RESEARCH HIGHLIGHTS

Organic ammonium halides enhance the performance of Pb–Sn perovskite solar cells

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With the efforts of scientists around the world, the power conversion efficiency (PCE) of perovskite solar cells (PSCs) has reached 25.7%. To further improve the efficiency and break through the Shockley-Queisser (S-Q) limit, it is promising to construct all-perovskite tandem solar cells *via* combining wide-bandgap and narrow-bandgap perovskites[1–5]. As the key light-harvesting material for the bottom cell in all-perovskite tandem devices, the narrow-bandgap Pb–Sn mixed perovskites have attracted increasing interest in recent years[6–8]. However, the Pb–Sn mixed perovskites suffer from uncontrollable crystallization, easy oxidation of Sn^{2+} and high defect density, which significantly limit PCE improvement[9, 10]. Organic ammonium halides can improve the efficiency and stability of Pb–Sn mixed PSCs.

Organic ammonium halides can be employed as additives to modulate the crystallization of Pb–Sn perovskite films, or passivate surface defects *via* post-treatment. Tong *et al.* found that the incorporation of guanidinium thiocyanate (GuaSCN) in $(FASnI_3)_{0.6}(MAPbI_3)_{0.4}$ perovskite film can significantly improve the optoelectronic properties[11]. SCN^- can increase grain size and improve film morphology, while Gua^+ can participate in constructing 2D phases at grain boundaries to prevent Sn vacancy diffusion and protect the film from oxygen erosion. The optimized film offered a prolonged carrier lifetime (>1 μs) (Fig. 1(a)), yielding PCEs of 20.5%, 25% and 23.1% for single-junction solar cell, four-terminal (4-T) and two-terminal (2-T) tandem devices, respectively. Similarly, Zhou *et al.* added 12% guanidinium bromide (GABr) into $FA_{0.7}MA_{0.3}Pb_{0.7}Sn_{0.3}I_3$ perovskite film with a bandgap of 1.34 eV[12]. They found that GABr can effectively reduce the defect density and facilitate charge transport. Consequently, GABr-modified Pb–Sn PSCs gave a PCE of 20.63% with enhanced environmental and thermal stability. To achieve vertically aligned crystals, Li *et al.* introduced 2-(4-fluorophenyl)ethylammonium iodide (FPEAI) into $(MAPbI_3)_{0.75}(FASnI_3)_{0.25}$ to form 2D/3D structure to induce oriented growth[13]. FPEAI-based perovskite film presented (110)-preferred orientation (Fig. 1(b)), which is beneficial for effective charge transport and extraction. Meanwhile, the 2D/3D structure can suppress Pb–Sn phase segregation. As a result, the 2D/3D hybrid Pb–Sn PSCs delivered a PCE of 17.51% with superior stability. Compared

with Ruddlesden-Popper (R-P) 2D phases formed by monovalent organic cations, the interlayer distance of Dion-Jacobson (D-J) 2D phases achieved by divalent organic cations is much shorter, and D-J 2D phase is less resistant to charge transfer[14]. Ke *et al.* developed a D-J 2D structure using a divalent 3-(aminomethyl)piperidinium (3AMP) spacer for $MA_{0.5}FA_{0.5}Pb_{0.5}Sn_{0.5}I_3$ perovskite films, affording a longer carrier lifetime of 657.7 ns and a PCE of 20.09% with an open-circuit voltage (V_{oc}) of 0.88 V[15]. To avoid excess formation of 2D phases which could block charge transfer, Wei *et al.* dexterously designed an ultrathin 2D layer capping Pb–Sn perovskite film surface[16]. Ethyl acetate (EA) with 0.5 mg/mL phenethylammonium iodide (PEAI) was applied as anti-solvent in film preparation. This approach not only passivated surface defects, but also avoided excess formation of 2D phases, yielding PCEs of 19.4% and 23.7% for single-junction and 2-T tandem solar cells, respectively. Low-dimensional structure treatment by using organic ammonium halides has been widely used to improve the performance of PSCs. However, most post-treatment results in the formation of one layer (1L) 2D structure on film surface, which could severely impede charge extraction. Ning *et al.* designed a new molecule 2-thiopheneethylamine thiocyanate (TEASCN) to construct bilayer (2L) quasi-2D structure that allowed effective charge transfer[17]. For comparison, 2-thiopheneethylamine iodide (TEAI) was also used for surface treatment. Interestingly, though both TEAI and TEASCN treatment formed 1L structure during spin-coating process, the 1L structure of TEASCN film transformed to 2L structure after annealing process, while 1L structure of TEAI film remained on the surface (Figs. 1(c) and 1(d)). The density functional theory (DFT) calculation revealed that the formation energy from $TEA_2SnI_2SCN_2$ to $TEA_2FASn_2I_5SCN_2$ is close to zero, suggesting the easy transformation from 1L to 2L, which explains the formation of the 2L structure. The 2L structure on the surface can not only ensure effective charge transfer, but also improve thermal stability of Pb–Sn perovskite films. TEASCN-treated Pb–Sn PSCs offered a PCE of 21.1%.

Besides forming 2D structures, organic ammonium halides are also effective passivators. Lee *et al.* introduced butylammonium (BA) halide (2%) into $FA_{0.83}Cs_{0.17}Pb_{0.5}Sn_{0.5}I_3$ precursor, and they found that BA cations allow self-aggregation on the surface and at the bottom of perovskite films[18]. The BA cations on the film surface can suppress the diffusion of Ag into perovskite film, while BA cations at the buried inter-
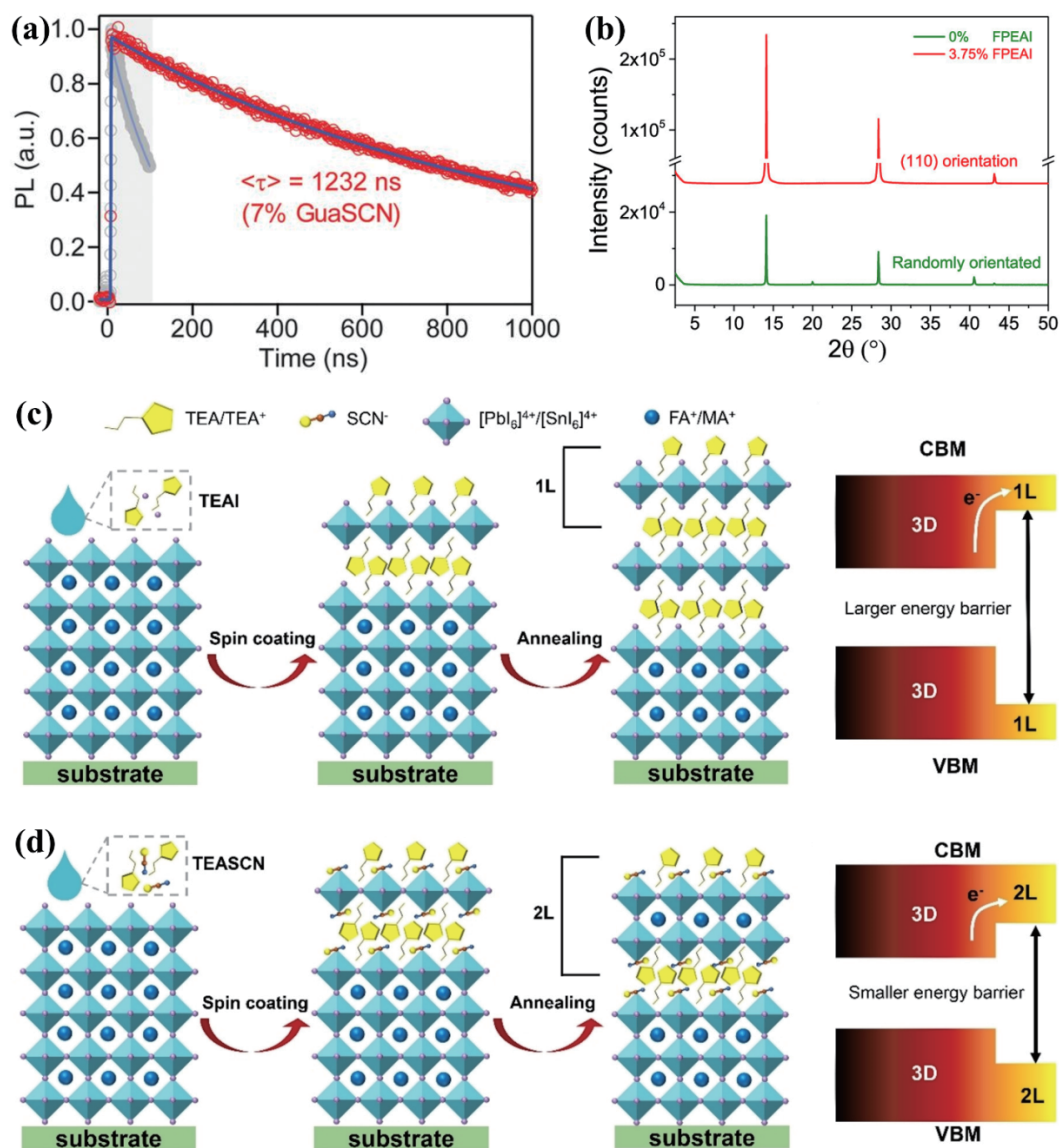
Fig. 1. (Color online) (a) Time-resolved photoluminescence of GuaSCN-based perovskite film. Reproduced with permission[11], Copyright 2019, Science Publishing Group. (b) X-ray diffraction patterns for the perovskite films with and without FPEAI. Reproduced with permission[13], Copyright 2020, American Chemical Society. Schematics for perovskite films treated with (c) TEAI and (d) TEASCN, and the corresponding energy level diagrams. Reproduced with permission[17], Copyright 2022, Wiley-VCH.

face can suppress the perovskite degradation induced by sulfonic acid groups in PEDOT:PSS. Most importantly, BA cations can induce a more phase-pure perovskite film with (100)-preferred orientation, reducing the trap states. With these merits, BA-based $FA_{0.83}Cs_{0.17}Pb_{0.5}Sn_{0.5}I_3$ solar cells gave a PCE of 18.66%. Liang *et al.* proposed a selective targeting anchor (STA) strategy *via* jointly employing PEAI and ethylenediamine diiodide ($EDAI_2$) to passivate surface defects of Pb–Sn perovskite films[19]. Combining DFT calculations and optoelectronic techniques, they demonstrated that PEA^+ and EDA^{2+} cations can selectively anchor $[PbI_6]^{4-}$ and $[SnI_6]^{4-}$ octahedron, respectively, through filling A-site vacancies (Fig. 2(a)). The STA strategy yielded a champion PCE of 22.51%, and the cells can retain 80% of the initial PCE after being stored in N_2 glovebox for 2700 h. Hu *et al.* modified the bottom surface of $Cs_{0.1}FA_{0.6}MA_{0.3}$- $Pb_{0.5}Sn_{0.5}I_3$ film *via* adding glycine hydrochloride (GlyHCl) into the perovskite precursor, and $GlyH^+$ cations can self-assemble at the bottom surface to passivate trap states[20]. They further passivated the surface defects by us-

ing $EDAI_2$. $GlyH^+$ and EDA^{2+} cations can form interface dipoles to facilitate charge extraction. A PCE of 23.6% was obtained, which is the record for Pb–Sn PSCs. In our previous work, we introduced a trace amount of propanediamine diiodide ($PDAI_2$) into $FA_{0.7}MA_{0.3}Pb_{0.5}Sn_{0.5}I_3$ precursor to induce oriented crystal growth[21]. PDA cations can anchor onto the nuclei to induce (100)-preferred orientation through strong interactions between PDA cations and $[PbI_6]^{4-}$ and $[SnI_6]^{4-}$ octahedron. Then, the nuclei would act as a surface template to modulate the crystal growth along (100) orientation, and PDA cations kept on the crystal surface (Fig. 2(b)). The DFT calculations and experimental characterizations confirmed that the (100)-oriented perovskite crystals have reduced trap states and higher carrier mobilities. Consequently, the PCE for PDA-based solar cells was improved from 16.62% to 20.03%. Owing to the relatively low light absorption coefficient, highly efficient Pb–Sn PSCs require thick (~1 μm) perovskite films. However, the short carrier diffusion lengths caused by severe trap states limit the carrier transport in thick Pb–Sn per-
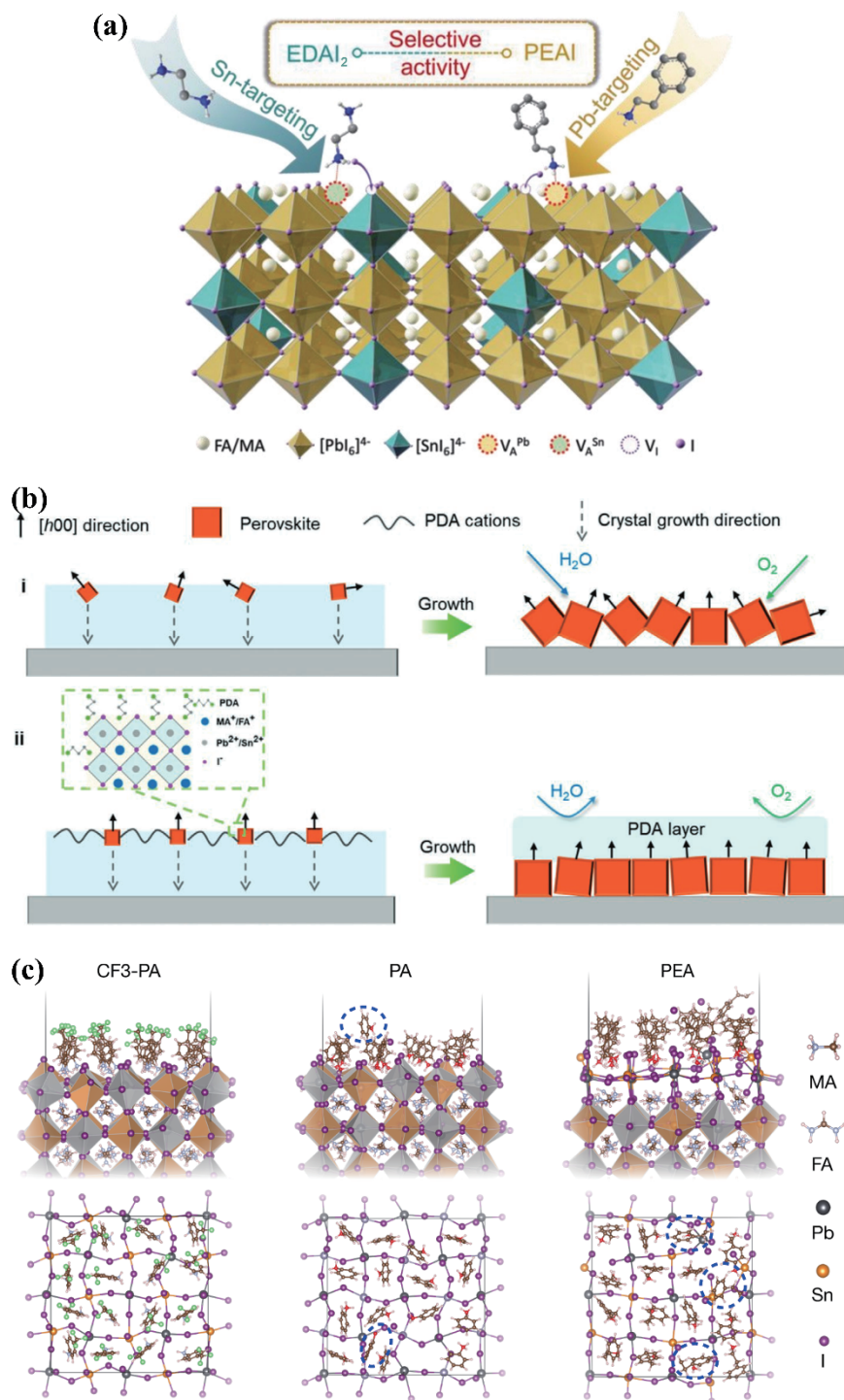
Fig. 2. (Color online) (a) Schematic for the selective targeting anchor strategy by using EDAI$_2$ and PEAI. Reproduced with permission[19], Copyright 2022, Wiley-VCH. (b) Schematic for the crystal growth without and with PDA cations. Reproduced with permission[21], Copyright 2022, Wiley-VCH. (c) Molecular dynamics snapshots and top views for perovskite surfaces anchored with CF3-PA, PA and PEA, respectively. Reproduced with permission[22], Copyright 2022, Nature Publishing Group.

ovskite films. Tan *et al.* developed a ~1.2 μm thick Pb–Sn perovskite film with long diffusion length exceeding 5 μm[22]. PEA, phenylammonium (PA) and 4-trifluoromethyl-phenylammonium (CF3-PA) cations were employed as passivators in the precursor solution. DFT calculations revealed that electrostatic potentials at the -NH$_3^+$ terminal of the three cations are different: PEA < PA < CF3-PA. High electrostatic potential is beneficial for molecules anchoring onto perovskite crystals. During the annealing process of perovskite films, CF3-PA cations showed the strongest tendency to anchor on the crystal sur-

face *via* filling A-site vacancies (Fig. 2(c)). Meanwhile, the strong interaction between CF3-PA and perovskite can also suppress the formation of iodine vacancies, I$_{Sn}$ and I$_{Pb}$ antisite defects. The significantly reduced trap states contributed to enhanced carrier lifetimes and diffusion lengths, yielding a PCE of 22.2% for single-junction solar cells and a PCE of 26.4% for tandem cells.

In short, organic ammonium halides can modulate crystal growth, passivate trap sites and modify interfaces of Pb–Sn mixed perovskite films to enhance the device perform-

ance. Rational molecular design of organic ammonium halides can help to develop efficient Pb–Sn mixed PSCs, applicable in all-perovskite tandem solar cells.

Acknowledgements

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