COMMENTARY

Surface regulation of perovskite nanocrystals for electroluminescence

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Metal-halide perovskite light-emitting diodes (PeLEDs) have emerged as a promising candidate for next-generation displays due to their ultrahigh color purity, excellent efficiency, and low processing cost. Despite the high efficiency of PeLEDs approaching the theoretical limit, their unsatisfactory operational lifetime remains a critical challenge. Besides, PeLEDs usually take several milliseconds to reach a steady state under pulse operation longer than one millisecond,[1] severely sacrificing brightness and bringing difficulty in brightness control. This millisecond-response time of PeLEDs is unfavorable for realizing high-refresh-rate display, which has been largely overlooked. Ion migration under electric fields has been proven to be one of the essential factors for operational stability and slow response time. It is known that ions prefer to migrate through halide vacancies, namely the defective surface and grain boundaries serve as ion migration channels. Relying on surrounding ligands rather than grain boundaries, perovskite nanocrystal (PeNC) films with fewer vacancies possess a higher energy barrier for ion migration than bulk film. Combined with unique strategies of in-situ surface modification, the ideal PeNC films with a perfect lattice and the absence of surface vacancies in every single PeNC would further increase the energy barrier, promising to inhibit ion migration under electric fields.

The type of organic acids used in PeNC synthesis plays an important role in surface construction. For the typical hot-injection method, the acid-base equilibrium of oleic acid (OA, acid, H-A) and oleylamine (OAm, base, B) binary ligand system are crucial for the crystallization and surface regulation of PeNC.[2] In detail, OAm will be protonated by H^+ ions released from OA, forming oleylammonium ions (RNH_3^+). Since OA is a weak acid with a dissociation constant (pKa) of 7.1, there are acid-base equilibria as shown in Figure 1, resulting in the co-existence of OA, H^+, OA^-, OAm, and RNH_3^+. OA^- and RNH_3^+ dynamically bonded with PeNC are insufficient to passivate the PeNCs surface, generating many incomplete $[PbX_6]^{4-}$ octahedrons with uncoordinated Pb. The concentration of ionized H^+ will influence the acid-base equilibria, which means that altering the type of organic acid ligands with various acidity can regulate the equilibrium of the protonation progress. The pKa of

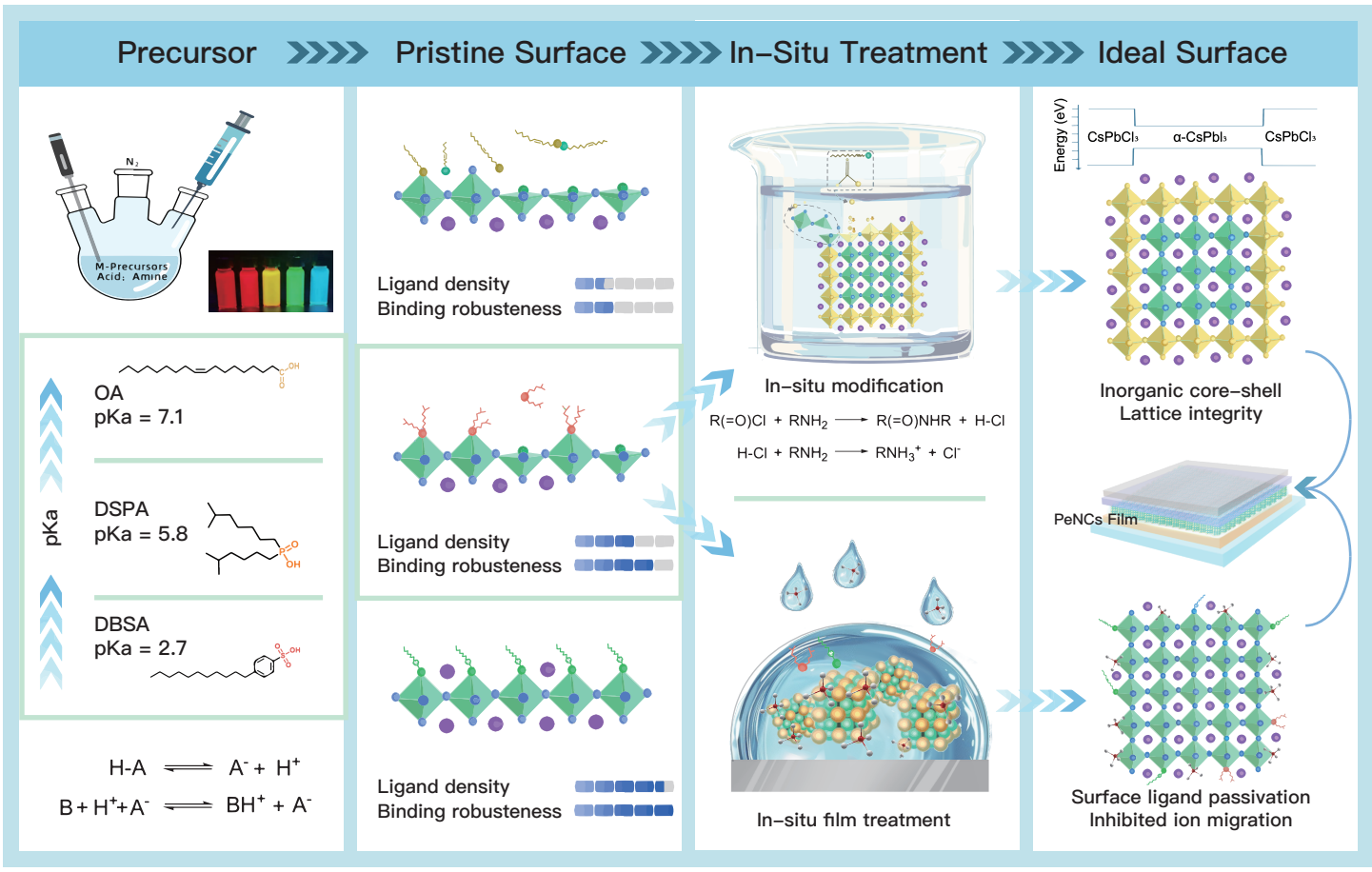

Figure 1. Schematic of surface regulation of perovskite nanocrystals for electroluminescence.

acid ligands decreases with increasing acidity (OA, 7.1 > diisooctylphosphinic acid (DSPA), 5.8 > dodecylbenzene sulfonic acid (DBSA), 2.7), and the increased ionized H^+ make the acid-base equilibrium shift to the right. Resultantly, more protonated amine (RNH_3^+) and acid radicals can coordinate on the surface of PeNC. Acid radicals anchor on the PeNC surface through their interaction with the uncoordinated Pb. The bonding robustness of this interaction depends on the orbital overlap of the electron cloud between Pb and acid radicals, which is determined by the electronegativity of the central element in the acids (S>P>C), the electron-withdrawing or donating ability of alkyl chains, and other functional groups. Combined with the acidity and bonding robustness of the acid ligands, these merits result in more activated ligands anchoring on the surface of PeNC, enhancing the surface lattice

integrity.

The surface configuration of the as-synthesized PeNCs, including their anchoring ligands and ligand density determined by precursors, significantly impacts the optoelectronic properties of PeNCs. Considering the weak bonding interaction between ligands and OA/OAm-capped PeNCs, the resulting halogen vacancies and diminished ligand density lead to a decrease in photoluminescence quantum yield (PLQY) and poor colloidal stability, raising challenges for the performance of PeLEDs. Compared with OA, the moderately acidic ligand (DSPA) bonds more strongly with uncoordinated Pb, showing a remarkable improvement in PLQY and stability of PeNCs. As acidity increases further, the DBSA-capped PeNCs exhibit sustained PLQY and persistent colloidal stability during multiple purifications, originating from the strongly bonded ligands that can be hardly peeled off or substituted. Though applying organic acids with strong acidity in synthesis can obtain PeNCs with perfect optical properties, the charge transport of the PeNC films is largely dependent on the type and density of the ligands. PeLEDs require an appropriate density of insulating alkyl chains that cap on the PeNC surface. Ligand-mediated synthesis can hardly resolve the trade-off between optical properties and charge transport.

Besides ligand regulation during synthesis, in-situ surface modifications during post-treatment are alternative strategies to construct ideal PeNCs for PeLEDs. Critically, in-situ treatments should be performed during the dissociation stage of the original ligands, such as the deprotonation process of OA/OAm-capped NCs and the spin-coating process of PeNC films. In the former case, the deprotonation of RNH_3^+ is an endothermic process in acid-base equilibria. At high temperatures, the intense deprotonation process leads to large amounts of OA^- and RNH_3^+ dissociating from the surface of the as-synthesized PeNCs. The exposed Pb and a few long-chain ligands provide opportunities for in-situ modification, such as shell growth or etching of incomplete lattice. As for the latter, although additional ligands can passivate PeNCs in solution, ligand loss is inevitable during solvent evaporation. Unfortunately, passivating PeNC film in a solid state is challenging due to its vulnerability to solvents in the absence of ligand protection. In-situ treatment during PeNC film deposition could be effective in constructing a perfect surface with fewer defects.

For instance, by utilizing the in-situ nucleophilic reaction between acyl halides and residual OAm at high temperatures, it is possible to successfully grow the $CsPbCl_3$ shell on the $CsPbI_3$ core. This process constructs the $CsPbI_3/CsPbCl_3$ core-shell NCs with a type I heterojunction.[3] When injected into the crude solution of PeNCs at high temperatures, acyl chlorides can immediately attack OAm. Chloride ions, as the product of nucleophilic reactions, are released immediately and coordinated with many exposed Pb atoms at high temperatures, enabling the growth of an ultrathin $CsPbCl_3$ shell on the $CsPbI_3$ surface. $CsPbI_3/CsPbCl_3$ core-shell NCs exhibit enhanced carrier confinement and surface stability with fewer defects, resulting in pure-red emission with near-unity PLQY and excellent stability. The $CsPbI_3$ NCs in the carrier-confined structure achieved high-performance pure-red PeLEDs with efficiencies exceeding 26%. Due to the significant difference in ionic radius between I^- and Cl^- and in lattice constants between $CsPbI_3$ and $CsPbCl_3$, the $CsPbCl_3$ shell strongly caps on $CsPbI_3$ NCs and effectively suppresses ion migration under constant electric fields. The core-shell PeNCs-based PeLEDs exhibited superior operational lifetime and stable electroluminescence spectra at high driving voltages. We anticipate that in-situ reactions are feasible strategies to construct the specific core-shell structure and surface composition of PeNCs, promising more stable PeLEDs.

Apart from the epitaxial growth of core-shell structure on PeNCs, the in-situ reaction also provides an opportunity for etching incomplete $[PbX_6]^{4-}$ octahedrons on the PeNC surface.[4] Utilizing the protic solvent, i.e., hydrogen halide (HX) or H_2O, to produce excessive RNH_3^+, makes the acid-base equilibrium shift in reverse and decreases OA^-. These surface ligands desorb from the PeNC surface and remove the poorly crystallized octahedrons, eventually presenting a neat and integral surface with a perfect lattice. In-situ etching can eliminate multiple carrier traps and ion-migration channels caused by surface vacancies, offering a facile strategy to further regulate the size of PeNCs and their optical properties.

Regarding in-situ treatment during deposition of PeNC film, pseudohalogen anions,[5] e.g., thiocyanate (SCN^-), tetrafluoroborate (BF_4^-), and hexafluorophosphate (PF_6^-) can fill the halogen vacancies due to their similar ionic radius to halogen ions, and improve the charge transport of the PeNC film due to the absence of insulating long alkyl chains. When dissolved in a mild polar antisolvent like ethyl acetate and rapidly added at the proper moment during the spin-coating of PeNCs films, pseudohalogen anions can strongly coordinate with the exposed Pb atoms through electrostatic interaction. The in-situ treatment should be applied to the PeNC films in a moist solvent microenvironment to ensure complete passivation of each individual particle is completely passivated. The method of in-situ film treatment via pseudohalogen anions can directly act during the film deposition stage and could be applicable for various PeNCs composed of mixed-halides or synthesized through different methods. We anticipate that the in-situ treated PeNC film can fully exploit its excellent crystallinity and sufficiently anchored surface ligands, enabling a defect-free film with a discrete nanostructure to inhibit ion migration. Furthermore, the impact of ions with various functional groups during the electroluminescent stage can be further investigated to improve the operational stability of PeLEDs.

In conclusion, surface regulation of PeNCs is crucial for enhancing the optoelectronic performance of electroluminescent devices. The compromise between surface ligand density and bonding robustness should be considered and carefully modulated by selecting an appropriate organic acid ligand with a moderate pKa in the synthetic stage of PeNCs. The in-situ treatment, either in the crude solution or during the film deposition, is essential to be conducted on the dynamical bonding surface to construct ideal PeNCs with a perfect surface lattice and the absence of vacancies. We anticipate that feasible in-situ treatments could tackle the challenges of ionic defects and ion migration in PeNCs and promote high-efficiency, spectra-stable, fast-response, and long-life PeLEDs.

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DECLARATION OF INTERESTS

The authors declare no competing interests.