RESEARCH HIGHLIGHTS

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Stabilizing α-phase $FAPbI_3$ solar cells

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Organic–inorganic hybrid perovskite solar cells (PSCs) have been recognized as a promising and cost-effective photovoltaic technology with the power conversion efficiency (PCE) exceeding 25%[1–3]. The high efficiency is attributed to the exceptional optoelectronic properties, such as high absorption coefficient, long carrier diffusion length, low non-radiative recombination rate, and so on[4–7]. Compared to methylammonium lead triiodide ($MAPbI_3$) perovskite, formamidinium lead triiodide ($FAPbI_3$) perovskite exhibits better thermal and structural stability. Meanwhile, it has a narrower bandgap, which is close to the optimum bandgap for reaching Shockley-Queisser limit (Fig. 1(a))[8]. So, $FAPbI_3$ is an ideal candidate for highly efficient single-junction PSCs. However, the black photoactive α-$FAPbI_3$ formed at high temperature (~150 °C) can readily convert to photoinactive δ-$FAPbI_3$ under ambient conditions[9–11], which is fatal to device performance and stability. Therefore, various approaches have been proposed to overcome the phase transition. Here, we will discuss three strategies: chloride-based additives, pseudo-halide anion engineering and ionic liquid engineering.

Chloride-based additives play an important role in improving the phase stability and crystallinity. The pioneer work was reported by Ding's group in 2014. They applied ammonium chloride (NH_4Cl) as the additive in perovskite precursor solution to manipulate the film morphology. An 80.11% FF was obtained[12]. Wang *et al.* indicated that less volatile additives such as formamidinium chloride (FACl) and methylammonium chloride (MACl) in precursor solution can form an intermediate phase to prohibit the crystallization of δ-$FAPbI_3$, which then converts to α-$FAPbI_3$ through thermal annealing[13]. Mu *et al.* reported that MACl acts as a transitional "stabilizer" to preserve the crystal structure and form black-phase $FAPbI_3$[14]. Xie *et al.* proposed a new "vertical recrystallization" method by using MACl additive to make FA-based perovskite films with high crystallinity, yielding a PCE of 20.6%[15]. Qing *et al.* described the synergistic effects of DMSO and MACl in assisting perovskite crystallization, leading to smoother surface, higher crystallinity, and lower defect densities[16]. Kim *et al.* studied the function of MACl additive in the formation of α-phase $FAPbI_3$ *via* analyzing the photophysical properties and using density functional theory. By optimizing MACl content, they achieved a certified PCE of 23.48% (Fig. 1(b))[17]. Min *et al.* further stabilized α-$FAPbI_3$ by incorporating methylenediammonium dichloride ($MDACl_2$) into $FAPbI_3$ perovskite lattices, obtaining a certified PCE of 23.7%[18].

Pseudo halides can also improve perovskite crystallinity and phase stability, due to their similar properties as halides. Thiocyanate anion (SCN^-), one of the pseudo halide anions, has received attention during past few years[19]. Lu *et al.* used a methylammonium thiocyanate (MASCN) vapor-assisted treatment to convert δ-$FAPbI_3$ to pure α-$FAPbI_3$, which was carried out below the thermodynamic phase-transition temperature. Molecular dynamics (MD) simulations revealed that SCN^- can promote the formation and stabilization of α-$FAPbI_3$. The resulted PSCs presented excellent performance and long-term operational stability (Fig. 1(c))[11]. Jeong *et al.* indicated that formate ($HCOO^-$) can suppress anion-vacancy defects at grain boundaries and perovskite film surface. By using formate additive, α-$FAPbI_3$ PSCs offered a PCE of 25.6% (certified 25.2%)[3].

Ionic liquid engineering is also an effective approach to stabilize black α-$FAPbI_3$. DMF and DMSO are usually used in combination to retard perovskite crystallization, and the experiment was processed in an inert atmosphere with strict control of both temperature and humidity[20]. Hui *et al.* used ionic liquid methylamine formate (MAFa) to replace DMF:DMSO as solvent of PbI_2 in the two-step deposition. The strong interactions with PbI_2 through C=O···Pb chelation and N–H···I hydrogen bonds promote the vertical growth of PbI_2, forming nanoscale channels to facilitate the penetration of FAI into PbI_2 film. This enables rapid conversion to α-$FAPbI_3$ regardless of humidity and temperature. A PCE of 24.1% was achieved (Fig. 1(d))[21].

In summary, many efforts have been put into making pure α-$FAPbI_3$ solar cells, and the phase stability and long-term operational stability should be further improved. Understanding the phase transition and optimizing the fabrication methods will further enhance the performance and stability of PSCs for commercialization.

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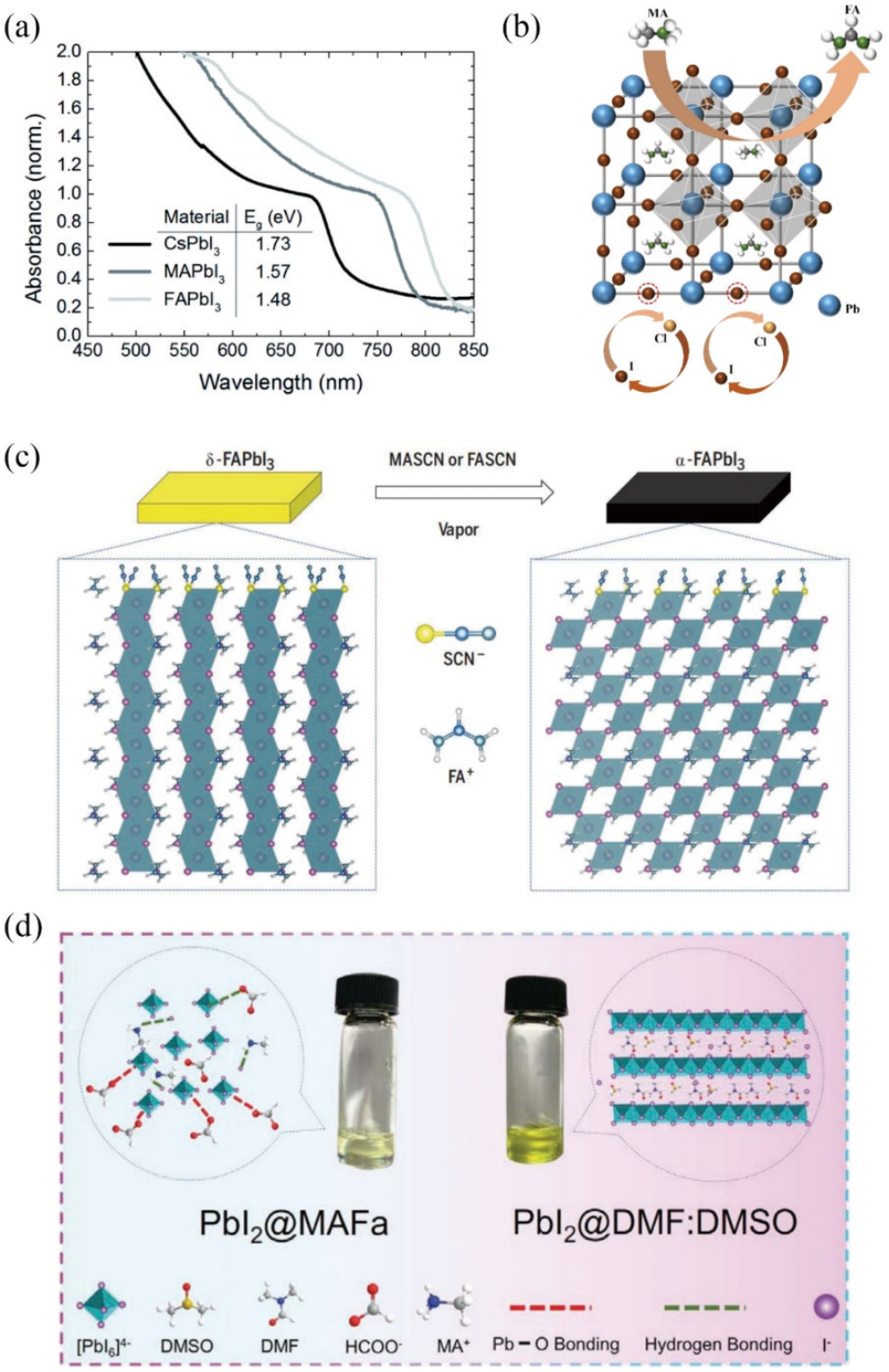

Fig. 1. (Color online) (a) UV–Vis absorption spectra for $APbI_3$ perovskites, where A is either Cs, MA or FA[8]. Copyright 2014, Royal Society of Chemistry. (b) Illustration for the interaction between MACl and $FAPbI_3$[17]. (c) Using MASCN or FASCN vapor treatment to convert yellow δ-$FAPbI_3$ film to pure α-$FAPbI_3$ film[11]. Copyright 2020, The American Association for the Advancement of Science. (d) Images for PbI_2@MAFa and PbI_2@DMF:DMSO solutions and schematic for interactions in solutions[21]. Copyright 2021, The American Association for the Advancement of Science.

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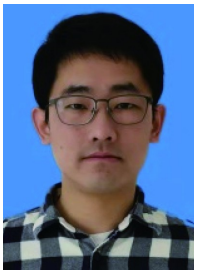

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