2D/3D tin perovskite layer benefit from low trap-assisted recombination, low shunt losses of the charge carriers and efficient charge collection. Moreover, the improved crystallinity of the active layer results in more stable HPSCs.

In stark contrast, reference films using only SnF$_2$ as a reducing agent have a high degree of structural disorder, a high density of sharp grain boundaries and randomly oriented 3D grains. This facilitates the formation of a high density of tin vacancies and causes a high p-doping level. As a consequence, the best reference cell has a PCE of 6%, and suffers from severe trap-assisted recombination and high leakage current.

Finally, by adding trace amount of 2D tin perovskite in FASnI$_3$ we overcome the bottleneck that has long been faced by tin-based HPSCs and demonstrate a way forward to further improve their performance.

### Experimental Section

**Materials**: PEDOT:PSS water dispersion (Clevios VP Al 4083) was acquired from Heraeus. PEAI (>98%) and FAI (>98%) were purchased from TCI EUROPE N.V. SnI$_3$ (99.99%), SnF$_2$ (>99%), C$_{60}$ (>99.9%), BCP (99.9%), DMF (99.8%), and DMSO (99.8%) were purchased from Sigma Aldrich. All the materials were used as received without further purification.

**SEM Measurement**: SEM images were recorded in air on a FEI NovaNano SEM 650 with an acceleration voltage of 10 kV.

**XRD**: XRD patterns (Figure S1, Supporting Information) of the perovskite films were collected using a Vantec500 detector (1024 × 1024 pixel array with pixel size 136 × 136 μm) located 93 mm away from the sample. The perovskite films were placed in reflection geometry at certain incident angles $\alpha_i$ with respect to the direct beam using a Huber goniometer. GIWAXS patterns were acquired using incident angles from 0.25° to 2° in order to probe the thin film structure at different X-ray penetration depths. For an ideally flat surface, the value of the X-ray penetration depth (i.e., the depth into the material measured along the surface normal where the intensity of X-rays falls to 1/e of its value at the surface) depends on the X-ray energy (wavelength $\lambda$), the critical angle of total reflection, $\alpha_t$, and the incident angle, $\alpha_i$, and can be estimated using the relation: $\Lambda = \frac{\lambda}{2} \sqrt{\frac{(\alpha_t - \alpha_i)^2}{4} + 4\beta^2 - (\alpha_t - \alpha_i)^2}$, where $\beta$ is the imaginary part of the complex refractive index of the compound. The estimated X-ray penetration depth is 10 and 40 nm at incident angle of 0.25°, and 350 and 600 nm at incident angle of 2° for the pure 3D and 2D perovskites, respectively. For the calculation, the densities of 3.56 and 2.35 g cm$^{-3}$ were used for the pure 3D and 2D perovskites, respectively. The direct beam center position on the detector and the sample-to-detector distance were calibrated using the diffraction rings from standard silver behenate and Al$_2$O$_3$ powders. All the necessary corrections for the GIWAXS geometry were applied to the raw patterns using the GIXGUI Matlab toolbox. The reshaped GIWAXS patterns, taking into account the inaccessible part in reciprocal space (wedge-shaped corrected patterns), are presented as a function of the vertical and parallel scattering vectors $q_x$ and $q_y$. The scattering vector coordinates for the GIWAXS geometry are given by

$$q_x = \frac{2\pi}{\Lambda}(\cos(2\theta_h)\cos(\alpha_i) - \cos(\alpha_t))$$

$$q_y = \frac{2\pi}{\Lambda}(\sin(2\theta_h)\cos(\alpha_t))$$

$$q_z = \frac{2\pi}{\Lambda}(\sin(\alpha_i) + \sin(\alpha_t))$$

where $2\theta_h$ is the scattering angle in the horizontal direction and $\alpha_t$ is the exit angle in the vertical direction. The parallel component of the scattering vector is thus calculated as $q_z = \sqrt{q_x^2 + q_y^2}$.

**Steady-State and Time-Resolved PL Measurement**: Steady-state and time-resolved PL measurements were conducted by exciting the samples with the second harmonic (400 nm) of a mode-locked Ti:Sapphire femtosecond laser (Mira 900, Coherent). The repetition rate of the laser is 76 MHz; a pulse picker was inserted in the optical path to decrease the repetition rate of the laser pulses. The laser power...
(0.7 μJ cm⁻²) was adjusted using neutral density filters. The excitation beam was focused with a 150 mm focal length lens, and the emission was collected and coupled into a spectrometer with a 50 lines mm⁻¹ grating. The steady-state PL was recorded with an Image EM CCD camera from Hamamatsu (Hamamatsu, Japan). Time-resolved PL was measured with a Hamamatsu streak camera working in single sweep mode.

**Electrical Conductivity, Seebeck Coefficient, and C–V Measurement:**
For the electrical conductivity measurements, parallel line-shaped Au electrodes with a width (w) of 13 mm and a channel length (L) of 200 μm were deposited on clean glass substrates as bottom contacts. Different perovskite films were spin-coated on the patterned glass following the same recipe used for photovoltaic device fabrication. Voltage-sourced two-point conductivity measurements were conducted using a probe station in a N₂ glovebox. The electrical conductivity (σ) was calculated according to the formula \( \sigma = J/V \times L/(w \times d) \), where \( d \) is the thickness of the perovskite films. The Seebeck coefficient was measured with a home-built setup in a vacuum probe station. Temperature steps were imposed across the devices to measure the thermal voltages of perovskite thin films at different temperatures, which were detected by a standard constantan wire (127 μm from Omega, Seebeck coefficient of ~39 μV K⁻¹).

The capacitance–voltage (C–V) measurements were conducted under dark condition at a frequency of 10 kHz with an ac drive voltage of 20 mV and DC bias in the range of −0.6 to 0.6 V on a Solartron 1260 impedance gain-phase analyzer.

**UV–vis Measurement:**
UV–vis spectra of the perovskite films were recorded on Shimatsu UV-Vis-NIR spectrophotometer (UV 3600). The perovskite samples were encapsulated with quartz using UV light curing adhesive.

**Device Fabrication:**
ITO glasses were cleaned using an ultra-sonication bath in soap water and rinsed sequentially with de-ionized water, acetone and isopropanol alcohol. A PEDOT:PSS layer was then spin-coated onto the ITO substrates at 4000 rpm for 60 s and dried at 140 °C for 20 min. The 2D/3D tin perovskite films was then annealed at 65 °C under vacuum of 10⁻⁶ mbar. The J–V curves of the perovskite solar cells were measured at 295 K using a Keithley 2400 source meter under simulated AM 1.5 G solar illumination using a Steuernagel Solar constant 1200 metal halide lamp in a nitrogen-filled glove box. The light intensity was calibrated to be 100 mW cm⁻² by using a Si reference cell and correcting the spectral mismatch. A shadow mask (0.04 cm²) was used to exclude lateral contributions beyond the device area.

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

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**Conflict of Interest**
The authors declare no conflict of interest.

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background charge carrier density, crystallinity, grain boundaries, tin perovskite solar cells, tin vacancies