

Ionic liquids in perovskite solar cells

Wensi Cai¹, Zhigang Zang^{1, †}, and Liming Ding^{2, †}

¹Key Laboratory of Optoelectronic Technology & Systems (MoE), Chongqing University, Chongqing 400044, China

²Center 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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Metal halide perovskites have gained a lot of attention particularly in recent years due to their excellent optoelectronic properties and simple scalable processability^[1–3]. One major application of halide perovskites is solar cells, however, despite the power conversion efficiencies (PCEs) have already reached around 25%^[4, 5], the long-term stability issue of such devices still impedes their commercialization. Ionic liquids, which contain a large asymmetric organic cation and an organic or inorganic anion, have recently been applied to perovskite solar cells (PSCs), not only increasing the efficiency but also remarkably improving the long-term stability^[6, 7].

While the addition of ionic liquids into transport layers and/or at transport layer/perovskite interfaces could improve energy level alignment and passivate interface defects^[8, 9], the addition of them into perovskite precursors might control the crystallization dynamics of perovskite films. For example, Huang *et al.* incorporated methylammonium acetate (MAAc) into the precursor solution of MAPbI₃, which formed an intermediate phase called MAPbI_{3-x}Ac_x and slowed down the reaction between MAI and PbI₂ in the solution to manage the crystal growth^[10]. Besides, the MAAc additive was found to induce a crystalline reconstruction of MAPbI₃ from (110)/(002) planes to (112)/(200) planes^[11]. By precisely controlling the content of MAAc, PbI₂ could preferentially crystallize in a (101) phase, inducing a reconstruction of PbI₆ octahedral framework during annealing and resulting in dense perovskite films with large grains along (112)/(200) planes.

Similarly, Sonmegoglu *et al.* employed an ionic liquid, 1-hexyl-3-methylimidazolium iodide (HMII), to avoid the easy phase change of FAPbI₃ from black α -phase to yellow δ -phase^[12]. Owing to the high polarity and high boiling-point of HMII, the liquid domains between neighboring grains are yielded and the activation energy of the grain-boundary migration is reduced, resulting in a grain coarsening of FAPbI₃ crystals and micron-sized grains with reduced parasitic traps (Figs. 1(a) and 1(b)). This effective trap passivation also suppresses non-radiative recombination and improves overall charge-carrier dynamics, leading to an efficiency of 20.6% and an increase of open-circuit voltage by 80 mV compared with HMII-free ones. Most importantly, the HMII treatment also improves the device stability under both high humidity and thermal stress, retaining >80% of their initial efficiencies under 60 ± 10% relative humidity (RH) and ~95% at 65 °C, re-

spectively (Fig. 1(c)).

The improvement of efficiency and long-term stability were also reported by Snaith *et al.*, who incorporated BMIM-BF₄ into perovskite precursors (Fig. 1(d))^[13]. While BF₄⁻ anions are found mainly located at the buried interface, the BMIM⁺ cations exist not only at the buried interface but also throughout the whole film, suggesting an accumulation of ion pairs of BMIM⁺ and BF₄⁻ at the perovskite/NiO interface (Fig. 1(e)). The accumulation of BMIM⁺ cations at the surface and grain boundaries of the perovskite film could suppress the degradation of perovskites and improve the film stability. As a result, the PSCs show a *J-V*-derived efficiency degradation of only 5% even after being aged under full-spectrum sunlight at 70–75 °C for more than 1800 h.

Owing to the easy decomposition in air, hybrid perovskites are usually prepared in a dry or inert environment, which increases the manufacturing cost. By incorporating ionic liquids with hydrophobic groups, the humidity sensitive issue of perovskites could be overcome by the molecular encapsulation. Recently, Dyson *et al.* reported that a self-polymerizing hydrophobic ionic liquid, called 1,3-bis(4-vinylbenzyl)imidazolium chloride ([bvbm]Cl) (Fig. 1(f)), can effectively improve the moisture resistance of perovskites, enabling them to be made under humid environment while still maintaining a high device performance^[14]. During the crystallization of the perovskite film, the added [bvbm]Cl formed an insoluble and hydrophobic cross-linked polymer *via* self-polymerization, which effectively reduced the moisture sensitivity during device fabrication and yielded a decent PCE of 19.9% for FAMAPbI₃ solar cells made under ~50% RH. Such ionic liquids were also applied to MAPbI₃ solar cells, which showed an improved long-term stability with >80% of their initial performance maintained even after being stored in air for more than 2900 h (Fig. 1(g)).

Ionic liquids can also be used to replace traditional solvents. Recently, Huang *et al.* reported that by substituting traditional DMF:DMSO with an ionic liquid called methylamine formate (MAFa) to prepare precursor solutions, they made stable α -FAPbI₃ films regardless of humidity and temperature^[15]. While PbI₂@DMF:DMSO thin films have a random orientation distribution and hence an energy barrier to form α -phase FAPbI₃, the excellent vertically oriented crystallization of PbI₂@MAFa thin films enabled the quick entering of FA⁺ into the interior crystals and a rapid reaction between FA⁺ and PbI₂ to produce stable α -phase FAPbI₃. Besides, the strong Pb...O and hydrogen-bond interactions between residual MAFa and PbI₂ framework prevented the film decomposition. As a result, the device performance was dramatically im-

Correspondence to: Z G Zang, zangzg@cqu.edu.cn; L M Ding, ding@nanoctr.cn

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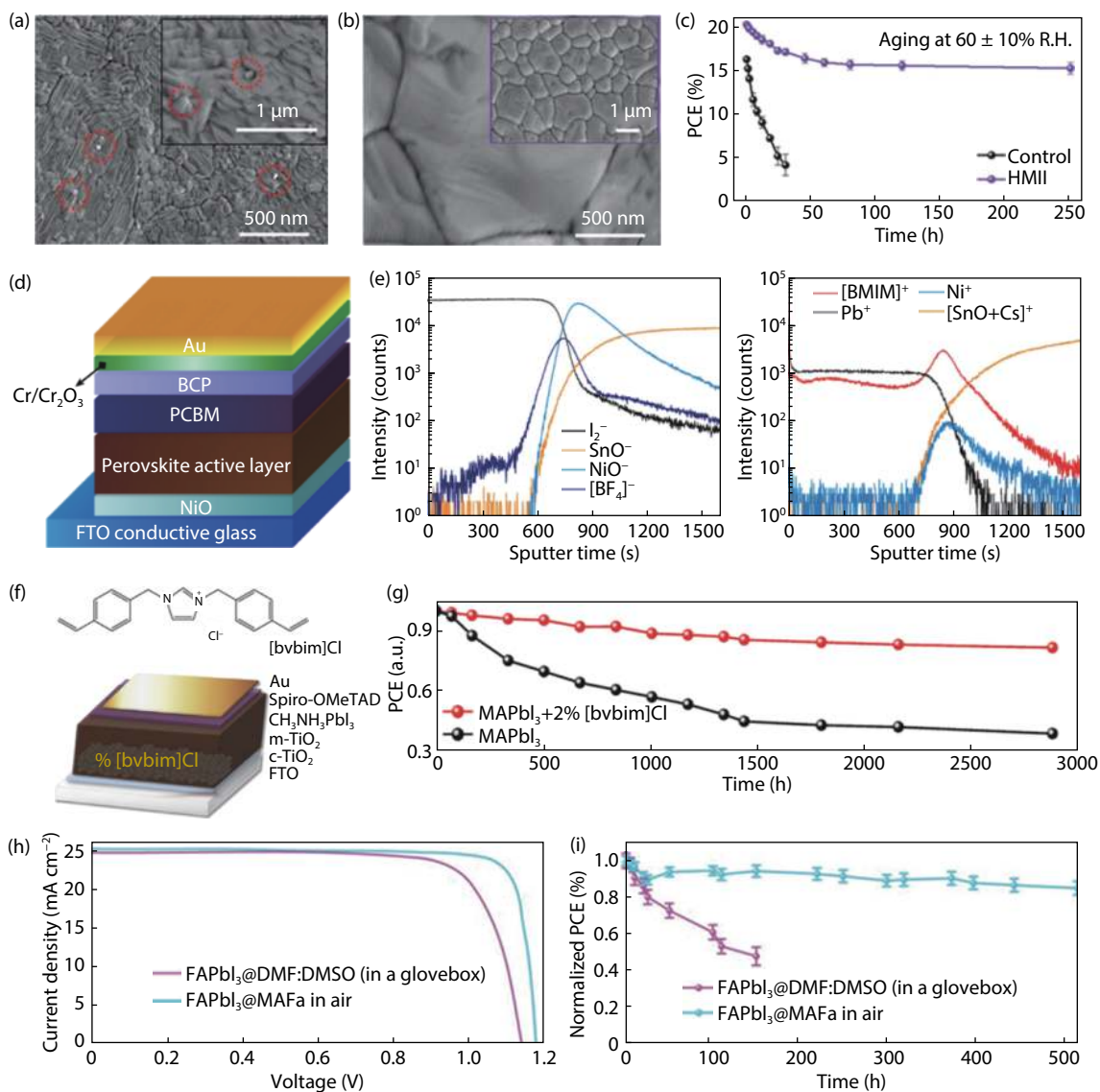


Fig. 1. (Color online) SEM micrographs for FAPbI₃ films (a) without and (b) with HMII. (c) Stability curves for the devices aged under ambient conditions (25 °C, 60 ± 10% RH). Reproduced with permission^[12], Copyright 2021, Wiley-VCH. (d) The structure for a p-i-n solar cell. (e) ToF-SIMS depth profiles for BMIM-BF₄-containing perovskite film on an NiO/FTO glass substrate. Reproduced with permission^[13], Copyright 2021, Nature. (f) [bv bim]Cl (top) and the PSC (bottom). (g) Device stability study. The cells were stored in air (50% RH, room temperature). Reproduced with permission^[14], Copyright 2021, Wiley-VCH. (h) *J-V* curves for champion cells based on FAPbI₃@MAFa and FAPbI₃@DMF:DMSO films. (i) Thermal stability comparison between two unencapsulated devices under continuous heating at 85 °C in a N₂ glovebox. Reproduced with permission^[15], Copyright 2021, Science.

proved (Fig. 1(h)), showing a PCE of 24.1%. Moreover, even the unencapsulated FAMAPbI₃@MAFa cells could maintain 80% and 90% of their initial efficiencies for 500 h at 85 °C (Fig. 1(i)) and under a continuous light stress, respectively, demonstrating the great potential of this approach.

The above research and results clearly demonstrate the effectiveness of ionic liquids in performance enhancement of perovskite solar cells. However, deep understanding on solution chemistry as well as the effects of residual ionic liquids in perovskite films is still required in order to design more versatile ionic liquids and further improve the device performance.

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Wensi Cai received her PhD degree from University of Manchester in 2019. She joined Chongqing University as a postdoc in 2020. Her research focuses on oxide semiconductor- and perovskite-based electronic devices.



Zhigang Zang received his PhD degree from Kyushu University in 2011. He joined School of Optoelectronic Engineering, Chongqing University as a professor in 2014. His research focuses on the synthesis of II-VI, III-V semiconductor materials and their applications in solar cells, photodetectors and LEDs.



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 innovative materials and devices. He is RSC Fellow, the nominator for Xplorer Prize, and the Associate Editors for Science Bulletin and Journal of Semiconductors.