

Carrier Cascade: Enabling High Performance Perovskite Light-Emitting Diodes (PeLEDs)

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Abstract

In recent years, hybrid lead-halide perovskites have emerged as promising solution-processed semiconductors for thin-film optoelectronics with a growing focus on light-emitting diode (LED) applications. Perovskites exhibit remarkable flexibilities in structure and composition tuning and possess excellent intrinsic properties such as band gap tunability over a visible range, high color purity emission, high photoluminescence quantum yield (PLQY) and high exciton binding energies. Recently, perovskite based light-emitting diodes (PeLEDs) have exhibited external quantum efficiency (EQE) of 14.36% and have revealed the potential for further improvement. High PLQY is a key requirement for better PeLED performance. This can be realized by controlling the grain-size of the perovskite films with optimum active layer thickness and utilizing reduced-dimensionality perovskite emitters to spatially confine charge carriers for enhanced radiative recombination. In this short review, we discuss the critical parameters required for the efficient PeLEDs, the recent progress mainly highlighting the energy transfer mechanism within Ruddlesden Popper (RP) structures and graded size nanoparticles (NPs) films. We also outline the recommendations and strategies for further improvement.

Keywords: Perovskites, PeLEDs, LEDs, carrier cascade, energy funnelling, nanoparticles (NPs)

Introduction

The light-emitting diode (LED) is an economic light source, with advantages of low energy consumption, high efficiency, and long lifetime. Often explored material systems include III-V semiconductors, organic molecules and quantum dots, which are at various levels of commercial application in displays and lighting. In recent developments, solution processable metal halide perovskites (AMX_3 , where A-monovalent organic/inorganic cation, M-divalent metal ion and X-halide anion) based LEDs (PeLEDs) have shown a great potential to fill the ‘green gap’ and can be a strong contestant to organic and quantum dot LEDs.[1, 2] This is due to their unique intrinsic properties, which include tunable band gap (E_g), high colour purity, tunable binding energies (E_b), slow bimolecular recombination, low deep trap density, cost effectiveness and easy solution processability at low temperature. [3, 4*] Since the first reports of lasing [5] and light emission in 2014 (current efficiency (CE) of 0.3 cd A^{-1} and external quantum efficiency (EQE) $< 0.1\%$), [6] many promising improvements have been made in both material and device engineering to achieve very significant performance improvements; with efficiencies of 62.4 cd A^{-1} of CE and 14.36% of EQE recently achieved.[5, 6, 7**] This encouraging progress has raised expectations that PeLEDs may reach a stage of development where industrialisation could be considered in applications such as large area illumination.[8, 9**]

This review highlights the recent developments in PeLEDs, to achieve improved performance with an emphasis on the ‘charge cascade’ phenomenon in thin films and nanoparticles. In the context of PeLEDs, the terms ‘energy cascade’, ‘energy funnelling’, or ‘carrier cascade’ refer to the transfer of ‘energy’ or ‘charge’ from a high band gap (E_g) to a low E_g domain within the emitter, comprising multi-dimensional phases possessing a range of band-gaps. Another approach has utilised nanoparticle size variation (and subsequently the bandgaps) to improve performance. Films with graded band gaps display significant reduction in nonradiative recombination, as a results of funnelling phenomenon, thus leading to significant improvements in devices.

Ruddlesden–Popper (RP) perovskites

The insertion of a larger cation (A') in AMX_3 leads to the reconstruction of the 3D framework to mixed dimensional (2D-3D) RP-multi-quantum-wells (MQWs, $A'A_{n-1}M_nX_{3n+1}$.) or ‘quasi-2D’ perovskite structures. In RP-MQWs structures, the inorganic layer acts as a ‘quantum well’

and the organic layer as a ‘barrier’.[1] These RP structures are defined in terms of $\langle n \rangle$, which represents the number of inorganic layers (MX_6) within the perovskites structures as illustrated in **Figure 1a**, while pure 3D, pure 2D and quasi-2D systems are denoted by $\langle n \rangle = \infty$, $\langle n \rangle = 1$, and $\langle n \rangle > 1$ respectively. In RP structures, both E_g and exciton binding energy (E_b) increase with decrease in $\langle n \rangle$, mainly due to the quantum confinement effect. High E_b (~ 320 eV) in RP structures favour fast and efficient excitonic recombination (charge density $< 10^{15} \text{ cm}^{-3}$) which can result in a high PLQY as compared to their bulk counterpart. (**Figure 1b**).[10, 11]

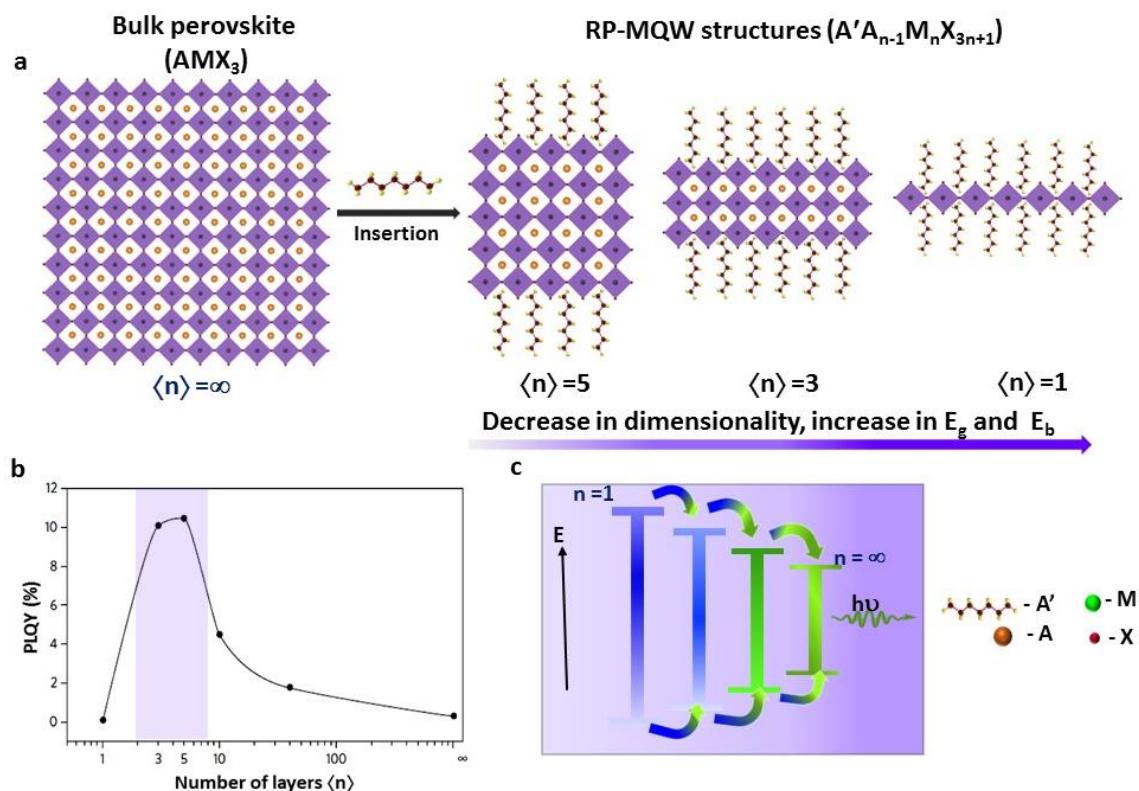


Figure 1 a) Schematic illustrations of unit cell structure of bulk (3D) and quasi-2D perovskites i.e. Ruddlesden popper multi quantum well (RP-MQWs) structures with different $\langle n \rangle$ values formed after insertion of long chain organic cation, showing the evolution of dimensionality from 3D ($n = \infty$) to 2D ($n = 1$). The band gap (E_g) and exciton binding energy (E_b) increases with decrease in $\langle n \rangle$. (b) summary of the photoluminescence quantum yield (PLQY) for perovskite films with different $\langle n \rangle$ values at a low excitation intensity (6 mW cm^{-2})[12*] (c) Schematic representation of charge transfer process within the RP-MQW perovskite film with various $\langle n \rangle$ values (i.e. different band gap), from high band gap phase (low $\langle n \rangle$) to small band gap (high $\langle n \rangle$) phase. The arrows represent the carrier transfer direction.

Detailed studies of PeLED devices based on RP emitters were carried out using transient absorption (TA) and time-resolved photoluminescence (TRPL) spectroscopic measurements. The analyses revealed energy cascade or funnelling phenomenon as illustrated in Figure 1c.[13]

PeLEDs based on RP-MQW perovskites structures have exhibited more efficient electroluminescence over small grain sized 3D films and have become the system of interest for efficient PeLEDs.[12, 13, 14*, 15].

Concept of carrier funnelling/cascade

RP-MQW / Quasi 2D films

RP-MQW/quasi 2D films typically comprise of mixed perovskite phases with various $\langle n \rangle$ values, i.e. a film with different bandgap domains. The steady-state absorption and PL measurements clearly indicate presence of multiple perovskite phases, whereas the electroluminescence (EL) appears as a single emission peak of the lowest bandgap (Figure 2a). As an example, CsPbBr₃ perovskite displays a PL emission peak at $\lambda = 526$ nm, while quasi-2D PEABr: CsPbBr₃ (0.8: 1) films, demonstrate a higher PL intensity emission peak at $\lambda = 511$ nm (peak shift attributable to grain size effect) along with the weak intensity peaks at different emission wavelengths λ_1 , λ_2 and λ_3 (each corresponding to different $\langle n \rangle$ values). This implies that most of the emission originated from the 3D perovskite phase rather than the quasi-2D phases, confirming efficient funnelling. The energy funnelling effect could also be noted in TRPL measurements, where a longer lifetime of $\tau_{ave} = 11.41$ ns was observed for quasi-2D PEABr: CsPbBr₃ (0.8: 1) films over the pure 3D film ($\tau_{ave} = 5.56$ ns) (Figure 2b).[16] From TRPL, the fast decay component was attributed to non-radiative recombination processes, while the slower process corresponded to radiative recombination.[12, 16] Longer lifetimes at lower emission wavelength ($\lambda = 526$ nm) confirmed funnelling within the active emitter layer.[12, 16] "Eventually, the efficient funnelling process led to quasi-2D PeLEDs with CE of 6.16 cd A⁻¹ and EQE of 1.97%, which is more than 50 times that of the 3D device." [16]

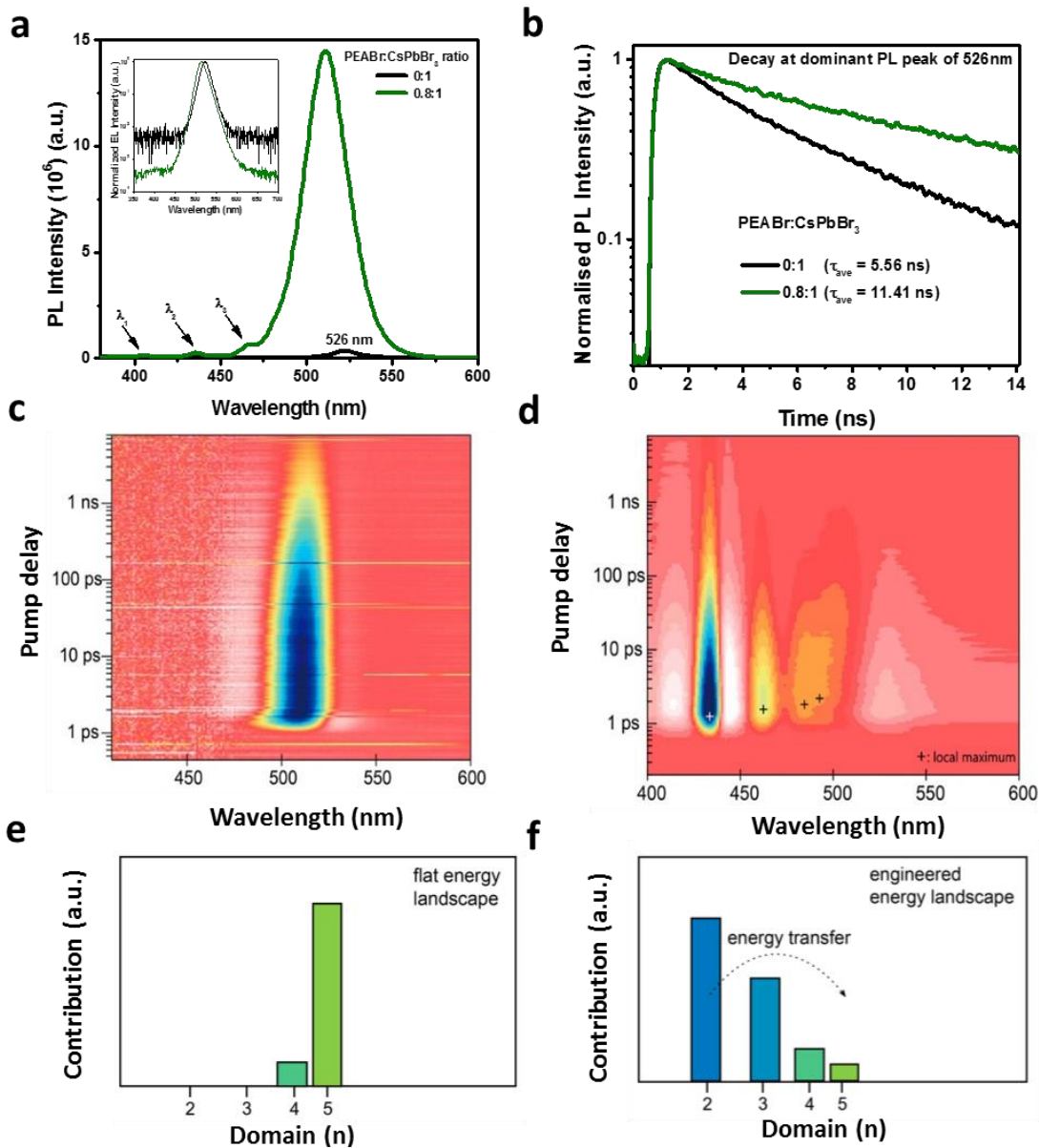


Figure 2: (a) Superimposed steady state PL (absorbance corrected) spectra of pristine CsPbBr₃ film and with the addition of excesses of PEABr i.e. PEABr:CsPbBr₃ = 0.8:1. Inset shows the electroluminescence (EL) spectra of the corresponding PeLEDs devices. (b) TRPL spectra for pristine CsPbBr₃, and PEABr:CsPbBr₃ = 0.8: 1 perovskite films at 526 nm emission wavelength. [16] Transient absorption spectra of (c) flat quasi-2D films exhibit no energy transfer process and (d) energy-landscape engineered $\langle n \rangle \geq 3$ quasi-2D perovskite films exhibit the energy transfer process. (e) Flat energy landscape, $n = 5$ dominates, n energy transfer. (f) Energy landscape-engineered films instead consist of a set of different domains where energy funnels into the final $n = 5$ domain.[14]

Ultrafast transient absorption spectroscopy (TA) measurements also confirmed the signature of energy funnelling from larger band gap domains at picosecond (ps) timescales. As shown in Figure 2c, the ground state bleach signature (GSB) revealed no energy transfer process within the film whereas the energy transfer process is clearly depicted in figure 2d, showing several relative intensity GSB peaks with different decay time constants (100 fs -100 ps). The slower

decay kinetics observed for the lower energy gap domains as compared to larger bandgap domains supports the energy-funnelling phenomenon. In these RP perovskite systems, an artificial increase in the concentration of carriers in the 3D system through funnelling allows traps to be filled up quickly, thereby enhancing radiative recombination and achieving higher PLQY along with improved device performance. It has been highlighted that the distribution of high and small band gap energy domains in the film is crucial for achieving high PLQY and better LED performance (**Figure 2e and 2f**). [14] However, more detailed theoretical as well as experimental investigations are required to understand the effect of population of different domains and its contribution to the energy funnelling process, as the optical and electrical properties vary based on the perovskites compositions.[14] An interesting effort in this direction studied the modulation in the electrical and optical signatures of the energy cascading mechanisms for a $(\text{C}_8\text{H}_{17}\text{NH}_3)_2(\text{CH}(\text{NH}_2)_2)_{m-1}\text{Pb}_m\text{Br}_{3m+1}$ RP system and revealed the signatures of an efficient funnelling.[15]

Perovskite films

Perovskite NPs have excellent optoelectronic properties which include high PLQY of up to 100%, narrow bandwidth, as well as precise and facile tunable luminescence over the entire visible spectrum.[17] NPs formation represents a more ideal approach to obtain perovskites with high PLQY due their high E_b induced by effective confinement of excitons at the nanometer-scale (< 20 nm) in contrast to polycrystalline perovskite films with large grain sizes (> 100 nm). Just as in RP-MQW's perovskite structures, the energy-funnelling mechanism have been previously demonstrated in colloidal nanostructures. For instance, efficient Förster resonance energy transfer (FRET) has been demonstrated for the artificially assembled PbS colloidal nanostructures with a graded band gap.[18] Efficient exciton funnelling and recycling of trap state-bound excitons observed in CdTe nanocrystal assemblies with gradually changing band gaps and yielded significantly improved luminescence efficiencies.[19, 20]

Unlike RP-MQW structures, the bandgap of NPs is determined by their sizes due to the more pronounced quantum confinement effect. The smaller particle size corresponds to higher band gap and vice versa. Therefore, energy funnelling occurs in the system with a wide particle size distribution. TA measurements carried out within suspension of perovskites NPs aggregates (containing NPs and nanoplatelets of various size) reflect the variation in the lifetime with respect to the excitation wavelength. The PL lifetime increases significantly with respect to longer excitation wavelengths, which is an evidence of the energy transfer process between nanostructures.[21] In short, the smaller nanoparticles rapidly recombine and provide short-

lived emissions on the picosecond timescale, or form charge-transfer states (CTSs) across adjacent domains, resulting in longer-lived photoluminescence in the millisecond timescale for the larger NPs. Interestingly, in our very recent study, the energy cascade approach has been demonstrated for the perovskite NCs of graded size coupled with microplatelets of octylammonium lead bromide perovskites. Steady-state PL spectrum has confirmed the multi-bandgap features of the system as depicted in **Figure 3(a)**. The PeLEDs fabricated with these hierarchically structured perovskite NCs films have exhibited PLQY of over 80% and LEDs with impressively high efficiencies in excess of 57.6 cd A^{-1} and an EQE above 13% (**Figure 3b and 3c**) without any light-outcoupling structures.[9, 22] The process is easily scalable to fabricate bright and extremely efficient halide PeLEDs for potential applications in large area illumination.

The advantages of nanostructure formation could also be harnessed in thin films as well. Initially, thin film based PeLEDs were restricted to low performance (EQE <1 %) mainly due to the large perovskite grain size and small E_b (~9-50 meV), which often led to predominant non-radiative recombination resulting in low PLQY.[23-25] Subsequently, highly efficient PeLEDs with enhanced radiative recombination have been accomplished by reducing perovskite crystal size to spatially confine the injected charge carriers. A novel approach of nanocrystal pinning (NCP) in 3D films, led to controlled grain growth, and exhibited enhanced PeLEDs performance with CE of 42.9 cd A^{-1} with and EQE of 8.53%.[26]** This work proved to be a milestone for PeLEDs based on 3D thin films.

Subsequent efforts towards improved PeLEDs were also made in the direction of material engineering by using different additives to control the grain growth as well as in device engineering.[27-32] In one of the approaches, long chain organic cations (A' e.g. phenylethylammonium (PEA), butyl ammonium (BA), octylammonium (OA) etc.) were added into the perovskite precursor solution (e.g. methyl ammonium lead bromide, MAPbBr_3) to impede grain growth in 3D perovskites.[33, 34] The optimum amount of octylammonium (OA) addition in the perovskite precursor led to *in-situ* nanoparticle film formation accompanied by enhanced PLQY ~ 20.5% vs. 3.40 % (bulk film) and increased excitonic nature of the emission. [29] Films fabricated with BA halides (BAX, X = I, Br) resulted in smaller grain size smoother films (roughness to 1 nm) with reported PeLEDs performance of 10.4% and 9.3% (EQE) for the MAPbI_3 and MAPbBr_3 perovskites respectively.[34]* In such nano-grained systems induced by the utilisation of additives, carrier cascading effects could be occurring, however a careful deconvolution of the various effects is challenging. A critical factor to consider is the

necessity for surface passivation in many of these systems. Even in RP-MQWs, which yield better PeLED performance with effective carrier funnelling, the reduction of crystal sizes can enhance the possibility of defect formation due to the larger surface and grain boundary area. Consequently, it has been reported that surface passivation with trioctylphosphine oxide (TOPO) on perovskite thin film surface has provided a further boost in the performance with a CE of 62.4 cd A^{-1} and EQE of 14.36% (figure 3d).[7]**, the highest efficiency for PeLEDs reported to date.

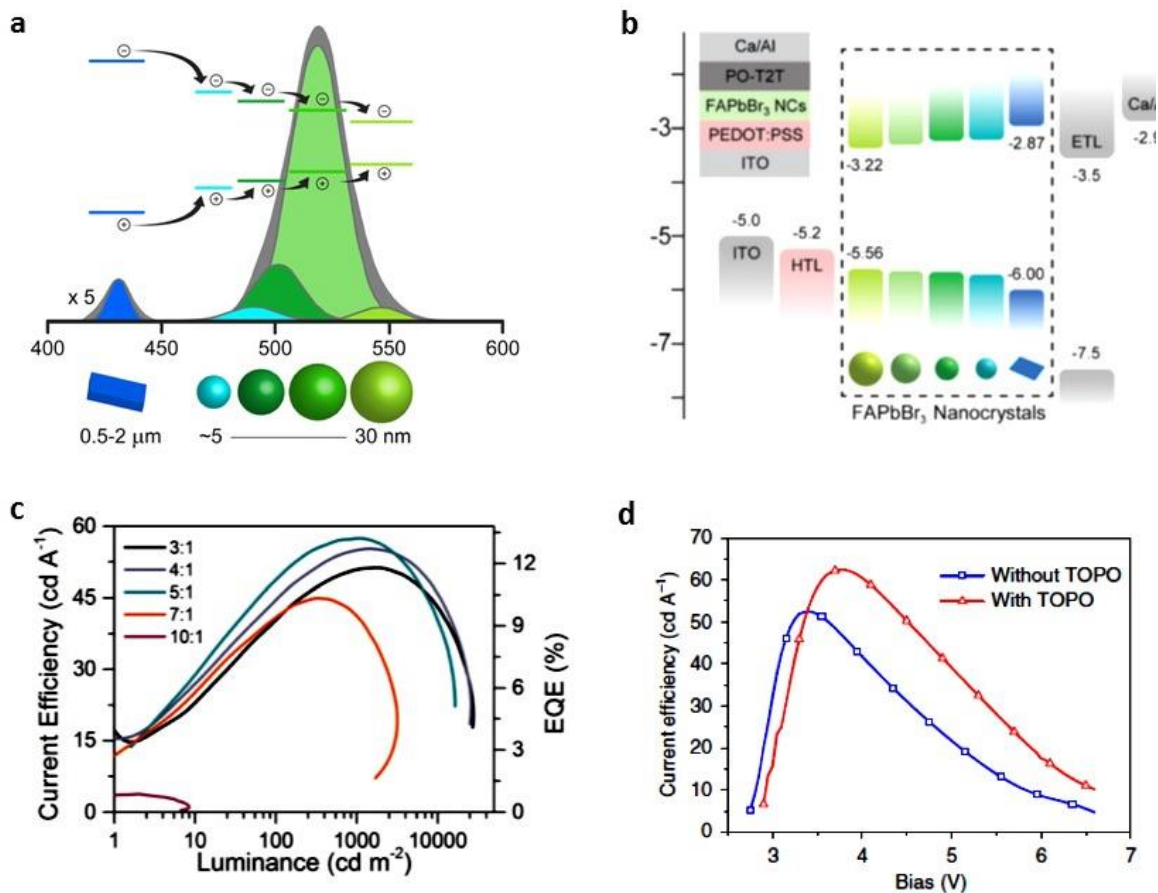


Figure 3a) Conceptual diagram representing the energy cascade mechanism from 2D microplatelets (MPLs) to FAPbBr₃ NCs of graded size, where the deconvolution of the steady-state PL spectrum clearly displays the different PL contribution at varying NC sizes. Note: Deconvolution of the PL spectrum into 4 Gaussians is only used to illustrate the energy cascading from the smallest to largest NCs (i.e. largest to smallest bandgap) and corresponding (b) schematic band diagram of the NCs LEDs. (c) Characteristic current efficiency/EQE versus luminance (device area: 3mm²). Black, grey, dark cyan, orange, and purple curves show NCs with molar ratios of 3 : 1, 4 : 1, 5 : 1, 7 : 1, and 10 : 1 of OA: PbBr₂, respectively.[9] (d) Current efficiency–voltage (CE-V) curves of PEA₂(FAPbBr₃)_{n-1}PbBr₄ (n = 3 composition) devices with and without TOPO passivation layer.[7]

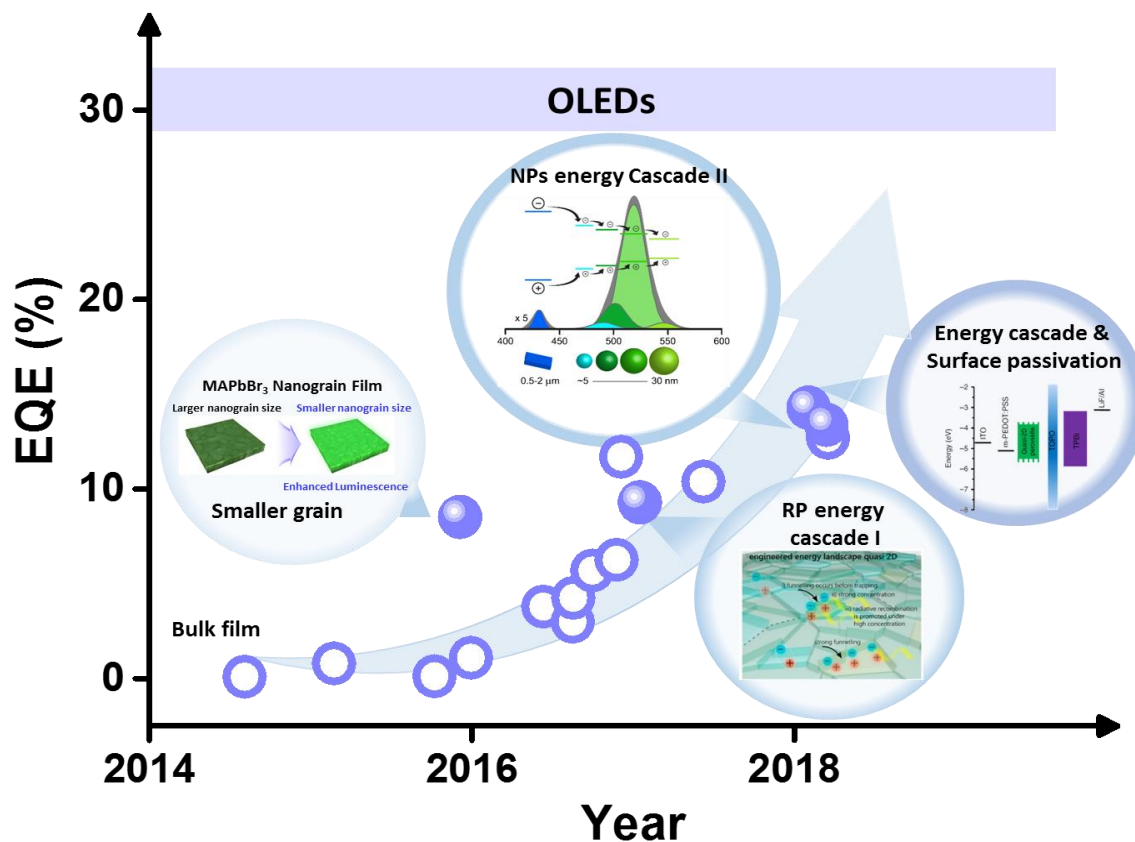


Figure 4 Overview of the best reported external quantum efficiency (EQE) values for perovskite LED (PeLED) devices. Four milestones with smaller grain,[26] Ruddlesden-Popper (RP)[12, 14] energy cascade, nanoparticles (NPs) energy cascade [9], RP-energy cascade together with surface passivation approaches [7] are indicated in the circles in details. The current status of EQE values for organic-LED (OLED) [35, 36] is also marked for comparison. EQE values taken from the references cited in the supporting information of reference [9].

The overview of the best reported EQE values for PeLED along with the various significant milestones are illustrated in Figure 4. Within a few years, development in the emitter layer (from bulk 3D films, RP structures to NPs films) has boosted performance up to 13.4% and the surface passivation strategy led to the maximum EQE value of 14.36% till date. Compared to the current state-of-the-art with organic LEDs (OLEDs, ~30%), [35, 36] PeLEDs still have a long way to go in performance as well as stability improvement.

Future prospects

More detailed theoretical and experimental investigations on the energy domain distribution in the RP structures, viz. optimum domain size as well steps involved in charge transfer process, as well as optimum size and population of NPs are required to achieve efficient charge transfer processes to enhance radiative recombination. In order to boost both performance and stability of PeLEDs, further exploration is required in the area of surface passivation of NPs and thin

films. Usually, the efficiency roll-off in PeLEDs occur mainly due to luminescence quenching which is likely caused by non-radiative Auger recombination. This can be effectively suppressed by increasing the width of quantum wells in the RP-MQWs, which facilitate confinement of charge carriers and enhance the probability of radiative recombination and reduces efficiency roll-off. [13, 37, 38] For instance, stable PeLEDs under a high current density of 500 mA cm^{-2} (retaining the EQE of 6.6%) have been demonstrated using FA-Cs-based MQW structures (addition of 1-naphthylmethylamine iodide (NMAI) cation in the FAPbI₃). [37] Further investigation in order to improve the operational, colour (due to phase segregation) and environmental stability (moisture) of PeLEDs need to be conducted. Finally, interfacial engineering for balanced charge injection requires judicious exploration into new organic and inorganic interface materials."

Acknowledgements

This research was supported by the National Research Foundation, Prime Minister's Office, Singapore under its Competitive Research Programme (CRP Award No. NRF-CRP14-2014-03) and through the Singapore–Berkeley Research Initiative for Sustainable Energy (SinBeRISE) CREATE Program. Authors thank Dr. S.A. Veldhuis, Dr. Xin Yu Chin and Mr. Ng. Yan Fong for discussion and valuable comments during the preparation of this manuscript.

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*Paper of special interest

** Paper of outstanding interest

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