Perspective

Low-dimensionality perovskites yield high electroluminescence

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Light-emitting diodes (LEDs) are changing the energy and lighting industry due to their high power efficiencies, low energy consumption, and long operational lifetimes. While epitaxially-grown LEDs are the current industry standard, their incompatibility with large-area displays and flexible substrates precludes their use in many applications. Solution-processed light-emitting materials are more versatile and can be easily coated onto a variety of substrates using modern deposition techniques such as vapor deposition, spin-coating, dip-coating, and spray-painting. With these advantages, organic light-emitting diodes (OLEDs) have been widely applied to TVs, cell phones, and semi-transparent displays. They, however, suffer from resolution-transparency trade-off and incompatibility with high-temperature processes. Quantum dot (QD) light-emitting diodes (QLEDs) have sharper emission features and higher stabilities. However, QD emitting layers also have low mobilities, and thus the devices require large voltages for operation due to the presence of surface organic ligands.

Metal halide perovskites have emerged as promising light-emitting materials simply because they hold the most promise of high-efficiency, high-transparency, and low-cost. Perovskites also possess high mobilities and high colour purity [1]. More importantly, their wavelength can be tuned by tailoring the composition and the grain size, allowing more vibrant colors than conventional LEDs. However, further material development is needed to establish highly stable perovskites with high external quantum efficiencies.

Metal halide perovskites share a general chemical formula ABX₃, where A is a monovalent cation such as inorganic cations (e.g., Cs⁺) and organic ammoniums (e.g., methylammonium (MA)), B is a metal cation center such as Pb²⁺ and Sn²⁺, and X represents a halide group (e.g., Cl⁻, Br⁻, and I⁻). When small A-site cations are fully or partially substituted by large aliphatic or aromatic cations, the original cubic or pseudocubic three-dimensional (3D) inorganic framework is “cleaved” into a structure with layered, localized two-dimensional (2D) boundaries (Fig. 1a). The LD structure can be easily tuned between a purely 2D material and a 3D crystal where the quasi-2D intermediates are layered perovskites synthesized by introducing large organic cations such at a predesigned stoichiometry to yield compounds with different inorganic layer (n) values in the series A't(A''n)₁,BX₃n₋₁ (A' = large organic cation). Here, n = 1 corresponds to a purely 2D structure and n > 1 to the LD crystallite. A 3D perovskite (i.e., ABX₃) would correspond to n = ∞ in this notation.

One of the most salient features of the LD perovskites is the enhanced photoluminescence quantum yield (PLQY) even at low excitation densities [2]. It has been reported that LD perovskite with high transparency can exhibit sufficient light output with very thin layers of material. The high PLQY originates from a “cascade”-like mixed quantum well structure (Fig. 1c): upon light excitation or electrical injection, the generated charge carriers funnel from polycrystalline grains with lower “n” value (i.e., larger bandgap) to higher “n” grains (i.e., smaller bandgap), thereby effectively collecting charge carriers in close proximity. This promotes radiative recombination over trap-mediated non-radiative channels, enabling efficient luminescence. The high mobility of the LD component with large “n” value also reduces the required voltage for device turn-on and efficient operation, therefore, improving the LED efficiency [3].

In a typical perovskite LED architecture (Fig. 1c), a thin layer of perovskite polycrystalline emission layer is sandwiched between the charge transport layers built using organic materials and/or metal oxides. Different from their 3D counterparts, LD perovskite typically feature specific crystal lattice cuts along certain directions such as (1 0 0), (1 1 0), and (1 1 1) direction of 3D structures. These crystal orientations can be reflected by the nano- or micro-scaled grain stacking within the solution-processed LD perovskite film [6]; the distribution of the quantum well structure is also varied by the selection of the inorganic/organic components and solvents, stoichiometry of the precursors, and even the materials deposition technique [7]. Recently reports also demonstrate that the energy and charge transport between adjacent inorganic and organic layers can be engineered through the insertion of various conjugated intercalating ligands [8]. In this regard, we discuss several challenges in the development of the LD perovskite emission layer.
and summarize recent research progress of the LED performance. We sought to connect the chemical structures and photophysics of the layered perovskites with their device performance.

**Tailoring the quantum-well structures.** In 3D perovskites, charge carrier diffusion is usually faster than the localized radiative recombination. The free charge carriers are mostly trapped by the defects at the grain boundary, yielding low PLQYs. Due to the insertion of large organic cations, quantum wells with different thickness dominate the LD perovskite thin-film. The excitons are therefore confined within the quantum wells, which significantly improves the PLQY. Because the band position and the electronic bandgap of the LD component can be different as the \( n \) value of each grain may vary, the structure of the downward energy cascade needs to be carefully engineered to improve the radiative properties. The general process of the LD perovskite emission layer includes two synthetic steps: spin-casting and thermal annealing. During these processes, the solvent (or the solvent combination) evaporates, and the perovskite precursors are released and begin to nucleate, yielding the assembly of quantum well structures. While crystal grains with various \( n \) values are randomly distributed within the as-formed thin-film, the probability distribution of the \( n \) value of the inorganic component can be primarily determined by the stoichiometric quantities of the inorganic components and the intercalating organic cations. The energy landscape constructed by the assembly of LD quantum wells can be controlled to benefit radiative combination to achieve a high PLQY of LD perovskite emissive layer even at low excitation intensities [3]. The dynamics of the energy transfer through radiative or non-radiative recombination processes can be monitored using ultra-fast spectroscopic studies: multiple bleaching decays shall be observed from the LD perovskite films with engineered energy landscape as the notion of the multi-step (but fast) energy transfer.

The high PLQY of the LD perovskites with tailored quantum well sizes and distributions also originates from the active photoexcited “bright” states in the small subpopulation of the quantum well assemblies. It is important to note that the efficient emission from those LD perovskites usually from the quantum well with the smallest bandgap, which effectively collects the charge carriers and excitons from the energy funnel. The redshift of the absorption and PL features are thus commonly found from the LD perovskite films, and the central wavelength of the PL and EL is usually assigned to the radiative recombination at the large-\( n \) quantum wells [2,4]. One of the facile approaches to create LD perovskite thin-films with emission at 400–500 nm is to reduce the \( n \) value. The phase-pure LD perovskites with \( n = 1 \) and 2 have relatively large exciton binding energy and stable emission in the blue-green regime. For instance, it is reported that the LEDs with \( n = 1 \) perovskite PEA\(_2\)PbBr\(_4\) and PEA\(_2\)PbI\(_4\) (PEA = phenylethylammonium) emit at 410 and 526 nm, respectively [9,10]. Phase-pure LD perovskites have been widely investigated for solar cell applications, but far less investigated as LED active materials. The insulating nature of the large organic cations and the relative large exciton binding energy impair the charge carrier injection and radiative recombination within the phase-pure LD perovskite with lower \( n \) values. These processes can be improved the aid of the engineering of crystal orientation and intercalating ligands mentioned below.

**Controlling the grain orientations.** The control of the orientation of the inorganic crystal domains within the LD perovskite film is crucial for high-performance LEDs. Ideally, all inorganic grains should grow perpendicularly to the substrate and the top electrode. In that case, the charge carriers can transport along the vertical standing inorganic grains without being influenced by the electrically insulating organic intercalating cations, and effectively recombine and generate light within the quantum well. However, the formation of a smooth and bright LD perovskite thin-film generally requires a series of rapid and dynamic growth processes (e.g., solution deposition, solvent evaporation, post-synthetic annealing), and the fast growth of thin-film would yield crystal grains with varied orientations (Fig. 1c). The effective control of LD crystal grain growth is one of the keys to further improve the radiative recombination rate of LD perovskite thin-films and devices.

Generally, the film-formation technique holds the key to controlling the orientation of the crystal grains. Recent findings demonstrate that the optimized hot-cast film deposition method can yield high degrees of crystal grain orientation of LD perovskite
The selection of intercalating ligands can also influence the crystal orientations. It has been found that LD perovskite films with aromatic ligands (e.g., PEA) have a higher probability to yield oriented grains compared to their counterparts with aliphatic ligands (e.g., butylammonium) [7]. This may be because of the stronger van der Waals interaction between aromatic rings that regulate the formation of the inorganic quantum wells with preferred orientation during the post-synthetic annealing process. Some intercalating ligands can also regulate the formation of 3D components with specific morphologies that benefit charge transport. Lai et al. [16] observed the formation of nanorod-like quantum well domains in LD perovskite films when thiophenemethylammonium (TMA) is applied as the intercalating cation. Further optimization of the monovalent cation ratio (i.e., MA-to-TMA) enables the formation of LD perovskite films with vertically aligned grains, thus facilitating efficient charge transport. It is expected that similar ligand-induced orientation effects happen on LD perovskites with other classes of organic functional ligands.

LD perovskites have demonstrated encouraging luminescence properties and the efficiencies of the devices have advanced rapidly in the last four years. The studies of the LD perovskite materials will therefore become more important as their reduced dimensionality, compositional flexibility, and excellent photophysical properties have been widely used in optoelectronic devices. Combining higher device performance and long-term stability under device operating conditions is a top priority. As for the further optimization of the materials, the emissive layer is required to have better and balanced charge carrier transport, higher density of radiative recombination center, and improved materials stability against light, heat, and moisture. The concert efforts on the design of the LD structures, including the optimization of quantum well assembly and ligand engineering, are anticipated to address this important challenge.

Conflict of interest

The authors declare that they have no conflict of interest.

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References

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