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RESEARCH HIGHLIGHTS

Compositional engineering for lead halide perovskite solar cells

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Since metal halide perovskites were utilized as visible-light-harvesting materials for solar cells in 2009, power conversion efficiencies (PCEs) for metal halide perovskite solar cells (PSCs) have already reached to a certified value of 25.7%, making PSCs to be a promising next-generation photovoltaic technology[1–5]. Compositional engineering of perovskite materials is an effective approach for achieving highly efficient and stable PSCs[6–8]. Typical perovskite materials have a general formula ABX_3, where A is a monovalent cation, B a divalent metal cation and X a halogen anion. The radii of each component in perovskite material *via* Goldschmidt tolerance factor (t) determine the crystallographic stability and the formation of the 3D crystal structure[9]. Therefore, cation and anion with different size like Cs, methylammonium (MA), formamidinium (FA), I, Br, and Cl can be adopted to construct perovskite crystals, resulting in bandgap variation. In 2009, MA-based perovskites were first used as sensitizers in liquid-state solar cells, producing a PCE of 3.81% with extremely poor stability (Table 1)[1]. Kim *et al.* used $MAPbI_3$ in solid-state mesoporous solar cells, achieving dramatically improved performance (Table 1)[10, 11]. Since then, composition engineering based on $MAPbI_3$ has sprung up. In 2013, Seok *et al.* produced bandgap tunable $MAPbX_3$ solar cells *via* substituting I with Br[6]. Combined with solvent engineering, a substitution of 10–15 mol% I with Br in $MAPbI_3$ greatly improved the device stability in ambient atmosphere and a certified PCE of 16.2% was achieved for $MAPb(I_{1-x}Br_x)_3$ (x = 0.1–0.15) PSCs[12]. $MAPbI_{3-x}Cl_x$ perovskites exhibit much longer carrier diffusion length and the related PSCs gave PCEs >12% and >14% for mesoporous and planar structure, respectively[13, 14]. Cl can aid film crystallization to improve device performance and stability[15–17].

In order to further improve PCE and stability, FA and Cs were successively applied in composition engineering. The bandgap of $MAPbI_3$ is about 1.5 eV, which is far from Shockley-Queisser (S-Q) optimum[18, 19]. Substituting MA with a slightly larger monovalent cation FA could reduce the bandgap of perovskite to S-Q optimum. What's more, FA exhibits better thermal stability than the volatile MA cation[20]. However, the degradation of black-phase $FAPbI_3$ to yellow non-perovskite phase under ambient conditions restricts the development of $FAPbI_3$ PSCs. It was found that the incorporation of MA and Br ions into $FAPbI_3$ can effectively stabilize black-phase perovskite and enhance the crystallinity[21]. As a result, $FA_{1-x}MA_xPb(I_{1-y}Br_y)_3$ composition drew attention and dominated for a long time[22–24]. PCEs exceeding 22% was achieved in $FA_{1-x}MA_xPb(I_{1-y}Br_y)_3$ PSCs (Table 1), together with a long-term stability, especially the thermal stability[25]. In 2016, Saliba *et al.* introduced Cs into $FA_{1-x}MA_xPb(I_{1-y}Br_y)_3$ to further improve crystallinity of the perovskite film and the thermal stability of PSCs[26]. They found that Cs-containing PSCs could steadily work over hundreds of hours under continuous illumination. Since then, $FA_{0.95-x}MA_xCs_{0.05}Pb(I_{1-y}Br_y)_3$ composition has become one of the dominant recipes (Table 1)[27, 28]. Besides Cs, other alkali metals are used in composition engineering[29].

Though the introduction of MA and Br is beneficial for producing high-quality perovskite films, it induces a blue shift of absorption, limiting the further enhancement of J_{sc} and PCE. And Br can cause phase segregation under long-term illumination[30]. With the volatile nature of MA, introducing Br and MA into FA-based perovskite decreases the stability of PSCs[31]. Therefore, scientists continued focusing on $FAPbI_3$ and devoted great efforts to obtain MA- and Br-free pure α-phase $FAPbI_3$[32]. Adding methylammonium chloride (MACl) into $FAPbI_3$ precursor solution could overcome phase transformation of α-$FAPbI_3$[33]. MACl induces the growth of (001) plane of α-$FAPbI_3$ and increases the crystallinity. Seok *et al.* added methylenediammonium dichloride ($MDACl_2$) into $FAPbI_3$ to stabilize α-$FAPbI_3$ and achieved a J_{sc} of 26.7 mA/cm²[31]. More than 90% of the initial PCE was maintained after 600-h operation. Besides the phase transformation, anion-vacancy defects at grain boundaries and at $FAPbI_3$ film surface inhibit PCE improvement. Jeong *et al.* used pseudo-halide anion formate (HCOO−) to suppress anion-vacancy defects and to increase film crystallinity[34]. The resulting solar cells gave a PCE of 25.6% (certified 25.2%) (Table 1).

Though PCE has been greatly improved, the long-term stability of organic/inorganic hybrid perovskites cannot satisfy commercial requirements. To tackle this issue, all-inorganic $CsPbX_3$ and low-dimensional (LD) materials are tried. Without volatile organic components, all-inorganic $CsPbX_3$ cells exhibit excellent thermal stability and desired bandgaps for tandem solar cells[35]. Because of more easily formed defects and poor surface morphology, the PCE for all-inorganic PSCs is still inferior to inorganic–organic hybrid counterparts[36]. Similar to $FAPbI_3$, how to stabilize the black phase and passivate the defects of $CsPbX_3$ is very important for achieving high PCE[37]. By using a sequential dripping method and octylammonium iodide post-treatment, Seok *et al.* made uniform and pinhole-free $CsPbI_3$ film, and the cells gave a PCE of

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Table 1. Advances in composition engineering of lead halide perovskite solar cells.

Year	Composition of perovskites	Device structure	PCE (%)	Ref.
2009	$MAPbI_3$	FTO/TiO_2/perovskite/liquid electrolyte/Pt	3.81	[1]
2012	$MAPbI_3$	FTO/c-TiO_2/m-TiO_2/perovskite/Spiro-OMeTAD/Au	9.7	[10]
2012	$MAPbI_2Cl$	FTO/c-TiO_2/m-Al_2O_3/perovskite/Spiro-OMeTAD/Au	10.9	[11]
2017	$MA_{0.05}FA_{0.95}Pb(I_{0.95}Br_{0.05})_3$	FTO/c-TiO_2/m-TiO_2/perovskite/PTAA/Au	22.1	[25]
2020	$Cs_{0.05}(MA_{0.05}FA_{0.95})_{0.95}Pb(I_{0.95}Br_{0.05})_3$	ITO/PTAA/perovskite/PI/C_{60}/BCP/Ag	23.37	[27]
2021	$FAPbI_3$	FTO/c-TiO_2/m-TiO_2/perovskite/OAI/Spiro-OMeTAD/Au	25.6	[34]
2022	$CsPbI_3$	FTO/c-TiO_2/perovskite/PTAI/Spiro-OMeTAD/Au	21.0	[39]
2022	$(4F\text{-}PEA)_2FA_4Pb_5I_{16}$	ITO/PTAA/perovskite/$PC_{61}BM$/BCP/Ag	21.07	[43]

Note: c-TiO_2, compact TiO_2; m-TiO_2, mesoporous TiO_2; m-Al_2O_3, mesoporous Al_2O_3; PTAA, poly(triarylamine); OAI, octylammonium iodide; PI, piperazinium iodide; BCP, bathocuproine; PTAI, phenyltrimethylammonium iodide.

20.37%[38]. Most recently, Meng *et al.* reported a facile and effective defect passivation method for high-quality $CsPbI_3$ films and efficient devices[39]. They found that the in-situ grown phenyltrimethylammonium iodide (PTAI)-based LD perovskites (1D $PTAPbI_3$ and 2D PTA_2PbI_4) located at $CsPbI_3$ grain boundaries and the film surface, which can not only suppress non-radiative recombination but also stabilize black-phase $CsPbI_3$ to prevent moisture intrusion. As a result, the $CsPbI_3$ cells exhibited a record efficiency of 21.0% with high stability (Table 1). Owing to excellent stability in ambient environment and under operating conditions, 2D Ruddlesden–Popper (RP) perovskites with a formula of $A_2B_{n-1}Pb_nI_{3n+1}$ are recognized as another promising candidate for PSCs[40, 41]. Their performances are still lower than 3D counterparts. The lower PCE is mainly ascribed to quantum confinement effect, the enlarged bandgap and in-plane orientation of 2D RP perovskite with respect to the substrate[42]. Various approaches, including solvent, additives, and cations engineering have been proposed to make vertically directed 2D RP perovskite to improve device performance. Zhang *et al.* reported pure FA-based 2D PSCs with the assistance of MACl and $PbCl_2$ additives, which gave a record PCE of 21.07% (Table 1)[43].

In short, improving device stability while maintaining high PCE stays a hot topic in PSC field. Adjusting cations to enhance the performance of 2D or quasi-2D perovskite solar cells will be an interesting approach.

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