

Ion migration in perovskite solar cells

Xiaoxue Ren^{1, ‡}, Lixiu Zhang^{2, 3, ‡}, Yongbo Yuan^{1, †}, and Liming Ding^{2, 3, †}

¹Hunan Key Laboratory of Super Microstructure and Ultrafast Process, School of Physics and Electronics, Central South University, Changsha 410083, China

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

³University of Chinese Academy of Sciences, Beijing 100049, China

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The past few years have witnessed a remarkable progress of perovskite solar cells (PSCs), which can be attributed to the high light absorption coefficient, tunable bandgap, long carrier diffusion length, solution processability at low temperature and relatively low cost of perovskite materials. Up to now, the highest certified power conversion efficiency (PCE) of PSCs has reached 25.5% (<https://www.nrel.gov/pv/cell-efficiency.html>), shedding light on the commercialization of PSCs. Nevertheless, the stability issues of PSCs severely limit the field deployment of solar cell modules. Notably, ion migration in organic-inorganic halide perovskite (OIHP) originating from the ionic nature of perovskite materials has been suggested to be responsible for many instability problems and cannot be eliminated through encapsulation. With crucial significance being attached to the long-term durability of PSCs during operation, it is of profound implication to clarify the fundamental mechanism and potential influence of ion migration on device performance.

To date, numerous researchers have provided evidences for the existence of ion migration in hybrid PSCs, including dynamic electrical characterizations, such as the J - V hysteresis, the giant dielectric constant, and the switchable photocurrent, and direct elemental mapping, e.g. TPIR, focused XPS, TOF-SIMS, *et al.* However, ion migration in OIHP solar cells has not drawn much attention until Snaithe *et al.* in 2013 MRS fall meeting reported the J - V hysteresis phenomenon and speculated that ion migration might be one of the three possible origins^[1], and Xiao *et al.* in 2014 reported the giant switchable photovoltaic effect and firstly proved the significant ion migration in perovskites at RT^[2]. In the giant switchable photovoltaic effect, the perovskite layer can be poled under external bias, making the direction of photoinduced current completely reversible with the applied bias (Fig. 1(a)). Schematically, Fig. 1(b) shows positively charged ions drift along the direction of the field and accumulate at the cathode region, while negatively charged ions are just the opposite. Moreover, the perovskite material adjacent to anode turned transparent under constant poling, indicating the existence of ion drifting from anode^[2].

The species of migrating ions are suggested to be either

intrinsic ions, such as MA⁺, I⁻, within the perovskite, or extrinsic ions from interfacial layers, e.g. Li⁺, H⁺, Na⁺. Based on the first-principle calculation, Eames *et al.* simulated the corresponding activation energies of three conventional ion migration mechanisms, where I⁻ travels along an octahedron edge with a lowest activation energy, MA⁺ moves to the neighboring octahedral vacancy with a moderate activation energy and Pb²⁺ migrates along the diagonal direction $\langle 110 \rangle$ with a highest activation energy^[3]. It reveals that the most easily occurred migration is I⁻, followed by MA⁺, and Pb²⁺ turns to be difficult to migrate. At the same time, Azpiroz *et al.* analyzed the activation energies of four typical point defects (I vacancies, MA vacancies, Pb vacancies and I interstitials) related to ion migration and raised four plausible diffusion pathways^[4], which are illustrated in Fig. 1(c). Despite the different numerical values of activation energy from different computational models, it can still be elucidated that I interstitials and I vacancies are the easiest to migrate compared with other defects.

Experimentally, the fact of ion migration was confirmed by Yuan *et al.* in 2015, when they first observed the migration of MA⁺ under a poling voltage in MAPbI₃ PSCs through PTIR^[5]. In addition, a p-i-n structured device (with switchable polarity) was discovered to form in-situ in perovskite layer due to the chemical doping effect induced by excessive ions. Furthermore, Li *et al.* quantitatively monitored the distribution of I/Pb ratio (within a lateral structure device) after electrical poling process and found it went much higher around anode region^[6]. After withdrawing poling bias, I⁻ ion showed reversible diffusion and returned back into its original state, verifying the drifting and accumulation of I⁻ ion at anode under poling voltage. Except for intrinsic ions, Li *et al.*^[7] pointed out that extrinsic ions like Li⁺, H⁺, and Na⁺ can also penetrate through perovskite film and accumulate in the counter transport layer, as evidenced by the distribution profile of different elements in a common structured cell (TiO₂/perovskite/spiro-OMeTAD) derived from TOF-SIMS.

Recent studies have indicated that the migration of ionic species has critical impacts on the performance and long-term operational stability of PSCs.

The migration and accumulation of ions have been demonstrated to affect the charge carrier transport and electronic properties in the perovskite film. As shown in Fig. 1(b), Xiao *et al.* reported the switchable photovoltaic effect^[2], the ion migration under the applied electric field induces a self-doping effect and local band bending, forming a p-i-n or n-i-p type junction. The concentration of accumulated ions

Xiaoxue Ren and Lixiu Zhang contributed equally to this work.

Correspondence to: Y B Yuan, yuanyb@csu.edu.cn; L M Ding, ding@nanoctr.cn

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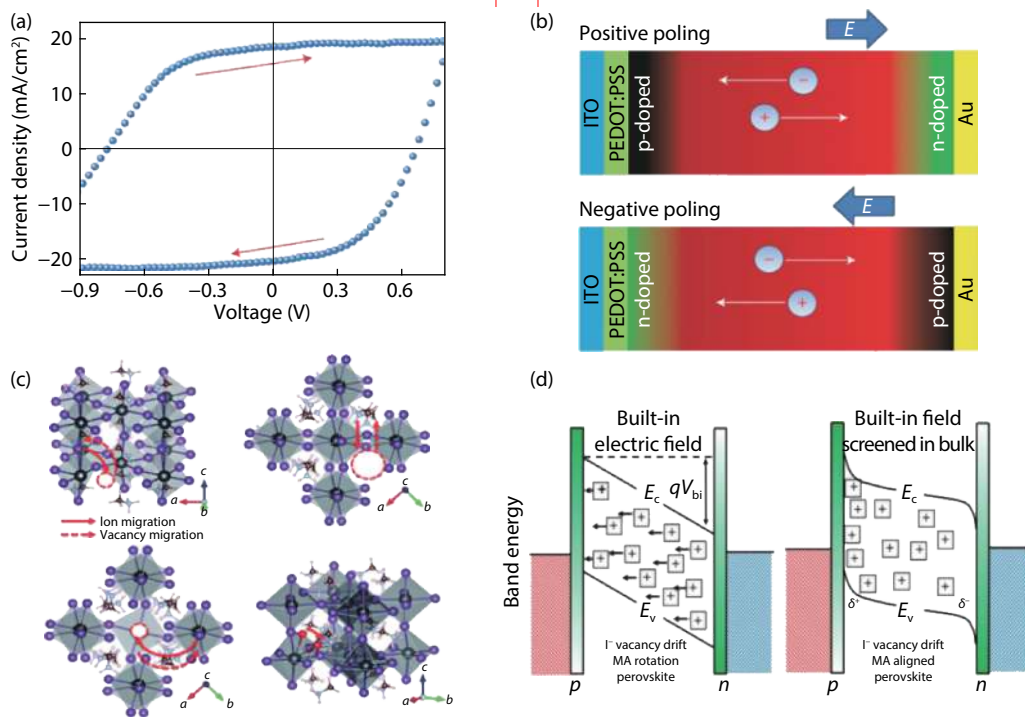


Fig. 1. (Color online) (a) Giant switchable photocurrent curve in a non-selective contact structured device. Reproduced with permission^[2], Copyright 2014, Nature Publishing Group. (b) Schematic representation of ion migration in a perovskite solar cell when applying forward (left) and reverse bias (right). Reproduced with permission^[2], Copyright 2014, Nature Publishing Group. (c) The possible migrating paths for I⁻ vacancies, MA vacancies, Pb vacancies and I interstitial defects. Reproduced with permission^[4], Copyright 2015, The Royal Society of Chemistry. (d) Schematic diagrams indicating the influence of vacancy drift on the band energies of a p-i-n device at short circuit^[3].

could be 10^{17} cm^{-3} or higher, which severely quench the photoluminescence (PL) intensities. Eames^[3] proposed that the migration of ion species can generate a local electric field which partially shield the built-in electric field and influence the collection efficiency of photogenerated carriers (Fig. 1(d)). A high concentration of opposite ions accumulated around grain boundaries (GBs) would form tunneling junctions with sharp surface potential change^[8]. Xu *et al.* reported that the formation of I-Pb antisite defects with excessive I⁻ ions on the surface of perovskite film could form deep level traps according to the density functional (DFT) calculation, which are responsible for the non-radiative recombination loss of charge carrier^[9].

A key reason for the mobile ions play diverse roles in perovskite is their very low threshold electrical field to migrate, e.g. $0.3 \text{ V}/\mu\text{m}$, which is much smaller than the built-in electrical field in solar cells or local band bending induced by buildup charges^[5]. Faster ion migration along GBs than bulk was experimentally proved by Shao *et al.* based on an in-situ mapping of I and Pb elements around jointed single-crystals with GB parallel to the electrical field direction^[10]. The dramatic morphology change and the I element redistribution along GB under applied bias demonstrated GBs as the priority ion migration channels.

The migration and redistribution of ion species also result in the instability of perovskite phase, eventually causing decomposition of the films and device failure. Yuan *et al.* discovered the phase transformation between MAPbI_3 perovskite and PbI_2 crystals under an external electric field due to the migration of mobile ions (MA^+ , I^-)^[11]. This structural transformation can be recovered at 330 K. Moreover, the per-

ovskites with mixed halides compositions tend to be phase segregated under light illumination or applied electric field, which was verified to lead to reversible performance loss for PSCs. As shown in Fig. 2(a), Hoke *et al.* discovered the reversible photoluminescence shift in $\text{MAPb}(\text{Br}_x\text{I}_{1-x})_3$ mixed perovskite^[12]. This indicated that light illumination can cause the ion redistribution and halide segregation into iodide-rich and bromide-rich domains. Zhang *et al.* studied the phase-segregation effect in $\text{CsPbBr}_{1.2}\text{I}_{1.8}$ nanocrystal ensemble, suggesting that it is the local electric field to break the iodide bonds that triggers the ion migration process^[13]. More importantly, the mobile ion species migrate across the perovskite layer and react with the function layer, leading to irreversible performance degradation and severely stability issues of PSCs. Kato *et al.* observed that the mobile I⁻ could react with the electrode and form AgI interface layer, which progressively reduced the PSCs performance^[14]. Li *et al.*^[7] highlighted the important roles of extinct ions migration such as Li^+ , Na^+ and H^+ dopant used in the hole transport layer (HTL) can also provoke hysteresis and intensified PSCs performance attenuation.

Remarkably, since the redistribution of mobile ions is driven by dynamic equilibrium, the detrimental effect of ion migration in stability can be healed when the loss of mobile ions is ignorable. The light induced ion redistribution was also found to be able to cure the performance of PSCs. deQuilettes^[15] illustrated the photo-induced 'clean effect' due to the migration and redistribution of iodide ions, which contributes to the reduction of the trap density in the perovskite films (Fig. 2(b)). Furthermore, Motti *et al.*^[16] investigated the defect formation process due to the migration of ion species in

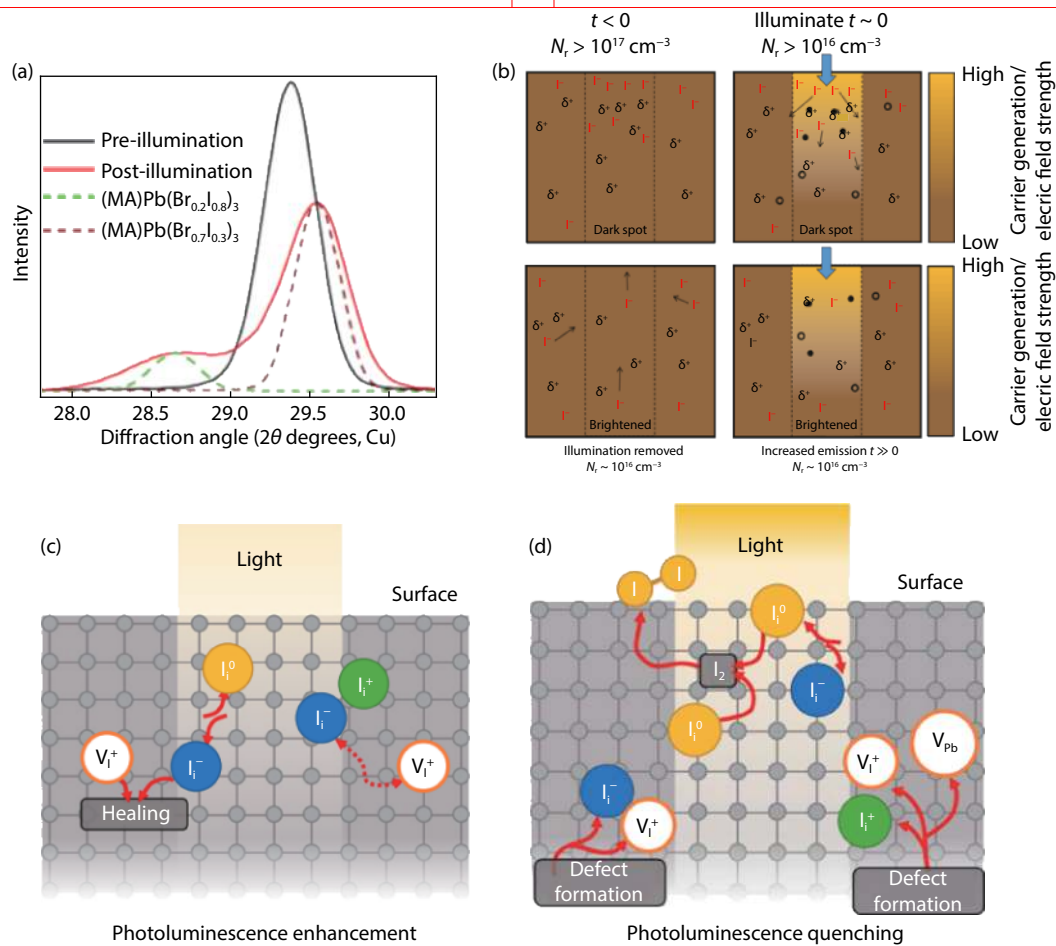


Fig. 2. (Color online) (a) The 200 XRD peak of an $x = 0.6$ film before (black) and after (red) white-light soaking for 5 minutes at $\sim 50 \text{ mW/cm}^2$. XRD patterns of an $x = 0.2$ film (dashed green) and an $x = 0.7$ film (dashed brown) are included for comparison. Reproduced with permission^[12], Copyright 2015, Royal Society of Chemistry. (b) Proposed mechanism of photo-induced cleaning by halide redistribution. Reproduced with permission^[15], Copyright 2016, Nature Publishing Group. (c) (d) Photoluminescence enhancement and quenching mechanisms. (c) Ion dynamics in MAPbI₃ thin film promoting PLIE, when the probability of I_i^0 species encounters is small and Frenkel pair annihilation is boosted by electron trapping, and PLID (d) when the probability of I_i^0 species encounters is high, boosting I_2 molecule formation. (c/d) Reproduced with permission^[16], Copyright 2019, Nature Publishing Group.

various quality of perovskite films. The long-living halide carriers can heal the defect through Frenkel defects annihilation when the trap density of the perovskite film is relatively low, as Fig. 2(c) depicted. On the contrary, the high-density traps provide binding sites for photogenerated species, boosting I_2 molecule formation and eventually leading to material degradation (Fig. 2(d)). Consequently, covering perovskite with compact materials possessing surface defect passivation effect is an effective strategy to prevent ion loss as a promising direction^[17].

Recently, significant research efforts have been devoted to suppress the ion migration from the perspective of composition, crystallization, and dimension engineering. Compared to MAPbI₃, the ion migration tendency is lower in FA-based and all-inorganic PSCs, indicating the sensitivity of material stabilities on its compositions. Lin *et al.*^[18] applied the temperature-dependent conductivity experiment and demonstrated that the ion migration in 2D (BA)₂(MA)₃Pb₄I₁₃ perovskite is dramatically suppressed due to the confinement effect of organic spacers. In addition, Liu *et al.* introduced the (2D) A₂PbI₄ perovskite layer between the 3D perovskite layer and the HTL to form the 2D/3D heterogeneous junction, meanwhile redu-

cing the ion migration in the device and protecting the perovskite from environmental moisture damage^[19]. Wei *et al.* utilized the strong energy of the cation- π interaction between aromatic rubrene and organic cation, locking the MA⁺ firmly in place. Hence effectively inhibit the migration of organic cations^[20]. Zhao *et al.* clarified that the residual strain in crystal impacts a lot on the ion migration, i.e. the compressive lattice strain tends to inhibit mobile ions. However, the tensile lattice strain plays the opposite role, which highlights the importance of strain engineering on improving the intrinsic stability of perovskites. All these advances provide deep insights to mitigate the ion migration and enhance stability of PSCs^[21].

To summarize, ion migration is detrimental to performance and long-term operational stability, which is still hindering the large-scale and commercial development of PSCs. Therefore, systematical research on the mechanism of ion migration induced phase segregation can supply the theoretical foundation for effectively eliminating hysteresis and enhancing the stability of PSCs. However, more efforts will be required to elucidate the ion migration phenomenon in halide perovskite materials. If ion loss is prevented, the dynamic equilibrium nature of mobile ion can be utilized to design state of

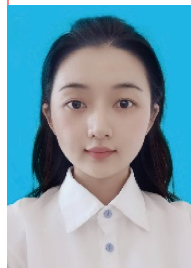
the art high performance and stable perovskite optoelectronic devices.

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Xiaoxue Ren got her BS from Xinjiang University in 2019. Now she is a MS student at Central South University under the supervision of Prof. Yongbo Yuan. Her research interests focus on perovskite solar cells.



Lixiu Zhang got her BS from Soochow University in 2019. Now she is a PhD student at University of Chinese Academy of Sciences under the supervision of Prof. Liming Ding. Her research focuses on organic solar cells and perovskite solar cells.



Yongbo Yuan got his BS degree in 2004 and PhD degree in 2009 at Zhongshan University. Then he joined Jinsong Huang Group at University of Nebraska-Lincoln as a postdoc. In March 2016, he joined Central South University as a full professor. His research interests include perovskite/polymer solar cells, organic thin-film transistors and photodetectors.



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 functional materials and devices.