

# Complete Suppression of Phase Segregation in Mixed-Halide Perovskite Nanocrystals under Periodic Heating

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Under continuous light illumination, it is known that localized domains with segregated halide compositions form in semiconducting mixed-halide perovskites, thus severely limiting their optoelectronic applications due to the negative changes in bandgap energies and charge-carrier characteristics. Here mixed-halide perovskite CsPbBr<sub>1.2</sub>I<sub>1.8</sub> nanocrystals are deposited onto an indium tin oxide substrate, whose temperature can be rapidly changed by  $\approx 10$  °C in a few seconds by applying or removing an external voltage. Such a sudden temperature change induces a temporary transition of CsPbBr<sub>1.2</sub>I<sub>1.8</sub> nanocrystals from the segregated phase to the mixed phase, the latter of which can be permanently maintained when the light illumination is coupled with periodic heating cycles. These findings mark the emergence of a practical solution to the detrimental phase-segregation problem, given that a small temperature modulation is readily available in various fundamental studies and practical devices of mixed-halide perovskites.

diodes (LEDs).<sup>[8,9]</sup> However, the primary challenge for the further advancements is the instability issue, which is manifested as lowered open-circuit voltage<sup>[10]</sup> and decreased emission-color purity<sup>[11]</sup> under long-term operations. The instability of mixed-halide perovskites is closely linked to the phase-segregation effect,<sup>[12–15]</sup> wherein light illumination or electrical biasing would give rise to iodide- and bromide-rich domains that severely modify the otherwise homogeneous energy landscape for charge carriers. Several driving forces have been proposed so far for anion migration<sup>[16–18]</sup> in this intriguing process, mainly including polaronic strain caused by hole localization,<sup>[19,20]</sup> density gradient or electric field imposed by charge carriers,<sup>[16,21,22]</sup> free-energy variation of the system,<sup>[23–26]</sup> and iodide

## 1. Introduction

Lead mixed-halide perovskites of APbBr<sub>x</sub>I<sub>3-x</sub> ( $0 < x < 3$ ), with A being CH<sub>3</sub>NH<sub>3</sub><sup>+</sup> (MA<sup>+</sup>), HC(NH<sub>2</sub>)<sub>2</sub><sup>+</sup> (FA<sup>+</sup>) or Cs<sup>+</sup>, are featured with high fluorescence quantum yield,<sup>[1]</sup> long carrier diffusion length,<sup>[2]</sup> good defect tolerance,<sup>[3]</sup> and tunable emission wavelength covering a wide spectral range from the visible to the near infrared.<sup>[4,5]</sup> These superior optoelectronic properties have rendered them excellent candidates as absorbers and emitters for highly efficient solar cells<sup>[6,7]</sup> and light-emitting

oxidation/repulsion promoted by photogenerated holes.<sup>[27–29]</sup> Various strategies to improve the materials quality have been developed to mitigate the phase-segregation effect, e.g., by increasing the grain size,<sup>[30]</sup> improving the film crystallinity,<sup>[31]</sup> passivating the surface defect,<sup>[32]</sup> mixing the A-site cations,<sup>[33]</sup> and minimizing the interface recombination.<sup>[6,34]</sup> However, these alternations in materials could pose a stringent limit on the available bandgap energies and even induce unwanted changes of carrier recombination and transport dynamics.<sup>[35]</sup>

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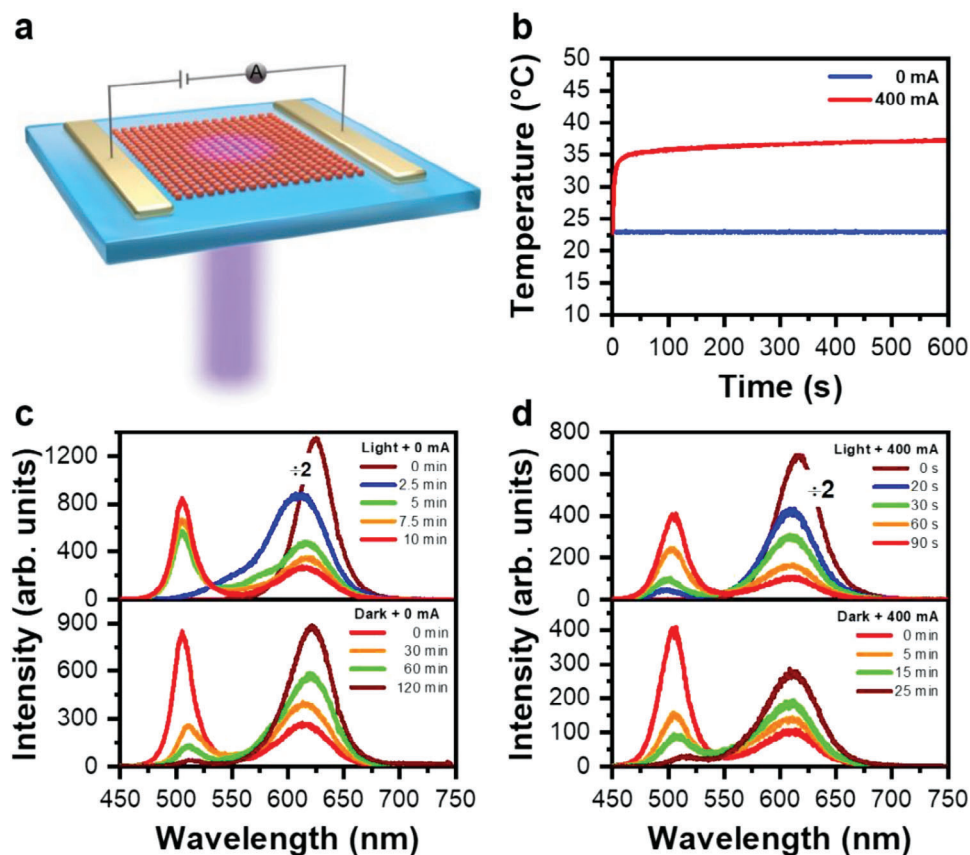
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**Figure 1.** Phase segregation and remixing studies of CsPbBr<sub>1.2</sub>I<sub>1.8</sub> NCs at static temperatures. a) Experimental setup for the heating/cooling operations and the optical studies. b) Temperature evolution of CsPbBr<sub>1.2</sub>I<sub>1.8</sub> NCs after a current flow of 400 mA is induced in the ITO substrate, as compared to that measured at room temperature (0 mA). PL spectra measured during the light-induced phase-segregation (top) and dark-recovered phase-remixing (bottom) processes of CsPbBr<sub>1.2</sub>I<sub>1.8</sub> NCs at c) room temperature and d)  $\approx 35^\circ\text{C}$ .

The phase-segregation effect can also be controlled by some external stimuli such as hydrostatic pressure<sup>[36,37]</sup> and light intensity.<sup>[26,38,39]</sup> In the former case, a compressive strain can be induced by the external pressure,<sup>[40]</sup> which is capable of suppressing phase segregation by increasing the activation energy for anion migration.<sup>[40,41]</sup> In the latter case, a threshold light intensity is required to yield the segregated phase<sup>[26,38]</sup> which, however, can be reversed to the mixed phase at sufficiently high light intensities due to polaron formation across the length scale larger than the average separation of segregated domains.<sup>[39]</sup> Despite providing in-depth information on the underlying mechanism, it is impractical to apply the large compressive strain or high light intensity to a working device of mixed-halide perovskites.

Here, we report on the complete suppression of phase segregation in mixed-halide CsPbBr<sub>1.2</sub>I<sub>1.8</sub> nanocrystals (NCs) by means of a mild periodic heating method. This is achieved by depositing a dense film of CsPbBr<sub>1.2</sub>I<sub>1.8</sub> NCs on top of an ITO (indium tin oxide) substrate, which is capable of changing the sample temperature very rapidly upon the application or removal of an external voltage. When the phase segregation has already been induced in the NCs under light illumination, a sudden temperature increase would convert them completely to the mixed phase within just several seconds. Intriguingly, the light-induced segregated phase of heated CsPbBr<sub>1.2</sub>I<sub>1.8</sub> NCs can also be reverted to the mixed

phase within several seconds after a sudden decrease of the sample temperature. After either of the above heating and cooling operations, the mixed phase of CsPbBr<sub>1.2</sub>I<sub>1.8</sub> NCs can only be kept temporarily and it would finally switch back to the segregated phase under elongated light illumination. However, when continuous light illumination is coupled with periodic heating durations realized by alternatively switching on and off an external voltage applied to the ITO substrate, the CsPbBr<sub>1.2</sub>I<sub>1.8</sub> NCs would remain at the mixed phase without any detectable halide segregation. We explain this intriguing phenomenon by the contributions of two main factors to the change of the system free energy, namely the thermal entropy and lattice strain that are increased during the heating and cooling processes, respectively.

## 2. Results and Discussion

Following the same procedure as reported previously,<sup>[42]</sup> we synthesize cuboid CsPbBr<sub>1.2</sub>I<sub>1.8</sub> NCs with an average edge length of  $\approx 23$  nm (see the Experimental Section and Figure S1, Supporting Information, for the transmission electron microscopy images). As depicted in Figure 1a, we then place a high-density film of CsPbBr<sub>1.2</sub>I<sub>1.8</sub> NCs (see Figure S2, Supporting Information, for the structural characterizations) in between two electrodes on top of an ITO substrate, which stays at room temperature of

$\approx 23\text{--}24$  °C without any current (0 mA, Figure 1b). When an external voltage of 6 V is applied to the ITO substrate, its temperature first increases quickly to  $\approx 32$  °C within 10 s and then rises further slowly to  $\approx 37$  °C after  $\approx 600$  s of current heating (400 mA, Figure 1b). Compared to the traditional method of heating by a hot plate,<sup>[43,44]</sup> the current heating of ITO substrate can achieve temperature change of the deposited CsPbBr<sub>1.2</sub>I<sub>1.8</sub> NCs very promptly, thus allowing us to explore how a dynamic variation of the thermal environment affects the phase segregation and remixing processes. To this end, we use an immersion-oil objective to focus the 405 nm output beam from a 5 MHz picosecond diode laser onto the sample (Figure 1a). Optical signals of CsPbBr<sub>1.2</sub>I<sub>1.8</sub> NCs excited at a power density of  $\approx 50$  W cm<sup>-2</sup> are collected by the same objective and sent through a spectrometer to the CCD (charge-coupled device) camera for the photoluminescence (PL) measurements (see the Experimental Section).

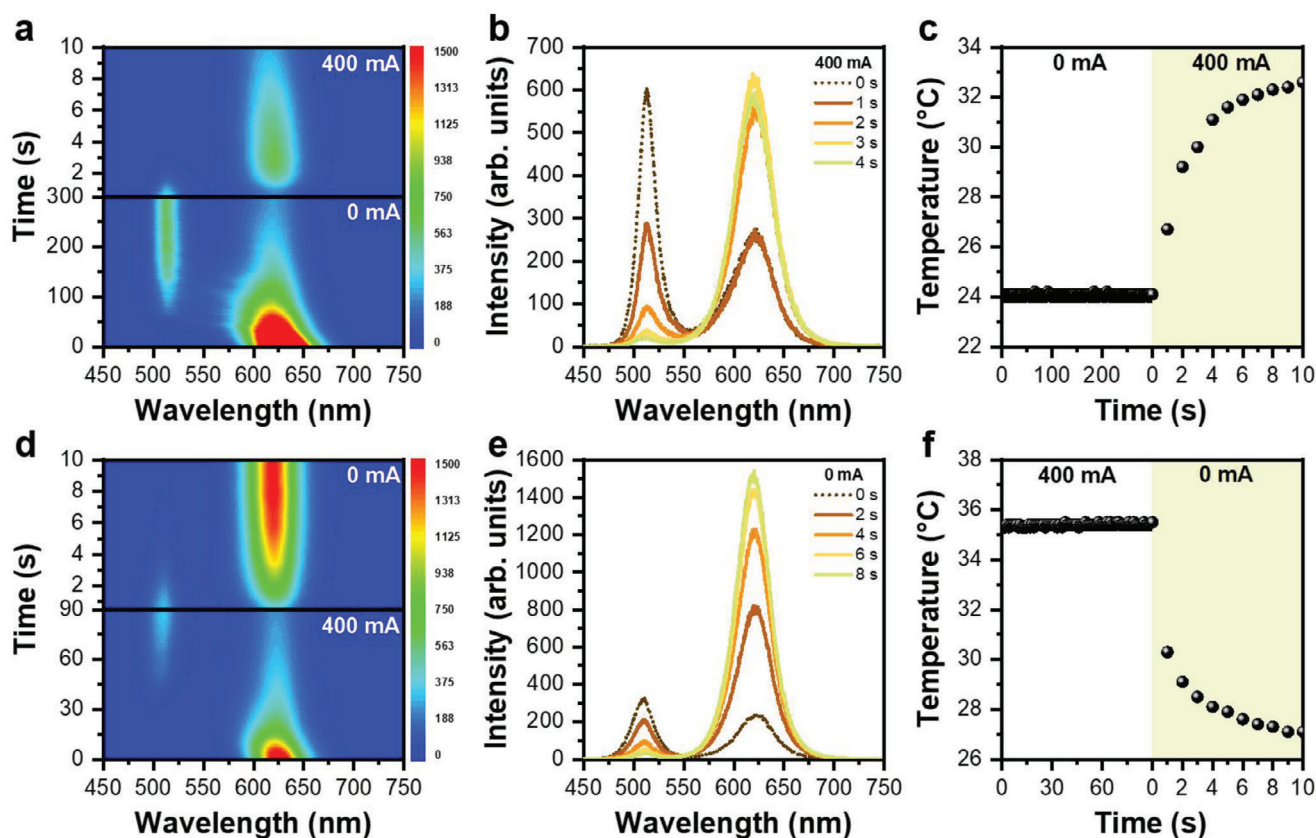
At room temperature without any current heating, the phase segregation of CsPbBr<sub>1.2</sub>I<sub>1.8</sub> NCs completes within  $\approx 10$  min of light illumination, which is evidenced by the optical measurements in the top panel of Figure 1c. During this process, the PL spectrum shifts from the initial peak wavelength of  $\approx 626$  nm ( $\approx 37.4$  nm linewidth) to the final one of  $\approx 505$  nm ( $\approx 18.4$  nm linewidth), indicating the formation of CsPbBr<sub>3</sub> NCs as a result of halide segregation.<sup>[42]</sup> In addition to the new PL peak, a residual one can also be seen at  $\approx 626$  nm, which originates from those CsPbBr<sub>1.2</sub>I<sub>1.8</sub> NCs located at the edge of the laser spot without receiving enough power density to trigger phase segregation.<sup>[26,36]</sup> The bottom panel of Figure 1c shows the recorded PL spectra when the sample is then left in the dark while the laser beam is unblocked for 1 s only at several time points. Compared to the light-illuminating duration of  $\approx 10$  min to fully induce phase segregation, a much longer time of  $\approx 120$  min is needed for the recovery of mixed phase.

In the next experiment, we apply an external voltage to the ITO substrate to induce a current flow of 400 mA in the dark and a stable temperature of  $\approx 35$  °C can be achieved after 300 s without triggering phase segregation in the CsPbBr<sub>1.2</sub>I<sub>1.8</sub> NCs (see Figure S3, Supporting Information). The PL spectrum measured for a film location right after laser excitation is plotted in the top panel of Figure 1d (see Figure S4a, Supporting Information, for the inhomogeneous distribution of PL peak wavelengths in the film), which is associated with a broadened linewidth of  $\approx 42.3$  nm and a blueshifted peak wavelength of  $\approx 1.2$  nm relative to that acquired at room temperature (see Figure S4b, Supporting Information, for the temperature-dependent PL spectra). These heating-induced changes can be jointly contributed by the enlarged crystal lattice and the enhanced exciton–phonon coupling commonly observed in perovskite materials.<sup>[45,46]</sup> Compared to the time duration of  $\approx 10$  min for the completion of phase segregation at room temperature, a much shorter time of  $\approx 90$  s is now needed at  $\approx 35$  °C due to the more active diffusion kinetics of halide anions.<sup>[17,41,47]</sup> After the above treatment, the sample film is left in the dark still at  $\approx 35$  °C while the PL spectra are measured at several time points in the bottom panel of Figure 1d to monitor the reversal process. PL intensity of the mixed-phase peak increases and gets to a stable value after  $\approx 25$  min, significantly shorter than the room-temperature time of  $\approx 120$  min due to the enhanced entropic effect.<sup>[48]</sup>

Consistent with previous results,<sup>[41,49,50]</sup> the light-induced phase segregation proceeds at much faster rates than those of the dark-recovered phase remixing at both room temperature and  $\approx 35$  °C. This observation implies that the driving force provided by light illumination is dominant over that of the entropic mixing, so that phase segregation of CsPbBr<sub>1.2</sub>I<sub>1.8</sub> NCs is always preferred at static temperatures. However, a critical point completely neglected in previous studies is that the system entropy can respond instantly to the temperature change, while the ion migration requires a much longer time in the perovskites.<sup>[17,51,52]</sup> This motivates us to introduce the tuning knob of dynamic temperature change to our perovskite system of CsPbBr<sub>1.2</sub>I<sub>1.8</sub> NCs, thinking that a sudden heating or cooling operation might shift the balance between the forward phase-segregation and the reverse phase-remixing processes.

To confirm this hypothesis, we monitor the time-dependent PL spectra of CsPbBr<sub>1.2</sub>I<sub>1.8</sub> NCs during two separate experiments, where we show the phase segregation can be suppressed by either the application of heating to the ITO substrate or the removal of heating from it. For the first experiment, as shown in the bottom panel of Figure 2a, the segregated phase is first induced by  $\approx 300$  s of light illumination at room temperature. Then right after a current heating of 400 mA is applied to the ITO substrate, the segregated phase completely shifts back to the mixed phase within  $\approx 4$  s while the CsPbBr<sub>1.2</sub>I<sub>1.8</sub> NCs are still being illuminated (top panel, Figure 2a). The corresponding PL spectra extracted at several time points in Figure 2b demonstrate the fast phase-remixing process, during which the sample temperature increases from  $\approx 24$  to 31 °C within  $\approx 4$  s since the start of current heating (Figure 2c). We then perform a second experiment by first inducing phase segregation in another film location of CsPbBr<sub>1.2</sub>I<sub>1.8</sub> NCs after  $\approx 90$  s of continuous light illumination under the current heating at 400 mA (bottom panel, Figure 2d). As can be seen from the time-dependent spectral image in the top panel of Figure 2d, the segregated phase is converted back to the mixed phase within  $\approx 8$  s after the current heating has been removed. The corresponding PL spectra extracted at several time points are plotted in Figure 2e for this phase-remixing process, during which a decrease of the sample temperature from  $\approx 35$  to 27 °C can be monitored within  $\approx 8$  s in Figure 2f. In Figures S5 and S6 in the Supporting Information, we present quite similar results obtained at other current values of 300 and 500 mA, while the 400 mA current is employed in our experiment as the result of a trade-off between fast heating/cooling and moderate impact of the thermal accumulation. Moreover, we have shown in Figures S7 and S8 in the Supporting Information that the mixed phase of segregated CsPbBr<sub>1.2</sub>I<sub>1.8</sub> NCs can be achieved more quickly at a faster temperature change or a higher starting temperature, respectively.

We note that despite the observations in Figure 2 that a sudden start (stop) of current heating can restore the mixed phase within  $\approx 4$  s ( $\approx 8$  s), the segregated phase would be resumed again when the CsPbBr<sub>1.2</sub>I<sub>1.8</sub> NCs are exposed to further light illumination (see Figure S9, Supporting Information). Since the mixed phase can be restored temporarily by either increasing or decreasing the temperature, we speculate that a well-designed timing of periodic heating and cooling could help to maintain the mixed phase just before it starts to segregate. We achieve this by regulating the time width ( $t$ ) of a single 400 mA pulse within a given time



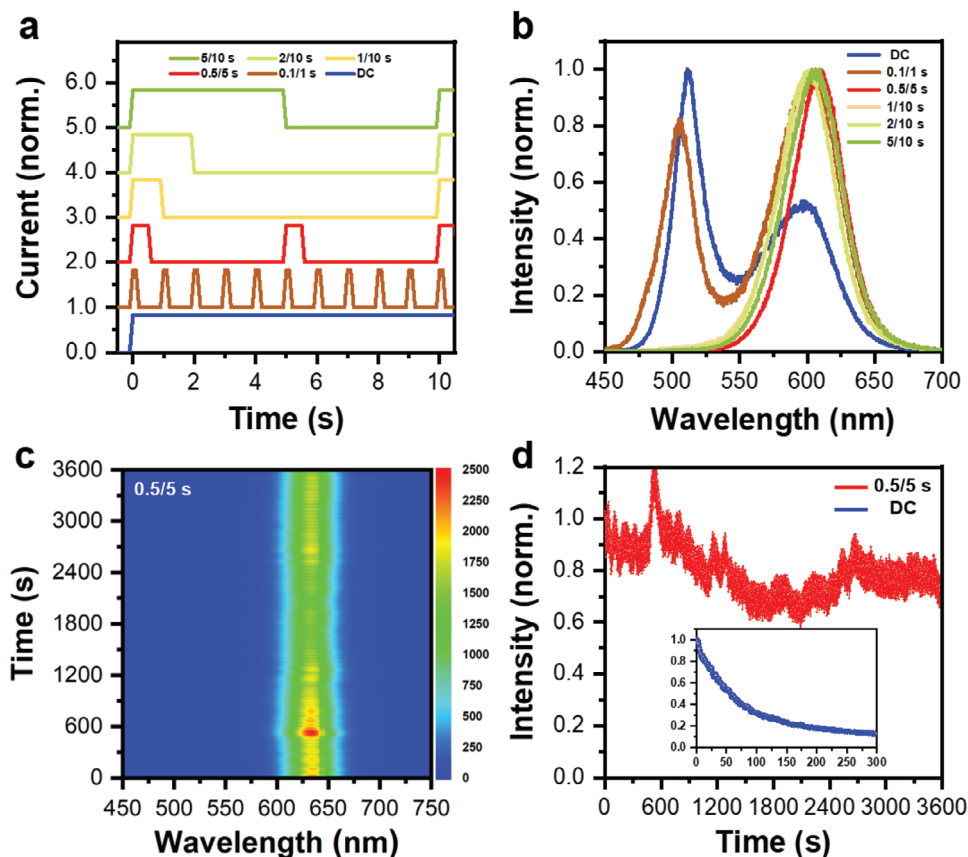
**Figure 2.** Phase segregation and remixing studies of CsPbBr<sub>1.2</sub>I<sub>1.8</sub> NCs at dynamic temperatures. a) Time-dependent spectral images measured before (bottom) and after (top) a current flow of 400 mA is induced in the ITO substrate. b) PL spectra extracted from the top panel of a) at several time points between 0 and 4 s. c) Sample temperatures monitored before and after a current flow of 400 mA are induced in the ITO substrate. d) Time-dependent spectral images measured before (bottom) and after (top) a current flow of 400 mA are removed from the ITO substrate. e) PL spectra extracted from the top panel of d) at several time points between 0 and 8 s. f) Sample temperatures monitored before and after a current flow of 400 mA is removed from the ITO substrate. In (a), (b), (d), and (e), the CsPbBr<sub>1.2</sub>I<sub>1.8</sub> NCs are continuously excited at  $\approx 50 \text{ W cm}^{-2}$  by a 405 nm pulsed laser.

period ( $T$ ). The time-dependent current curves with five different  $t/T$  combinations are plotted in Figure 3a, together with the direct-current (DC) one where the 400 mA current is flowing all the time across the ITO substrate.

After 180 s of light illumination with different  $t/T$  combinations of the applied current, it can be seen from the PL spectra in Figure 3b that severe phase segregation occurs in the DC and 0.1/1 s cases, while it is much milder under the conditions of 1/10, 2/10, and 5/10 s. Meanwhile, there is no sign of phase segregation in the  $t/T$  combination of 0.5/5 s, which can be further revealed from the time-dependent PL spectral evolution in Figure 3c. As shown in Figure 3d, the extracted PL intensities remain stable during the 3600 s measurement except the occurrence of small variations caused by periodic heating and cooling cycles. In contrast, the sample under DC current exhibits a drastic trend of PL decaying (inset of Figure 3d) caused by phase segregation at the first place and then by thermal quenching of the photogenerated excitons. In fact, even for the 0.5/5 s case that allows 4.5 s of sample cooling within every 5 s, local heat can still be built up to cause a slight blueshift in the PL peak and a reduced PL intensity during the simultaneous light-illumination and current-heating processes (see Figure 3c). Such thermal instability can be circumvented in practice such as by improving the

ventilation condition and adopting a heat sink, which are common procedures in the operations of perovskite optoelectronic devices.<sup>[53]</sup>

We emphasize that for the optical experiments performed in Figures 2 and 3, the 405 nm pulsed laser excitation at  $\approx 50 \text{ W cm}^{-2}$  is always supplied to the CsPbBr<sub>1.2</sub>I<sub>1.8</sub> NCs during the sudden change of sample temperature, highlighting that the segregated phase can be reversed to the mixed phase even under such a harsh condition (see Figure S10, Supporting Information for similar measurements at  $\approx 5 \text{ W cm}^{-2}$  and with a continuous-wave laser). Now if the segregated CsPbBr<sub>1.2</sub>I<sub>1.8</sub> NCs are left in the dark instead, a sudden temperature change would also promote a fast appearance of the mixed phase (see Figure S11, Supporting Information). Thereafter, no further phase segregation occurs due to lack of the driving force provided by light illumination. These results allow us to decouple the effect of light illumination with that of sample heating/cooling, and then the main scientific question is how the latter operation could accelerate the phase-remixing process in the dark. Since previous experimental<sup>[12,26,44,48]</sup> and theoretical<sup>[23–26]</sup> studies of mixed-halide perovskites were mostly done at static temperatures, a new mechanism should be at play in our case for the dynamic temperature response of segregated CsPbBr<sub>1.2</sub>I<sub>1.8</sub> NCs toward phase remixing.

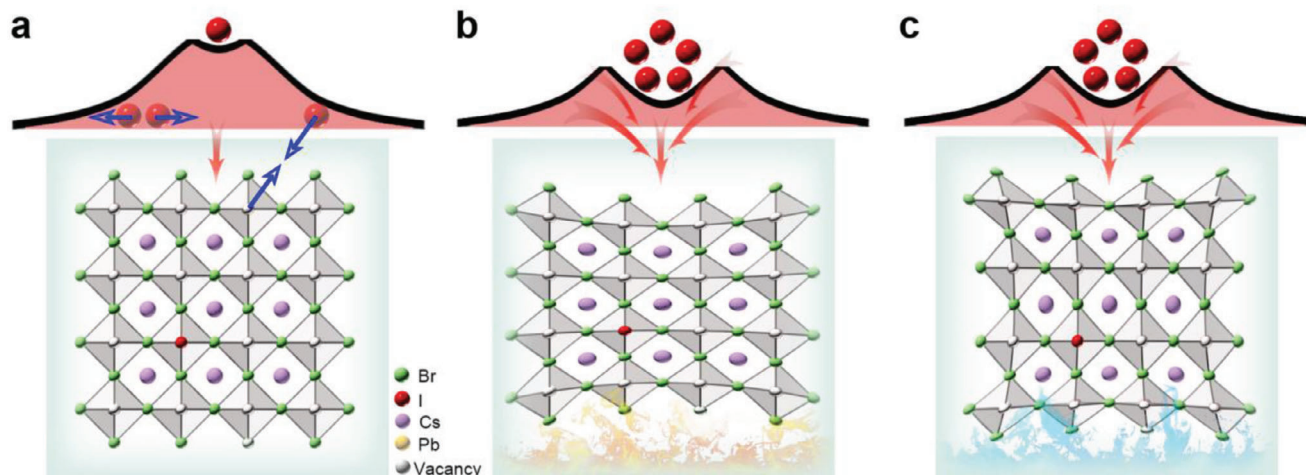


**Figure 3.** Complete suppression of phase segregation in CsPbBr<sub>1.2</sub>I<sub>1.8</sub> NCs. a) Different current patterns applied to the ITO substrate each with the maximum amplitude of 400 mA. b) PL spectra measured for CsPbBr<sub>1.2</sub>I<sub>1.8</sub> NCs after different current patterns have been applied to the ITO substrate for 180 s. c) Time-dependent spectral image of CsPbBr<sub>1.2</sub>I<sub>1.8</sub> NCs measured with the current pattern of 0.5/5 s. d) Time-dependent PL intensities of CsPbBr<sub>1.2</sub>I<sub>1.8</sub> NCs extracted from a) for the current pattern of 0.5/5 s. For comparison, the mixed-phase PL intensity of CsPbBr<sub>1.2</sub>I<sub>1.8</sub> NCs is plotted in the inset as a function of time for the DC current pattern. In (b)–(d), the CsPbBr<sub>1.2</sub>I<sub>1.8</sub> NCs are continuously excited at  $\approx 50 \text{ W cm}^{-2}$  by a 405 nm pulsed laser.

As can be noticed from the top panel of Figure 2a after the induction of a 400 mA current in the ITO substrate, the segregated CsPbBr<sub>1.2</sub>I<sub>1.8</sub> NCs are converted instantly to the mixed phase with a PL intensity significantly lower than that measured before light-induced phase segregation in the bottom panel. This PL intensity drop should be a direct consequence of the thermal quenching effect, which can be deduced from the representative PL spectra plotted in Figure S4b in the Supporting Information at several static temperatures. However, according to the energy-level diagram depicted in Figure S12 in the Supporting Information,<sup>[54]</sup> it is possible for charge carriers to be injected into the CsPbBr<sub>1.2</sub>I<sub>1.8</sub> NCs right after the ITO substrate has been biased by an external voltage.<sup>[55,56]</sup> To exclude this charging effect as a possible origin for the PL intensity drop via the nonradiative Auger process,<sup>[57]</sup> we insert a  $\approx 60 \text{ nm}$  thick hBN (hexagonal boron nitride) flake between the CsPbBr<sub>1.2</sub>I<sub>1.8</sub> NCs and the ITO substrate (see Figure S13a, Supporting Information) to block the charge injection channel if it really exists. As can be seen from Figure S13b in the Supporting Information, the PL intensity of CsPbBr<sub>1.2</sub>I<sub>1.8</sub> NCs shows a sudden drop once a current flow of 400 mA is induced in the ITO substrate, the degree of which is comparable to that measured in Figure 2a between the original

and reverted mixed phases. Consequently, we can safely conclude that there are no injected holes from the ITO substrate to introduce the iodide oxidation effect<sup>[27,28]</sup> into the phase-remixing process of CsPbBr<sub>1.2</sub>I<sub>1.8</sub> NCs. Moreover, due to the absent injection of high-density charge carriers into the CsPbBr<sub>1.2</sub>I<sub>1.8</sub> NCs, we can also exclude the polaron merging effect<sup>[39]</sup> as the underlying mechanism for the phase remixing induced by current heating.

Before setting up a plausible model to accommodate the promotion of mixed phase by a dynamic temperature change, we first need to understand how the CsPbBr<sub>1.2</sub>I<sub>1.8</sub> NCs behave in the light-induced phase-segregation process. Under light illumination, the excited charge carriers in a single CsPbBr<sub>1.2</sub>I<sub>1.8</sub> NC could be captured by surface traps to create local electric fields<sup>[22,32]</sup> that are capable of breaking the lead-halide bonds.<sup>[42]</sup> The freed iodide and bromide anions are mobile and have the tendency of refilling the vacancies left in the NC under the entropic driving force.<sup>[23,25]</sup> The respective vacancy-refilling rates of iodide and bromide anions should be smaller and larger than those of the opposite bond-breaking reactions. The above judgement is based on the fact that the Pb–Br bond is associated with a larger binding energy than that of the Pb–I bond<sup>[42,58]</sup> and is firmly corroborated



**Figure 4.** Underlying mechanism for heating- and cooling-induced phase remixing in the dark. a) Spatial distribution of freed iodide anions in close proximity to the surface of a single CsPbBr<sub>3</sub> NC, with the central one just about to fill the internal vacancy to restore a broken Pb–I bond. This spatial distribution of iodide anions is maintained by their mutual repulsions and the attractions from internal vacancies, which are represented by the two tail-to-tail and head-to-head blue arrows, respectively. b) When the CsPbBr<sub>3</sub> NC is suddenly heated to have a lattice expansion, more iodide anions in the distribution center would refill the vacancies to cause a fast restoration of the mixed phase. c) When thermal heating is suddenly removed from the CsPbBr<sub>3</sub> NC to induce a lattice contraction, more iodide anions in the distribution center would refill the vacancies to cause a fast restoration of the mixed phase.

by the eventual formation of a single CsPbBr<sub>3</sub> NC after phase segregation.

To confirm the existence of freed iodide anions on the surface, we have performed Kelvin probe force microscopy measurements on the CsPbBr<sub>1.2</sub>I<sub>1.8</sub> NCs during their light-induced phase-segregation and dark-recovered phase-remixing processes (see Figure S14, Supporting Information). In the former case, the surface potential of CsPbBr<sub>1.2</sub>I<sub>1.8</sub> NCs is progressively reduced to signify that abundant iodide anions are released to the surface from the broken Pb–I bonds. In the latter case, the surface potential increases sequentially to suggest that the crystal lattice becomes more charge-neutral as the internal vacancies are filled by the iodide anions. As proposed previously,<sup>[42]</sup> the ≈23 nm size of a single CsPbBr<sub>1.2</sub>I<sub>1.8</sub> NC might be not enough to favor the formation of a large-polaron or iodide-rich domain normally with a spatial size of ≈8 nm.<sup>[59]</sup> As such, the freed iodide anions tend to migrate to the strained NC surface,<sup>[60]</sup> just like what they have been reported to do with the grain boundaries in mixed-halide perovskites.<sup>[61,62]</sup> Consequently, a blueshift in the PL peak is observed from the remaining CsPbBr<sub>3</sub> material in the NC core, instead of the redshifts reported in the literature for other types of mixed-halide perovskite NCs.<sup>[63,64]</sup> Of special note is that some of the surface iodide anions could be lost via the molecular formation and the subsequent sublimation processes,<sup>[15,42,65]</sup> resulting in the small amount of residual CsPbBr<sub>3</sub> emission after the majority of segregated CsPbBr<sub>1.2</sub>I<sub>1.8</sub> NCs have been converted to the mixed phase (see, e.g., the bottom panels in Figure 1c,d). This unexpected loss of iodine elements becomes more obvious when the CsPbBr<sub>1.2</sub>I<sub>1.8</sub> NCs are illuminated by the laser light for longer times (see Figure S15, Supporting Information, for the energy dispersive X-ray spectroscopy measurements), which can be suppressed by various strategies such as the growth of a PbSO<sub>4</sub> shell on the NC surface.<sup>[66]</sup>

Due to the slow ion migration process in perovskite materials,<sup>[17,51,52]</sup> it is surprising to see in our experiment that the internal vacancies of a single CsPbBr<sub>3</sub> NC can be occupied by iodide anions within several seconds after a sudden temperature change (Figure 2a,d). This contradiction can be reconciled by assuming that the freed iodide anions are located in close proximity to the CsPbBr<sub>3</sub> NC with a Gaussian-like distribution, as depicted in Figure 4a. This spatial distribution is a result of the competition of the attraction from internal vacancies to keep iodide anions piling up on the CsPbBr<sub>3</sub> NC surface, with the repulsion among iodide anions to push some of them to nearby regions.

For the coupled system in Figure 4a where a single CsPbBr<sub>3</sub> NC is surrounded by freed iodide anions on the surface, the phase-remixing process can be conveniently assumed to start from a vacancy-filling event involving an iodide anion located at the center of the spatial distribution. A neighboring iodide anion will take the void position left by its predecessor due to the vanished Coulomb repulsion, thus bringing about another round of vacancy-filling and anion-shifting motions until a single CsPbBr<sub>1.2</sub>I<sub>1.8</sub> NC is completely restored after tens of minutes (bottom panels, Figure 1c,d). As shown in Figure 4b for the segregated phase, a sudden operation of sample heating with an elevated entropic driving force promotes vacancy fillings by more iodide anions as compared to the mild situation in Figure 4a. The greatly reduced Coulomb repulsion triggers an avalanched movement of iodide anions toward the central region and speeds up the collapse of their spatial distribution, so that phase remixing can be reached in just a few seconds (top panel, Figure 2a). Bearing the above picture in mind to depict the phase-remixing process after a sudden temperature increase, it is counter-intuitive to understand why the same thing happens after a sudden temperature decrease that seems to attenuate the entropic driving force of halide remixing.

Due to the size difference between bromide ( $\approx 196$  pm) and iodide ( $\approx 220$  pm) anions,<sup>[67]</sup> the crystal lattice of a single CsPbBr<sub>1.2</sub>I<sub>1.8</sub> NC hosts extensive local strains, which can be effectively attenuated from the single CsPbBr<sub>3</sub> NC depicted in Figure 4a owing to a total loss of the iodide elements. Being exposed to a sudden decrease of temperature, as shown in Figure 4c, the CsPbBr<sub>3</sub> NC experiences a compressive strain in the contracted lattice. To mitigate such strain, the iodide anions in the distribution center at the surface of the NC are activated to fill the internal vacancies. This analysis is consistent with the literature scenarios, where the polaronic region<sup>[19,20]</sup> and grain boundary<sup>[61,62]</sup> with abundant strains are preferred as the migration destinations of iodide anions to reduce the system free energy. Here, the strain-relieving driving force is larger than just compensating the reduced entropy-mixing force, as can be deduced from the fact that a single CsPbBr<sub>1.2</sub>I<sub>1.8</sub> NC is recovered within several seconds after a sudden temperature decrease. According to first principles calculations,<sup>[68–70]</sup> when the temperature decreases from 310 to 300 K, the lattice constants of CsPbBr<sub>3</sub> and CsPbI<sub>3</sub> change from the initial values of  $\approx 5.807$  and  $\approx 6.080$  Å to the final ones of  $\approx 5.802$  and  $\approx 6.075$  Å, respectively. These cumulative changes in the whole crystal give rise to the respective lattice strains of  $\approx 0.086$  and  $\approx 0.082\%$ , which should be close to the corresponding value of CsPbBr<sub>1.2</sub>I<sub>1.8</sub> studied in our experiment. In a previous work conducted on single CsPbI<sub>3</sub> NCs,<sup>[60]</sup> the surface-induced strain was estimated to be within a comparable range of  $\approx 0.05$ – $0.17\%$ . The above analysis suggests that a temperature change of  $\approx 10$  K can be sufficient to modify the strain profile of the mixed-halide CsPbBr<sub>1.2</sub>I<sub>1.8</sub> NCs. Now we can have another look at Figure 4b for the temperature-increasing case, where tensile strains are induced by lattice expansion of the single CsPbBr<sub>3</sub> NC. Under this situation, the pairing of iodide anions and internal vacancies should not increase the tensile strains any further if not decreasing them, so that the enhanced entropic driving force serves as the main factor for a fast recovery of the mixed phase.

**3. Conclusion** To summarize, we demonstrate in CsPbBr<sub>1.2</sub>I<sub>1.8</sub> NCs that a sudden temperature change of  $\approx 10$  °C in the dark can reduce the transition time from segregated to mixed phases by more than two orders of magnitude as compared to that measured at static temperatures. Even under laser excitation at a high power density of  $\approx 50$  W cm<sup>-2</sup>, this mixed phase can still be temporarily obtained by a sudden temperature change, and it can be further kept permanently when the CsPbBr<sub>1.2</sub>I<sub>1.8</sub> NCs are periodically heated with a well-designed time interval. To explain all the experimental findings, we propose that the iodide anions are released from the broken Pb–I bonds of a single CsPbBr<sub>1.2</sub>I<sub>1.8</sub> NC under light illumination and migrate to the surface to form a Gaussian-like spatial distribution around the converted CsPbBr<sub>3</sub> NC. This spatial distribution of surface-accumulated iodide anions is kept by the balancing forces of their mutual repulsion and the attraction from internal vacancies, which can be interrupted under an appropriate driving force such as the sudden change of sample temperature. This temperature change increases either the entropic driving force in the case of heating or the lattice strain in the case of cooling for the segregated phase. To minimize system free energy, the internal vacancies of a single CsPbBr<sub>3</sub> NC start to be refilled in an avalanched fashion to promote a fast restoration of the mixed phase.

Besides the CsPbBr<sub>1.2</sub>I<sub>1.8</sub> composition focused here, the temperature-modulation strategy of suppressing phase segregation is also applicable for CsPbBr<sub>x</sub>I<sub>3-x</sub> NCs with other  $x$  values (see Figure S16, Supporting Information) as well as for the organic–inorganic hybrid FAPbBr<sub>0.9</sub>I<sub>2.1</sub> NCs (see Figure S17, Supporting Information). Moreover, we have also performed similar studies on bulk CsPbBr<sub>2</sub>I microplates (see Figure S18, Supporting Information), seeing that the heating operation can also drive a fast transition from the segregated to the remixed phases. However, the remixed phase cannot be fully accessed when a segregated CsPbBr<sub>2</sub>I microplate undergoes the cooling operation, possibly because the uniform strains induced by a temperature variation in bulk perovskites can be easily relaxed through the global volume changes.<sup>[19]</sup> It would be necessary in future works to synthesize different-sized CsPbBr<sub>x</sub>I<sub>3-x</sub> NCs by changing the reaction conditions, not only to monitor the PL shift directions during phase segregation but also to estimate how the modified strain profiles affect phase remixing upon a sudden temperature change. Overall, the above findings in different mixed-halide perovskites have greatly deepened the current understanding of their phase segregation and remixing mechanisms, which will promote the rational design of potent schemes to increase the operation stabilities of relevant optoelectronic devices.

### 3. Experimental Section

**3.0.0.1. Sample Preparations:** To prepare the Cs-oleate precursor, 0.814 g Cs<sub>2</sub>CO<sub>3</sub>, 2.5 mL oleic acid, and 40 mL octadecene were loaded into a 100 mL three-neck flask. After being degassed and dried for 10 min in vacuum, the solution was heated first at 120 °C for 1 h and then at 150 °C for 2 h under the N<sub>2</sub> gas to completely dissolve the Cs<sub>2</sub>CO<sub>3</sub>. To prepare the CsPbBr<sub>1.2</sub>I<sub>1.8</sub> NCs, 0.105 g PbI<sub>2</sub>, 0.052 g PbBr<sub>2</sub>, 1.0 mL oleic acid, 1.0 mL oleylamine, and 10 mL octadecene were loaded into a 25 mL three-neck flask. After the solution had been degassed in vacuum and dried for 1 h at 120 °C, the flask was connected to the N<sub>2</sub> gas. The solution temperature was then raised to 160 °C for 10 min, after which 1.0 mL of the Cs-oleate solution preheated to 120 °C was quickly injected. The reaction was stopped with ice bath after 5 s and the resulting solution was centrifuged for 20 min at 5000 rpm. The precipitate was redispersed in 10.0 mL hexane and centrifuged again for 20 min at 5000 rpm to get the final product of CsPbBr<sub>1.2</sub>I<sub>1.8</sub> NCs in the supernatant. To prepare a high-density film for the optical measurements, one solution drop of the as-synthesized CsPbBr<sub>1.2</sub>I<sub>1.8</sub> NCs was spin-coated between two electrodes separated by 14 mm on top of an ITO substrate. Each of the deposited electrodes had a width of 2 mm and consisted of the Cr and Au layers (from bottom to top) with the thicknesses of 5 and 70 nm, respectively.

**3.0.0.2. Experimental Measurements:** The sample substrate was attached to a home-built confocal scanning optical microscope, where the CsPbBr<sub>1.2</sub>I<sub>1.8</sub> NCs were excited by a 405 nm picosecond diode laser operated at the repetition rate of 5 MHz. After passing through an immersion-oil objective with the numerical aperture of  $\approx 1.4$ , the laser beam was focused onto the sample substrate with a spot size of  $\approx 500$  nm and a power density of  $\approx 50$  W cm<sup>-2</sup>. Optical emission from the CsPbBr<sub>1.2</sub>I<sub>1.8</sub> NCs was collected by the same objective and sent through a 0.5 m spectrometer to a CCD camera for the PL spectral measurement with an integration time of 0.5 s. For the heating operation, a bias voltage was applied to the two electrodes on the ITO substrate by a digital source meter (Keithley2636B). The surface temperature of the NC film was monitored by a noncontact thermometer, with the obtained data being recorded and processed by a TH11S-B software. Due to differences in the surrounding environment, the ITO substrate, and the heat-dissipating power of immersion oil, the exact temperature and its current-induced change in the CsPbBr<sub>1.2</sub>I<sub>1.8</sub> NCs may vary from experiment to experiment.

## Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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## Conflict of Interest

The authors declare no conflict of interest.

## Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

## Keywords

mixed-halide perovskite, nanocrystal, periodic heating, phase remixing, phase segregation

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