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Hybrid sequential processing of mixed Sn–Pb
narrow-bandgap perovskite solar cellsYasemin Saygili,^a Federico Ventosinos,^b Mohammad Dehnavi,^c
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Hybrid vapor-solution sequential deposition of perovskites is a well-established method that enables large-area processing of perovskite films and solar cells. In this study, for the first time, we applied the hybrid sequential deposition method to the fabrication of narrow-bandgap mixed Sn–Pb perovskite films. We obtained compact, large-grained perovskite films with power conversion efficiency values exceeding 10% under 1 sun illumination with hole-transport-material-free devices. The applied method eliminates the oxidative degradation risks of solvents during perovskite formation and provides an easy way to develop additive and passivation strategies to improve photovoltaic properties.

Metal halide perovskites have gained considerable attention among the emerging photovoltaic technologies over the last decade. The advancements in perovskite film morphology, composition and device optimization have led to the development of single-junction and tandem perovskite solar cells (PSCs) with remarkable efficiency and promising stability.^{1–4} The general ABX₃ perovskite structure allows tuning of the photophysical and chemical properties by employing different compositions of monovalent cations, divalent metals, and halides.⁴ Record photovoltaic performance has been mostly obtained when Pb²⁺ occupies the B site; however, partial or full substitution of Sn²⁺ has several advantages. With partial Sn²⁺ substitution, the bandgap (E_g) can be lowered in the energy region of the radiative efficiency limit for single-junction solar cells (approximately 1.34 eV).⁵ Sn²⁺-substituted narrow-bandgap (1.1–1.3 eV) absorbers can also be employed as the rear sub-cells in all-perovskite tandem solar cells.^{6,7} In addition, reducing the toxic Pb²⁺ content or full replacement

with less toxic Sn²⁺ is reported to reduce the possible health risks.^{8,9} However, Sn²⁺ or mixed Sn²⁺/Pb²⁺ perovskites exhibit poorer optoelectronic properties compared to the Pb²⁺ counterparts.^{8,10} Sn²⁺ oxidation to Sn⁴⁺ appears to be the main challenge in terms of device performance and stability.^{8,11,12}

Metal halide perovskite films can be deposited using different methods. Most of these techniques rely on solution processing, either one-step anti-solvent assisted deposition^{6,13,14} or two-step spin-coating.^{15–18} However, the use of polar aprotic solvents (e.g., dimethylformamide, DMF) in combination with heavy metals and the use of anti-solvents (e.g., chlorobenzene) raise ecotoxicity and health concerns.¹⁹ Besides, solution-processing might be a practical barrier for sustainable, large-area and industrial-scale PSC production.²⁰ In addition to the aforementioned drawbacks, the interaction of dimethyl sulfoxide (DMSO) with tin halides remains controversial in the literature. In some studies, it was observed that DMSO played a crucial role in slowing down the crystallization and thereby enhancing the crystal quality, while other reports highlighted its detrimental effect on the oxidation of Sn²⁺ to Sn⁴⁺.^{11,12,21} Alternative thin-film deposition processes to obtain Sn²⁺ or Sn²⁺/Pb²⁺ narrow bandgap perovskites are vacuum deposition,^{22–27} vapor-assisted solution processing^{16,28} and hybrid methods.^{29,30}

Herein, we applied the well-known hybrid sequential deposition method^{31–33} for the first time to fabricate mixed FA_yMA_(1–y)Pb_xSn_(1–x)I₃ perovskite devices. This method is widely studied for mid- and wide-bandgap perovskites,^{34,35} enabling high efficiencies without the use of DMF/DMSO, and offering good scalability to large areas. Although Mitzi and co-workers¹⁵ studied this method for Sn-based perovskites in 1998, so far, to the best of our knowledge, no narrow bandgap PSC has been reported using this fabrication method. We first deposited the inorganic Pb_xSn_(1–x)I₂ films through simultaneous co-evaporation of PbI₂, SnI₂ and SnF₂ in a vacuum chamber. The sublimation rates were monitored through individual microbalance crystal sensors. Depending on the desired nominal Sn/Pb composition, the precursor sublimation rates

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were controlled by manipulating the source temperatures. SnF_2 was employed as a stabilizing additive during evaporation.^{36–39} The concentration of SnF_2 was consistently kept low to prevent phase segregation on the perovskite surface³⁶ (at 4–6% with respect to SnI_2 rate).²⁴ In the second step, perovskite formation and crystallization are induced by spin coating of an organic cation solution, followed by a rapid annealing step. Hole-transport-material (HTM)-free indium tin oxide (ITO) substrates were used not only to avoid complexity in the device architecture but also because ITO/perovskite heterojunctions are already reported to be stable and energetically well aligned, at least in the case of mixed Sn/Pb PSCs.⁴⁰

In the sequential deposition method, the cation solution plays a key role in the resulting perovskite crystal size and film morphology.^{41,42} Therefore, we tested alternative cation solutions employing different solvents, cation concentrations and additives and analyzed the effect through absorbance spectra of the perovskite films. The ultraviolet-visible (UV-vis) absorption spectra for $\text{Pb}_{0.5}\text{Sn}_{0.5}\text{I}_2$ seed film and $\text{FA}_{0.7}\text{MA}_{0.3}\text{Pb}_{0.5}\text{Sn}_{0.5}\text{I}_3$ perovskite film deposited on ITO are given in Fig. 1(a). While SnF_2 was used as a stabilization agent during the evaporation step, the need for another additive in the cation solution was evaluated. Accordingly, we added

metallic Sn powder⁷ to the cation solution and examined its effect on the optical properties of the perovskite films. However, the addition of metallic Sn did not produce any significant change in the absorbance spectra of the prepared perovskite films (Fig. S1).

X-ray diffraction (XRD) signals of the $\text{Pb}_{0.5}\text{Sn}_{0.5}\text{I}_2$ seed layer and perovskite film fabricated on ITO are given in Fig. 1(b). The seed film shows a strong peak at 12.6° , indicating crystalline $(\text{Pb/Sn})\text{I}_2$ phase.³⁰ For the perovskite film, the XRD reflections appearing at 14° , 28° , and 43° are associated with the (110), (220), and (330) planes of the perovskite tetragonal crystal structure, respectively.⁴³ In most cases, the peak at 12.6° disappeared, owing to full conversion to perovskite, but some films still exhibited unconverted $(\text{Pb/Sn})\text{I}_2$ content (Fig. S2(a)). In addition to HTM-free ITO substrates, perovskite conversion was also tested on poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) and poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine] (PTAA). The effect of substrate choice on perovskite formation was assessed qualitatively using XRD measurements. Some perovskite films employing PEDOT:PSS showed an additional diffraction at 25° , which is attributed to the orthorhombic perovskite structure.^{36,38} The rest of the peaks showed an XRD pattern

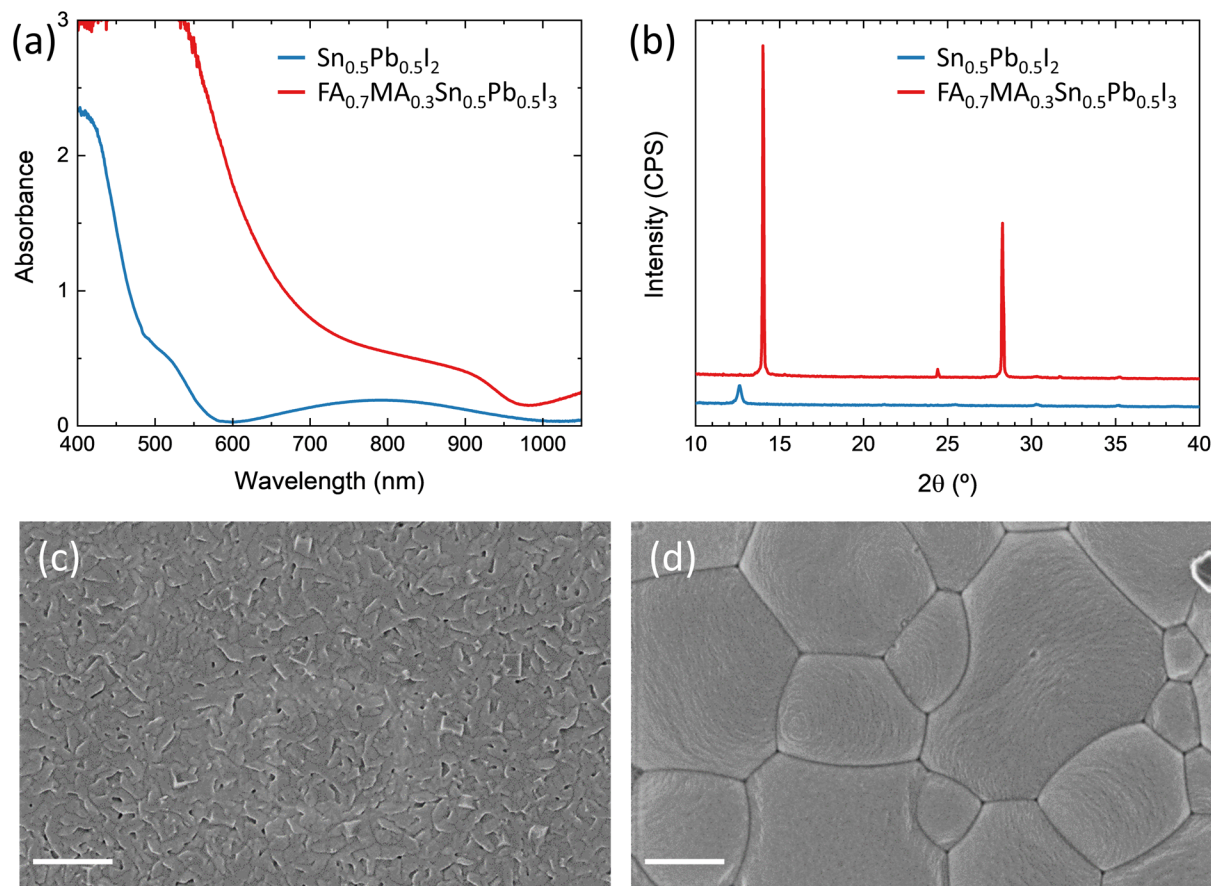


Fig. 1 (a) UV-vis spectra of an evaporated $\text{Pb}_{0.5}\text{Sn}_{0.5}\text{I}_2$ film and fabricated perovskite film. (b) XRD data of the evaporated $\text{Pb}_{0.5}\text{Sn}_{0.5}\text{I}_2$ film and perovskite film. (c) SEM image of the evaporated $\text{Pb}_{0.5}\text{Sn}_{0.5}\text{I}_2$ film. (d) SEM image of the fabricated perovskite film (bar scales 300 nm).



with {110} growth orientation, as in the case of ITO substrates (Fig. S2(b)). The samples employing PTAA exhibited a strong 12.6° diffraction after perovskite conversion, which implies incomplete perovskite formation (Fig. S2(c)). The differences in XRD patterns arising from the choice of substrate can be attributed to the formation of nucleation seeds, wetting behaviour, and diffusion of organic cations into the porous inorganic seed layer during conversion.

Top-view scanning electron microscopy (SEM) images of the inorganic seed layer and perovskite films fabricated on ITO are given in Fig. 1(c) and (d), respectively. The evaporated $\text{Pb}_{0.5}\text{Sn}_{0.5}\text{I}_2$ films exhibit uniform surface coverage with porous

morphology. The porous structure of the inorganic film is expected to facilitate cation insertion through the film during the conversion step.²⁸ The SEM image of the obtained $\text{FA}_{0.7}\text{MA}_{0.3}\text{Pb}_{0.5}\text{Sn}_{0.5}\text{I}_3$ perovskite films on ITO (Fig. 1(d)) shows high crystallinity with uniform, smooth and defect-free morphology. With the hybrid conversion technique, up to $1.8\ \mu\text{m}$ grain size was obtained, with the average grain size of $1.01 \pm 0.47\ \mu\text{m}$.

Minority carrier diffusion lengths (L_d) were measured using the steady-state photocarrier grating (SSPG) technique.^{44,45} Details of the theory behind the technique may be found elsewhere.⁴⁶ While this technique was mainly developed to study

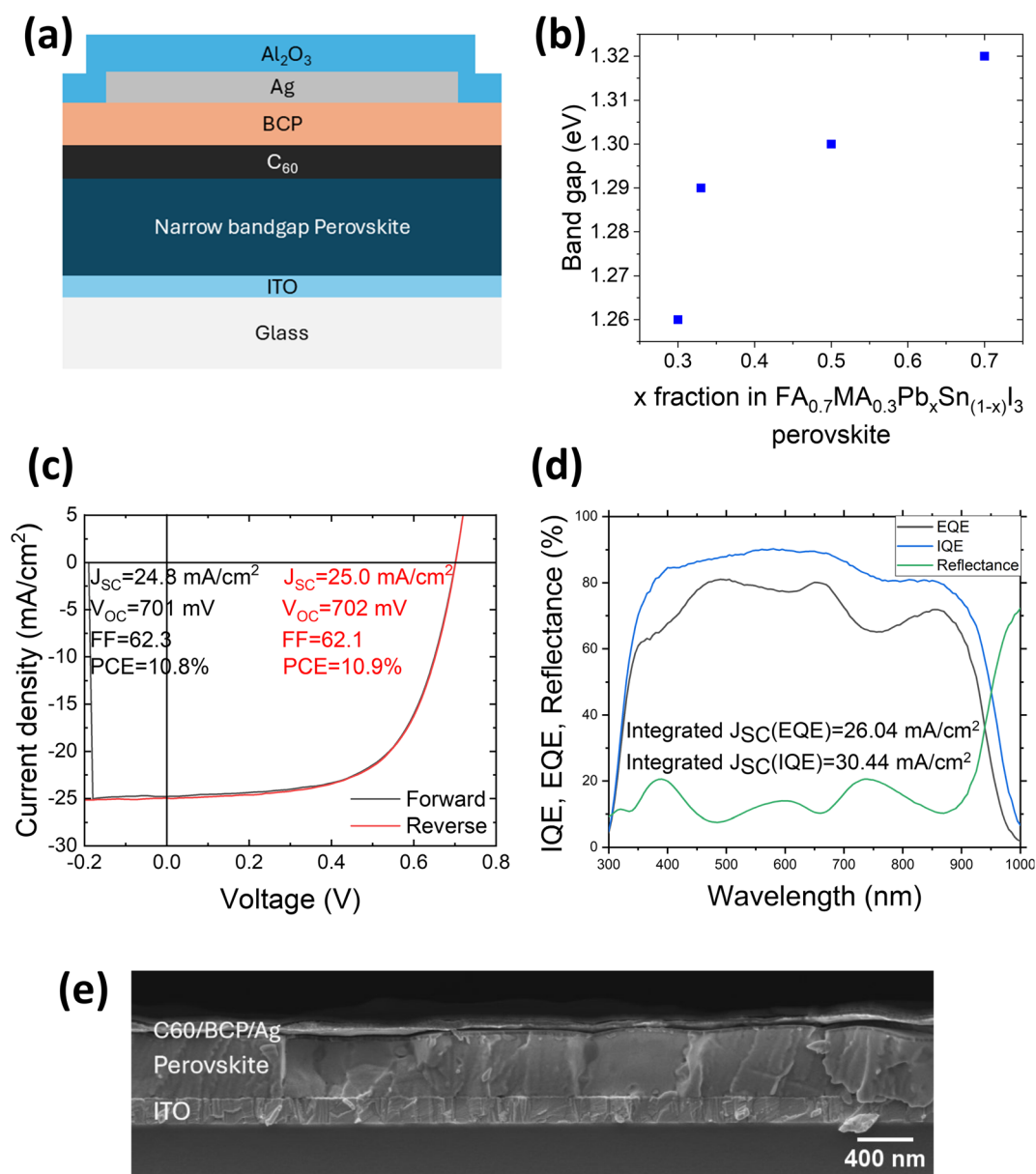


Fig. 2 (a) Scheme of the fabricated devices. (b) Bandgap values derived from the derivative of EQE spectrum for perovskite devices employing different nominal Pb/Sn ratios. Performance metrics of a typical device fabricated through the conversion of evaporated $\text{Pb}_{0.5}\text{Sn}_{0.5}\text{I}_2$ films. (c) J - V curves measured under standard AM 1.5G illumination. (d) EQE, IQE and reflectance spectra. (e) Cross-sectional SEM image of a typical device.



amorphous silicon films, its applicability to perovskite films has already been addressed.^{47–49} As usual with SSPG, the measurements were carried out on samples with coplanar contacts (gold in this case), thus measuring a diffusion length in the lateral plane. Nevertheless, the obtained information is known to be associated with device performance, grain size and recombination mechanisms.⁴⁹ For the $\text{FA}_{0.7}\text{MA}_{0.3}\text{Pb}_{0.5}\text{Sn}_{0.5}\text{I}_3$ film deposited on glass, the ambipolar diffusion lengths (which are dominated by the minority carriers) started around 300 nm for full intensity (giving a generation rate (G) of $G = 1 \times 10^{22} \text{ cm}^{-3} \text{ s}^{-1}$) and increased upon lowering the flux up to 470 nm (for 10% of full flux, see Fig. S3). This dependence of L_{d} on G has been found for other semiconductors like amorphous silicon,⁴⁹ but differs from that reported by Levine *et al.*⁴⁷ for their perovskite films (MAPbI_3 and $\text{MAPbI}_3(\text{Cl})$), where it was found to be constant. Regarding the diffusion length values, we found similar values to the ones reported for MAPbI_3 perovskites obtained by solution processing technique,^{49,50} and higher than the MAPbI_3 films done by co-evaporation in our laboratory, which are around 250 nm for full flux and around 300 nm for 10% of full flux (the SSPG measurement data and the model fitting curves are given in Fig. S4).

The perovskite films formed by the hybrid conversion method were tested in HTM-free p–i–n devices. The devices employed evaporated carbon 60 fullerene (C60) (20 nm)/bathocuproine (BCP) (7 nm) as electron transport layer and Ag metallic contacts, encapsulated with an atomic layer deposition (ALD) of Al_2O_3 . A schematic of the fabricated device is given in Fig. 2(a). The effective band gap values as a function of the nominal Pb and Sn content were estimated from the first derivative of the external quantum efficiency (EQE, Fig. 2(b)).^{51–53} We obtained the lowest bandgap value of 1.26 eV with the conversion of $\text{Pb}_{0.3}\text{Sn}_{0.7}\text{I}_2$ seed films (normalized EQE plots and a typical photoluminescence (PL) spectrum are provided in Fig. S5 and S6, respectively). Bandgap values tend to increase with increasing nominal Pb content; however, within the range of the studied compositions, we did not observe a clear trend in relation to bandgap bowing behavior.⁵⁴ The absence of clear bandgap bowing may be due to the limited composition range and effects related to material defectivity. Higher concentrations of Sn were not studied, as the device performance deteriorated with increasing Sn content. Therefore, the reported bandgap evolution should be interpreted as reflecting a trend with nominal precursor ratios rather than quantitative compositional bandgap mapping. The

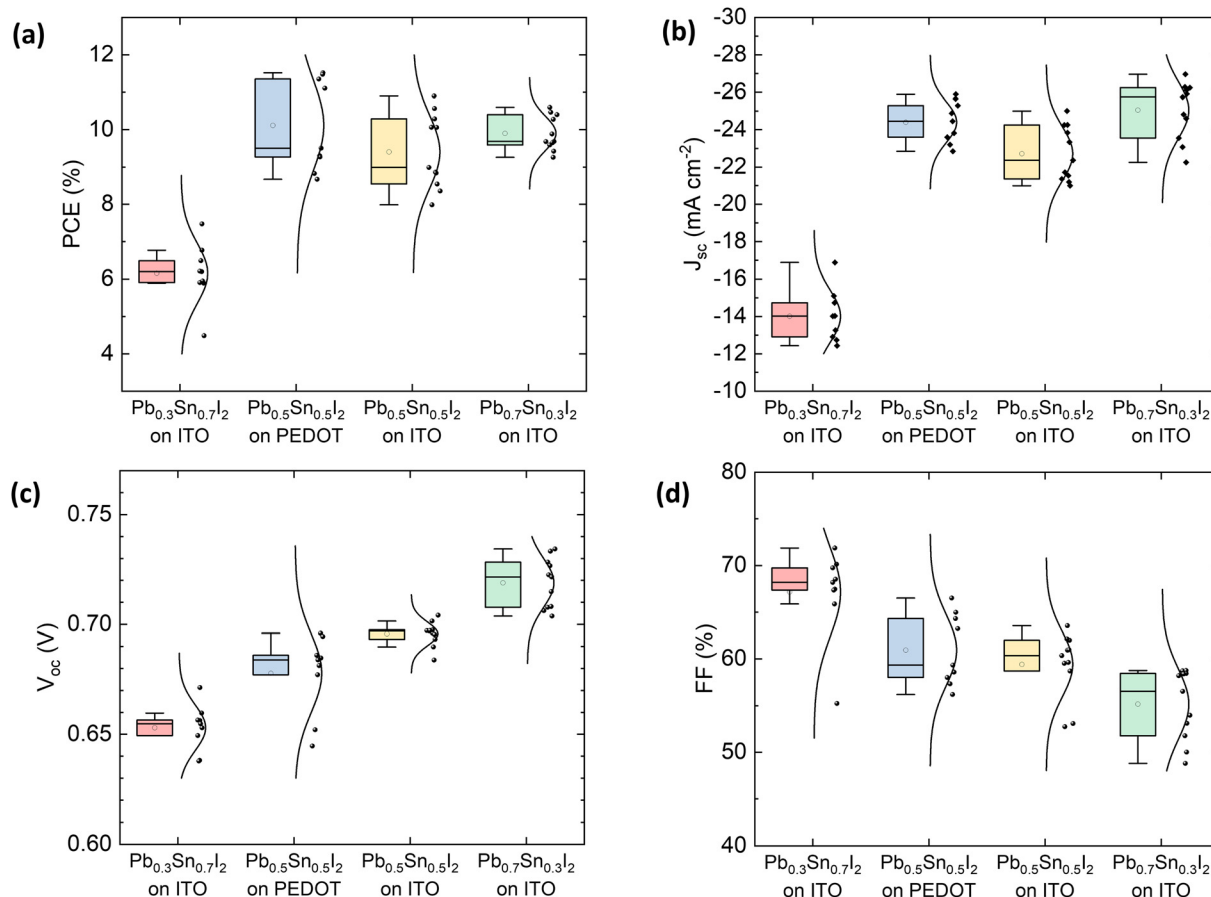


Fig. 3 Statistics of (a) power conversion efficiency, (b) short-circuit current density, (c) open-circuit voltage, and (d) fill factor values of the devices obtained through the conversion of $\text{Pb}_x\text{Sn}_{(1-x)}\text{I}_2$ seed films.



optimum photovoltaic performance was typically recorded with perovskite films with a band gap of 1.3 eV, which were obtained through the conversion of $\text{Pb}_{0.5}\text{Sn}_{0.5}\text{I}_2$ inorganic seed films. For the best device within a typical batch, the power conversion efficiency (PCE) was recorded as 10.9% from the photocurrent density vs. voltage (J - V) curve (reverse scan) under simulated solar illumination (AM 1.5G, 100 mW cm^{-2}), with a short-circuit current density (J_{sc}), open circuit voltage (V_{oc}) and fill factor (FF) of 25.0 mA cm^{-2} , 702 mV and 62.1%, respectively (Fig. 2(c)). The external quantum efficiency (EQE), internal quantum efficiency (IQE), and reflectance (R) spectra of the same device are given in (Fig. 2(d)). The integrated EQE spectrum for the same device remains in accordance with the J_{sc} value obtained from the J - V curves (the mismatch can be related to the difference in equipment light sources). By accounting for the reflectance, the integrated IQE spectrum gives a maximum J_{sc} of 30.44 mA cm^{-2} , which indicates that device performance can be enhanced not only by minimizing reflectance losses but also by improving charge collection within the device. The lower EQE at long wavelengths also indicates insufficient perovskite thickness, which was measured as $429 \pm 22 \text{ nm}$, as shown in the cross-sectional SEM view of a typical device (Fig. 2(e)). Although the devices fabricated on PEDOT:PSS substrates resulted in efficiency values reaching over 11% (Fig. S7), further analyses were carried out on HTM-free devices, considering the stability issues reported for PEDOT:PSS and for simplicity in device architecture.⁴⁰ With PTAA (Fig. S8), the J - V curves exhibited the S-shaped characteristic, independent of the employed HTM thickness. For these samples, we presume that the unconverted (Pb/Sn) I_2 acts as an insulating domain or has unfavorable band alignment, which obstructs the charge collection and, accordingly, the device performance.⁵⁵ With PTAA, the resulting PCE values were lower compared to those reported for one-step solution-processed mixed PSC.¹⁸

Perovskite devices employing different nominal Sn/Pb ratios were fabricated through the conversion of $\text{Pb}_x\text{Sn}_{(1-x)}\text{I}_2$ seed layers. The photovoltaic parameters are summarized by the statistical box charts in Fig. 3. Solar cells with $\text{FA}_{0.7}\text{MA}_{0.3}\text{Pb}_{0.5}\text{Sn}_{0.5}\text{I}_3$ films on PEDOT:PSS have higher PCE values compared to the HTM-free counterparts, which can be attributed to a better energy alignment and/or better film crystallization. Although the EQE onset spectra (Fig. S5) exhibit a red shift with increasing nominal Sn/Pb ratios, the corresponding bandgap reduction is more pronounced at lower Pb fractions. Conversion of $\text{Pb}_{0.3}\text{Sn}_{0.7}\text{I}_2$ film yields a bandgap of approximately 1.26 eV, whereas the conversions with $\text{Pb}_{0.5}\text{Sn}_{0.5}\text{I}_2$ and $\text{Pb}_{0.7}\text{Sn}_{0.3}\text{I}_2$ films result in bandgaps of 1.3 eV and 1.32 eV, respectively. This nonlinear trend suggests that, from a detailed balance perspective, performance differences attributed solely to bandgap variation may be masked by statistical fluctuations.

The theoretical short-circuit current density from the Shockley-Queisser (SQ)⁵⁶ limit for a bandgap of 1.32 eV is 35.44 mA cm^{-2} , while for 1.3 eV, it is slightly higher at 35.82 mA cm^{-2} . In our experimental data, however, the device

with a 1.3 eV bandgap exhibits a marginally lower J_{sc} (mean value of 22.7 mA cm^{-2} , compared to 25.1 mA cm^{-2} for the higher bandgap device). This variation, however, falls within the experimental statistical spread. According to Fig. 3(b), the J_{sc} values show an increasing trend for higher nominal Pb/Sn ratios. As depicted in Fig. 3(c), the open-circuit voltage follows the expected detailed balance trend, with slightly higher values observed for the higher bandgap device (0.72 V to 0.70 V of mean values). Nevertheless, the experimental spread in V_{oc} values is sufficiently large that we cannot conclusively attribute these differences to bandgap and conduction band edge⁵⁴ variations alone. We also illustrated the J - V characteristics of the solar cells employing $\text{FA}_{0.7}\text{MA}_{0.3}\text{Pb}_{0.3}\text{Sn}_{0.7}\text{I}_3$, $\text{FA}_{0.7}\text{MA}_{0.3}\text{Pb}_{0.5}\text{Sn}_{0.5}\text{I}_3$, and $\text{FA}_{0.7}\text{MA}_{0.3}\text{Pb}_{0.7}\text{Sn}_{0.3}\text{I}_3$ perovskites on ITO using SCAPS-1D.⁵⁷ The set values for the parameters

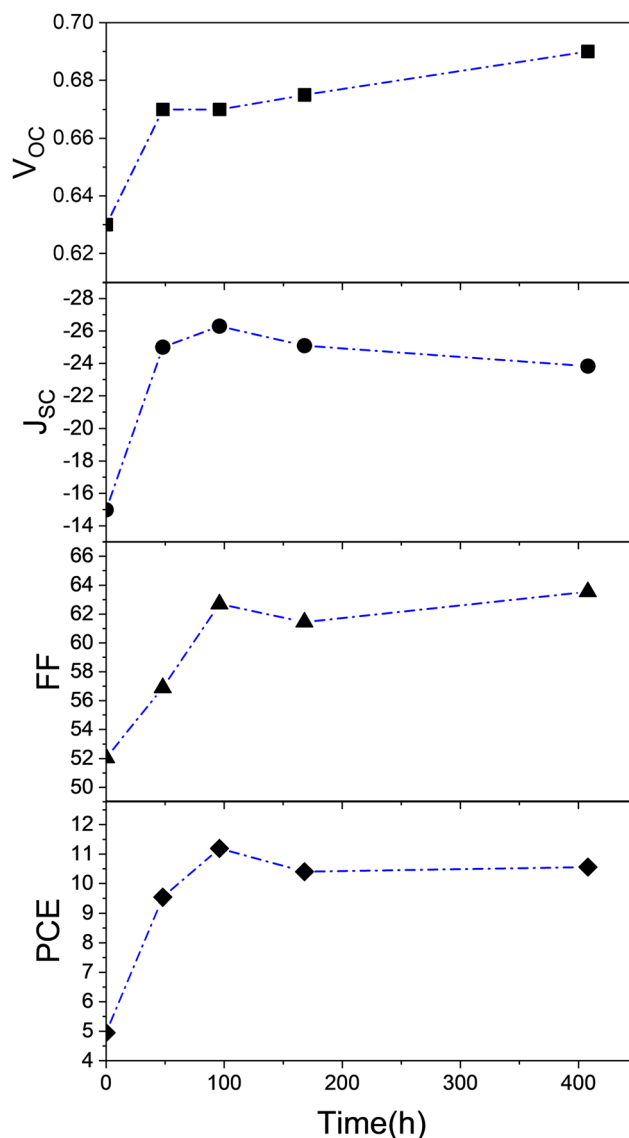


Fig. 4 Change of photovoltaic parameters of an Al_2O_3 encapsulated perovskite solar cell fabricated on ITO as a function of time (samples stored in the dark and under inert atmosphere).



and the device metrics obtained through the simulations are given in Tables S1–S4 and Fig. S9.

The stability of the encapsulated $\text{FA}_{0.7}\text{MA}_{0.3}\text{Pb}_{0.5}\text{Sn}_{0.5}\text{I}_3$ PSCs stored in a dark glovebox atmosphere was monitored through J - V measurements (Fig. 4). The photovoltaic parameters exhibited improvement (most significantly, the current density values) within a couple of days after fabrication and then stayed mostly stable for 500 h. Although the origin is unclear, based on the similar trends reported in literature, this initial enhancement in the PCE value is consistent with reports of aging-induced reorganization^{58,59} and self-healing processes⁶⁰ reported for polycrystalline perovskites.^{58–60} Self-healing in Sn-based solution-processed perovskites is related to the reversible chemical effects, *i.e.*, the reduction of Sn^{4+} back to Sn^{2+} .⁶⁰ Selectivity of coalescence is reported to be favorable when the degree of misorientation at the grain boundaries is low, which conforms with our case (Fig. 1(b)).⁵⁹ We can speculate that spontaneous coalescence and, similarly, additive-induced Ostwald ripening^{61,62} can be used in Pb/Sn mixed perovskites to alleviate the drawbacks of fast crystallization and resulting poor film morphologies.

In conclusion, a hybrid sequential deposition method was effectively used for the first time for fabricating narrow-bandgap mixed Pb/Sn perovskite solar cells. With this method, we obtained PCE values reaching over 10% both with HTM-free and PEDOT:PSS substrates. We expect that with certain additives and surface passivation strategies, the photovoltaic performance can be enhanced further. Avoiding the use of DMF and DMSO during perovskite formation provides a more environmentally friendly approach. Also, eliminating DMSO might help prevent Sn oxidation to $\text{Sn}(\text{iv})$. We expect that our findings can be used as a starting point for the manufacturing of mixed Pb/Sn perovskites, especially for tandem solar cell applications.

Conflicts of interest

The authors declare no conflicts of interest.

Data availability

The data supporting this article have been included as part of the supplementary information (SI). In addition, the simulation files and the related data for this work are accessible at <https://github.com/ODTUGUNAM/Mixed-SnPb-Perovskite-Simulation>.

Supplementary information: Experimental methods, UV-Vis spectra, XRD data, SSPG analysis, EQE spectra, PL spectra, Current density–photovoltage curves, Simulation tables. See DOI: <https://doi.org/10.1039/d5dt02879e>.

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