

Recent Insights for Achieving Mixed Halide Perovskites Without Halide Segregation

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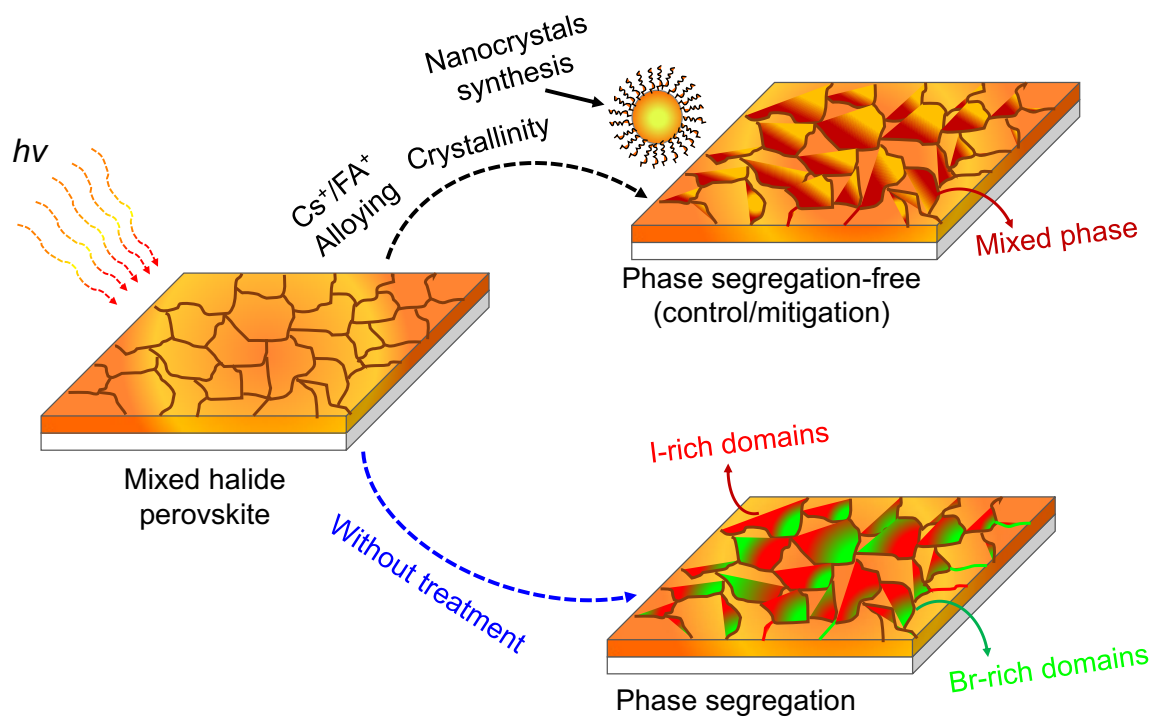
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Abstract

The incorporation of halide perovskites in optoelectronics have provided a fast advance in the fabrication of new sensitizers with a balanced light-harvesting, free carrier transportation, and a progressive overcoming of the low tolerance to the moisture. Within these emerging materials, mixed halide perovskites as $\text{APbX}_{3-x}\text{Y}_x$, ($\text{A} = \text{MA}^+$, Cs^+ , FA^+ ; $\text{X}, \text{Y} = \text{Cl}^-$, Br^- , I^-) have been highlighted due to their facile band gap tunability in the entire visible region by varying the halide composition, which making these systems enormously appealing for the design of optoelectronic devices. Nonetheless, their performance in real devices is strongly limited as mixed halide perovskites exhibit photoinduced and current-induced phase segregation, losing their original photophysical properties and effective band gap tunability to generate halide-rich domains. The phase segregation has been the key factor to decrease the photovoltaic parameters in solar cells as open-circuit voltage and photoconversion efficiency, also limiting the performance of tandem devices and the potentiality of color design in perovskite LEDs. This review summarizes recent trends to hinder the phase segregation.

Key words

perovskite, mixed halide perovskite, phase segregation, solar cells,

1. Introduction

Since their first application in solar devices in 2003, the halide perovskites with an ABX_3 -type structure ($\text{A} = \text{MA}^+$, Cs^+ , FA^+ , where $\text{MA}^+ = \text{CH}_3\text{NH}_3^+$, $\text{FA}^+ = \text{CH}(\text{NH}_2)_2^+$, $\text{B} = \text{Pb}^{2+}$; $\text{X} = \text{Cl}^-$, Br^- and I^-) have been widely studied worldwide due to outstanding characteristics as high ambipolar carrier transport and extraction capabilities, high absorption cross-section, and photoluminescence features.[1-6] The promising property of the perovskite has been successfully demonstrated in solar cell with photoconversion efficiency (PCE) over 23 % in few years.[7] One approach to control the band-gap of a perovskite is by varying its halide composition, achieving a spectral response range between ~ 1.6 - 2.3 eV just by varying the ratio between I and Br in a mixed halide composition.[8-11] The halide interchange has been proposed to tune the perovskite band gap mixed halide perovskites with the aim to improve photovoltaic parameters in solar cells, mainly the open-circuit voltage (V_{oc}) and incident photon to charge carrier efficiency (IPCE),[10, 12, 13] to optimize the band gap in tandem devices,[14, 15] or to tune the photoluminescence (PL) emission.[8] However, under continuous illumination[16, 17] or applied bias,[14, 18] mixed halide perovskites undergo phase segregation, creating Br-rich and I-rich domains, as it has been first reported by Hoke *et al.*[16] This

segregation leads to the losing of initial optical/electrical properties of mixed phase, favoring the formation of two high- and low-band gap states.[12, 19, 20] It has been reported that the segregated I-rich domain acts as primary free carrier recombination centers in the mixed halide perovskite, blocking electron flow into a solar device and limiting consequently the performance,[21, 22] and red shifting the PL emission limiting the color design in LEDs.[14, 18] This segregated phase behaves as effective charge trap site, producing an increase of recombination and therefore a drop in the V_{oc} , being more evident this decrease as increases the bromine content in mixed Br/I perovskites, that is the mix of halides most studied.[12, 17, 19] in this sense, minimization of halide segregation in mixed halide perovskites is mandatory to optimize the performance of the optoelectronic devices produced with these materials.

To reduce halide segregation some works have established diverse points of view from the composition,[23-27] crystallinity,[28-30] and chemical passivation[31, 32] of mixed halide perovskites. However, a strategy to prepare phase segregation-free perovskites has not been widely discussed, likely as the possible reasons for occurring the segregation effect are not completely understood. In this review, we highlight recent alternatives to decrease the phase segregation into mixed halide perovskites as the starting point to propose novel strategies for achieving phase stability.

2. Background about phase segregation: monitoring, dependence and influence on optoelectronics

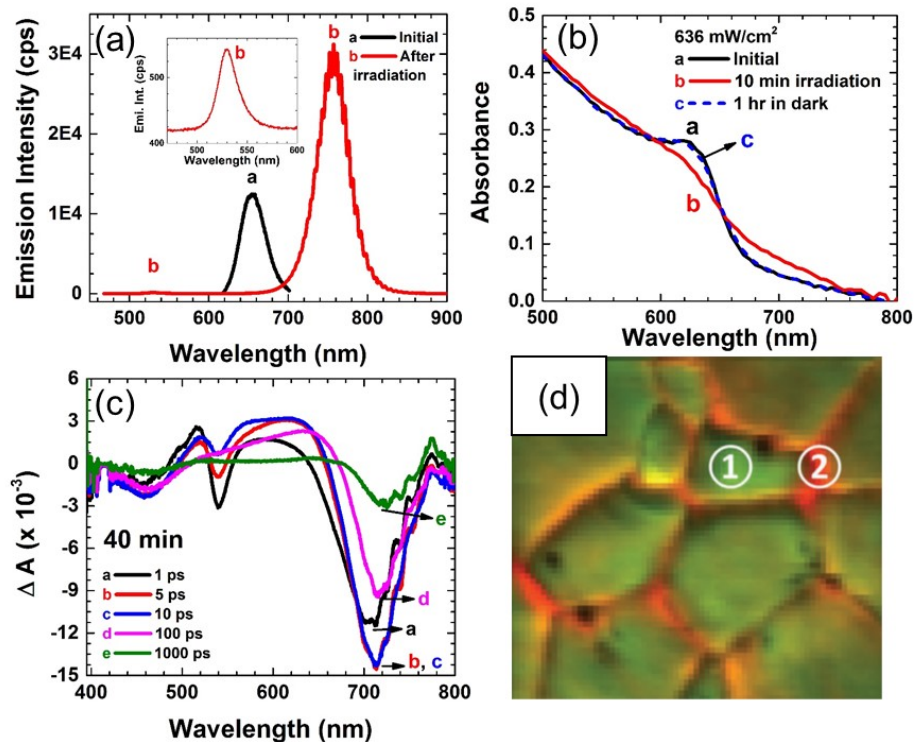


Figure 1. (a) Emission spectra and (b) absorption spectra of CH₃NH₃PbBr_{1.3}I_{1.7} film before and after laser irradiation (a: 1 min, b: 10 min). (c) Time-resolved difference absorption spectra of CH₃NH₃PbBr_{1.3}I_{1.7} film recorded following 387 nm laser pulse (pump) excitation after subjecting the sample to 40 min laser irradiation. (a-c, reprinted with permission from reference.[22] Copyright 2016 American Chemical Society) (d) SEM image of CsPbBr₂I film with overlapped catholuminescence spectra (Reproduced from reference[33] with permission from The Royal Society of Chemistry). The color code in (d) indicates the emitted light wavelength in which orange regions suggest a longer emitted light wavelength than green regions.

McGehee and coworkers demonstrated reversible PL and structural change under illumination.[16] Through monitoring XRD patterns under the illumination, about 20% of two segregated domains with 20% and 70% of bromide component were found and their estimated size is around 33 nm and 51 nm, respectively. Kamat and coworkers presented that the phase segregation can be tracked through absorption and transient absorption spectroscopic technique, see Figure 1a-c.[22] By monitoring the spectral change over time under a suitable continuous wave laser (Figure 1a,b), the initial emission/absorption peaks of the mixed phase is decreased, while two new different signals appear, increasing their intensity with rate constant of 0.3 s⁻¹. [21, 22] It has been described that the presence of both the low-energy and high-energy peaks correspond to the segregated Br-rich

and I-rich domains and charge transfer rate between them is about $\sim 3 \times 10^{11} \text{ s}^{-1}$ (Figure 1c).[22] Also, after the photoirradiation, the spectral features from segregated domains are bleached, returning the original peak of the mixed phase. This recovery process takes longer than the initial segregation process, in tens of minutes to hours.

To understand the fundamental mechanism of phase segregation, various efforts have been applied. Through theoretical calculation, Brivio *et al.*, proposed the phase diagram with dependence on Br/I components under different temperatures.[20] Thermodynamically, MAPbX_3 prefers to have a segregated domain if the Br content in the perovskite is between 15% and 75%, referred to as a “miscibility gap”. Without photoirradiation and after 2 weeks, the emission shift of $\text{MAPbBr}_{1.2}\text{I}_{1.8}$ from 625 nm to 740 nm supports this thermodynamically preferred segregation, presented by Friend and coworkers.[34] However, phase segregation is a quite fast and reversible phenomenon compared to gradual segregation under dark after 2 weeks. It is necessary to consider the role of free carriers in the perovskite matrix. Furthermore, Hillhouse and coworkers reported injected free carriers through both photoirradiation and applied bias induced phase segregation.[14] The generated free carriers interact in the perovskite matrix and induce lattice strain through electron-phonon coupling, referred to as polarons.[35] To reduce the lattice strain, phase segregation occurs by forming a cubic Br-rich phase and an orthorhombic I-rich domain.[35] Furthermore, the segregated domains are stabilized by the accumulation of polarons and the domains grow up to 30 ~ 55 nm.[16, 21, 35] To track the location of the segregated domains, by combining morphological and spectral characterization, the segregated domain locates at the grain boundary to release the lattice strain, see Figure 1d.[33] To occur phase segregation at the grain boundary, early literatures calculated the activation energy for ion migration and the importance of defects, especially iodide movement through ion vacancies is the key to form segregated domains.[35-37] Note that the activation of halide ion migration through the ion vacancy has the lowest values than other A or B site cations in the perovskite.[37] Therefore, here are key points to control phase segregation as follows: thermodynamics, grain boundary where the phase segregation occurs, defect density, and electron-phonon coupling.

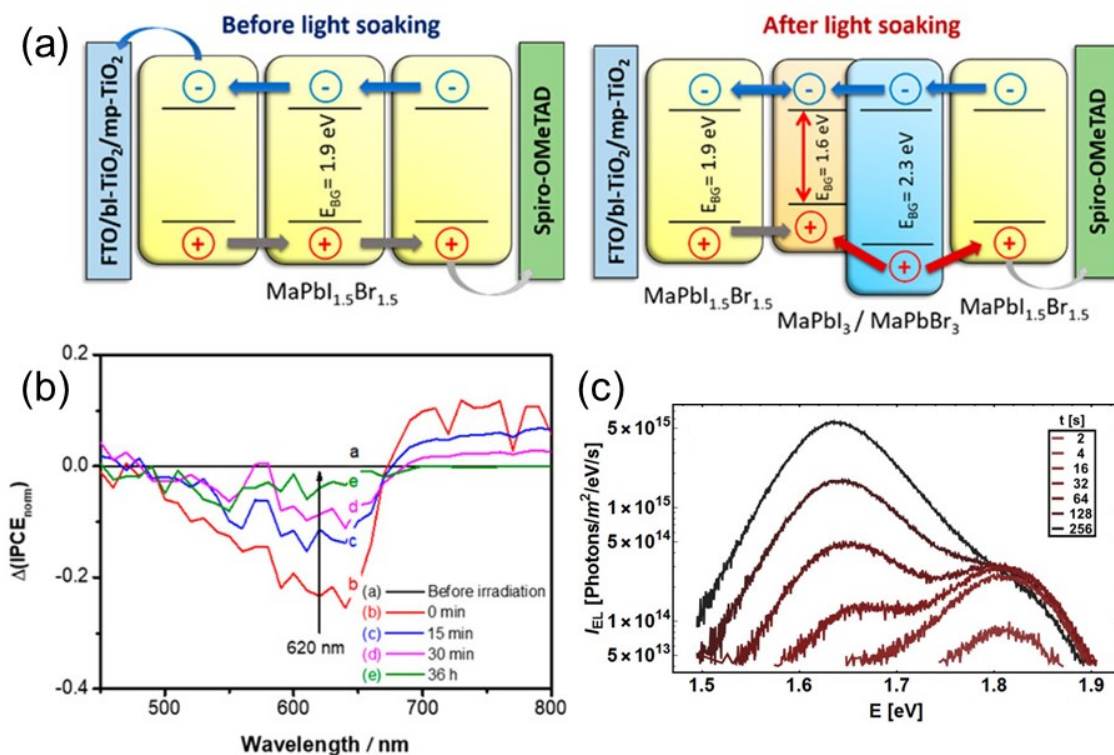


Figure 2. Effect of phase segregation to performance of solar cell (a,b) or LED (c) (Reprinted from reference.[12] Copyright 2017 American Chemical Society). (a) Schematic diagram of $\text{MAPbI}_{1.5}\text{Br}_{1.5}$ before/after illumination in solar cell device and charge flow process (b) Difference IPCE spectra showing the recovery of the solar cell response in the 600–700 nm region. (c) Electroluminescence spectra at selected times of a $\text{MAPbBr}_{1.2}\text{I}_{1.8}$ device being injected with a constant current density of 19.2 mA/cm^2 for 5 min (Reprinted with permission from reference.[14] Copyright 2017 American Chemical Society).

From the practical point of view, phase segregation produces a negative effect on the performance of optoelectronic devices, as it is summarized in Figure 2. In Figure 2a, the photogenerated electron/hole pairs in the Br-rich or mixed phase can be transferred to the low-band gap I-rich domains after light soaking.[12] The trapping of free carriers to I-rich domain is the main factor to decrease the performance of solar cells, where the carrier transport is blocked, decreasing the photovoltaic parameters as V_{oc} , IPCE (Figure 2b) and the photoconversion efficiency (PCE) of device.[12] In the case of LEDs, the applied potential can promote the phase segregation due to charge injection and generated free carrier in the perovskite, see Figure 2c, changing the color of the emission.[14]

3. Strategies to control phase segregation in mixed halide perovskites

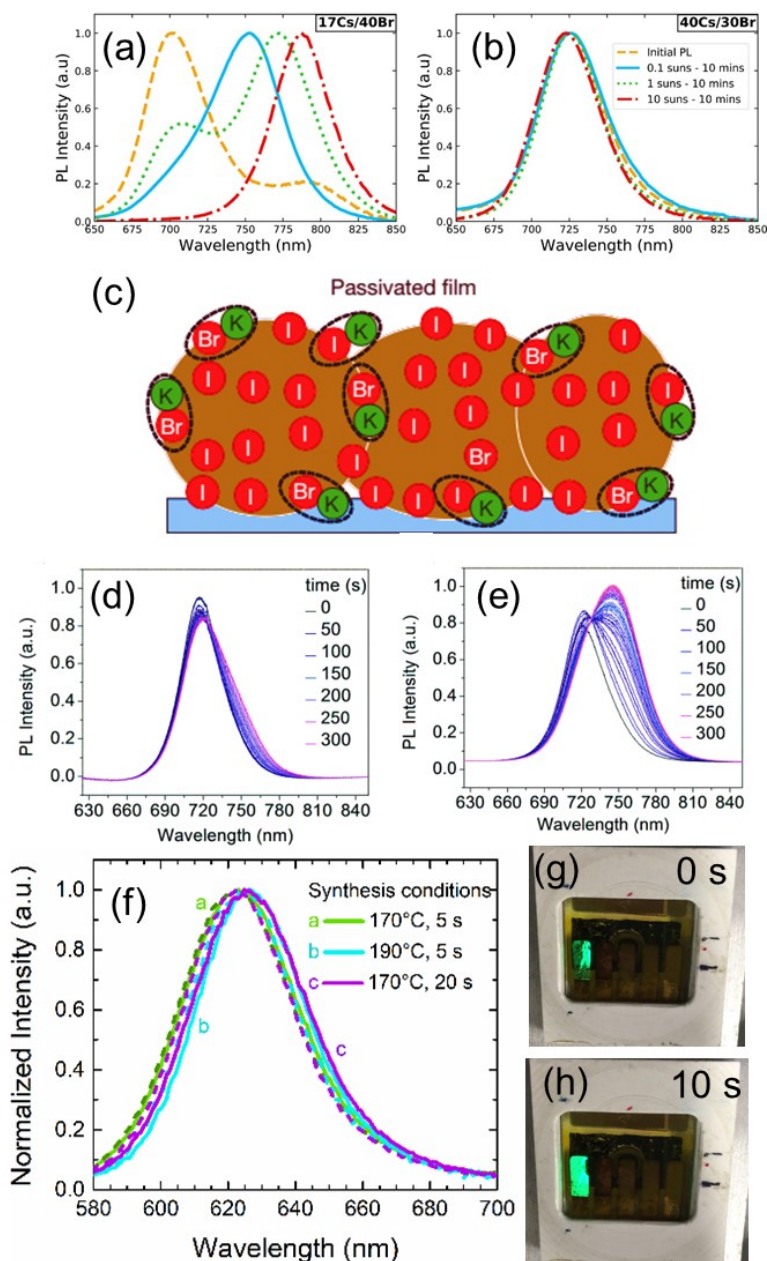


Figure 3. (a,b) PL from mixed cation and halide perovskite in device comparing (a) $\text{Cs}_{0.17}\text{FA}_{0.87}\text{PbBr}_{1.2}\text{I}_{1.8}$ (Cs17/Br40) and (b) $\text{Cs}_{0.40}\text{FA}_{0.60}\text{PbBr}_{0.9}\text{I}_{2.1}$ (Cs40/Br30) perovskites with a roughly 1.75 eV band gap. The initial PL peak is shown as the orange dashed curve. The final PL peaks after 0.1, 1, and 10 suns of excitation for 10 min with a 488 nm laser are shown for each composition. Devices were held at open circuit during the measurement. (Reprinted with permission from reference.[24] Copyright 2018 American Chemical Society) (c) Schematic of a cross-section of a film showing halide-vacancy management in cases of excess halide, in which the surplus halide is

immobilized through complexing with potassium into benign compounds at the grain boundaries and surfaces (Reprinted with permission from reference.[31] Copyright 2018 Springer Nature). (d,e) PL spectra under illumination with an interval of 10 sec for MAPbBr_{0.8}I_{2.2} film (d) grown on PTAA with larger grain size and (e) grown on PEDOT:PSS with smaller grain size (Reproduced from reference[28] from The Royal Society of Chemistry). (f) PL spectra of CsPbBr_{3-x}I_x NPs films (x = 1.5) before (solid line) and after (dash line) 40 s under 532 nm CW laser excitation ($I_{exc} = 500 \text{ mWcm}^{-2}$), varying the synthesis conditions of colloidal solutions (g,h) Green-light emission while electroluminescence measurement for TiO₂/CsPbBr_{2.37}I_{x0.63} NPs/spiro-OMeTAD based LED device under 9 V (g) before and (h) after 10 s.

Different strategies have been applied to reduce phase segregation in mixed halide perovskites. We summarize the most representing ones in this section:

i) One of the alternatives to mitigate phase segregation has been the partial replacing of cations. Conventional MA⁺ can be replaced partially by Cs⁺, FA⁺, or combination of these cations (Figure 3a,b).[23-27, 38-40] The incorporation of the later cations affects the lattice strain and the grain size of the material. The mixed cation perovskites as Cs_{1-y}MA_yPbBr_{3-x}I_x or FA_{1-y}Cs_yBr_{3-x}I_x exhibit smaller grain sizes than conventional MAPbBr_{3-x}I_x or CsPbBr_{3-x}I_x. Increasing the Cs⁺ (y = 0.4)[27] or FA content (y = 0.60)[23] makes thermodynamically unfavorable the I-rich and Br-rich redistribution and consequently avoids phase segregation, (Figure 3a,b). Similarly, the replacing of B-cation into perovskite has been also studied. Yang *et al.*, investigated the interchange of Pb²⁺ by smaller Sn²⁺ cations into MASn_{1-y}Pb_yBr_{3-x}I_x (y = 0.25), deducing by PL and XRD measurements that Sn²⁺ increase the microstrain in the perovskite lattice and acts as a barrier for the halide migration.[38] Both approaches suggest the decrease of the trap-assisted non-radiative recombination induced by GB. Even so, most of mixed cation-mixed halide perovskites are free from the phase segregation but still it is possible find some mixed cation-mixed halide perovskites in which phase segregation is observed, see Figure 3a where halide perovskite with mixing portion (17% Cs 83% FA) shows phase segregation.

ii) To avoid the formation of halide-rich clusters in grain boundary of mixed cation/halide perovskites, the potassium passivation has been performed.[31] Stranks and coworkers synthesized a triple-cation (Cs, FA, MA)PbBr_{3-x}I_x, dissolving certain amount of potassium iodide (KI) into the perovskite precursor solution.[31] They proposed that iodide ions from KI can fill the halide vacancies, while the K⁺ cations act as a “halide-sequesters” near to the grain boundary into the perovskite (Figure 3c). In this way, halide migration can be suppressed, enhancing the PCE of perovskite-based solar cells. An alternative passivation approach considers the use of organic ligands

to fill the trap states, defects or react with halides under diffusion process into the perovskite.[32] Organic as choline chloride or PCBM acts as Lewis acids favoring the halide coordination, which can also retard the halide migration to the trap states as grain boundary.

iii) Another interesting alternative to control halide segregation comes from a morphological point of view. As reported by Huang and coworkers, improved crystallinity of the $\text{MAPbBr}_{3-x}\text{I}_x$ film on PTAA as a hole transporter can facilitate/hinder phase segregation into material (Figure 3d). Conversely, poor crystalline perovskite film grown on PEDOT:PSS generates small grains with larger content of defects or grain boundary and so the segregation is facilitated in the poor crystalline perovskite films (Figure 3e).[28]

iv) Lastly, an efficient strategy to inhibit the halide segregation has been achieved to incorporate a new synthetic route for mixed halide perovskites by the preparation of materials with lower dimensionality. The use of long-chain ammonium ligand capped nanometer-sized crystallites, as n-butylammonium, producing 2D/3D perovskite architectures can inhibit phase segregation and preserve a real LED color tunability.[18] Further reduction of dimensionality by the use of colloidal perovskite nanoparticles (NPs) can also inhibit phase segregation in mixed halide perovskites.[21] Despite, the preparation of perovskite NPs has been recently reported, these materials produces very high PLQY with simple synthesis processes.[11, 41, 42] Our group has prepared colloidal $\text{CsPbBr}_{3-x}\text{I}_x$ NPs by hot injection method,[11, 41] varying the synthesis temperature and reaction time. Finally, we have produced thin films by drop casting, using perovskite NP from colloidal solutions as building blocks. Through PL measurements of $\text{CsPbBr}_{1.5}\text{I}_{1.5}$ NP films by using a high intensity continuous waver laser (532 nm, 500 mWcm^{-2}), we observed that the emission peak position of materials was not shifted over the time, concluding that nanocrystals are phase-segregation free, (Figure 3f). The NPs did not show agglomerations to generate interfacial electron traps or GB, inhibiting the halide migration and thereby the segregation effect. Consequently, optoelectronic devices fabricated with perovskite NPs do not suffer of phase segregation. As shown in Figure 3g,h, an unchanged emissive green-color was achieved in a $\text{CsPbBr}_{3-x}\text{I}_x$ QDs ($x = 0.75$) based LED device under 9 V, confirming the mitigation of segregation effect.

4. Conclusions

The mixed halide perovskites are, without doubts, an essential factor to improve the performance of optoelectronic devices for energy conversion and light production in coming years. However, the halide segregation under photoirradiation limits the expansion of their applicability, due to the perovskite features as composition, morphology and crystallinity. These characteristics are closely

associated with the generation of structural defects as halide vacancies or grain boundaries, which are considered as the critical points to induce the halide migration, accumulation and thereby, the assumption of segregation effect. By a comprehensive understanding of the A-cation and B-cation alloying, passivation process of structural defects, enhancing the crystallinity and the reduction of the perovskite dimensionality, not only the halide segregation can be retarded, but also the preparation of phase segregation-free mixed halide perovskites can be achieved. In this way, the full potential of these materials can be unlocked.

Declarations of interest

The authors declare no competing financial interest.

Acknowledgments

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The authors presented detailed mechanism of phase segregation through both experimental and theoretical ways. By developing the model for phase segregation, they provided various factors to affect rate of segregation and recovery. Furthermore, with dependence on diffusion length and excitation power density, the authors provided phase diagram and demonstrated stable region against to phase segregation by forming few nanometer sized dot shape.

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