

Renaissance of tin halide perovskite solar cells

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Halide perovskite solar cells (PSCs) have attracted wide interests in photovoltaics field due to the prominent advantages of perovskite materials. To date, the certified power conversion efficiency (PCE) of lead-based PSCs has reached to 25.5%^[1]. However, the toxicity of lead in PSCs limits the practical application. Tin (Sn)-based perovskites are the most promising candidates because of their narrow bandgap and comparable optoelectronic properties to lead analogues. The relatively narrower bandgap of Sn-perovskites possess expanded absorption of sunlight. The pioneering Sn-based PSCs based on MASnI₃ (MA = methylammonium) gave 5%–6% PCEs^[2]. Notably, the inferior device performance and stability restrict the explorations due to the facile oxidation of Sn²⁺ to Sn⁴⁺, fast crystallization, low formation energy of Sn vacancies and high level of self-doping^[3, 4]. Currently, efforts are devoted to the development of reducing reagents, manipulation of the perovskite dimensionality, and optimization of the interfacial energy level alignment of Sn-based PSCs. As summarized in Fig. 1(a), the PCE of Sn-based PSCs break double digits recently, indicating a renaissance of the Pb-free PSCs exploration. Here, the most recent advances of Sn-based PSCs are highlighted.

To probe the defect chemistry of Sn-perovskites, the lattice instability and electronic disorder act as triggers for unfavorable oxidation from Sn²⁺ to Sn⁴⁺^[5]. Besides, the calculation of defect formation energy (Figs. 1(b) and 1(c)) indicated that Sn²⁺ was only stable within the bandgap of bulk and Sn⁴⁺ defects usually located in the deep valence band (VB)^[6]. The oxidation to Sn⁴⁺ could be activated at the surface acting as a surface electron trap (Fig. 1(c)). Therefore, the Sn⁴⁺ elevates the defect concentration and exacerbates carrier recombination, leading to a deterioration of device performance, especially the open-circuit voltage (V_{oc}).

To suppress the oxidation of Sn²⁺, various reducing additives such as hypophosphorous acid^[7], Sn(0) powder^[8], and hydrazine vapor^[9] were utilized. Liu *et al.* introduced phenylhydrazine hydrochloride (PHCl) into FASnI₃ (FA = formamidinium) perovskite films to reduce the existing Sn⁴⁺ since PHCl has a reductive hydrazine group and a hydrophobic phenyl group^[10]. The resulting PSC gave a PCE of 11.4%. Meanwhile, the unencapsulated device showed almost no decay in a glovebox for over 110 days. Suppressed oxidation of Sn²⁺ could effectively inhibit the carrier recombination, leading to long carrier

lifetime and accessible V_{oc} . Wakamiya *et al.* used 1,4-bis(trimethylsilyl)-2,3,5,6-tetramethyl-1,4-dihydropyridazine (TM-DHP) to react with SnF₂ to form Sn(0) nanoparticles (Fig. 1(d))^[8]. The formed Sn(0) nanoparticles in the precursor solution could scavenge Sn⁴⁺, thus enabling strong photoluminescence and prolonged decay of the deposited perovskite films. The PCE of resulting device increased to 11.5%, with a V_{oc} of 0.76 V. Most recently, Liu *et al.* introduced phenylhydrazine cation (PhNHNH₃⁺) to improve the illumination stability of FASnI₃^[11]. Therefore, the use of efficacious reducing additives gifts the Sn-PSCs with high performance and stability.

Particularly, the relatively fast crystallization of Sn-perovskite films with unfavorable defects and rough morphology poses a great challenge for achieving high PCE and stability for Sn-based PSCs. In this regard, Han *et al.* precisely controlled the crystallization process by reducing the surface energy with pentafluorophen-oxethylammonium iodide (FOEI)^[12]. This approach enabled highly oriented and smooth FASnI₃ films with lower defect density and longer carrier lifetime. The resulting PSCs offered a certified PCE of 10.16%. The crystallization process was further regulated with n-propylammonium iodide (PAI)^[14]. PAI could induce templated growth of FASnI₃ crystals by forming the intermediate phase (Fig. 1(e)), thus resulting in a highly crystallized FASnI₃ film with preferential orientation along (100) plane and reduced trap density. Finally, a stabilized PCE of 11.22% was achieved and the device kept over 95% of its initial efficiency after 1000 h operation at the maximum power point (MPP). These results indicate that the retarded grain growth promotes forming high-quality and oriented Sn-perovskite films.

Moreover, large organic cation (ethylenediammonium, EA⁺; phenylethylammonium, PEA⁺) were used to regulate the composition and structure of Sn-perovskites. The substitution of A-site cations with ethylenediammonium and guanidinium cations was proved to cause lattice strain relaxation of Sn-perovskites^[15, 16]. Hayase *et al.* reported the correlation between lattice strain relaxation and the PCE of Sn-based PSCs. Substituting the A-site cations with smaller cations could reduce the lattice distortion, leading to improved carrier mobility and higher photovoltaic performance^[17]. Han *et al.* also did mixed-cation engineering to stabilize the perovskite phase in a tin triplehalide amorphous layer with CsFASnI₃ polycrystals^[18]. This special structure could block the moisture, oxygen and ion diffusion in the devices. A certified PCE over 10% was achieved and over 95% of the initial PCE was retained after working at MPP for 1000 h. Hayase *et al.* incorporated large EA⁺ cation into MASnI₃ abiding by the Goldschmidt tolerance factor to make vertically-oriented 2D/3D mixed perovskite films^[19]. The resulting PSCs gave a

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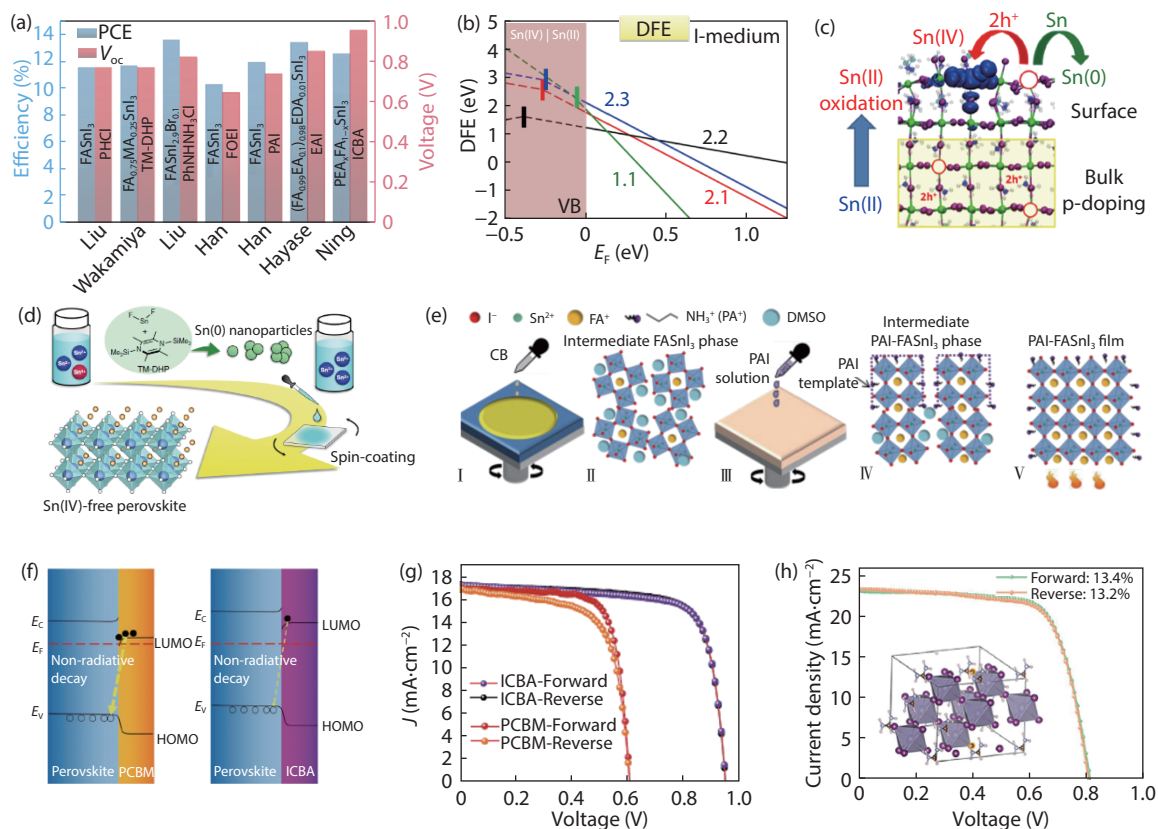


Fig. 1. (Color online) (a) Representative PCE and V_{oc} for Sn-based PSCs in 2020. Labels in the bar chart indicate perovskite components and additives (ICBA as ETL). (b) Defect formation energy diagram for bulk Sn(IV) defects in $MASn_3$ perovskites. (c) Schematic illustration of Sn^{2+} oxidation to Sn^{4+} . Bulk Sn^{4+} transforms to Sn^{2+} , releasing two holes to the valence band (VB) and p-doping the perovskite, while surface Sn^{4+} acts as a deep electron trap. Reproduced with permission^[6], Copyright 2020, American Chemical Society. (d) Schematic illustration of the Sn^{4+} -scavenging method with TM-DHP. Reproduced with permission^[8], Copyright 2020, Springer Nature. (e) Fabrication and crystallization of Sn-based films with PAI treatment. Reproduced with permission^[14], Copyright 2020, Royal Society of Chemistry. (f) The diagram for recombination at perovskite-ETL interface. (g) J - V curves for Sn-based devices with ICBA or $PC_{61}BM$ as ETL. Reproduced with permission^[13], Copyright 2020, Springer Nature. (h) J - V curves for Sn-based devices with $PhNH_3Cl$ treatment. Reproduced with permission^[11], Copyright 2020, Elsevier.

PCE of 9.24% and 95% of the initial efficiency was retained after being kept in a glovebox for 30 days without encapsulation.

Regarding the bandgap (1.35 eV) of Sn-based perovskites, reducing the voltage loss is a key challenge for getting high PCE for Sn-based PSCs. Good energy level alignment at interface affords effective electron extraction from perovskites to the electron-transport layer (ETL). Ning *et al.* introduced ICBA (indene- C_{60}) as ETL to replace $PC_{61}BM$ ([6,6]-phenyl- C_{61} -butyric acid methyl ester) and improved V_{oc} to 0.94 V (Figs. 1(f) and 1(g))^[13]. The shallower lowest unoccupied molecular orbital (LUMO) energy level of ICBA brought this V_{oc} gain. Meanwhile, suppressing the interfacial carrier recombination between Sn-based perovskites and ETL can increase V_{oc} . Interestingly, the surface Fermi level of Sn-based perovskites with EAI shifted to shallower value, thus effectively passivating Sn^{4+} traps/defects^[20, 21]. Liu *et al.* slightly substituted I^- with Br^- to form $FASn_{1.9}Br_{0.1}$ to realize better energy level alignment with C_{60} ^[11]. Br^- doping results in a larger lattice shrinkage and a slight increase of bandgap, in comparison to pure iodide perovskite^[11]. Owing to the strong s - p and p - p couplings^[22], the VB shifted downwards realizing an optimal energy level alignment between Sn-perovskites and ETL. The resulting device gave a PCE of 13.4% (certified

12.4%) with long-term durability, also setting a new PCE record for Sn-based PSCs (Fig. 1(h)).

In summary, the advances and recent renaissance of Sn-based PSCs are highlighted. The urgent challenge is to improve V_{oc} . Adjusting the composition and structure of perovskites with large organic cations, reducing crystal defects and charge carrier recombination, and selecting suitable ETLs for good energy level alignment are very crucial in enhancing the performance of Sn-based PSCs.

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