

# Low-bandgap Sn–Pb perovskite solar cells

Rui He<sup>1</sup>, Chuantian Zuo<sup>2</sup>, Shengqiang Ren<sup>1, †</sup>, Dewei Zhao<sup>1, †</sup>, and Liming Ding<sup>2, †</sup>

<sup>1</sup>College of Materials Science and Engineering, Engineering Research Center of Alternative Energy Materials & Devices (MoE), Sichuan University, Chengdu 610065, China

<sup>2</sup>Center for Excellence in Nanoscience (CAS), Key Laboratory of Nanosystem and Hierarchical Fabrication (CAS), National Center for Nanoscience and Technology, Beijing 100190, China

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Record power conversion efficiency (PCE) for organic–inorganic halide perovskite solar cells (PSCs) has been rapidly boosted from 3.8% to 25.5%, approaching the Shockley–Queisser (S–Q) limit for single-junction solar cells<sup>[1–3]</sup>. Multi-junction tandem solar cells provide a feasible approach to break the efficiency limit for single-junction solar cells by maximizing the use of the solar spectrum and photon energy. All-perovskite tandem solar cells have the advantages of tunable bandgaps, solution processability, and flexibility<sup>[4–6]</sup>. As long-wavelength-light absorbers, low-bandgap ( $E_g$ : ~1.1–1.3 eV) perovskites play a vital role in making efficient all-perovskite tandem solar cells<sup>[7, 8]</sup>. Generally, low- $E_g$  perovskites are prepared by partially substituting lead ( $\text{Pb}^{2+}$ ) with tin ( $\text{Sn}^{2+}$ )<sup>[9]</sup>. However, mixed Sn–Pb perovskites usually suffer from short carrier lifetimes, high defect density, and easy oxidation of  $\text{Sn}^{2+}$ <sup>[10]</sup>.

To obtain high-quality Sn–Pb perovskite films and efficient low- $E_g$  PSCs, many efforts have been devoted in the past years. Zhao *et al.* demonstrated an enhanced carrier lifetime up to ~250 ns in  $(\text{FASnI}_3)_{0.6}(\text{MAPbI}_3)_{0.4}$  (FA = formamidinium, MA = methylammonium) perovskite film with a bandgap of 1.25 eV by regulating its growth process. Improved crystallinity and enlarged grain size were obtained. The corresponding solar cells gave a certified PCE of ~17%<sup>[11]</sup>. They further reduced the defects, suppressed the trap-assisted recombination, decreased the dark saturation-current density in thicker Sn–Pb perovskite films *via* chlorine or bromine doping, enhancing the PCEs to 18.1% and ~19%, respectively<sup>[12, 13]</sup>. This enables making two-terminal (2-T) tandem solar cells with a PCE of 21%. In early 2019, Zhu *et al.* got a PCE of 20.5% for single-junction low- $E_g$  PSCs by incorporating guanidinium thiocyanate (GuaSCN) into perovskite<sup>[8]</sup>. GuaSCN greatly prolongs carrier lifetime to 1232 ns, which is almost ten times longer than that of the control one, resulting from reduced defect density in perovskite films. Tan group improved the efficiency of low- $E_g$  PSCs to 21.1% by adopting Sn powders to enable a comproportionation reaction of Sn and  $\text{Sn}^{4+}$  and thus suppress the oxidation of  $\text{Sn}^{2+}$ <sup>[14]</sup>, delivering high-quality low- $E_g$  perovskite films with long charge carrier diffusion length (~3  $\mu\text{m}$ ) and less defects.

Tan *et al.* used a surface-anchoring zwitterionic antioxidant, formamidine sulfonic acid (FSA), to reduce  $\text{Sn}^{4+}$  back to  $\text{Sn}^{2+}$  and meanwhile passivate both electron-donating and

electron-accepting defects on the grain surfaces (Fig. 1(a))<sup>[15]</sup>. They proposed that FSA can coordinate with perovskite precursor *via* dative bonding, resulting in delayed and more uniform crystallization due to the less volatile nature of FSA compared with DMSO. X-ray photoelectron spectroscopy (XPS) results indicated that  $\text{Sn}^{4+}$  was reduced significantly. The enhanced photoluminescence (PL) intensity and prolonged carrier lifetime indicated decreased defect density. More importantly, the PL imaging for the films (Figs. 1(b) and 1(c)) suggests that FSA significantly improved the uniformity of perovskite film. FSA-based PSCs gave PCEs of 21.7% and 18.8% for aperture areas of 0.049 and 1.05  $\text{cm}^2$ , respectively.

Though the efficiency of low- $E_g$  Sn–Pb PSCs has been greatly improved, the relatively poor stability originating from volatile  $\text{MA}^+$  inhibits the development of low- $E_g$  PSCs and their application in all-perovskite tandem solar cells. Li *et al.* designed a two-step bilayer interdiffusion growth method to reduce MA proportion in  $\text{FA}_{0.85}\text{MA}_{0.1}\text{Cs}_{0.05}\text{Sn}_{0.5}\text{Pb}_{0.5}\text{I}_3$  perovskite film<sup>[16]</sup>. Methylammonium thiocyanate (MASCN) was added into  $\text{SnI}_2/\text{PbI}_2$  precursor, followed by spin-coating on PEDOT:PSS substrates, and then FAI solution in isopropanol (IPA) was spin-coated (Fig. 2(a)). This two-step process could prolong the ion interdiffusion stage and slow down the crystallization. Moreover,  $\text{Sn}^{2+}$  oxidation was suppressed, which benefits from the strong bonding between  $\text{SCN}^-$  and  $\text{Sn}^{2+}$ . The temperature-programmed desorption mass spectrometry (TPD-MS) results suggested that  $\text{FA}_{0.85}\text{MA}_{0.1}\text{Cs}_{0.05}\text{Sn}_{0.5}\text{Pb}_{0.5}\text{I}_3$  has better thermal stability than one-step-processed  $(\text{FASnI}_3)_{0.6}(\text{MAPbI}_3)_{0.4}$  perovskite, which could be due to reduced MA content.

Time-of-flight secondary ion mass spectroscopy (TOF-SIMS) reveals that volatile  $\text{MA}^+$  tends to accumulate at the film surface and evaporates under heating, leading to increased recombination center caused by  $\text{MA}^+$  and  $\text{I}^-$  vacancies and deterioration of device performance. Hence, they proposed a strategy to passivate the surface and grain boundaries by introducing one-dimensional (1D)  $\text{PySn}_x\text{Pb}_{1-x}\text{I}_3$  perovskite on surface of mixed Sn–Pb perovskite film<sup>[16]</sup>. The photoluminescence (PL) was remarkably enhanced and the carrier lifetime was boosted from 670 to 1100 ns. Cross-sectional Kelvin probe force microscopy (KPFM) showed diminished electric-field difference at hole-transport layer (HTL)/perovskite interface and reinforced electric-field difference at perovskite/electron-transport layer (ETL) interface, further proving the surface passivation by  $\text{PySn}_x\text{Pb}_{1-x}\text{I}_3$  and improved junction quality. The PCE for 1.28 eV bandgap PSCs was improved to 20.4% with a high open-circuit voltage ( $V_{oc}$ ) of

Correspondence to: S Q Ren, [rensq@scu.edu.cn](mailto:rensq@scu.edu.cn); D W Zhao, [dewei.zhao@scu.edu.cn](mailto:dewei.zhao@scu.edu.cn); L M Ding, [ding@nanoctr.cn](mailto:ding@nanoctr.cn)

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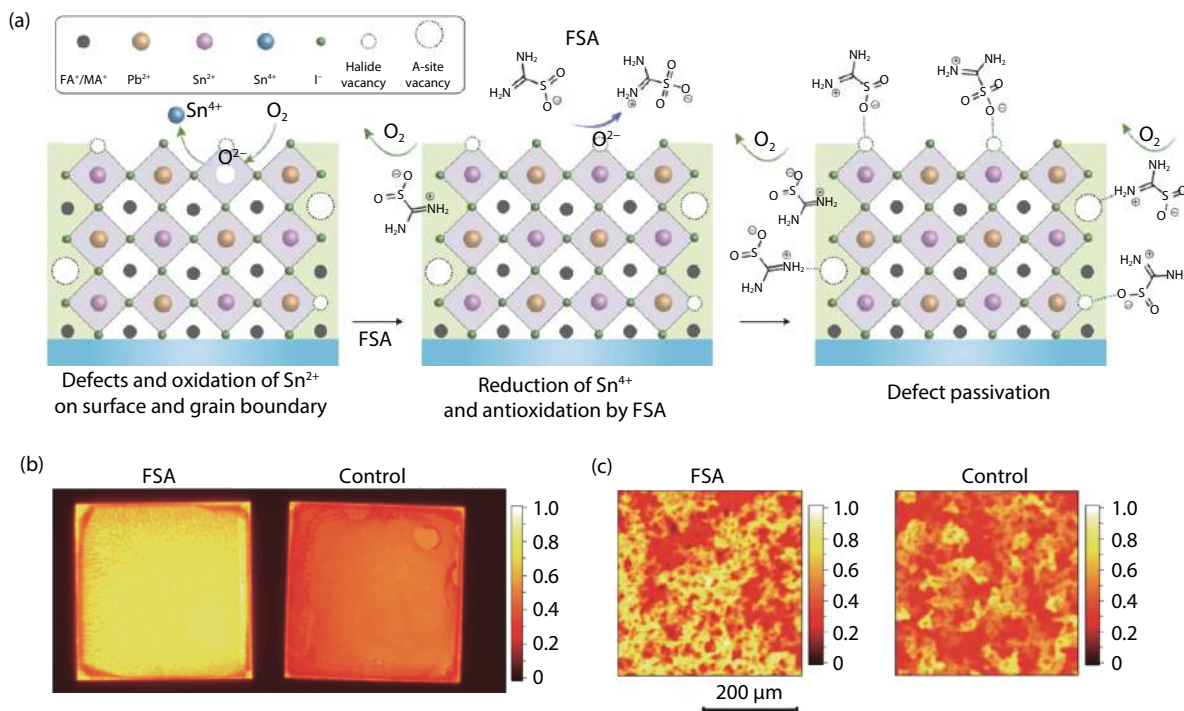


Fig. 1. (Color online) (a) Schematic illustration of antioxidantation and defect passivation by FSA at grain surfaces (including film surface and grain boundary) in mixed Pb–Sn perovskite films. A-site represents the site of monovalent cations. (b) PL imaging and (c) zoomed-in micro-PL mapping for the control and FSA-containing films on glass substrates (size  $2.5 \times 2.5 \text{ cm}^2$ ). The colour bars stand for the normalized PL intensity. Reproduced with permission<sup>[15]</sup>, Copyright 2020, Nature Publishing Group.

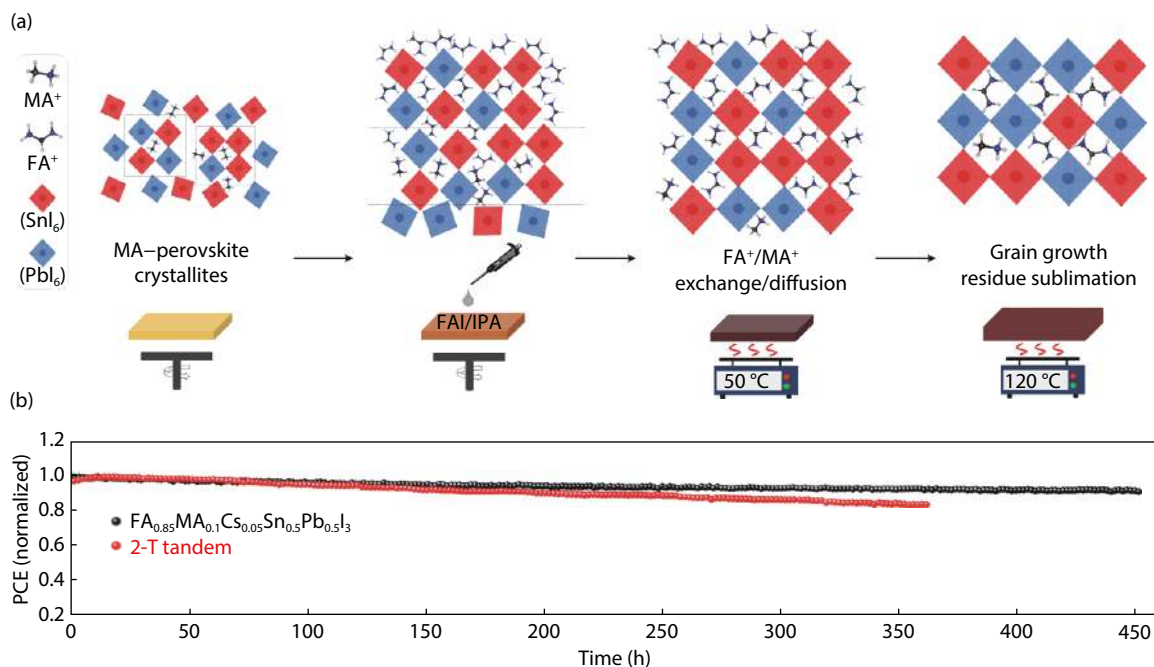


Fig. 2. (Color online) (a) Schematic illustration for the two-step bilayer interdiffusion growth process. (b) Maximum power point (MPP) tracking on a  $\text{FA}_{0.85}\text{MA}_{0.1}\text{Cs}_{0.05}\text{Sn}_{0.5}\text{Pb}_{0.5}\text{I}_3$  solar cell and a 2-T all-perovskite tandem solar cell with encapsulation measured in air under simulated AM 1.5G illumination. Reproduced with permission<sup>[16]</sup>, Copyright 2020, Nature Publishing Group.

0.865 V. An encapsulated cell remained 92% of its original PCE after maximum power point (MPP) tracking for 450 h under continuous one-sun illumination, showing good operational stability (Fig. 2(b)).

Additive engineering plays an important role in making high-quality low- $E_g$  perovskite films, but the underlying me-

chanisms are not fully understood yet. Herz *et al.* systematically investigated the effect of the commonly used  $\text{SnF}_2$  additive on the structure and optoelectronic properties of  $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Sn}_x\text{Pb}_{1-x}\text{I}_3$  ( $0 \leq x \leq 1$ ) perovskite films<sup>[17]</sup>. Detailed XRD characterizations on the films with different Sn:Pb ratios and  $\text{SnF}_2$  content indicated that  $\text{SnF}_2$  improved the quality of

mixed Sn–Pb perovskite films *via* preventing formation of Sn vacancies and associated lattice strain. Samples without SnF<sub>2</sub> exhibit significant tetragonal lattice distortion which can be greatly restrained by addition of SnF<sub>2</sub>. They also measured terahertz (THz) transmission spectra for the samples in dark to reveal the impact of Sn:Pb ratio and SnF<sub>2</sub> content. The background doping density caused by Sn oxidation in FA<sub>0.83</sub>CS<sub>0.17</sub>Sn<sub>x</sub>Pb<sub>1-x</sub>I<sub>3</sub> films was obtained by THz conductivity spectra and optical-pump-THz-probe (OPTP) measurements. The decrease in background hole doping density with the SnF<sub>2</sub> incorporation suggested that Sn oxidation was suppressed. Overall, the role of SnF<sub>2</sub> additive in mixed Sn–Pb perovskite films is reducing the background hole density *via* suppressing Sn<sup>2+</sup> oxidation, thus prolonging carrier lifetimes, mitigating energetic disorder, and improving carrier mobilities.

To further develop mixed Sn–Pb perovskite films and devices, attentions should be paid to following aspects: (1) Preventing the oxidation of Sn<sup>2+</sup> to Sn<sup>4+</sup>, which could result in short carrier lifetimes, short carrier diffusion lengths, and high defect density<sup>[14]</sup>. Better antioxidants and passivation materials are expected to eliminate the carrier recombination centers and make high-quality mixed Sn–Pb perovskite films<sup>[15]</sup>. (2) Slowing down the crystallization by regulating the preparation process or additives. Rapid crystallization generally results in small grains, leading to increased defects at grain boundaries or in grains, limiting device performance. (3) Improving the operational stability. Suppressing Sn<sup>2+</sup> oxidation and reducing MA<sup>+</sup> content are beneficial for stability enhancement. (4) Developing suitable techniques to make large-area Sn–Pb perovskite films and devices, and all-perovskite solar modules with a tandem structure<sup>[18]</sup>.

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**Rui He** is a PhD candidate under the supervision of Prof. Dewei Zhao in College of Materials Science and Engineering, Sichuan University. His research focuses on perovskite solar cells.



**Chuantian Zuo** received his PhD degree in 2018 from National Center for Nanoscience and Technology (CAS) under the supervision of Professor Liming Ding. Then he did postdoctoral research in CSIRO, Australia. Currently, he is an assistant professor in Liming Ding Group. His research focuses on innovative materials and devices.



**Shengqiang Ren** is a postdoc in College of Materials Science and Engineering, Sichuan University. He received his BS and PhD from Sichuan University in 2015 and 2019, respectively. His research focuses on optoelectronic materials and devices.



**Dewei Zhao** received his PhD from Nanyang Technological University, Singapore, in 2011. Since 2012, he worked as a postdoc at University of Michigan and University of Florida and as a research assistant professor in Prof. Yanfa Yan's group at University of Toledo. Currently, he is a professor at Sichuan University. His research focuses on organic/inorganic hybrid optoelectronic devices, such as thin-film solar cells, light-emitting diodes, and photodetectors.



**Liming Ding** got his PhD from University of Science and Technology of China (was a joint student at Changchun Institute of Applied Chemistry, CAS). He started his research on OSCs and PLEDs in Olle Inganäs Lab in 1998. Later on, he worked at National Center for Polymer Research, Wright-Patterson Air Force Base and Argonne National Lab (USA). He joined Konarka as a Senior Scientist in 2008. In 2010, he joined National Center for Nanoscience and Technology as a full professor. His research focuses on functional materials and devices. He is RSC Fellow, the nominator for Xplorer Prize, and the Associate Editors for Science Bulletin and Journal of Semiconductors.