TOPICAL REVIEW — Physics in micro-LED and quantum dots devices

Ion migration in metal halide perovskite QLEDs and its inhibition

Yuhui Dong(董宇辉)[1,2], Danni Yan(严丹妮)[1,2], Shuai Yang(杨帅)[1,2], Naiwei Wei(魏乃炜)[1,2], Yousheng Zou(邹友生)[1,2,†], and Haibo Zeng(曾海波)[1,2‡]

[1] *Institute of Optoelectronics & Nanomaterials, College of Materials Science and Engineering, Nanjing University of Science and Technology, Nanjing* 210094, *China*

[2] *Key Laboratory of Advanced Display Materials and Devices, Ministry of Industry and Information Technology, Nanjing* 210094, *China*

(Received 31 August 2022; revised manuscript received 16 November 2022; accepted manuscript online 2 December 2022)

Benefiting from the excellent properties such as high photoluminescence quantum yield (PLQY), wide gamut range, and narrow emission linewidth, as well as low-temperature processability, metal halide perovskite quantum dots (QDs) have attracted wide attention from researchers. Despite tremendous progress has been made during the past several years, the commercialization of perovskite QDs-based LEDs (PeQLEDs) is still plagued by the instability. The ion migration in halide perovskites is recognized as the key factor causing the performance degradation of PeQLEDs. In this review, the elements species of ion migration, the effects of ion migration on device performance and stability, and effective strategies to hinder/mitigate ion migration in PeQLEDs are successively discussed. Finally, the forward insights on the future research are highlighted.

Keywords: perovskite quantum dots, light-emitting diodes, ion migration, stability

PACS: 85.60.Jb, 61.82.Rx, 31.30.J–, 42.60.Lh **DOI:** 10.1088/1674-1056/aca7e8

1. Introduction

Metal halide perovskite quantum dots (PQDs) have gained increasing attention due to their inherent superiorities, including tunable emission wavelength,[1,2] high photoluminescence quantum yield (PLQY) >90%,[3,4] and narrow emission with linewidth below 20 nm,[5,6] which means high color purity. Given these excellent optoelectronic properties, PQDs are extensively used in solar cells,[7,8] lasers,[9,10] light-emitting diodes (LEDs),[11–13] and biosensing.[14,15] The predominant merits of high color purity and color-tunable wavelength have rendered them high-profile and lead to plenty of researches related to corresponding electroluminescent perovskite QDs-based LEDs (PeQLEDs) in the last few years.[16] Indeed, the PQDs have lived up to expectations. The device external quantum efficiencies (EQEs) of blue, green and red PeQLEDs have been elevated rapidly. At present, the highest EQEs of blue, green, and red PeQLEDs are 12.3%,[17] 23.4%,[18] and 23%,[19] respectively. The thin-film PeLEDs show higher efficiency. The highest EQE of quali-2D blue perovskite LED can reach 14.82%,[20] and the highest efficiency of red film LED has exceeded 28%.[21]

Compared to the rapid elevation in device efficiency, the progress in stability of PeQLEDs is still lagging behind. Up to now, the highest reported operational stability T_{50} (the time taken by the device to drop to 50% of its initial luminance or EQE) under the initial brightness of 100 cd/m^2 is less than 2500 h.[22,23] As for thin-film PeLEDs, the highest T_{50} is much longer than that of PeQLEDs, which is 32675 h at 3.2 mA/cm^2.[24] It has been greatly improved. However, the T_{50} of organic LEDs and QLEDs based on other kinds of QDs have exceeded 1000000 h.[25] The ion migration in metal halide perovskites has been widely acknowledged as the principal element causing the performance degradation of perovskite LEDs,[26–28] so as PeQLEDs.

Ion motion in metal halide perovskites (MHPs) was firstly observed in perovskite solar cells (PSCs) and manifested as the origin or an important contributing factor for the famous phenomenon of photocurrent hysteresis.[29] Fortunately, ion migration in PSCs does not appear to be a severe problem affecting operational stability due to the low electric field with thick film of perovskite. However, the electric field in PeQLEDs with the very thin perovskite layer ($\sim$ tens of nanometers) is much stronger than that of PSCs.[30,31] In addition, in PeQLEDs, the Joule heat generated during device operation can accelerate ion migration due to the increase in temperature. Based on these situations, ion migration is the major obstacle in PeQLEDs that needs to be overcome. So far, many studies have reported PeQLEDs degradation induced by ion migration, but further efforts are still needed.

Here, we will focus on the effect of ion migration on stability of metal halide perovskite QLEDs. The migratory element species in PeQLEDs is summarized, and the cause of ion migration is analyzed briefly. Then how does ion migration affect device stability of PeQLEDs is discussed, and the strategies to inhibit the ion migration are highlighted. Based

†Corresponding author. E-mail: yshzou75@njust.edu.cn
‡Corresponding author. E-mail: zeng.haibo@njust.edu.cn

© 2023 Chinese Physical Society and IOP Publishing Ltd

on the current progress reported in the literature, our perspectives to improve the device stability are finally presented.

2. Element species of ion migration in PeQLEDs

Origin of ion migration MHPs have a general chemical formula ABX_3, where A is a monovalent cation (e.g., Cs^+, $CH_3NH_3^+(MA^+)$, or $CH(NH_2)_2^+(FA^+)$), B is a divalent metal cation (e.g., Pb^{2+}, Sn^{2+}), and X is a halide anion (e.g., Cl^-, Br^-, I^-). The matrix of MHPs is a cubic lattice composed of BX_6^{4-} octahedra interconnected by corner-sharing in a three-dimensional space,[32] as shown in Fig. 1. Compared with conventional semiconductors, MHPs materials possess an ionic structure and mixed electronic and ionic conductivity. As an ionic compound, the activation energies (E_a) of halogen ions and A-site cations are not high, especially the former one, which are in the range of 0.1–0.6 eV,[33] verifying the possibility of ion migration in perovskites. In addition, the formation energies of MHPs are much lower than those of perovskite oxides counterparts, for example, the formation energy of $MAPbI_3$ is 0.11–0.14 eV per unit cell (4 $MAPbI_3$ units),[34] suggesting the soft matter nature. Therefore, the ion migration in the MHPs can easily occur under the illumination and heating,[35] and would even be accelerated under electrical stress as being an emitter in light-emitting devices.[32,36] As the result, the defects would be generated, and the crystal structure of MHPs would be distorted. Simultaneously, the diffusion of halide interstitials and vacancies generated by ion migration also plays a key role in the migration of halide ions.[37] Unfortunately, the MHP ionic crystals host a variety of defects, including Schottky detects, Frenkel defects, antisite defects, and structural defects with low defect formation energy.[36] Considering the high defect tolerance, which exists not only in bulk perovskites but also in PQDs,[38,39] the constituent ions can escape easily from the lattices, and can move along these defect sites.

Furthermore, the ions not only migrate in the perovskite layer under such high electric field in PeLEDs ($\sim 1 \times 10^8$ V/m), but also possibly diffuse into the charge transport layers and the electrodes.

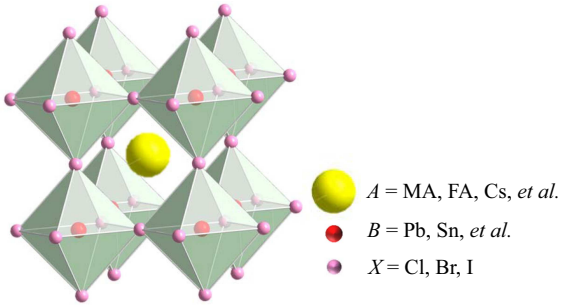


Fig. 1. Crystal structure of MHPs.

Species of migrated ions The PQDs are different from common polycrystalline as they have spatially confined electron–hole pairs in their particles ($\sim$ 10 nm) and passivated surface defects by organic ligands, which show efficient radiative recombination of excitons.[40] The lower dielectric constant k of organic ligands and relatively weaker van-der-Waals coupling between PQDs further confine the electron–hole pairs inside PQDs.[28] However, the ion migration in PQDs is still not completely inhibited, especially under very high electric field in PeQLEDs. The migrated ions in PeQLEDs can be divided into the following categories (shown in Fig. 2): (i) ion migration within QD layer; (ii) ion migration across device interfaces.

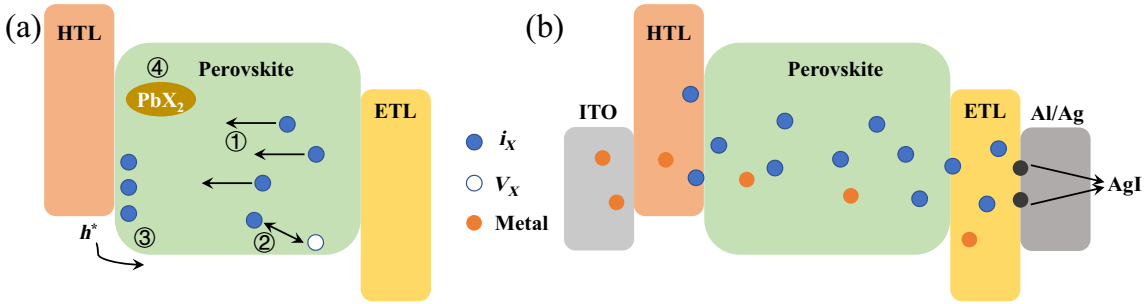


Fig. 2. Schematic diagrams of ion migration. (a) Ion migration inside PQDs: ① defect migration, ② annihilation and creation of Frenkel defects, ③ modification on charge injection, ④ distortion of crystal lattice, (b) ion migration across the interface which leads to electrode corrosion.

(i) Ion migration within PQD layer. In the forgoing discussion, the activation energy of halide ion migration is low, which makes it the most likely mobile ionic species in perovskites. We can even visualize halide ion migration by halide exchange between two nanocrystal suspensions,[41] which is usually used to tune the band gap of PQDs. Ion migration inside perovskites can lead to: ① defect migration, ② annihilation and creation of Frenkel defects, ③ modification on charge injection and ④ distortion of crystal lattice[30] (Fig. 2(a)). Parth Vashishtha and co-workers presented mixed halide $CsPbBr_{3-x}X_x$ (X = I or Cl) PeQLEDs, and studied the electroluminescence (EL) wavelength from yellow-orange to deep red (560–680 nm). They found evidence that field-driven halide migration in $CsPbBr_{3-x}X_x$ PQDs is responsible for the

observed red-shifting and splitting of the EL peaks,[42] which has a great impact on device stability. The diagram of ion migration creating green- and red-emitting NCs, as well as charging of red NCs at later time is shown in Fig. 3(a). Moreover, there are lots of evidences demonstrating that the deterioration of MHPs is induced by organic cation migration to some extent like MA^+.[43–45] The ions migration under high electric field could destroy the lattice of MHPs, induce surface defects and form charge-accumulated interfaces, leading to poor performance of PeQLEDs.

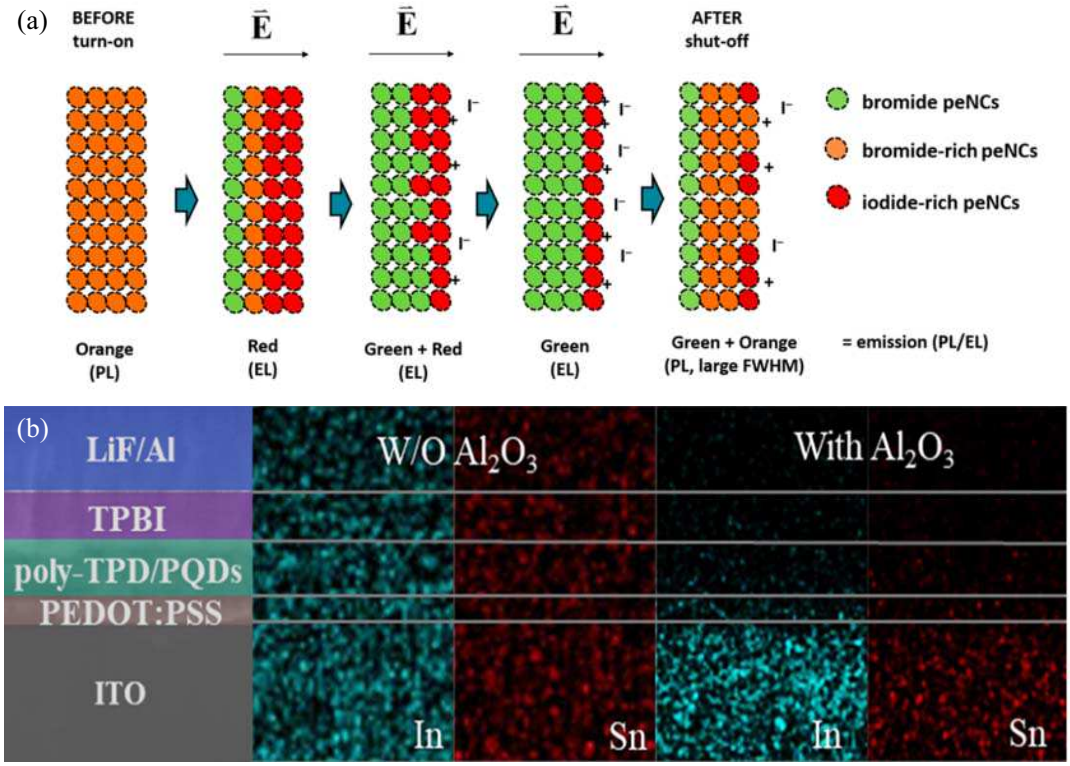


Fig. 3. (a) Diagram of ion migration creating green- and red-emitting NCs, as well as charging of red NCs at later time.[42] (b) EDS mappings of PeQLEDs with and without Al_2O_3 buffer layer.[46]

(ii) Ion migration across device interfaces. The halide ions are highly mobile as they can diffuse into transporting layers (Fig. 2(b)). This phenomenon is commonly seen in perovskite thin film LEDs. Zhao *et al.*[47] demonstrated $MAPbI_3$ perovskite LEDs with electrical stress influenced efficiency, and visual evidence by energy-dispersive x-ray spectroscopy (EDS) elemental depth profiles. The iodine is highly mobile as it can diffuse into both organic transport layers (1,3,5-tris (1-phenyl-1H-benzimidazol-2-yl) benzene (TPBi) and poly[N,N′-bis(4-butylphenyl)-N,N′-bis(phenyl)-benzi (poly-TPD)). The metal ions in electrodes can also diffuse to the emission layer. Geng *et al.* presented visual evidence of metal ions migration from ITO to emission layer of PQDs.[46] The device without buffer layer kept working at 4 V for 1 min, and the distribution of different elements was then scanned. As seen in Fig. 3(b), obvious In and Sn signals were observed, which showed the diffusion of metal ions and is harmful to the operational stability of PeQLEDs. In PeLEDs based on quasi-2D MHPs, *A*-site cation, i.e., PEA^+ and FA^+ can also migrate and get trapped in the electron transport layer (ETL), thus damaging the carrier transport property and causing deterioration of PeLEDs.[48]

Besides the halide ions and *A*-site cations, the protons (H^+)[49–51] and Li cation in LiF layer[52] can also participate in the ion migration of MHPs.

3. Effect on stability of PeQLEDs

These migrated ions in PeQLEDs could generate trap states and induce severe non-radiative recombination in the perovskite active layers, which dramatically deteriorate the device performance, mainly including spectral and operational instability. We will briefly discuss these phenomena in PeQLEDs in this part, and analysis how to suppress these effects in PeQLEDs by inhibiting ion migrations.

3.1. Spectral instability

The spectral instability is not uncommon phenomenon in PeQLEDs, especially in the device based on mixed halide PQDs,[53,54] only a few examples are briefly described here. Parth Vashishtha *et al.* systematically studied the spectral stability of mixed halide $CsPbBr_{3-x}X_x$ (X = I or Cl) PeQLEDs with different halide compositions during operation from 0 V to the maximal voltage of each device.[42] Furthermore, the EL

peaks of the PeQLEDs shifted significantly to redder wavelengths after operation at 7 V for 2 min, and the high bromide content used in the unstable orange-emitting PeQLEDs demonstrated unstable emission (shown in Fig. 4(a)). They ascribed the reason of spectral shift to the movement of ions within QDs and the composition changes during operation. And they found that a high iodide content in fact produces more stable PeQLEDs, which means high-iodide QDs appear to be more resistant to field-induced separation. Similarly, the $CsPb(Br_xCl_{1-x})_3$ QDs based blue LED demonstrated a redshift with increased applied voltage from 5 V to 8 V,[55] as shown in Fig. 4(b). This behavior was imputed to ion migration and phase transfer induced by enhanced electric field, especially in mixed halide perovskites.

3.2. Operational instability

Despite the high EQE of QLEDs, the operational stability is far behind that of commercial light sources. As an important factor affecting the stability of devices, it is very important to study the effect of ion migration on device stability of PeQLEDs. A $CsPbI_3$ QLED was demonstrated with very short T_{50} operational lifetime of 3.2 min due to poor charge transport and ion migration (Fig. 4(c)).[56] The corresponding E_a, which is mainly contributed by the activation of ion migration, is calculated from temperature-dependent conductivity measurement in the dark with a value of 0.779 eV. This value is not high enough to suppress ion migration, thus leading to poor operational stability. The pristine $CsPbI_3$ QLED without PbS capped demonstrated 48% drop of initial EL intensity under a low voltage of 2.5 V in 600 s as shown in Fig. 4(e), which is induce by ion migration in PQDs.[57] The diffusion of metal ions in electrodes also affected the operational stability of PeQLEDs.[46] The In and Sn ions of ITO can migrate to the emission layer under electric field, thus reducing the operational lifetime of PeQLEDs. The $CsPbBr_3$ QLED had a short T_{50} lifetime of 4.2 s without any protection, showing poor stability (Fig. 4(d)). Furthermore, metal electrodes used in device can also be corroded by ions migrated from the MHPs.[58,59] For instance, I^- anions released from emission layer can corrode Ag and create AgI.[60] These insulating components will induce deep traps or block efficient charge injection and extraction, thus destroying PeQLEDs.

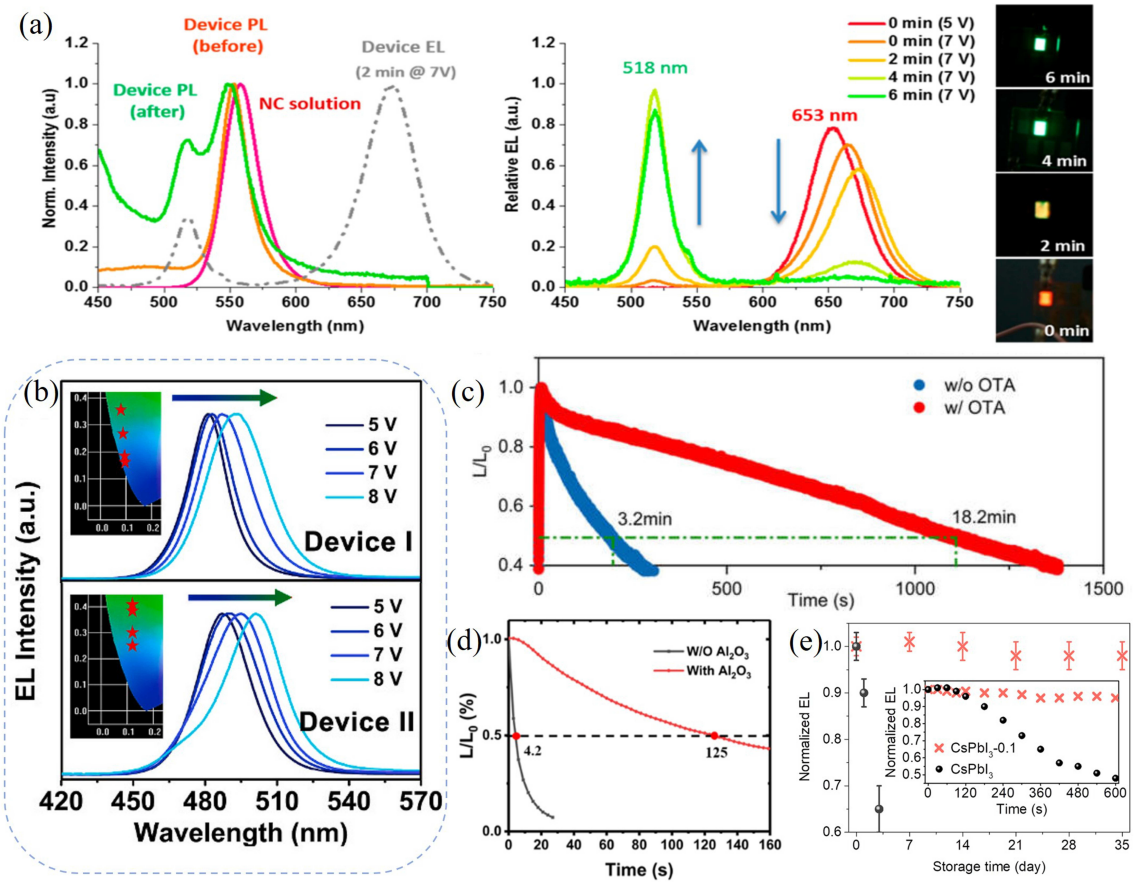


Fig. 4. (a) Photoluminescence spectrum (left chart) of a solution prior to thin film formation and of the finished ITO/PEDOT:PSS/pTPD/PQDs/TPBi/Al device before (orange line) and after (green line) device operation. The electroluminescence from the device after operation at 7 V for 2 min is included for reference (dashed gray line). After the initial PL measurements, the voltage for the LED was raised to the turn-on voltage of ~ 5 V until EL was observed and then switched to 7 V to ensure observation of ionic separation. Electroluminescence spectra (top center chart) and photos (top right) of the same LED were taken at the turn-on voltage and at 7 V and then at 2 min intervals until the spectrum had shifted completely.[42] (b) EL spectra, CIE of device I, II with different Br/I.[55] (c) Operational lifetimes of LEDs with/without octylamine (OTA).[56] (d) Lifetime of the PeQLEDs with/without Al_2O_3 film.[46] (e) Time-related storage stability of $CsPbI_3$ and $CsPbI_3$-0.1 QLEDs in nitrogen. Inset shows time-related EL intensities of pure and $CsPbI_3$-0.1 QLED at the same voltage of 2.5 V.[57]

Ion migration can also have beneficial effect on device operation in PeQLEDs.[61] MA^+ cation and X^- anions that accumulate on the cathode and anode induce p-doping and n-doping, i.e., p–i–n structure in MHP layers, which induce sharp tunneling barrier and facilitate injections of carriers from electrodes into emission layer.[62,63] In addition, short-distance migration of local excess ions will passivate defect states and improve the EQE of PeQLEDs.[5]

4. Inhibition of ion migration in PeQLEDs

The current commonly used methods to inhibit ion migration mainly have two aspects: one is from the PQDs light emitting layer itself, and the other is from the device structure design. Starting from the PQDs layer, the most frequently used idea is to consider how to stabilize the crystal structure of PQDs. The most easily thought of method is metal doping, including *A*-site or *B*-site doping, which is beneficial for tolerance factors of PQDs. Secondly, in view of the abundant ligand environment on the surface of PQDs, passivation and modification of surface ligands are also common methods to inhibit ion migration and improve its stability. Therefore, ligand engineering is the current research hotspot, which will be introduced in the following sections. In addition, it is also very effective and commonly used to inhibit ion migration between layers through reasonable design of device structure. Other strategies for improving PQDs, such as the formation of core–shell structure, structure design of PQDs films, and cross-linking, are also useful methods. However, due to the cubic structure of PQDs, the formation of complete core–shell structure is difficult to achieve, while organic molecular cross-linking and structure design of PQD films are mostly used in perovskite films, and there are a few reports on PQDs.

Metal doping Some metal ions are chosen as the dopant for PQDs to stabilize the perovskite structure[64] and improve the stability of PQDs, such as Ce^{3+}, Cu^{2+}, Mn^{2+}, etc.,[55,65–67] and simultaneously enhance the operational stability of PeQLEDs. Yao and co-workers proposed a Ce^{3+} doping strategy to enhance PL/EL efficiency of $CsPbBr_3$ QDs.[65] The Ce^{3+} ions was chosen by virtue of its similar ion radius and higher formation of energy level of conduction band with bromine compared with the Pb^{2+} cation to maintain the integrity of perovskite structure without introducing additional trap states (the schematic diagram is shown in Fig. 5(a)). The EQE is enhanced with the aid of Ce^{3+} doping from 1.6% to 4.4%, so as the operational stability. Zhang *et al.* demonstrated a strategy of La^{3+} doping in $CsPb(Br_xCl_{1-x})_3$ QDs to alleviate ion migration and phase separation benefiting from the constricted lattice and stronger interaction between La and Cl, and the spectral instability was effectively suppressed in the corresponding QLEDs as shown in Figs. 5(b) and 5(c).[55] Moreover, the maximum EQEs were significantly improved after La^{3+} doping. The Cu^{2+} cation was also used to stabilize PQD structure.[66] Zhang and co-workers presented enhanced stability of Cu^{2+}-substituted $CsPbBrI_2$ QDs with higher structural stability (Fig. 5(d)).[66] The incorporation of Cu^{2+} ions could increase the formation energy and cause slightly lattice contraction, which stabilized the cubic phase of PQDs.

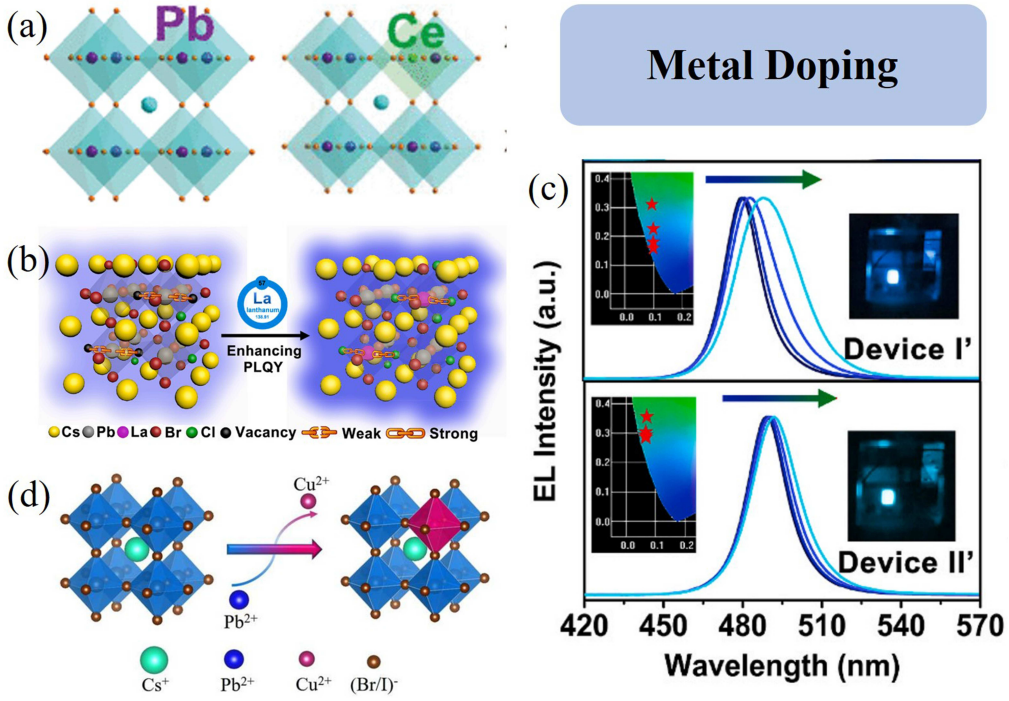


Fig. 5. (a) The schematic diagram of Ce^{3+} doped PQDs.[65] (b) The proposed PLQY increasing mechanism of La^{3+}-doped $CsPb(Br_{0.7}Cl_{0.3})_3$ PQDs. (c) EL spectra, CIE and corresponding device lighting photographs of device I', II' with different Br/I after La^{3+} doping.[55] (d) The schematic diagram of Cu^{2+} doped PQDs.[66]

Besides *B*-site doping, appropriate *A*-site cation mixing is also benefit to stabilize PQDs and MHP based devices.[68] Kim *et al.* exploited substitutional doping of $FAPbBr_3$ by guanidinium (GA^+) cations in PQDs,[18] which leads to an increased charge carrier confinement without inducing more defects on the PQD surfaces. In addition, the extra GA fit into the surface sites and stabilize the surface amino groups, and it is conducive to passivate/suppress defects, which is also conducive to inhibit ion migration. Meanwhile, they also introducing 1,3,5-tris(bromomethyl)-2,4,6-triethylbenzene (TBTB) interlayer ($\sim$ 5 nm) between PQDs and TPBi layers, which is a benzene ring structure rich in methyl bromide, and would heal the bromide vacancies and further suppress surface defects of PQDs. The two-pronged strategy showed obvious enhancement of operational stability of PeQLEDs, achieving a T_{50} of 132 min with 100 cd·m^{-2}, which is $\sim$ 5.3 relative to pristine $FAPbBr_3$ QLEDs (T_{50} = 25 min).

Ligand engineering To fabricate highly efficient PeQLEDs, the primary step is to obtain precise control of PQDs, especially the regulation of surface ligand process due to its significant effect on the stability of PQDs, some examples are shown in Fig. 6.[6,19,46,69,70] Dong *et al.* presented resurfacing $CsPbBr_3$ PQDs, and achieved a bipolar shell consisting of an inner anion shell and an outer shell comprised of cations and polar solvent molecules.[17] The inner and outer shells are held together by electrostatic adsorption. The PeQLEDs made using bipolar-shell QDs showed enhanced stability: a 60 min T_{50} at 1200 cd·m^{-2} for the green LEDs and a 20 min T_{50} at 90 cd·m^{-2} for the blue LEDs. In addition, the EQE of the blue PeQLED is the highest so far, benefiting from the reducing trap density, which would suppress the ion migration. Li *et al.* used octylamine (OTA) additive to maintain the integrity of PQDs and suppress the formation of defects (Fig. 6(a)).[56] The additive increased the E_a for ion migration from 0.779 eV to 0.819 eV, thus reduced the number of ion vacancies, i.e., decreasing the ion migration paths. As a result, the OTA additive led to 6-fold increase in operational lifetime of PeQLEDs. By the way, the QLEDs based on OTA-assisted Zn-doped $CsPbI_3$ QDs presented a high EQE of 15.3%.

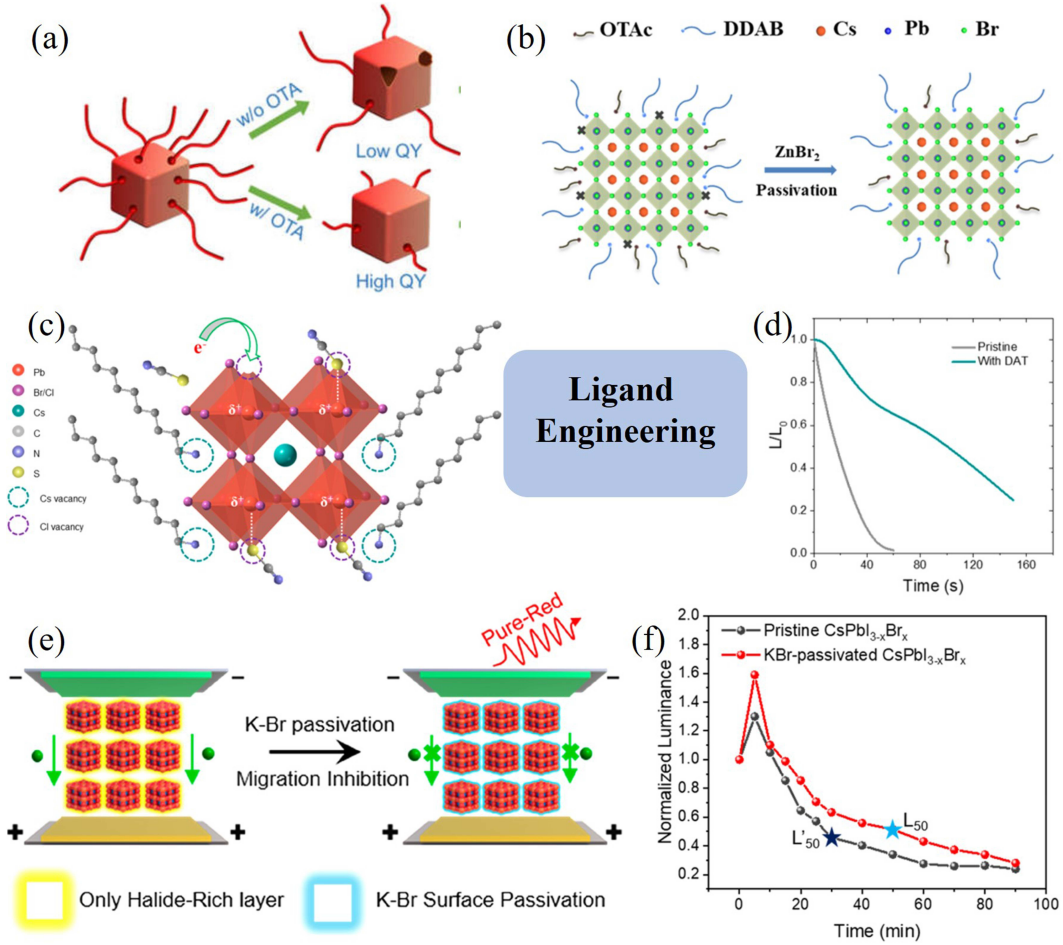


Fig. 6. (a) Comparison of two kinds of purification processes with/without octylamine (OTA).[56] (b) Schematic diagram of PQDs' passivation of $ZnBr_2$.[46] (c) Illustration of Cl vacancy-induced Coulomb trap site formation, electron trapping, and self-assembly of organic thiocyanate (RSCN) on the defect sites in PQDs. (d) Operational lifetimes for the pristine device and the DAT-treated device at a constant voltage bias of 4.5 V.[71] (e) Illustration of ion migration suppressed by potassium bromide-enriched surface passivation. (f) Operation lifetime for the devices based on prepared $CsPbI_{3-x}Br_x$ QDs measured at a constant driving voltage of 5.0 V. The luminance of the LEDs was normalized to their initial values.[72]

Halogen vacancies are the predominant defect species in inorganic lead halide QDs.[71] These defects initiate and catalyze device degradation by facilitating rapid ion migration and make perovskite more unstable. Therefore, suppressing halide vacancies is an effective way to achieve stable PeLEDs. Zheng *et al.*[71] demonstrated a facile strategy for passivating the Cl vacancy in PQDs with nonpolar solvent-soluble organic pseudohalides [n-dodecylammonium thiocyanate (DAT)] (Fig. 6(c)), and realized efficient blue ($\sim$ 470 nm) PeQLEDs with an EQE of 6.3% (vs. 3.5% for pristine devices) and a half-lifetime of $\sim$ 99 s (vs. $\sim$ 17 s for the pristine devices, Fig. 6(d)).

Baek and co-workers used ZnX_2 and tri-octyl phosphine oxide (TOPO) as surface capping agents for highly stable $CsPbX_3$ QDs.[73] Zn and TOPO were combined and these complexes were attached to the surface of the PQDs, and can effectively passivate the halide surface. The efficiency of PQDs is increased by the effect of reducing halide vacancy and surface oxides by excess ZnX_2, which is helpful to inhibit ion migration. Organic ammonium like diphenylpropylammonium chloride (DPPACl),[74] used as passivating agent, could also successfully prevent the spectral instability of blue $CsPbBr_2Cl$ PeLEDs by passivating the Cl^- vacancies. In addition, the device emitted stably in deep-blue spectral region (464 nm) with a T_{50} lifetime of 420 s. Yasser *et al.*[75] used multidentate ligands ethylene diaminetetraacetic acid (EDTA) and reduced L-glutathione to post-treat the synthesized $MAPb(I_xBr_{1-x})_3$ QDs, which inhibited the halide separation under electric field and enhanced the spectral stability of PeQLEDs. The EDTA and glutamine ligands bind strongly to Pb, hence the uncoordinated Pb on the surface of the PQDs would be removed by ligand exchange. Also, the ligand had a strong affinity with the QD surface, which improved the formation energy of the iodine Frankel defect, thereby suppressed the formation of this defect. The EL spectrum was stable under constant current density of 1.5 $mA{\cdot}cm^{-2}$ over 20 min. The acid etching-driven ligand exchange strategy was also proposed to achieve stable pure-blue small-sized $CsPbBr_3$ PeQLEDs.[76] The acid, HBr, was employed to etch imperfect $[PbBr_6]^{4-}$ octahedrons with halide vacancies to remove surface defects and excessive carboxylate ligands. Meanwhile, didodecylamine (DDDAM) and phenethylamine (PEA) were introduced to bond with the residual uncoordinated sites and realized *in situ* ligand exchange with original long-chain organic ligand. As a result, the vacancy density was suppressed, parallelly inhibiting ion migration by eliminating the active sites. The PeQLEDs exhibited robust durability with a T_{50} exceeding 12 h under continuous operation. KBr was also used to passivate PQDs to inhibit halide ion migration (Fig. 6(e)), benefitting from the high binding energy between potassium and halide ions in combination with the tendency for such ions to form halide-sequestering species.[72] After the treatment of $CsPb(Br/I)_3$ PQDs with KBr, pure red PeQLEDs were fabricated with more stable EL emission and a longer device lifetime (Fig. 6(f)). In addition, potassium passivation is useful in bulk MHPs.[77]

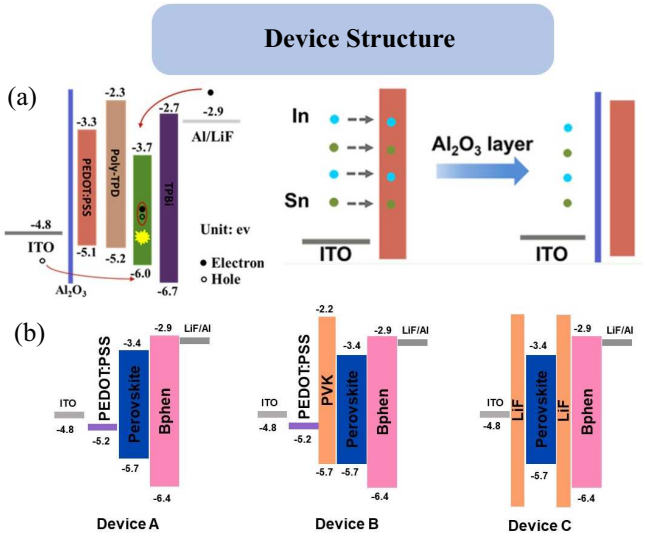


Fig. 7. (a) Schematic diagram of PeQLED energy band alignment with Al_2O_3 layer and suppressing ion migration.[46] (b) Schematic diagram of PeQLEDs of different architectures.[52]

Device structure architecture Except capping MHP layer utilizing ligand engineering and metal doping, introducing other layers to gain the novel device structure of LED is also an effective way to suppress ion migration. Geng *et al.* introduced the Al_2O_3 layer with ALD between ITO electrode and PEDOT:PSS transport layer in $CsPbBr_3$ QLED (schematic diagram in Fig. 7(a)),[46] which effectively inhibited the exciton quenching effect by preventing the migration of metal ions, which is responsible for the prolonged lifetime of the device. In addition, an inorganic $ZnBr_2$ ligand was used to passivate the Br vacancy on the surface of PQDs. The PLQY of PQDs was improved to near-unity. The stability of the PeQLEDs was tested under constant voltage (5 V) at room temperature. The T_{50} lifetime was extended by about 30 times. Wu *et al.* proposed the architecture of insulator–perovskite–insulator (IPI, schematic diagram shown in Fig. 7(b)) early on.[52] A thin LiF layer was evaporated on both surfaces of the MHP film. This structure significantly prevented ion migration between the MHP and the transport layer. Meanwhile, it effectively suppressed the quenching of excitons at the interface. The corresponding lifetime of LED is 96 h, which is about 24-fold enhancement compared to the controlled device. In the latest work, they introduced inorganic ZnS/ZnSe cascade electron transport layers to replace the previously used 4,7-diphenyl-1,10-phenanthroline (Bphen)[78] which further reduced the field-induced ion migrations of MHPs layers and diffusion of metal atoms from cathode into MHP layers. The prepared device showed an efficiency of 11.05% and a stability of 255 h at an initial luminance of 120 cd/m^2. Other

device structures changing transport layers to balance carriers injection[79] or composite emissive layer[80,81] may be expected to improve the device stability of PeQLEDs.

Core/shell structure To achieve better passivation of PQDs and inhibit ion migration, core/shell structure is a good choice. Zhang *et al.* reported a PbS capped $CsPbI_3$ PQDs structure with enhanced optical and phase stability.[57] PbS capping can passivated the surface defects of $CsPbI_3$ PQDs, and help to stabilize the QD surface and inhibit ion migration of QD films as shown in Fig. 8(a). In addition, the initial n-type PQDs switched to nearly ambipolar, and the corresponding LED with p–i–n structure presented an EQE of 11.8% along with enhanced operational stability.

Vikash Kumar Ravi *et al.* have successfully suppressed the halide ion exchange by capping $CsPbBr_3$ and $CsPbI_3$ QDs with $PbSO_4$–oleate, which means halide migration between QDs is prevented (Fig. 8(c)).[82] The QD suspensions were treated with a $PbSO_4$–oleate cluster, and the capping $CsPbBr_3$ and $CsPbI_3$ QDs suspensions were mixed to test stability. Compared with uncapping QDs, the capping mixture of QDs showed slightly shift ($\sim$ 30 nm) in the emission peak during several hours, which may arise from the halide ion exchange between poorly capped or uncapped QDs or from deterioration of stirring as seen in Figs. 8(d) and 8(e). Besides, a covalently bonded semiconductor shell could help to cut off the ion migration channel from PQDs, thus avoiding the efficiency deterioration of PQDs. Zhang and coworkers[83] capped $CsPbI_3$ PQDs with well-designed atomic crystal PbMgZnTe/$Mg_xZn_{1-x}Te$ shells as shown in Fig. 8(b), which simultaneously exhibited proper energy level arrangement to achieve balanced charge injection and suppressed efficiency roll-off of LEDs.

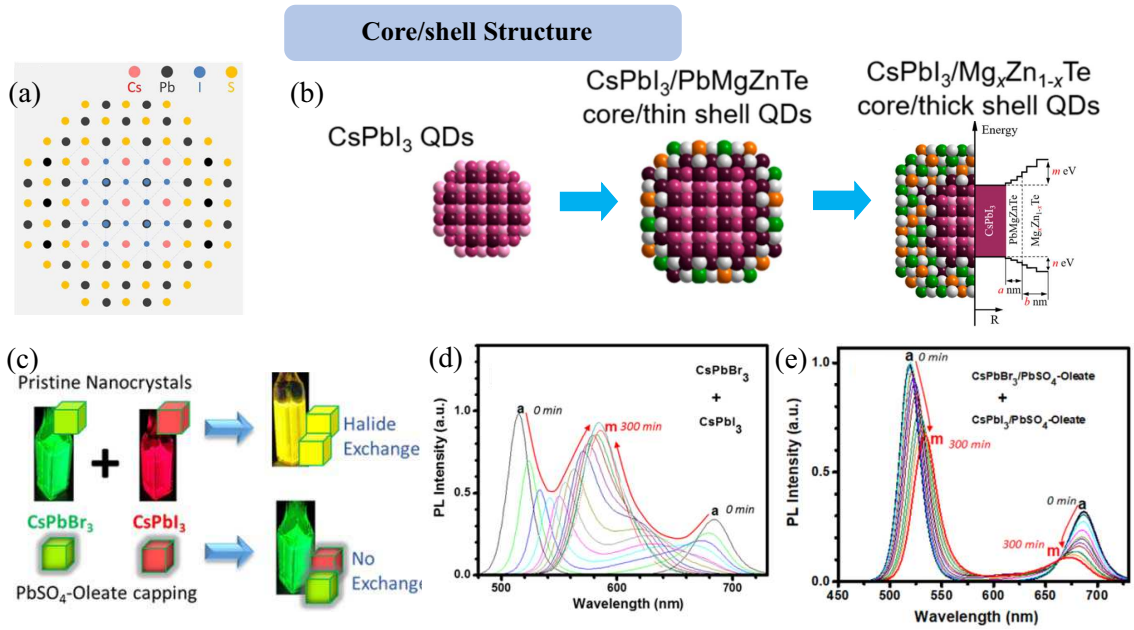


Fig. 8. (a) Proposed architecture of PbS capped $CsPbI_3$ QDs.[57] (b) Schematic of $CsPbI_3$ PQDs with well-designed atomic crystal PbMgZnTe/$Mg_xZn_{1-x}Te$ shells.[83] (c) Comparison of $PbSO_4$–oleate-capped $CsPbI_3$ QDs and the corresponding luminescences. (d) emission spectra of pristine $CsPbBr_3$ NCs and $CsPbI_3$ NCs in hexane ($\sim$ 40 nM each) recorded immediately after mixing. (e) Emission spectra of $PbSO_4$–oleate-capped $CsPbBr_3$ QDs and $PbSO_4$–oleate-capped $CsPbI_3$ QDs ($\sim$ 60 nM each) recorded immediately after mixing.[82]

Cross-linking Cross linking is also an effective way to suppress ion migration. Han *et al.* proposed a methylene-bis-acrylamide cross-linking strategy to both passivate defects and suppress ion-migration in PeLEDs.[84] The device exhibited operational stability with a T_{50} of 208 h under continuous operation with luminance of 100 cd·m^{-2}. In addition, the EQE of cross-linked LEDs could maintain above 15% during 25 times scanning as measured every 4 days. The improvement of operation stability is ascribed to the increases of binding energy from 0.54 eV to 0.92 eV and activation energy from 0.21 eV to 0.5 eV. The ligands breaking way and ion migration are suppressed, which inhibits ion migration inside and across crystals. Poly(maleic anhydride-alt-1-octadecene) (PMA) was used during PQD synthesis to achieve a stable red PeQLED.[85] The cross-linked PMA interacted with PbI_2 in the precursors via coupling effect between O groups in PMA and Pb^{2+}, and it significantly reduced the surface defect of $CsPbI_3$ QDs. Benefiting from the improved phase quality, the PLQY of PQDs increased a lot, and the corresponding LEDs achieved a high EQE of 17.8% and high lifetime ($T_{50} \sim$ 317 h at current density of 30 mA·cm^{-2}).

Film fabrication/structure design of PQDs films Liu and co-workers reported stable PQDs in a thin layer of precursor solution of perovskite,[23] and they used strained PQDs as nucleation centers to drive homogeneous crystallization of perovskite matrix. Benefiting from this novel structure,

the Auger bi-excitation recombination and ion migration have been suppressed, and a longer T_{50} ($\sim$ 2400 h) was obtained. Similarly, a thin film structure of PQDs stabilized in metal–organic framework (MOF) was demonstrated,[86] and the PeQLEDs device is free from ion migration with the protection of MOF matrix. As a result, the T_{50} is over 50 h under a constant high injection current density. Xue *et al.* achieved an enhanced stability of PeQLEDs by introducing preformed CdSe/ZnS core–shell QDs in anti-solvent during *in-situ* ligand assisted reprecipitation fabrication of PQDs films.[87] With this film fabrication method, the Cd-based QDs adjusted the electrical field distribution, and decreased the electrical field intensity within the perovskite film, thus suppressing the ion migration in PQDs films. The corresponding PeQLEDs demonstrated a T_{50} of 83 min under the initial luminance of 1021 cd/cm^2.

5. Summary and outlook

We have systematically reviewed the migratory element species in PeQLEDs and the origin of ion migration, the effect on the device stability. Then, the strategies to suppress the ion migration in PeQLEDs are highlighted. The phenomena of migrated ions in PeQLEDs are not uncommon due to low E_a and high electric field. The elements of ion migration are not only halogens, but also *A*-site cations, protons, metal ions in the transport layers. The spectral shift and the poor operational stability induced by ion migration are the main effects that we briefly discussed. It is worth noting that the effect of ion migration is not always bad, and a small amount of ion migration may lead to device performance improvement. The inhibition of ion migration in PeQLEDs takes up the bulk of this review, which mainly includes several aspects: i) metal doping. Appropriate *A*-site/*B*-site cation mixing has been verified benefit for suppress ion migration to stabilize PQDs and PeQLEDs. ii) Ligand engineering. In view of the abundant surface ligands of PQDs, surface ligand engineering has a great impact on their properties and stability, especially ligand passivation to reduce surface defects. iii) Device structure architecture. Introducing functional layers in PeQLEDs is also an effective method to impede ion migration within PQD layer and across device interfaces. iv) Core/shell structure. Fabricate appropriate core/shell structure of PQDs can passivate defects and inhibit ion migration. v) Cross linking. Some molecules are used as cross-linking agent to reduce defects of PQDs and suppress ion migration in PQDs. vi) Film fabrication/structure design of PQDs films. Embedding PQDs in different matrix materials to form composite films can also significantly inhibit ion migration. Although ion migration has been drastically mitigated by material design and device engineering, the operational lifetime of PeQLEDs cannot meet the industrial requirement. Even in our known reports, very few can achieve the lifetime of hundreds of hours for PeQLEDs. Therefore, there is a long way to go to study the inhibition of ion migration. We here give some perspectives for possible research directions as below.

Despite common passivation method to directly inhibit ion migration used in PeQLEDs, other ideas about passivate defects or different passivate agents utilized in 2D or bulk perovskite films have great potential to successfully suppress ion migration in PeQLEDs.[88–91] Nenon, *et al.* proposed a general surface passivation mechanism for $CsPbX_3$ perovskite,[4] and provided a systematic framework for full trap passivation, which is helpful to reduce the channels of ion migration. They suggested introducing softer, anionic, X-type Lewis bases that target under-coordinated Pb atoms in perovskite QDs, and near-unity PLQY of $CsPbBr_3$ QDs and $CsPbI_3$ QDs with full trap passivation were gained. This general mechanism is potential in suppressing ion migration due to the excellent surface passivation. Phenylalkylammonium iodide molecules of varying alkyl chain lengths were utilized to passivate perovskite films.[92] These molecules could stabilize the perovskites by suppressing iodide ion migration and reduce the surface defects, and stabilization effect enhanced with increasing chain length because of the stronger binding with perovskite surface. As a result, the perovskite LEDs with passivated film gained a T_{50} lifetime of 130 h under 100 mA·cm^{-2}. Furthermore, theoretical computation may provide a faster and more accurate screening scheme for the selection of passivation agents.

Manipulating method like low-temperature operation is also benefit for ion migration due to the lower energy provided from heat.[93] In addition, when the LED device is operating, the local temperature will rise to tens of degrees, which is very favorable for ion migration. Along this line of thinking, thermal management of PeQLED devices, wihch is little studied, may make good progress in inhibiting ion migration in the future. To sum up, this review will be helpful for designing highly stable PeQLEDs in the future.

Acknowledgements

This work was supported by the Natural Natural Science Foundation of China (Grant Nos. 61904081 and 51672132), the Natural Science Foundation of Jiangsu Province, China (Grant No. BK20190449), and the Postdoctoral Research Funding Program of Jiangsu Province, China (Grant No. 2020Z144).

References

[1] Ren X, Zhang X, Xie H, Cai J, Wang C, Chen E, Xu S, Ye Y, Sun J, Yan Q and Guo T 2022 *Nanomaterials* **12** 2243
[2] Li J, Xu L, Wang T, Song J, Chen J, Xue J, Dong Y, Cai B, Shan Q, Han B and Zeng H 2017 *Adv. Mater.* **29** 1603885

[3] Pan J, Shang Y, Yin J, De Bastiani M, Peng W, Dursun I, Sinatra L, El-Zohry A M, Hedhili M N, Emwas A H, Mohammed O F, Ning Z and Bakr O M 2018 *J. Am. Chem. Soc.* **140** 562

[4] Nenon D P, Pressler K, Kang J, Koscher B A, Olshansky J H, Osowiecki W T, Koc M A, Wang L W and Alivisatos A P 2018 *J. Am. Chem. Soc.* **140** 17760

[5] Fang T, Wang T, Li X, Dong Y, Bai S and Song J 2021 *Sci. Bull.* **66** 36

[6] De Roo J, Ibanez M, Geiregat P, Nedelcu G, Walravens W, Maes J, Martins J C, Van Driessche I, Kovalenko M V and Hens Z 2016 *ACS Nano* **10** 2071

[7] Chen K, Jin W, Zhang Y, Yang T, Reiss P, Zhong Q, Bach U, Li Q, Wang Y, Zhang H, Bao Q and Liu Y 2020 *J. Am. Chem. Soc.* **142** 3775

[8] Chen J, Jia D, Johansson E M J, Hagfeldt A and Zhang X 2021 *Energy Environ. Sci.* **14** 224

[9] Wang Y, Li X, Zhao X, Xiao L, Zeng H and Sun H 2016 *Nano Lett.* **16** 448

[10] Huang C Y, Zou C, Mao C, Corp K L, Yao Y C, Lee Y J, Schlenker C W, Jen A K Y and Lin L Y 2017 *ACS Photonics* **4** 2281

[11] Song J, Li J, Li X, Xu L, Dong Y and Zeng H 2015 *Adv. Mater.* **27** 7162

[12] Wang H C, Wang W, Tang A C, Tsai H Y, Bao Z, Ihara T, Yarita N, Tahara H, Kanemitsu Y, Chen S and Liu R S 2017 *Angew. Chem. Int. Ed.* **56** 13650

[13] Zhang B B, Yuan S, Ma J P, Zhou Y, Hou J, Chen X, Zheng W, Shen H, Wang X C, Sun B, Bakr O M, Liao L S and Sun H T 2019 *J. Am. Chem. Soc.* **141** 15423

[14] Dong Y, Tang X, Zhang Z, Song J, Niu T, Shan D and Zeng H 2020 *Matter* **3** 273

[15] Yang Z, Dong Y, Zong S, Li L, Yang K, Wang Z, Zeng H and Cui Y 2022 *Nanoscale* **14** 6392

[16] Mei X, Jia D, Chen J, Zheng S and Zhang X 2022 *Nano Today* **43** 101449

[17] Dong Y, Wang Y K and Yuan F 2020 *Nat. Nanotechnol.* **15** 668

[18] Kim Y H, Kim S and Kakekhani A 2021 *Nat. Photon.* **15** 148

[19] Wang Y K, Yuan F and Dong Y 2021 *Angew. Chem. Int. Ed.* **60** 16164

[20] Shen Y, Li Y Q, Zhang K, Zhang L J, Xie F M, Chen L, Cai X Y, Lu Y, Ren H, Gao X, Xie H, Mao H, Kera S and Tang J X 2022 *Adv. Funct. Mater.* **32** 2206574

[21] Liu Z, Qiu W, Peng X, Sun G, Liu X, Liu D, Li Z, He F, Shen C, Gu Q, Ma F, Yip H L, Hou L, Qi Z and Su S J 2021 *Adv. Mater.* **33** e2103268

[22] Ye F, Shan Q, Zeng H and Choy W 2021 *ACS Energy Lett.* **6** 3114

[23] Liu Y, Dong Y and Zhu T 2021 *J. Am. Chem. Soc.* **143** 15606

[24] Guo B, Lai R, Jiang S, Zhou L, Ren Z, Lian Y, Li P, Cao X, Xing S, Wang Y, Li W, Zou C, Chen M, Hong Z, Li C, Zhao B and Di D 2022 *Nat. Photon.* **16** 637

[25] Won Y H, Cho O, Kim T, Chung D Y, Kim T, Chung H, Jang H, Lee J, Kim D and Jang E 2019 *Nature* **575** 634

[26] Li N, Jia Y, Guo Y and Zhao N 2022 *Adv. Mater.* **34** e2108102

[27] Dong Q, Mendes J, Lei L, Seyitliyev D, Zhu L, He S, Gundogdu K and So F 2020 *ACS Appl. Mater. Interfaces* **12** 48845

[28] Xing G, Wu B, Wu X, Li M, Du B, Wei Q, Guo J, Yeow E K, Sum T C and Huang W 2017 *Nat. Commun.* **8** 14558

[29] Yuan Y and Huang J 2016 *Acc. Chem. Res.* **49** 286

[30] Dong Q, Lei L, Mendes J and So F 2020 *J. Phys.: Mater.* **3** 012002

[31] Wang H C, Bao Z, Tsai H Y, Tang A C and Liu R S 2018 *Small* **14** 1702433

[32] Xie M and Tian J 2022 *J. Phys. Chem. Lett.* **13** 1962

[33] Eames C, Frost J M, Barnes P R, O'Regan B C, Walsh A and Islam M S 2015 *Nat. Commun.* **6** 7497

[34] Conings B, Drijkoningen J, Gauquelin N, Babayigit A, D'Haen J, D'Olieslaeger L, Ethirajan A, Verbeeck J, Manca J, Mosconi E, Angelis F D and Boyen H G 2015 *Adv. Energy Mater.* **5** 1500477

[35] Zhang H, Fu X, Tang Y, Wang H, Zhang C, Yu W W, Wang X, Zhang Y and Xiao M 2019 *Nat. Commun.* **10** 1088

[36] Cho H, Kim Y H, Wolf C, Lee H D and Lee T W 2018 *Adv. Mater.* **30** e1704587

[37] Barker A J, Sadhanala A, Deschler F, Gandini M, Senanayak S P, Pearce P M, Mosconi E, Pearson A J, Wu Y, Kandada A R S, Leijtens T, Angelis F D, Dutton S E, Petrozza A and Friend R H 2017 *ACS Energy Lett.* **2** 1416

[38] ten Brinck S, Zaccaria F and Infante I 2019 *ACS Energy Lett.* **4** 2739

[39] Meggiolaro D, Mosconi E and De Angelis F 2019 *ACS Energy Lett.* **4** 779

[40] Kim Y H, Wolf C, Kim H and Lee T W 2018 *Nano Energy* **52** 329

[41] Kamat P V and Kuno M 2021 *Acc. Chem. Res.* **54** 520

[42] Vashishtha P and Halpert J E 2017 *Chem. Mater.* **29** 5965

[43] Wen Z, Xie F and Choy W C H 2021 *Nano Select* **3** 505

[44] Yuan Y, Wang Q, Shao Y, Lu H, Li T, Gruverman A and Huang J 2016 *Adv. Energy Mater.* **6** 1501803

[45] Prakasam V, Tordera D, Bolink H J and Gelinck G 2019 *Adv. Opt. Mater.* **7** 1900902

[46] Geng S, Wen Y, Zhou B, Wang Z, Wang Z, Wang P, Jing Y, Cao K, Wang K and Chen R 2021 *ACS Appl. Electron. Mater.* **3** 2362

[47] Zhao L, Gao J, Lin Y L, Yeh Y W, Lee K M, Yao N, Loo Y L and Rand B P 2017 *Adv. Mater.* **29** 1605317

[48] Cheng T, Tumen-Ulzii G, Klotz D, Watanabe S, Matsushima T and Adachi C 2020 *ACS Appl. Mater. Interfaces* **12** 33004

[49] Kim H, Kim J S, Heo J M 2020 *Nat. Commun.* **11** 3378

[50] Feng Y, Zhao Y, Zhou W K, Li Q, Saidi W A, Zhao Q and Li X Z 2018 *J. Phys. Chem. Lett.* **9** 6536

[51] Cardenas-Daw C, Simon T, Stolarczyk J K and Feldmann J 2017 *J. Am. Chem. Soc.* **139** 16462

[52] Shi Y, Wu W, Dong H, Li G, Xi K, Divitini G, Ran C, Yuan F, Zhang M, Jiao B, Hou X and Wu Z 2018 *Adv. Mater.* **30** e1800251

[53] Knight A J and Herz L M 2020 *Energy Environ. Sci.* **13** 2024

[54] Shynkarenko Y, Bodnarchuk M I, Bernasconi C, Berezovska Y, Verteletskyi V, Ochsenbein S T and Kovalenko M V 2019 *ACS Energy Lett.* **4** 2703

[55] Zhang S, Liu H, Li X and Wang S 2020 *Nano Energy* **77** 105302

[56] Li H, Dong W, Shen X, Ge C, Song Y, Wang Z, Wang A, Yang Z, Hao M, Zhang Y, Zheng W, Zhang X and Dong Q 2022 *J. Phys. Chem. C* **126** 1085

[57] Zhang X, Lu M, Zhang Y, Wu H, Shen X, Zhang W, Zheng W, Colvin V L and Yu W W 2018 *ACS Cent. Sci.* **4** 1352

[58] Xu B, Wang W, Zhang X, Liu H, Zhang Y, Mei G, Chen S, Wang K, Wang L and Sun X W 2018 *Sci. Rep.* **8** 15799

[59] Lee H, Ko D and Lee C 2019 *ACS Appl Mater Interfaces* **11** 11667

[60] Bi E, Chen H, Xie F, Wu Y, Chen W, Su Y, Islam A, Gratzel M, Yang X and Han L 2017 *Nat. Commun.* **8** 15330

[61] Kim Y H, Kim J S and Lee T W 2019 *Adv. Mater.* **31** e1804595

[62] Yuan Y, Chae J, Shao Y, Wang Q, Xiao Z, Centrone A and Huang J 2015 *Adv. Energy Mater.* **5** 1500615

[63] Li J, Shan X, Bade S G R, Geske T, Jiang Q, Yang X and Yu Z 2016 *J. Phys. Chem. Lett.* **7** 4059

[64] Futscher M H, Gangishetty M K, Congreve D N and Ehrler B 2020 *ACS Appl. Electron. Mater.* **2** 1522

[65] Yao J S, Ge J, Han B N, Wang K H, Yao H B, Yu H L, Li J H, Zhu B S, Song J Z, Chen C, Zhang Q, Zeng H B, Luo Y and Yu S H 2018 *J. Am. Chem. Soc.* **140** 3626

[66] Zhang J, Zhang L, Cai P, Xue X, Wang M, Zhang J and Tu G 2019 *Nano Energy* **62** 434

[67] Zou S, Liu Y, Li J, Liu C, Feng R, Jiang F, Li Y, Song J, Zeng H, Hong M and Chen X 2017 *J. Am. Chem. Soc.* **139** 11443

[68] Tan S, Yavuz I, De Marco N, Huang T, Lee S J, Choi C S, Wang M, Nuryyeva S, Wang R, Zhao Y, Wang H C, Han T H, Dunn B, Huang Y, Lee J W and Yang Y 2020 *Adv. Mater.* **32** e1906995

[69] Song J, Fang T, Li J, Xu L, Zhang F, Han B, Shan Q and Zeng H 2018 *Adv. Mater.* **30** e1805409

[70] Ye F, Zhang H, Wang P, Cai J, Wang L, Liu D and Wang T 2020 *Chem. Mater.* **32** 3211

[71] Zheng X, Yuan S and Liu J 2020 *ACS Energy Lett.* **5** 793

[72] Yang J N, Song Y, Yao J S, Wang K H, Wang J J, Zhu B S, Yao M M, Rahman S U, Lan Y F, Fan F J and Yao H B 2020 *J. Am. Chem. Soc.* **142** 2956

[73] Baek S, Kang S, Son C, Shin S J, Kim J H, Park J and Kim S W 2020 *Adv. Opt. Mater.* **8** 1901897

[74] Kim Y C, An H J, Kim D H, Myoung J M, Heo Y J and Cho J H 2020 *Adv. Funct. Mater.* **31** 2005553

[75] Hassan Y, Park J H, Crawford M L, Sadhanala A, Lee J, Sadighian J C, Mosconi E, Shivanna R, Radicchi E, Jeong M, Yang C, Choi H, Park S H, Song M H, De Angelis F, Wong C Y, Friend R H, Lee B R and Snaith H J 2021 *Nature* **591** 72

[76] Bi C, Yao Z, Sun X, Wei X, Wang J and Tian J 2021 *Adv. Mater.* **33** e2006722

[77] Abdi-Jalebi M, Andaji-Garmaroudi Z, Cacovich S, Stavrakas C, Philippe B, Richter J M, Alsari M, Booker E P, Hutter E M, Pearson A J, Lilliu S, Savenije T J, Rensmo H, Divitini G, Ducati C, Friend R H and Stranks S D 2018 *Nature* **555** 497
[78] Zhang L, Yuan F, Xi J, Jiao B, Dong H, Li J and Wu Z 2020 *Adv. Funct. Mater.* **30** 2001834
[79] Tan Z K, Moghaddam R S, Lai M L, Docampo P, Higler R, Deschler F, Price M, Sadhanala A, Pazos L M, Credgington D, Hanusch F, Bein T, Snaith H J and Friend R H 2014 *Nat. Nanotechnol.* **9** 687
[80] Zhao B, Bai S and Kim V 2018 *Nat. Photon.* **12** 783
[81] Cho H, Wolf C, Kim J S, Yun H J, Bae J S, Kim H, Heo J M, Ahn S and Lee T W 2017 *Adv. Mater.* **29** 1700579
[82] Ravi V K, Scheidt R A, Nag A, Kuno M and Kamat P V 2018 *ACS Energy Lett.* **3** 1049
[83] Zhang X, Yin W, Zheng W and Rogach A L 2020 *ACS Energy Lett.* **5** 2927
[84] Han B, Yuan S, Cai B, Song J, Liu W, Zhang F, Fang T, Wei C and Zeng H 2021 *Adv. Funct. Mater.* **31** 2011003
[85] Li H, Lin H, Ouyang D, Yao C, Li C, Sun J, Song Y, Wang Y, Yan Y, Wang Y, Dong Q and Choy W C H 2021 *Adv. Mater.* **33** e2008820
[86] Tsai H, Shrestha S, Vilá R A, Huang W, Liu C, Hou C H, Huang H H, Wen X, Li M, Wiederrecht G, Cui Y, Cotlet M, Zhang X, Ma X and Nie W 2021 *Nat. Photon.* **15** 843
[87] Xue X, Li M, Liu Z, Wang C, Xu J, Wang S, Zhang H, Zhong H and Ji W 2022 *Fundamental Research*
[88] Lee S, Park J H, Lee B R, Jung E D, Yu J C, Di Nuzzo D, Friend R H and Song M H 2017 *J. Phys. Chem. Lett.* **8** 1784
[89] Ma D, Todorovic P and Meshkat S 2020 *J. Am. Chem. Soc.* **142** 5126
[90] Han B, Yuan S, Fang T, Zhang F, Shi Z and Song J 2020 *ACS Appl. Mater. Interfaces* **12** 14224
[91] Chu Z, Ye Q, Zhao Y, Ma F, Yin Z, Zhang X and You J 2021 *Adv. Mater.* **33** e2007169
[92] Guo Y, Apergi S, Li N, Chen M, Yin C, Yuan Z, Gao F, Xie F, Brocks G, Tao S and Zhao N 2021 *Nat. Commun.* **12** 644
[93] Chen M, Shan X, Geske T, Li J and Yu Z 2017 *ACS Nano* **11** 6312