

# Managing excess $\text{PbI}_2$ for efficient perovskite solar cells

Xiaodong Li<sup>1</sup>, Jie Sun<sup>2</sup>, Bozhang Li<sup>3</sup>, Junfeng Fang<sup>1,†</sup>, and Liming Ding<sup>2,†</sup>

<sup>1</sup>School of Physics and Electronic Science, Engineering Research Center of Nanophotonics & Advanced Instrument (MoE), East China Normal University, Shanghai 200062, China

<sup>2</sup>Center for Excellence in Nanoscience (CAS), Key Laboratory of Nanosystem and Hierarchical Fabrication (CAS), National Center for Nanoscience and Technology, Beijing 100190, China

<sup>3</sup>East Chapel Hill High School, Chapel Hill, NC 27514, USA

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Perovskite solar cells (PSCs) have attracted much attention due to their low cost, high efficiency and easy processing. Recently, You *et al.* achieved a record efficiency of 26.1% (certified 25.6%) in PSCs with excellent stability<sup>[1]</sup>. Excess  $\text{PbI}_2$  in perovskite films was converted into inactive  $(\text{PbI}_2)_2\text{RbCl}$  to avoid its detrimental effect to device stability, while maintaining its positive effect to device efficiency.

Most highly efficient PSCs were achieved with excess  $\text{PbI}_2$  in either perovskite bulk or film surface. For example, Seo *et al.* fabricated PSCs with >25% efficiency by using perovskite precursor solution with excess  $\text{PbI}_2$ <sup>[2]</sup>. Besides, You *et al.* achieved planar PSCs with efficiency close to 20% in 2016 through annealing perovskite films at high temperature to induce its partial decomposition and form excess  $\text{PbI}_2$  spontaneously<sup>[3]</sup>. The increased efficiency in PSCs with excess  $\text{PbI}_2$  resulted from  $\text{PbI}_2$  passivation. Owing to the larger bandgap of  $\text{PbI}_2$ , a favorable type I band alignment was established between  $\text{PbI}_2$  and perovskite, forming energy barriers to block both electron and hole transport to grain boundaries (GBs) and repel them into perovskite grains<sup>[4, 5]</sup>. As a result, potential carrier recombination induced by defects at GBs was effectively inhibited, thus improving device efficiency. In addition, the excess  $\text{PbI}_2$  at perovskite/charge-transport layer interface can block possible interfacial recombination, further enhancing device efficiency.

However, scientists found that excess  $\text{PbI}_2$  in perovskite films could cause severe stability issues of PSCs especially under illumination, despite increased efficiency<sup>[6, 7]</sup>.  $\text{PbI}_2$  tended to decompose into metallic  $\text{Pb}^0$  and  $\text{I}_2$  under illumination, yielding  $\text{Pb}^0$  defects and thus decreasing device efficiency<sup>[8]</sup>.  $\text{I}_2$  product could further promote perovskite decomposition, even destroy charge-transporting layer<sup>[9, 10]</sup> and corrode metal electrode<sup>[11, 12]</sup>, accelerating device degradation. In addition, excess  $\text{PbI}_2$  can absorb adjacent  $\text{MA}^+$  (or  $\text{FA}^+$ ) and  $\text{I}^-$  during perovskite aging, yielding  $\text{MA}^+$  and  $\text{I}^-$  vacancies<sup>[13]</sup>. These vacancies can act as channels for ion migration in perovskite films, also leading to device degradation.

To reduce the negative effect of excess  $\text{PbI}_2$ , Zhu *et al.* reported a chemical polishing method to optimize perovskite films. They introduced excess  $\text{PbI}_2$  during perovskite growth to obtain high-quality perovskite films. Then they washed away excess  $\text{PbI}_2$  on perovskite surface through its

reaction with ammonium salts in the polishing agents (Fig. 1(a))<sup>[14]</sup>, avoiding  $\text{PbI}_2$ -induced perovskite degradation. The PSCs exhibited over 24% efficiency with good light and air stability. In addition, Luo *et al.* reported a ligand-modulated method (Fig. 1(b)) to regulate the shape and distribution of excess  $\text{PbI}_2$  in perovskite films via introducing cetyltrimethylammonium bromide (CTAB)<sup>[15]</sup>. CTAB caused  $\text{PbI}_2$  into 2D nanosheet, vertically sticking among perovskite grains. As a result, over 22% efficiency was obtained. Besides, Li *et al.* modulated excess  $\text{PbI}_2$  with ionic liquid [BMIM]X (Fig. 1(c))<sup>[16]</sup>. [BMIM]X could interact with  $\text{PbI}_2$  and form supramolecular structures, which could relax lattice distortion and release residual tensile strain in perovskite films, thus improving device stability.

Recently, You *et al.* managed excess  $\text{PbI}_2$  through  $\text{RbCl}$  doping in perovskite films<sup>[1]</sup>.  $\text{RbCl}$  reacted with  $\text{PbI}_2$  to form  $(\text{PbI}_2)_2\text{RbCl}$  (Fig. 2(a)).  $(\text{PbI}_2)_2\text{RbCl}$  promoted the formation and stabilization of black  $\text{FAPbI}_3$  phase through Pb-Cl bonding. On the other hand,  $(\text{PbI}_2)_2\text{RbCl}$  was inactive and could not react with  $\text{FA}^+$  or  $\text{I}^-$  of perovskite grains, thus inhibiting the formation of  $\text{FA}^+$  or  $\text{I}^-$  vacancies and suppressing ion migration (Fig. 2(b)). Besides,  $(\text{PbI}_2)_2\text{RbCl}$  is an intercalated compound and is more favorable to block ion migration in perovskite. As a result, a record efficiency of 26.1% (certified 25.6%) was realized in PSCs with good stability (Fig. 2(c)). The devices retained 96% of initial efficiency after aging in  $\text{N}_2$  for 1000 h and 80% of initial value after aging at 85°C for 500 h.

In short, future efforts on PSCs will focus on improving the module efficiency and stability for real commercialization.

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Correspondence to: J F Fang, [jffang@phy.ecnu.edu.cn](mailto:jffang@phy.ecnu.edu.cn); L M Ding, [ding@nanoctr.cn](mailto:ding@nanoctr.cn)

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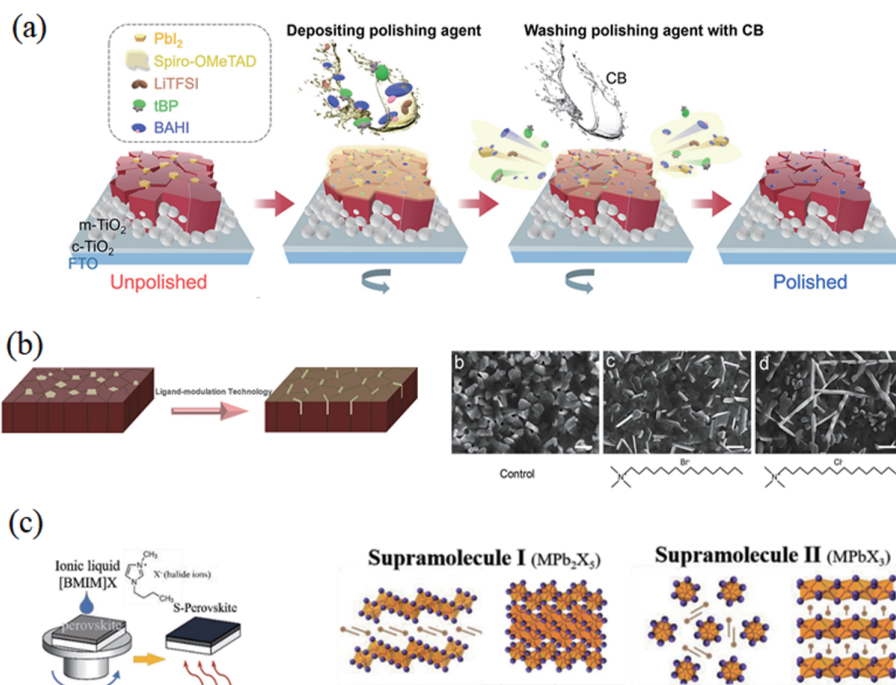


Fig. 1. (Color online) (a) Chemical polishing of perovskite surface to eliminate excess  $\text{PbI}_2$ . Reproduced with permission<sup>[14]</sup>, Copyright 2022, American Chemical Society. (b) Ligand-modulated  $\text{PbI}_2$  nanosheet in PSCs. Reproduced with permission<sup>[15]</sup>, Copyright 2020, Wiley. (c) Supramolecular engineering to modulate excess  $\text{PbI}_2$  in PSCs. Reproduced with permission<sup>[16]</sup>, Copyright 2022, Wiley.

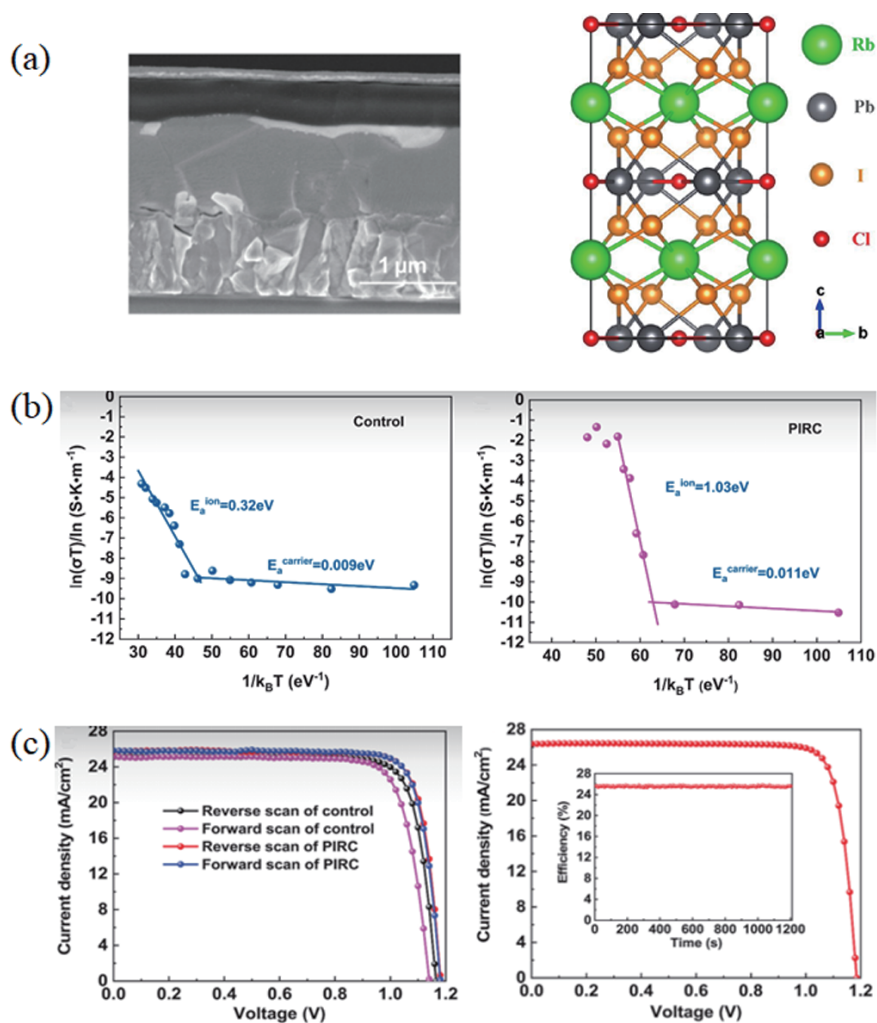


Fig. 2. (Color online) (a)  $(\text{PbI}_2)_2\text{RbCl}$  and its crystal structure in PSCs. (b) Ion-migration activation energy in control perovskite or perovskite with  $(\text{PbI}_2)_2\text{RbCl}$ . (c)  $J$ - $V$  curves for PSCs with  $(\text{PbI}_2)_2\text{RbCl}$ . Reproduced with permission<sup>[1]</sup>, Copyright 2022, the American Association for the Advancement of Science.

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**Xiaodong Li** got his PhD in 2016 from Ningbo Institute of Material Technology & Engineering (CAS). Then he started his postdoctoral research in NIMTE on OSCs and PSCs from 2016 to 2019. He joined East China Normal University in 2019 and became a full professor in 2022. His work focuses on perovskite solar cells.



**Junfeng Fang** got his PhD in 2006 from Changchun Institute of Applied Chemistry (CAS). He started his postdoctoral research in Umeå University (Sweden) and University of Cambridge (UK) from 2006 to 2010. He worked at Ningbo Institute of Material Technology & Engineering (CAS) as a professor from 2011 to 2019. Then he joined East China Normal University in 2019 and has been working as the director of Engineering Research Center of Nanophotonics & Advanced Instrument (MoE). His work focuses on perovskite solar cells.



**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, and the Associate Editor for *Journal of Semiconductors*.