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Monolithic all-perovskite tandem solar cells with 24.8% efficiency exploiting comproportionation to suppress Sn(ii) oxidation in precursor ink

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**Combining wide-bandgap and narrow-bandgap perovskites to construct monolithic all-perovskite tandem solar cells offers avenues for continued increases in photovoltaic (PV) power conversion efficiencies (PCEs). However, actual efficiencies today are diminished by the subpar performance of narrow-bandgap subcells. Here we report a strategy to reduce Sn vacancies in mixed Pb–Sn narrow-bandgap perovskites that use metallic tin to reduce the Sn4+ (an oxidation product of Sn2+) to Sn2+ via a comproportionation reaction. We increase, thereby, the charge-carrier diffusion length in narrow-bandgap perovskites to 3 μm for the best materials. We obtain a PCE of 21.1% for 1.22-eV narrow-bandgap solar cells. We fabricate monolithic all-**

**perovskite tandem cells with certified PCEs of 24.8% for small-area devices (0.049 cm2) and of 22.1% for large-area devices**

**(1.05 cm2). The tandem cells retain 90% of their performance following 463 h of operation at the maximum power point under full 1-sun illumination.**

wing to long carrier diffusion lengths, low trap densities and high tolerance to defects, lead halide perovskite solar cells (PSCs) have recently seen rapid advances in power

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conversion efficiency (PCE), reaching certified efficiencies of 24.2% (refs. 1–3). Combining Pb-based wide-bandgap perovskites (~1.8 eV) with mixed Pb–Sn-based narrow-bandgap perovskites (~1.2 eV) to construct monolithic tandem solar cells offers the potential to achieve even higher PCEs than single-junction PSCs4–6.

Alloying Pb and Sn in metal halide perovskites provides a route to obtain narrow bandgaps (*E*g) down to 1.17 eV for Sn content of 50–60% (refs. 7–9). However, a key element in these perovskites, Sn2+, is prone to oxidation, forming Sn4+, especially in precursor solutions and SnI2 solids, leading to high trap densities and short diffusion lengths in tin-containing perovskites10–12. To address this limitation, tin source purification and antioxidant additives such as SnF2, SnF2- pyrazine complex and hydroxybenzene sulfonic acid have been used to reduce defect densities related to Sn2+ oxidation in Sn-halide perovskites13–17. Device engineering strategies such as engineering the interface18–20, enlarging grains21,22, introducing lattice strain23 and alloying using halides22,24 have been exploited in mixed Pb–Sn narrow-bandgap PSCs to achieve improved PCEs of 17–19%. Guanidinium thiocyanate was recently reported to passivate grain boundaries and reduce surface defect densities; this increased the carrier lifetime and thus the diffusion length of mixed Pb–Sn perovskites, and led to PCEs of 20.2% (with a short-circuit current density *J*sc of ~30 mAcm−2) for single-junction narrow-bandgap PSCs and 23.1% (area ~0.1 cm2) for monolithic all-perovskite tan- dem solar cells25. We reasoned that reducing the in-grain defect density (that is, Sn vacancies) would enable us to improve the PCE further.

The efficiency of all-perovskite tandem solar cells remains below its potential due to the low external quantum efficiencies (EQEs) in the near-infrared range22,25–28, and lags behind the single-junc- tion Pb-based PSCs. It is particularly noticeable for commercially relevant large-area (≥1 cm2) devices: a highest PCE of 13.3% was

reported for all-perovskite tandems whereas Pb-based single-junc-

tion PSCs have demonstrated certified PCEs of 20.9% (refs. 3,27). Long-term device operational stability of all-perovskite tandems has also remained far inferior to that of Pb-based single-junction devices22,25–27,29.

The tunnel recombination junction in monolithic all-perovskite tandems typically relies on a sputtered indium tin oxide (ITO) layer to protect the underlying layers during solution processing of the back narrow-bandgap subcells22,25,26,30. The thick ITO layer not only induces parasitic absorption loss in the near-infrared spectral range, but it also causes shunting between subcells that severely constrains the performance of large-area devices and prevents the cell-to-cell monolithic integration in thin-film modules31. Recently, Palmstrom et al. showed that the thick ITO layer can be avoided by forming a dense recombination layer via atomic layer deposition, resulting in improved performance in all-perovskite tandem solar cells32.

Here we report a simple and effective tin-reduced precur- sor (TRP) solution strategy that prevents the oxidation of Sn2+ to Sn4+ in the precursor solution of narrow-bandgap perovskites by adding a small amount of metallic tin powders; the leftover tin gran- ules are removed before film fabrication via filtering solution. By using this strategy, we are able to reduce the Sn vacancies inside the

grains and thereby achieve a long carrier diffusion length of 3 μm in mixed Pb–Sn perovskite films, with electronic quality compa- rable to high-quality full Pb-based perovskites that have a diffusion

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length of 3.5 μm and PCEs higher than 22%. We obtained the highest PCE of 21.1% for 1.22-eV mixed Pb–Sn narrow-bandgap PSCs, together with a fill factor (FF) above 80% and *J*sc values

higher than 32 mAcm−2. We further developed a recombination junction that avoids using sputtered ITO by taking the advantage of a robust and compact SnO2 layer processed with atomic layer deposition. These enabled us to fabricate monolithic all-perovskite tandem solar cells with certified PCEs of 24.8% for a small-area device (0.049 cm2) and 22.1% for a large-area device (1.05 cm2) under reverse scans. The tandem solar cells exhibited promis- ing stability, retaining 90% of their initial performance following 463 h of operation at the maximum power point (MPP) under full 1-sun illumination.

## Low-*E*g perovskites thin films via comproportionation

The performance and operational stability of mixed Pb–Sn narrow- bandgap PSCs suffers from a high defect density (that is, Sn vacan- cies) in the bulk and surfaces of mixed Pb–Sn perovskites due to the ready oxidation of Sn2+ to Sn4+. This occurs especially in the precursor solutions and in SnI2 solids10,33,34. It leads to short charge- carrier lifetimes and thus short diffusion lengths in tin-containing perovskite films, resulting in poor charge transport/extraction and low FF values in solar cells.

We observed that as-prepared yellow perovskite precursor solu- tion, which contained a mixture of SnI2, PbI2, SnF2, formamidinium iodide (FAI) and methylammonium iodide (MAI) in mixed dimeth- ylformamide (DMF) and dimethylsulfoxide (DMSO) solvents, became orange-red rapidly following exposure to air (Fig. 1a and Supplementary Fig. 1). This indicates that Sn2+ readily oxidizes to Sn4+ in the precursor solution, and that the commonly used reduc- ing agent additive SnF2 does not prevent completely the oxidation of Sn2+, and does not sufficiently reduce Sn4+ to Sn2+ once Sn4+ forms in the precursor solution.

We posited that the trap density in mixed Pb–Snperovskites could be reduced if the undesired Sn4+—already formed in perovskite pre- cursor solution—could be avoided in the precursor solution before film formation. In contrast with purely Sn-based perovskites, mixed Pb–Sn perovskites (in their solid film form) with SnF2 embedded in the grains are tolerant to Sn2+ oxidation even in ambient air26,27,35, and the oxidation of Sn2+ to Sn4+ is expected to occur mainly before film formation in mixed Pb–Sn perovskite systems.

We pursued a reducing agent that is insoluble in precursor solu- tion on its own, but becomes a part of the perovskite lattice once oxidized by Sn4+ to form Sn2+. We constructed the Frost diagram for Sn of different oxidation states (Supplementary Fig. 2) and found that metallic Sn readily reduces Sn4+ in the precursor solution via

the comproportionation reaction Sn+Sn4+ → 2Sn2+; the standard redox potential of this reaction is *E*o= 0.29 V, exhibiting negative Gibbs energy Δ*G*o *= –nFE*o < 0 (ref. 36), where *n* is the electron transfer number and *F* is the Faraday constant. Indeed, when we

added metallic Sn powders into oxidized Pb–Sn perovskite precur- sor solution, the red solution became bright yellow again, even in the presence of oxygen, indicating that Sn4+ had been reduced to Sn2+ in the presence of metallic Sn (Supplementary Fig. 1).

The transmittance spectra of the precursor solution further confirmed the colour changes at different stages (Supplementary Fig. 2). We found that the absorption edge of the pristine precur- sor solution blue-shifted slightly following the introduction of Sn powders, a finding we attribute to the reduction of Sn4+ formed already in the solution (even in the glovebox) in the absence of Sn powders. In comparison, the precursor solution with Sn powders maintained its bright-yellow colour even after exposure to air for at least 2 weeks. We believed that the formation of Sn vacancies due to the presence of Sn4+ in the precursor solution could potentially be suppressed in perovskite films processed from Sn4+-free precursor solution (Fig. 1b).

We fabricated mixed Pb–Sn narrow-bandgap perovskite films with a composition of MA0.3FA0.7Pb0.5Sn0.5I3 from pristine (referred to as control from hereon) and TRP solutions using the antisolvent method. The metallic Sn powders (microparticles with a diam- eter of ~150 μm) were completely removed via filtering through

a 0.2-μm polytetrafluoroethylene (PTFE) membrane filter; no

metallic Sn was detected via X-ray photoemission spectroscopy

(XPS; Supplementary Fig. 3) in the TRP perovskite films. The TRP perovskite films showed a substantially reduced concentra- tion of Sn4+ compared to control films (Supplementary Fig. 3a–c). The Sn4+ in control films is assigned principally to the precursor solids (SnI2) and further oxidation of Sn2+ to Sn4+ in the precursor solution. We found that even highest-purity (99.999%) SnI2 beads available from Alfa Aesar and Sigma-Aldrich exhibited a substan- tial amount of Sn4+ (Supplementary Fig. 3d). We noted also that the SnI2 beads, marked as the same purity (99.999%), exhibited differ- ent colours for materials provided by Alfa Aesar and Sigma-Aldrich (Supplementary Fig. 4), and the colour of beads varied from batch to batch from the same provider.

The narrow-bandgap perovskite films showed an optical bandgap (defined at absorption onset) of 1.22 eV (Supplementary Fig. 5). The control and TRP perovskite films exhibited a pure perovskite phase with similar crystallinity and crystallographic orientation (Fig. 1c). Both films exhibited photoluminescence peaks at 1,000 nm, but the TRP perovskite film showed stronger photoluminescence intensity due to reduced non-radiative recombination (Fig. 1d). Both control and TRP films are smooth and pinhole-free, with uniform and large grains (Fig. 1e,f). Cross-sectional scanning electron microscopy (SEM) images (Supplementary Fig. 6) indicated that mixed Pb–Sn narrow-bandgap perovskite films form vertically oriented grains, offering potential benefits to charge transport in solar cells.

## Charge transport characteristics of low-*E*g perovskites

To measure the charge transport characteristics, we carried out femtosecond- and nanosecond-resolved optical-pump terahertz- probe (OPTP) spectroscopy, a non-destructive method of prob- ing the photoinduced conductivity and charge-carrier mobility37,38.

Transient THz spectroscopy (1 THz ≈ 4.1 meV) is suitable for the sensing of photocarriers and their dynamics, since THz spectros- copy is sensitive to the free charge carriers but not to the bound

carriers such as excitons and trapped carriers. Fluence-dependent femtosecond OPTP transients exhibited accelerated decay dynam- ics at higher initial photoinjected charge-carrier densities due to the enhanced contributions from bimolecular and Auger recom- bination (Fig. 2a,b). We calculated recombination rate constants and charge-carrier mobilities of 72 and 79 cm2 V−1 s−1 for control and TRP samples, respectively. The derivation of mobility and other parameters from OPTP transients is detailed in Methods and Supplementary Note 1.

We then performed nanosecond OPTP spectroscopy and extracted charge-carrier lifetimes of 3 ns versus 43 ns for control and TRP perovskite films (Fig. 2c). The much longer lifetime in TRP film agrees with the picture of a significantly lowered trap density. We derived the charge-carrier diffusion lengths (*L*D) as a function of the charge-carrier density *n* following the equation37: *L*D = [*μk*B*T*/

(*qR*)]1/2, where *R* = *k*1+*nk*2+*n*2*k*3 is the total recombination rate, *k*B

is the Boltzmann constant, *T* is the absolute temperature and *q* is

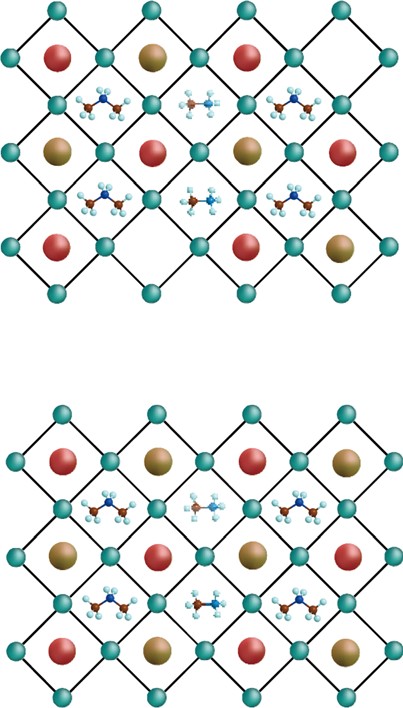
the elementary charge. Under 1-sun solar illumination conditions (*n* ≈ 1015 cm−3)38, the diffusion lengths of control and TRP perovskite films are 0.75 and 2.99 μm, respectively. The diffusion length of TRP narrow-bandgap perovskites is therefore several times longer than the thickness (~1 μm) required for complete incident light absorp- tion in solar cells, and this fact ensures efficient carrier extraction in

thick solar cells as required for efficient light harvesting in tandem devices. The TRP mixed Pb–Sn perovskites show a diffusion length comparable to those in high-quality Pb-based 1.53-eV perovskites

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***a* b**

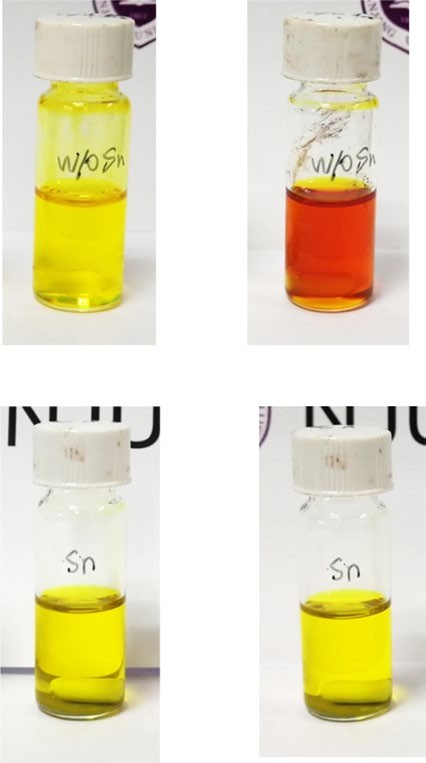
Solution Film



*V*Sn

*V*Sn

Sn vacancy



Air exposure

Sn2+ ‹ Sn4+

Without Sn

Air exposure

Sn4++Sn ‹ 2Sn2+

With Sn

With Sn4+



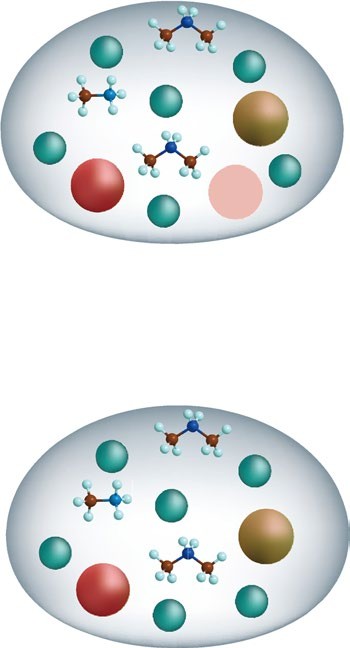
FA+

MA+

Pb2+

Sn2+

I–



I–

FA+ I–

I–

2+

I

– MA+

Sn

Pb2+

I–

I–

Sn4+

Without Sn4+

I–

I

FA+ I– I–

– MA+ Sn2+

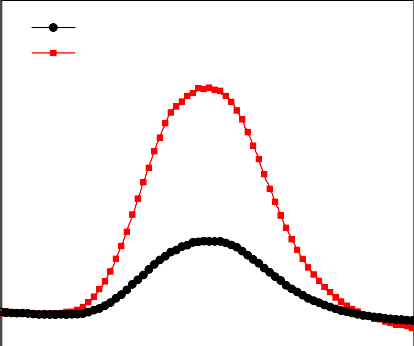
Pb2+

I–

I–

***c* d**

Control TRP



Control

TRP

Intensity (a.u.)

Photoluminescence intensity (a.u.)

10 20 30 40 50 60 850 900 950 1,000 1,050 1,100 1,150

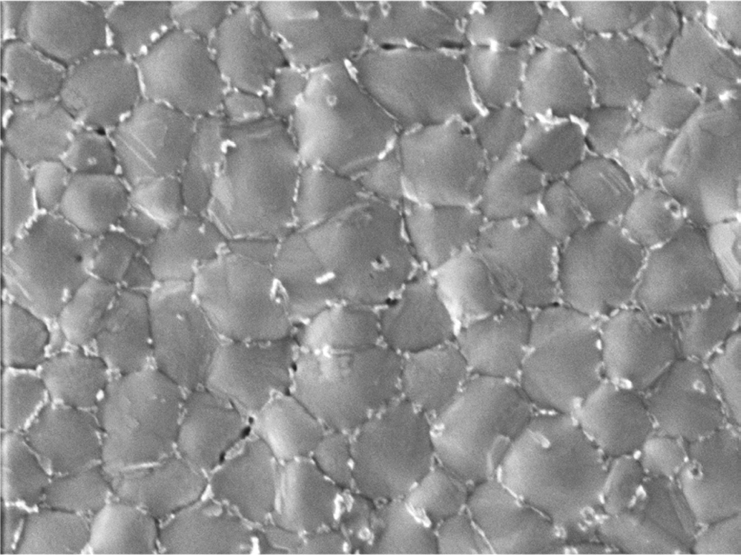
1. Control

2 *º* (°)

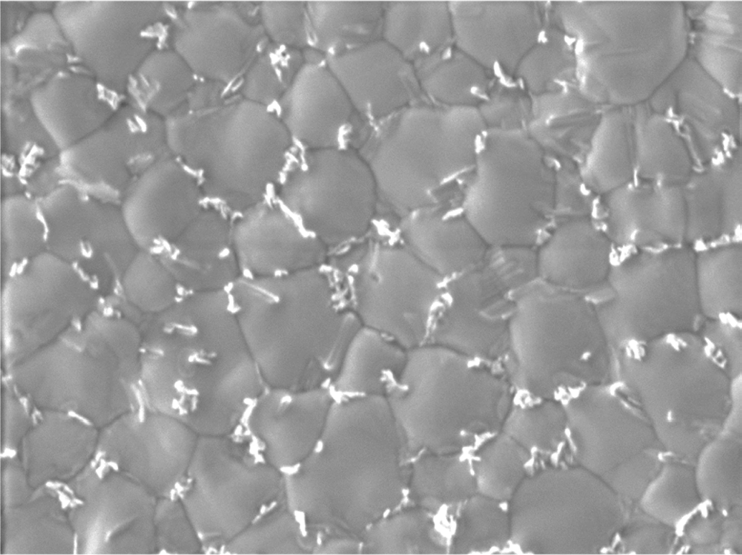
1. TRP

Wavelength (nm)

## 



2 µm



2 µm

**Fig. 1 |** Mixed Pb–Sn narrow-bandgap perovskite films fabricated from Sn4**+**-containing and Sn-reduced (Sn4**+**-free) precursor solutions. **a**, Photographs showing the ease of oxidation of Sn2+ to Sn4+ in ambient air and the facile reduction of Sn4+ to Sn2+ by metallic Sn powders. **b**, Illustration of the formation of Sn vacancies in mixed Pb–Sn perovskite due to the presence of Sn4+ in the precursor solution and the suppression of Sn vacancy formation in TRP perovskite because of the absence of Sn4+. **c**, X-ray diffraction patterns of control and TRP narrow-bandgap perovskite films. a.u., arbitrary units.

**d**, Photoluminescence spectra of control and TRP narrow-bandgap perovskites films deposited on bare glass substrates. **e**,**f**, SEM images of control

(**e**) and TRP (**f**) narrow-bandgap perovskite films.

(*L*D= 3.45 μm) with a composition of Cs0.05MA0.05FA0.9PbI2.85Br0.15

that delivers PCEs higher than 22% (Supplementary Figs. 7–9).

To explore the origins of improved charge-carrier lifetimes and diffusion lengths in TRP narrow-bandgap perovskites, we carried out space-charge-limited current and Mott–Schottky plot measure- ments to estimate the trap density and hole concentration for con- trol and TRP films (Supplementary Figs. 10 and 11). As expected, mixed Pb–Sn perovskites exhibit a high hole concentration, and

the density of hole traps is higher than the density of electron traps due to the tendency to form Sn vacancies in the material (Table 1). By avoiding Sn4+ in the precursor solution, the density of hole traps is reduced from 2.14 × 1016 cm−3 for the control samples to

1.06 × 1016 cm−3 for the TRP films. Correspondingly, the hole con- centration is significantly decreased from 1.4 × 1016 cm−3 in the con- trol samples made from Sn4+-containing solution to 0.54 × 1016 cm−3 in the TRP ones.

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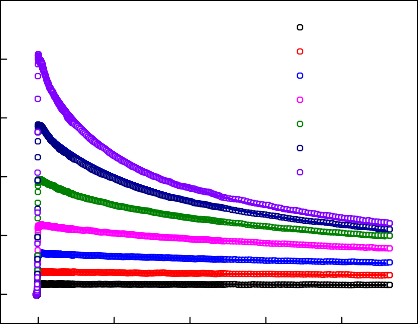
# Articles

**a** 0.10

Control *µ* = 72 cm2 V–1 s–1

1.8 µJ cm–2

**b** 0.10

TRP

*µ* = 79 cm2 V–1 s–1

1.5 µJ cm–2

3.0 µJ cm–2

8 –1

3.0 µJ cm–2

0.08

*k*1 = 3.3 × 108 s–1

–10

3 –1

5.5 µJ cm–2

8.0 µJ cm–2

0.08

*k*1 = 0.23 × 10 s

*k* = 3.0 × 10–10 cm3 s–1

5.5 µJ cm–2

*k*2 = 3.5 × 10

cm s

–2

2

–28

6 –1

9.0 µJ cm–2

0.06

–6*T*/*T*

0.04

*k*3 = 3.2 × 10–28 cm6 s–1

12 µJ cm

20 µJ cm–2

30 µJ cm–2

0.06

0.04

–6*T*/*T*

*k*3 = 3.5 × 10

cm s

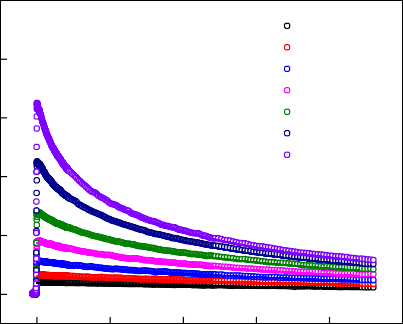
15 µJ cm–2

23 µJ cm–2

32 µJ cm–2

0.02 0.02

0.00 0.00

0 500

1,000

1,500

2,000

2,500

0 500

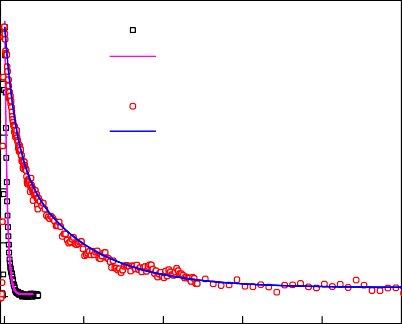
1,000

1,500

2,000

2,500

Pump-probe time delay (ps)

**c d**

1.0 Control - exp

Fitting, lifetime 3.0 ns

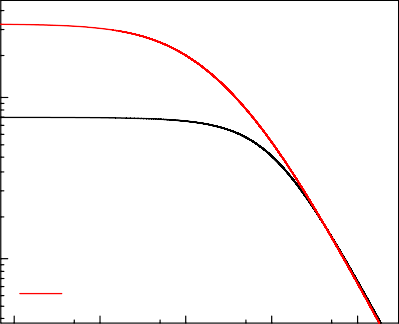
Pump-probe time delay (ps)

0.8

–6*T*/*T* (norm.)

0.6

TRP - exp 1

Fitting, lifetime 43.2 ns

Diffusion length (µm)

0.4

0.2

0.0

0

100

200

300

400

500

0.1 Control, *L*D(1015 cm–3) = 0.75 µm TRP, *L*D(1015 cm–3) = 2.99 µm

1015 1016 1017 1018 1019

Pump-probe time delay (ns)

Carrier concentration (cm–3)

**Fig. 2 |** Charge dynamics of mixed Pb–Sn narrow-bandgap perovskites. **a**,**b**, Femtosecond OPTP transients for control (**a**) and TRP (**b**) perovskite films measured after excitation with a 90-fs light pulse of 800 nm wavelength with various fluences. The rate constants (*k*) associated with different

recombination processes were fitted globally to these transients according to the equation d*n*(*t*)/d*t* = –*k*3*n*3 – *k*2*n*2 – *k*1*n*, where *t* is decay time, and *k*1, *k*2, *k*3

are rate constants associated with monomolecular recombination, bimolecular recombination and Auger recombination, respectively. The mobilities are calculated to 72 and 79 cm2 V−1 s−1 for the control and TRP samples, respectively. **c**, Nanosecond OPTP transients for the control and TRP perovskite films measured after excitation with a 0.8-ns light pulse of 800 nm wavelength with a low fluence. The lifetimes were obtained by the monoexponential fit. All OPTP measurements were carried out in a N2 atmosphere to avoid potential degradation of samples in ambient air. norm., normalized; exp, experimental data. **d**, Charge-carrier diffusion lengths (*L*D) of control and TRP perovskite films as a function of charge-carrier concentration. At 1-sun condition (a carrier

density of approximately 1015 cm−3), the control and TRP samples show diffusion lengths of 0.75 and 2.99 μm, respectively.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| **Table 1 |** Material characteristics of mixed Pb–Sn perovskites and full Pb-based perovskite | | | | | | | |
| Material | Composition | *N*trap, electron | *N*trap, hole | *N*hole | Mobility | Lifetime | *L*D |
|  |  | (1016 cm−3) | (1016 cm−3) | (1016 cm−3) | (cm2 V−1 s−1) | (ns) | (**μ**m) |
| Pb–Sn, control | MA0.3FA0.7Pb0.5Sn0.5I3 | 0.38 | 2.14 | 1.40 | 72 | 3 | 0.75 |
| Pb–Sn, TRP | MA0.3FA0.7Pb0.5Sn0.5I3 | 0.24 | 1.06 | 0.54 | 79 | 43 | 2.99 |
| Full Pb, 1.53 eV | Cs0.05MA0.05FA0.9Pb(I0.95Br0.05)3 | 0.13 | 0.38 | – | 55 | 82 | 3.45 |
| *N*trap, electron, density of electron traps; *N*trap, hole, density of hole traps; *N*hole, hole density. | | | | | | | |

## PV performance of low-*E*g PSCs

We fabricated a series of mixed Pb–Sn narrow-bandgap PSCs with various absorber layer thicknesses to evaluate solar cell per- formance (Fig. 3a and Supplementary Table 1). The devices had an inverted planar structure comprising ITO/PEDOT:PSS/mixed Pb–Sn perovskite/C60/BCP/Cu (Supplementary Fig. 6), where PEDOT:PSS is poly(3,4-ethylene dioxythiophene)-poly(styrene sulfonate), C60 is fullerene and BCP is bathocuproine. For very thin devices, that is, at a thickness of 220 nm, both control and TRP devices were not limited by their diffusion lengths and they exhibited comparable performance. As the thickness of perovskite absorber increased from 350 to 920 nm, the TRP devices exhib- ited considerably better performance than the control devices. The

average FF value of TRP devices was substantially constant for all thicknesses investigated, and the average *J*sc value gradually increased with thickness due to increased light absorption when the thicker absorber was used, and this was achieved without com- promising the carrier collection, as indicated by the EQE curves in Fig. 3b. By contrast, the average FF value of control devices decreased with thickness, consistent with the shorter diffusion length. Correspondingly, the control devices initially showed increased *J*sc with thickness up to 650 nm, up to which the charge transport was not severely constrained by the diffusion length. As the thickness increased beyond their diffusion length, that is, at 860 and 920 nm thickness, the control devices exhibited reduced *J*sc with increased thickness and photogenerated charge carriers were

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**a** 0.85



Control

0.80 



*V*oc (V)

0.75

0.70

0.85

TRP

0.80  

*V*oc (V)

0.75 

0.70

**b** 100

80



TRP

220 nm, 24.8 mA cm–2

380 nm, 28.0 mA cm–2

650 nm, 30.4 mA cm–2

860 nm, 31.3 mA cm–2

920 nm, 31.5 mA cm–2

Control

75     80

FF (%)

EQE (%)

70 60

80 40



TRP

FF (%)

75 20

70

0

Thickness (nm)

32



Control

*J* (mA cm–2)

30 



28 

26

sc

24

32  



TRP

*J* (mA cm–2)

30 

28

26



sc

24

Thickness (nm)

22



Control

20

PCE (%)

18 

16 



14

22



TRP

20   

PCE (%)

18

16



14

**c**

1.0

0.8

Photovoltage (norm.)

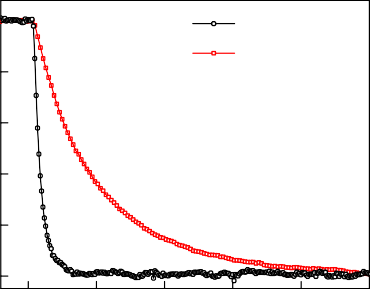
0.6

0.4

0.2

0.0

Wavelength (nm)



Control, *t* = 6 µs TRP, *t* = 48 µs

Thickness (nm)

**d**

60

40

Counts

20

0

**e** 35

30

Current density (mA cm–2)

25

20

15

10

5

0

Thickness (nm)

**f** 100

Reverse

Forward

*V*oc *J*sc

FF

(V) (mA cm–2) (%)

Reverse 0.831 31.4 80.8

Forward 0.827 31.4 80.3

PCE (%) 21.1

20.9

80

60

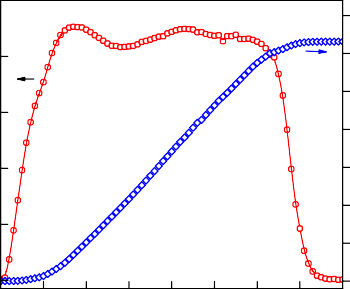
EQE (%)

40

20

0

Decay time (µs)

35

30

25

*J*sc (mA cm–2)

20

15

10

5

0

PCE (%)

Voltage (V)

Wavelength (nm)

**Fig. 3 |** PV performance of mixed Pb–Sn narrow-bandgap PSCs. **a**, PV parameters of control and TRP solar cells with various perovskite layer thicknesses.

**b**, Representative EQE curves of TRP solar cells with various perovskite thicknesses. **c**, Transient photovoltage decay of control and TRP solar cells with a thickness of 860 nm. The recombination lifetime (*τ*) is monoexponentially fitted. **d**, Histogram of PCEs over 126 TRP devices with a perovskite layer thickness of 860 nm. The devices exhibit an average PCE of 20.1 ± 0.6%. **e**, *J*–*V* curves of the best-performing TRP device. **f**, EQE curve of the best- performing TRP device, showing an integrated *J*sc of 31.6 mA cm−2.

not efficiently extracted, as indicated by the EQE curves shown in Supplementary Fig. 12.

The best performance for control devices was achieved at a thickness of 650 nm, with an average PCE of 17.8% and a best PCE of 18.3% (*V*oc= 0.811 V, FF = 77.7%, *J*sc= 29.1 mAcm−2 where *V*oc is open-circuit voltage; Supplementary Fig. 13), which is comparable

to previously reported performance22–24. The TRP devices obtained their best performance using an 860-nm-thick absorber, resulting in a considerably higher average PCE of 20.1%. Further increasing the thickness beyond this thickness did not lead to an obvious increase in *J*sc due to almost complete light absorption. The devices with thick absorbers reached highest *J*sc values above 32 mAcm−2, which is amongst the highest values reported24–26,32. It is interesting to note that the average *V*oc of TRP solar cells increases with thickness up to 860 nm. This can be ascribed to the larger grain size formed at a higher concentration of precursor solution (Supplementary Fig. 14) and is consistent with previous studies21,26. The best *V*oc (0.84 V)

**868**

achieved in our devices is still below the best reported values (0.85–0.89 V)19,22,24. Further optimization of perovskite composition, device interface and grain passivation offers the potential to achieve higher *V*oc and FF values19,20,24,25,28. We performed transient photo- voltage decay under the open-circuit condition for control and TRP solar cells (Fig. 3c) and found that the charge-recombination life-

time *τ* of the TRP device (48 μs) was substantially longer than that of the control device (6 μs), consistent with the longer charge-carrier lifetime and lower trap density in TRP perovskite films (Fig. 2 and

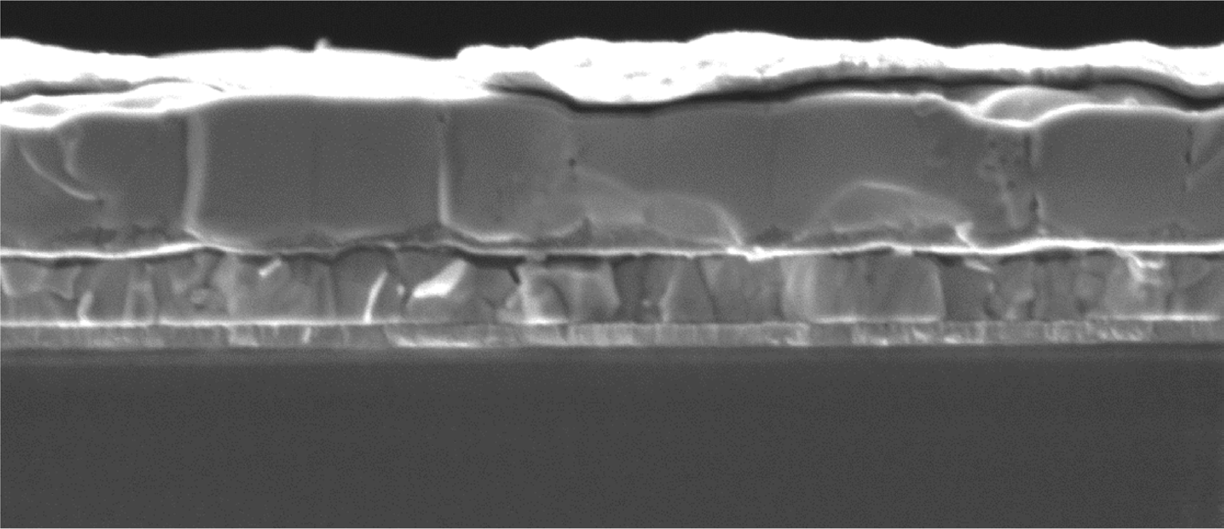
Table 1). The TRP solar cells also exhibited lower dark saturation- current density (Supplementary Fig. 15), in agreement with lower trap density and lower hole concentration in TRP perovskite films24. Figure 3d shows a histogram of PCE values over 126 TRP narrow- bandgap PSCs at the optimal thickness of 860 nm. The devices have

an average PCE of 20.1 ± 0.6%, and the narrow PCE distribution indicates an excellent reproducibility for devices processed from the TRP solution. The best TRP narrow-bandgap PSC achieved a high

NATuRE ENERGY | VOL 4 | OCTOBER 2019 | 864–873 | [www.nature.com/natureenergy](http://www.nature.com/natureenergy)

**Nature eNergy** Articles

**a**



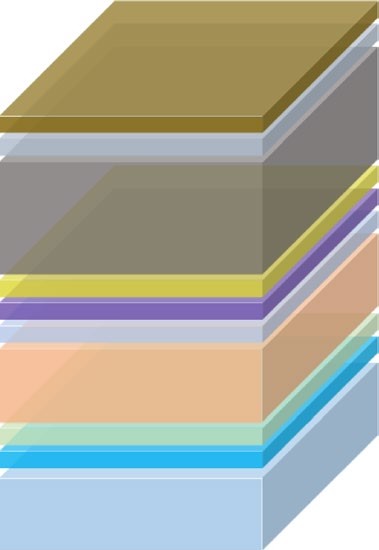
Low-*E*g perovskite

Wide-*E*g perovskite

ITO

glass

2 µm



Cu C60/BCP

1.22-eV low-*E*g perovskite

PEDOT:PSS ALD-SnO2/Au C60

1.77-eV wide-*E*g perovskite

PTAA ITO

Glass

Cu C60/BCP

PEDOT:PSS

ALD-SnO2/Au C60

PTAA

**b**

16

Current density (mA cm–2)

12

8

4

0

**e** 16

Voltage (V)

**c** 18

15

Current density (mA cm–2)

12

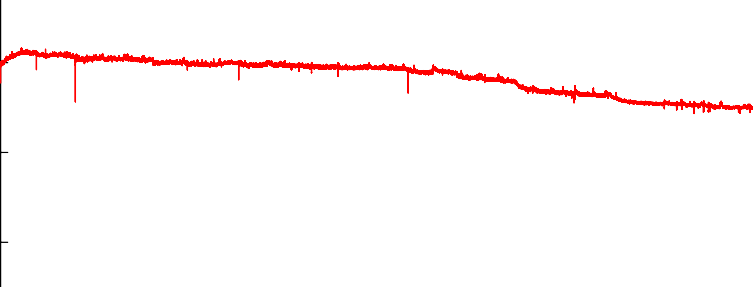
9

6

3

0

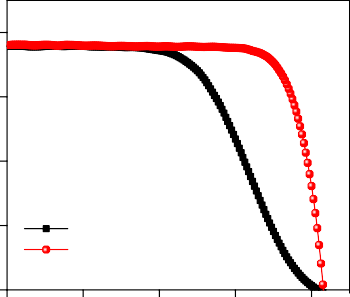
**f**



MPP tracking under full AM1.5 illumination

*T*90 = 463 h

Voltage (V)



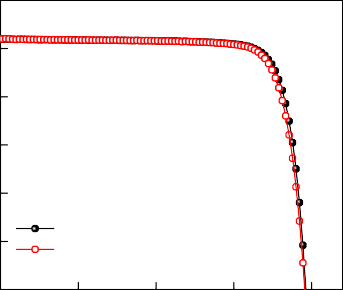
Without Au

With Au



Front, *J*sc = 15.7 mA cm–2

Back, *J*sc = 15.5 mA cm–2



Area: 0.073 cm2

Reverse, PCE = 24.8%

Forward, PCE = 24.5%

**d**

100

80

60

EQE (%)

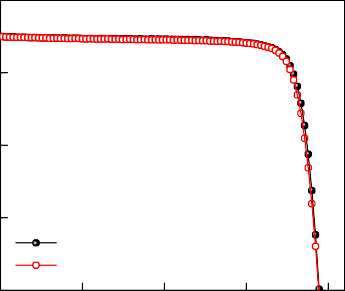
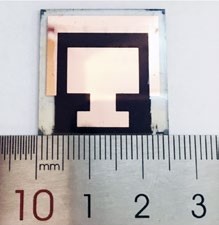
40

20

0

Wavelength (nm)

12 1.0



Aperture area: 1.05 cm2

Reverse, PCE = 22.3% Forward, PCE = 22.3%

Current density (mA cm–2)

PCE (norm.)

8 0.8

4

0.6

0

0.0 0.5 1.0 1.5 2.0

Voltage (V)

0 50 100 150 200 250 300 350 400 450 500

Time (h)

**Fig. 4 |** Performance and stability of monolithic all-perovskite tandem solar cells. **a**, Device structure and corresponding cross-sectional SEM image of a tandem solar cell. **b**, *J*–*V* curves of tandem solar cells without and with an ultrathin Au layer in the tunnel recombination junction. **c**, *J*–*V* curves of the best- performing small-area tandem solar cell (0.073 cm2), showing PCEs of 24.8% and 24.5% under reverse and forward scans, respectively. **d**, EQE curves

of the best-performing small-area tandem cell, showing integrated *J*sc values of 15.7 and 15.5 mA cm−2 for the front and back subcells, respectively. **e**, *J*–*V* curves of a large-area tandem solar cell (1.05 cm2). The inset shows the digital photo of the large-area device. **f**, MPP tracking of an unencapsulated small- area tandem solar cell for 463 h in a glovebox under full simulated AM1.5 solar illumination (100 mW cm–2) without ultraviolet filter. The device retained 90% of its initial efficiency after operation for 463 h (*T*90 = 463 h). AM1.5, Air Mass 1.5.

PCE of 21.1% under reverse scan and a PCE of 20.9% under for- ward scan, showing low hysteresis (Fig. 3e). The stabilized power output of 20.9% is consistent with the PCEs determined from the current density–voltage (*J–V)* sweeps (Supplementary Fig. 16). The integrated *J*sc value from the EQE curve is 31.6 mAcm−2, which is in good agreement with the values obtained from *J*–*V* measurements (Fig. 3f). The devices show a spectral response up to 1,050 nm wavelength and exhibit high EQE values in the near-infrared spec- tral range (above 80% for wavelengths up to 940 nm). We sent a narrow-bandgap solar cell to an accredited independent PV test laboratory (SIMIT, Shanghai, China) for certification (see Methods about the PV certification at Shanghai Institute of Microsystem and Information Technology (SIMIT)), and the device delivered a certi- fied PCE of 19.83% (Supplementary Fig. 17). Another device was sent to Newport PV test laboratory (Montana, USA), and the device

delivered a comparable certified PCE of 19.53% (Supplementary Fig. 18). Minor drops in PCE (~5% relatively) were observed after exposure to ambient air during shipping to and testing at SIMIT and Newport.

## Performance and stability of all-perovskite tandems

We fabricated monolithic all-perovskite tandem cells using a 1.77- eV wide-bandgap front subcell (~300 nm) and a 1.22-eV TRP narrow-bandgap back subcell (~800 nm) as depicted in Fig. 4a. The wide-bandgap perovskite had composition Cs0.2FA0.8PbI1.8Br1.2. The tandem cells had a device configuration of glass/ITO/PTAA/ wide-*E*g perovskite/C60/ALD-SnO2/Au(~1 nm)/ PEDOT:PSS/low- *E*g perovskite/C60/BCP/Cu, where PTAA is poly(triarylamine). Here we took advantage of depositing a compact thin layer of SnO2 using atomic layer deposition (ALD) to avoid the necessity of ITO layer in

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|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Table 2 |** PV performance of monolithic tandem solar cells and single-junction subcells | | | | | |
| Cells | Scan direction | *V*oc (V) | *J*sc (mA cm−2) | FF (%) | PCE (%) |
| 1.77-eV single Reverse | | 1.216 | 17.0 | 79.7 | 16.5 |
| Forward | | 1.202 | 17.0 | 79.9 | 16.3 |
| 2T tandem Reverse | | 1.965 | 15.6 | 81.0 | 24.8 |
| (0.073 cm2) Forward | | 1.957 | 15.6 | 80.2 | 24.5 |
| 2T tandem | Reverse | 1.945 | 14.0 | 82.0 | 22.3 |
| (1.05 cm2) | Forward | 1.943 | 14.0 | 81.8 | 22.3 |
| Reverse, scan from *V*oc to *J*sc; forward, scan from *J*sc to *V*oc; 2T, two-terminal. | | | | | |

the tunnel recombination junction. The ALD-SnO2 layer provides excellent electron extraction and leads to slightly improved perfor- mance for the wide-bandgap front cells (Supplementary Fig. 19). This compact and robust ALD-SnO2 layer (~20 nm thick) allowed us to fabricate tandems free of ITO layer, as the SnO2 layer can pre- vent damage to the deposited-underlying front subcells during the solution processing of back subcells. An ultrathin Au layer (~1 nm) was deposited between the SnO2 and PEDOT:PSS layers by thermal evaporation to facilitate electron–hole recombination in the tun- nel recombination junction. Tandem solar cells without the ultra- thin Au layer exhibited an obvious S shape in the *J*–*V* curves near the open-circuit voltage and thus have low FF values (Fig. 4b and Supplementary Table 2).

Figure 4c,d presents the *J*–*V* and EQE curves of the best-per- forming tandem solar cells; the corresponding PV parameters are summarized in Table 2. The champion tandem device exhibits a high PCE of 24.8% under reverse scan, with a high *V*oc of 1.965 V, a *J*sc of 15.6 mAcm−2 and a high FF of 81.0%. The *V*oc of tandem cells closely approaches the summed photovoltages of the two subcells, indicating negligible voltage loss in the interconnecting recombina- tion junction. The PCE of tandem cells reported herein are appre- ciably higher than that of each subcell, indicating the benefits of the monolithic tandem configuration. The tandem devices and corresponding single-junction subcells exhibit low hysteresis between reverse and forward scans (Table 2). The PCEs from *J*–*V* sweeps are consistent with the stabilized PCE of 24.5% in tandem devices (Supplementary Fig. 20). These PCEs are high when com- pared to other monolithic all-perovskite tandem solar cell reports. The integrated *J*sc values of the front and back subcells from EQE curves (Fig. 4d) are 15.7 and 15.5 mA cm−2, respectively, agreeing well with the *J*scdetermined from *J*–*V* measurements. Supplementary Table 3 shows the summary of performance over 26 tandem

solar cells processed among several batches. The tandem devices provide an average PCE of 22.6 ± 0.9%, best *V*oc values exceeding

2.0 V and a relatively narrow PCE distribution indicative of promis-

ing reproducibility.

(aperture area 0.049 cm2) and a large-area (1.05 cm2) tandem solar cell to SIMIT (Shanghai, China) for certification, and the devices delivered certified PCEs of 24.8% and 22.1% under reverse scans, respectively (Supplementary Figs. 22 and 23).

Stability is another crucial parameter for commercialization of PSCs. We anticipated that reducing the lattice defects, that is, the Sn vacancies, in the TRP narrow-bandgap perovskites would allow us to improve the stability of tandem solar cells39,40. We first inves- tigated the shelf lifetime of tandem solar cells, storing the devices in a glovebox in the dark and tracking the evolution of PCEs. Supplementary Fig. 24 shows that there is no obvious degradation in performance following dark storage in a nitrogen atmosphere for 1,650 h. This indicates that the stability of mixed Pb–Sn perovskites is achievable using suitable encapsulation.

We also investigated the operational stability of unencapsulated tandem cells under full 1-sun illumination and MPP operation in a glovebox without ultraviolet filter. The PCE of tandem cells increased slightly in the first tens of hours of illumination, which may be related to light-induced defect healing in perovskites41,42. The tandem solar cells exhibited promising stability for Sn-containing PSCs and retained 90% of their initial performance following opera- tion for 463 h under 1-sun illumination with MPP tracking (Fig. 4f).

## Conclusions

In summary, we have developed a strategy to reduce Sn vacancies in mixed Pb–Sn narrow-bandgap perovskites via a comproportion- ation reaction, and increased thereby the performance and stability of monolithic all-perovskite tandem solar cells. We obtained a PCE of 21.1% (certified 19.5%) for mixed Pb–Sn single-junction solar cells, and achieved certified PCEs of 24.8% and 22.1% for small-area and large-area all-perovskite tandem cells, respectively. The tandem cells exhibit promising stability and retain 90% of their performance after 463 h of operation at the MPP under full 1-sun illumination. Efficiency of the monolithic all-perovskite tandem solar cells is still limited by the large *V*oc deficit in the wide-bandgap front cell and the optical loss caused by the tunnel recombination junction. The sum of the EQEs in the tandem solar cell is considerably lower than that of single-junction narrow-bandgap solar cells over 680–1,000 nm wavelength range due to optical reflection and parasitic absorp- tion by the PEDOT:PSS layer in the recombination junction (Supplementary Fig. 25). Further advances in wide-bandgap PSCs and tunnel recombination junctions should enable PCEs exceeding 25%, making all-perovskite tandem PV technologies promising, in view of the potential for low cost combined with higher efficiencies.

## Methods

**Materials.** Unless otherwise stated, all materials were purchased from Sigma- Aldrich or Alfa Aesar and used as received without further purification. Unless otherwise stated, all films and devices discussed herein were fabricated using SnI2 (99.999% purity) purchased from Alfa Aesar without further purification. The organic halide salts were purchased from GreatCell Solar (Australia). PEDOT:PSS aqueous solution (Al 4083) was purchased from Heraeus Clevios (Germany). Tin powders were purchased from Sigma-Aldrich (<150 μm, 99.5%).

**Perovskite precursor solution.** To make narrow-bandgap FA MA Pb Sn I

To evaluate the upscaling potential of tandem cells, we also fab-

0.7

0.3

0.5

0.5 3

ricated large-area devices (1.05 cm2 aperture area) with processing and perovskite absorbers as used in small cells. The large-area cells exhibited a high PCE of 22.3% (*V*oc =1.945 V, *J*sc = 14.0 mA cm−2

and FF = 82.0%) without detailed optimization for current match-

ing between subcells (Fig. 4e). The *J*sc value is lower than that of

the small-area cell due to the use of a thicker front ITO electrode— this leads to stronger parasitic absorption in the near-infrared spectral range and thus lower photocurrent in the back subcell (Supplementary Fig. 21). The *V*oc and FF values of large-area devices are comparable to those seen in small-area devices (Table 2). The performance of these large-area tandems indicates promise in upscaling all-perovskite tandem solar cells. We sent a small-area

perovskite films with various thicknesses, the precursor solution (with various concentrations of 0.8, 1.2, 1.6, 1.8 and 2.0 M) was prepared in mixed solvents of DMF and DMSO with a volume ratio of 3:1. The molar ratios for FAI/MAI and PbI2/SnI2 were 0.7:0.3 and 0.5:0.5, respectively. The molar ratio of (FAI+MAI)/

(PbI2+SnI2) was 1:1. SnF2 (10 mol% relative to SnI2) was added in the precursor

solution. The precursor solution was stirred at room temperature for 2 h and then filtered through 0.20-μm PTFE membrane before use. To reduce Sn4+ in the precursor solution, tin powders (5 mgml−1) were added in the precursor and

stirred at room temperature for 10 min before use. The precursor solution with the remaining tin powders was filtered through 0.20-μm PTFE membrane before the perovskite films were made. XPS measurements did not detect any residual metallic Sn in the perovskite films. It should be noted that SnF2 additive is still necessary

in TRP solution to achieve high performance in solar cells (see Supplementary

Figs. 26 and 27). To make wide-bandgap FA0.8Cs0.2Pb(I0.6Br0.4)3 perovskite films, the precursor solution (1.1 M) was prepared in mixed solvents of DMF and

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DMSO with a volume ratio of 4:1. The molar ratios for FAI/FABr/CsI/CsBr and PbI2/PbBr2 were 0.48:0.32:0.12:0.08 and 0.6:0.4, respectively. The molar ratio of

(FAI+FABr+CsI+CsBr)/(PbI2+PbBr2) was 1:1. The precursor solution was stirred at 50 °C for 2 h and then filtered through a 0.20-μm PTFE membrane before use.

**Pb–Sn narrow-bandgap PSC fabrication.** The pre-patterned ITO glass substrates were sequentially cleaned using acetone and isopropanol. PEDOT:PSS (Al

4083) was spin-coated on ITO substrates at 4,000 r.p.m. for 30 s and annealed on a hotplate at 150 °C for 10 min in ambient air. After cooling, we transferred the substrates immediately to a nitrogen-filled glovebox for the deposition of

perovskite films. The perovskite films were deposited with two-step spin-coating procedures: (1) 1,000 r.p.m. for 10 s with an acceleration of 200 r.p.m. s–1 and (2) 4,000 r.p.m. for 40 s with a ramp-up of 1,000 r.p.m. s–1. Ethyl acetate (200 µl) was dropped on the spinning substrate during the second spin-coating step at 20 s

before the end of the procedure. Ethyl acetate was chosen here since it is less toxic and more environmentally friendly than commonly used chlorobenzene. The substrates were then transferred to a hotplate and heated at 100 °C for 10 min.

After cooling down to room temperature, the substrates were transferred to the evaporation system. Finally, C60(20 nm)/BCP(7 nm)/Cu(100 nm) were sequentially deposited on top of the perovskite by thermal evaporation.

**Monolithic all-perovskite tandem solar cell fabrication.** PTAA (2 mg mL−1 in chlorobenzene) layers were firstly spin-coated on ITO substrates at 5,000 r.p.m. for 30 s and annealed on a hotplate at 150 °C for 10 min in a glovebox. After cooling, the wide-bandgap perovskite films were deposited on top of PTAA with a two-step spin-coating procedure. The first step was 2,000 r.p.m. for 10 s with an acceleration of 200 r.p.m. s–1. The second step was 6,000 r.p.m. for 40 s

with a ramp-up of 2,000 r.p.m. s–1. Chlorobenzene (100 µl) was dropped onto the spinning substrate during the second spin-coating step at 20 s before the end of the procedure. The substrates were then transferred on a hotplate and heated at

100 °C for 15 min. After cooling down to room temperature, the substrates were transferred to the evaporation system, and 20-nm-thick C60 film was subsequently deposited on top by thermal evaporation at a rate of 0.2 Å s–1. The substrates were then exposed to air and transferred to the ALD system to deposit a 20-nm SnO2 layer at low temperatures. After ALD deposition, the substrates were exposed

to air again and transferred to the thermal evaporation system to deposit an ultrathin layer of Au clusters (~1 nm) on SnO2. PEDOT:PSS layers were spin-cast on top of the SnO2-protected front cell and annealed in air at 120 °C for 20 min. After the substrates had cooled, we immediately transferred the substrates to a nitrogen-filled glovebox for the deposition of narrow-bandgap perovskite films with identical procedures used for the single-junction devices. We found that the thickness of the Pb–Sn narrow-bandgap perovskite film was slightly thinner than that of the film in the single-junction device even though we used identical process and precursor solution. Finally, 20-nm C60, 7-nm BCP and 100-nm Cu films were sequentially deposited by thermal evaporation at the rates of 0.2, 0.2 and 1.0 Å s–1, respectively.

**Characterization of single-junction narrow-bandgap solar cells.** The *J–V* characteristics were measured using a Keithley 2400 sourcemeter under the illumination of the solar simulator (EnliTech, Class AAA) at a light intensity of 100 mW cm−2 as checked with a calibrated reference solar cell (NREL) with a quartz window (a KG-5 reference cell was used for the measurements of the wide-bandgap solar cell). Unless otherwise stated, the *J*–*V* curves were all measured in a nitrogen-filled glovebox with a scanning rate of 100 mVs−1 (with a voltage step of 10 mV and a delay time of 100 ms). The steady-state PCE, PCE(*t*), was measured by setting the bias voltage to the *V*MPP and then tracing the current density, where the *V*MPP at MPP was determined from the *J–V* curve. The active

area was determined by the aperture shade mask (0.073 cm2) placed in front of the

solar cell to avoid overestimation of the photocurrent density. An aperture mask with a smaller open area (0.049 cm2) was used for the measurements at Newport or SIMIT to avoid misalignment between the cell and the mask; however, this underestimated the measured open-circuit voltages. EQE measurements were performed in ambient air without encapsulation using a QE system (EnliTech) with monochromatic light focused on the device pixel and a chopper frequency of 20 Hz. The reference cell used for the calibration of EQE measurements was calibrated by NREL.

**Characterization of tandem solar cells.** The *J–V* characteristics were measured with a dual-lamp (xenon and halogen) class AAA solar simulator (Yamashita Denso, YSS-T155-2M). The two lamps (xenon and halogen) were finely tuned to ensure that spectra mismatch was within 3% over 400–500, 500–600, 600–700, 700–800 and 800–900 nm wavelength ranges (Supplementary Fig. 28). The solar simulator was set at a light intensity of 100 mWcm−2 as checked with a calibrated crystalline silicon reference solar cell with a quartz window. EQE measurements were performed in ambient air with bias voltages of 1.1 and 0.7 V for front and back subcells, respectively. We noticed that there was no obvious difference for the EQE measurements with or without bias voltages. The bias illumination from highly-bright light-emitting diodes (LEDs) with emission peaks of 850 and 460 nm were used for the measurements of the front subcells and back subcells,

respectively. The operational stability tests were carried out under full AM1.5G illumination (xenon lamp solar simulator, 100 mWcm−2) in a glovebox by fixing the voltage at *V*MPP and then tracking the current output. The solar cells were not encapsulated and no ultraviolet filter was applied. The solar cell temperature increased to ~32 °C during the long-time MPP tests as no passive cooling was implemented. The illumination intensity was regularly calibrated to compensate for the gradual degradation of the xenon lamp. The dark long-term stability assessments of solar cells (without encapsulation) were carried out by repeating the *J*–*V* characterizations over various times and the devices were stored in a N2 glovebox.

**Femtosecond and nanosecond OPTP spectroscopy.** For femtosecond OPTP spectroscopy, a commercial titanium–sapphire amplified laser (Libra, Coherent) with a pulse duration of 90 fs, centre wavelength of 800 nm and repetition rate of 1 kHz was used to generate THz radiation via optical rectification in a 0.5-mm-

thick ZnTe(110) nonlinear single crystal and detect it using free space electro-optic sampling in a 0.5-mm-thick ZnTe(110) crystal. Perovskite thin films deposited

on z-cut quartz substrates were photoexcited at 800 nm with fluences in the range 1.5–50 μJ cm−2. The change in THz amplitude was monitored as a function of the time delay between the 800-nm optical-pump pulse and THz probe pulse using

a translation stage. For nanosecond OPTP spectroscopy, we used a frequency- doubled subnanosecond laser (Picolo AOT MOPA, InnoLas) with a pulse duration of ~0.8 ns to excite the samples at 532 nm. The laser was synchronized to the THz probe pulse with an electronic delay generator (SRS DG645, Stanford Research System). All measurements were carried out in a nitrogen-purged environment to avoid potential degradation of perovskite films in ambient air.

As the excitation fluence increased, the OPTP transients exhibited accelerated decay dynamics at higher initial photoinjected charge-carrier densities due to enhanced contributions from bimolecular recombination and Auger recombination. We extracted the rate constants associated with different recombination mechanisms by global fits to these transients according to the following rate equation37:

dn t

ð Þ ¼ �k n3 2

dt 3 � k2n � k1n

The femtosecond OPTP transients did not exhibit obvious decay dynamics at low excitation density, which makes it difficult to extract an accurate rate constant *k*1. To extract *k*1 as well as charge-carrier lifetime, we then performed nanosecond OPTP spectroscopy by changing the photoexcitation source while keeping the sample inside the measurement chamber. The samples were photoexcited at a

low fluence to reduce the effects of bimolecular and Auger recombination. The nanosecond OPTP transients were fitted with a monoexponential decay function. A carrier density of 1015 cm−3 (1-sun condition) was used as being representative of typical operating conditions for a solar cell.

**Space-charge-limited current.** The hole-only or electron-only devices were fabricated to obtain the density of hole traps or electron traps using the following architectures: ITO/PEDOT:PSS/perovskite/PTAA/Au for holes, where the PTAA layer was doped with 5 wt% 4-isopropyl-4'-methyldiphenyliodoniumtetrakis (pentafluorophenyl)borate43, and ITO/TiO2-Cl/PCBM/perovskite/C60/BCP/Cu for electrons, where PCBM is [6,6]-phenyl C61 butyric acid methyl ester. Measurements were carried out in a glovebox using a Keithley 2400 sourcemeter. The applied voltages started from 0 V and rose to 5 V with an interval of 0.01 V and a delay

time of 100 ms. The trap density *N*trap is determined by the equation *V*TFL= *qN*trap*L*2/ (2*ɛɛ*0), where *V*TFL is thte trap-filled limit voltage, *L* is the thickness of perovskite film, *ɛ* is the relative dielectric constant of perovskite (32 for all samples) and *ɛ*0 is the vacuum permittivity.

**Other characterizations.** SEM images were obtained using a TESCAN microscope with an accelerating voltage of 2 kV. X-ray diffraction patterns were collected

using a Rigaku MiniFlex 600 diffractometer equipped with a NaI scintillation counter and using monochromatized Cu Kα radiation (wavelength *λ* = 1.5406 Å). XPS analysis was carried out using a Thermo Scientific Al K-Alpha XPS system with energy steps of 0.1 eV. Optical absorption measurements were carried

out in a Lambda 950 ultraviolet/visible spectrophotometer (Perkin Elmer). Photoluminescence was measured using a FLS980 fluorescence spectrometer (Edinburgh Instruments) equipped with time-correlated single-photon-counting system. The light was illuminated from the perovskite film side and the excitation wavelength was 405 nm. Transient photovoltage decays were measured on a home- made system. A 540-nm green LED was used to modulate the *V*oc with a constant light bias and the repetition rate was set to 2,000 Hz. A white LED was focused on the active area of the solar cell under study for the constant light bias. The intensity of the pulsed illumination was set in a way that the modulated *V*oc was ~10 mV

to ensure a perturbation regime. The open-circuit voltage transient, induced by

the light perturbation, was measured with a digital oscilloscope set to an input impedance of 1 MΩ. The charge-recombination lifetime was fitted by a single exponential decay. The Mott–Schottky plot measurements were performed on a CHI660 electrochemical workstation (CH Instrument Inc.) at a frequency of 1 kHz from −0.8 to 0.8 V with a voltage step of 10 mV.

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**PV certification at SIMIT (Shanghai, China).** The PV certification tests were performed by the Test and Calibration Centre of the New Energy Device

and Module, SIMIT, Chinese Academy of Sciences, which is accredited by China National Accreditation Service for Conformity Assessment (CNAS) to ISO/IEC 17025 and by the International Laboratory Accreditation Cooperation (ILAC) Mutual Recognition Arrangement. CNAS was the accreditation body member of the International Accreditation Forum and ILAC, and is also a member

ofthe Asia Pacific Laboratory Accreditation Cooperation and Pacific Accreditation Cooperation.

The *J-V* characteristics were measured using a steady-state class AAA dual-lamp (xenon and halogen) super solar simulator under standard test conditions according to IEC 60904-1:2006. The *J*–*V* curves were measured in forward and reverse scans with a scanning speed of 50 mVs−1. A World PV Scale (WPVS) silicon reference solar cell calibrated by NREL was used to

set the irradiance at 100 mWcm−2. The spectral mismatch was calculated and mismatch correction was performed according to IEC 60904-7:2008. The spectral irradiance of the solar simulator was measured by a calibrated spectroradiometer (Opto Research Corporation), and the EQE of the device under test was measured with a three-grating monochromator spectral response measurement system.

The measurements of tandem solar cells were performed according to IEC 60904-1-1 for *J*–*V* measurements and to IEC 60904-8-1 for EQE measurements. The full-spectral mismatch factor of the solar simulator for our tandem solar cells was 1.00 ± 0.01, representing an excellent spectrum matching with AM1.5G.

**Reporting summary.** Further information on research design is available in the Nature Research Reporting Summary linked to this article.

## Data availability

All data that support the findings in this study are present in the paper and the Supplementary Information. Additional data related to this study are available from the corresponding authors upon reasonable request.

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## Author contributions

H.T. conceived the idea and directed the overall project. R.L., K.X., C.Z., J.Z., E.H.S. and

H.T. designed the experiments. R.L. and K.X. fabricated all the devices and conducted the characterization. Z.Q., C.Z. and M.X. carried out the THz measurements and corresponding data analysis. Q.H., M.W., M.I.S. and Y.G. helped on the device fabrication and characterization. A.L. helped on ALD processing. J.X. helped on ultraviolet–visible– near-infrared spectroscopy measurements. H.T. and E.H.S. wrote the manuscript, and all authors read and commented on the manuscript.

## Competing interests

The authors declare no competing interests.

## Additional information

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