

Ultrafast Thermodynamic Control for Stable and Efficient Mixed Halide Perovskite Nanocrystals

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Low photoluminescence quantum yield (PLQY) and spectra instability, the two most difficult challenges in blue-emitting CsPbBr_xCl_{3-x} NCs, have not yet been solved. Quickly controlling the reaction thermodynamics is crucial to enhance crystallinity, thus PLQY and spectra stability, but it has been ignored until now. An ultrafast thermodynamic control (UTC) strategy is designed by utilizing liquid nitrogen to instantaneously freeze the superior crystal lattices of CsPbBr, Cl_{3-r} NCs formed at high temperature. The average cooling rate exhibits a 33-fold increase compared to conventional ice-water cooling (from 1.5 to 50 K s⁻¹). This UTC can make the reaction thermodynamic energy of the system lower than the threshold very quickly. Therefore, abrupt termination of further crystal growth can be achieved, which also avoids additional nucleation at low temperature. With the assist of defect passivation, the final blue-emitting CsPbBr_xCl_{3-x} NCs exhibit an absolute PLQY of 98%, representing the highest value in Pb-based blue perovskites to date. More importantly, they exhibit superior spectra instability. This UTC strategy not only represents a new avenue to synthesize perovskite NCs with excellent crystal quality and ultrahigh PLQY, but also provides a good reference to deal with the recognized bottleneck of spectra instability.

1. Introduction

As emerging semiconductor materials, the solution-processed all-inorganic metal halide perovskite (CsPbX₃, X = Br, Cl, or I) nanocrystals (NCs) have experienced explosive developments in recent years, owning to the inspiring photovoltaic properties.^[1] Especially their high color purity with narrow spectra full width at half maximum (FWHM), long charge carriers mobility, low cost, and large-area processing features,^[2,3] render them the most ideal candidate for next-generation high-resolution displays and efficient white light illumination, which require three

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primary colors (red, green, and blue) with high photoluminescence quantum yields (PLQYs) and stability simultaneously.^[4] With unremitting efforts in recent years, the PLQYs of red and green emitting perovskite have leaped to near unity.[5,6] However, the PLQY of blue-emitting perovskite has struggled to match this such admirable value.^[7-11] This exceedingly unbalanced development of three primary colors triggered by the low blue photoluminescence efficiency seriously hinders the further practical application of perovskite.[12-14] Although recent remarkable efforts have been devoted to remedy this regret,^[15-18] at present, it is generally recognized that achieving high blue emitting PLQY with stable and pure spectra is challenging.^[3,11,13,14,19]

In general, two strategies have been developed to achieve blue emission: Dimension engineering and component engineering.^[8,13,20–22] The dimension engineering is constructing quantum

well structures by synthesizing 2D or quasi-2D Br-based perovskite, allowing the emission wavelength to shift toward the blue region based on the quantum confinement effect.^[23] Recently, lots of outstanding work regarding dimension engineering have greatly promoted the research of blue emitting perovskite.^[12,19,21,22,24,25] However, it is unavoidable that as the dimension decreases, the surface-to-volume ratio increases rapidly, which will induce a large number of surface defects, thus low PLQY.^[11] Since a bluer emission entails a lower dimensional quantum well structure, this means that more PLOY will be sacrificed.^[12,26,27] As a result, achieving high PLQY in the pure blue spectra range is very challenging based on this strategy, especially in the deep blue spectra range. So, most of the blue LEDs based on dimension engineering have emission wavelengths at 480 nm or larger, close to sky blue, including the recently reported highest and second most efficient blue LEDs.^[21,22,28-31] Moreover, such range could not meet the standard of National Television System Committee, which indicates that the emission of blue LED must be located at around 470 nm or bluer.^[9] In addition, controlling the formation of single quantum wells or achieving effective charge transfer between different quantum wells is challenging, which usually results in multiple emission peaks.^[23,28] Furthermore, it is relatively inconvenient to tune the emission color precisely by

dimension engineering. Fortunately, based on component engineering, the mixed halide perovskite $CsPbBr_xCl_{3-x}$ NCs could well remedy the aforementioned shortcoming, as its unique advantages of high blue emitting purity and the easily-tailored bandgap covering the whole blue spectra range.^[7]

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However, two serious obstacles of $CsPbBr_xCl_{3-x}$ NCs currently inhibited the researches and the more widespread applications of such materials severely: i) A large number of vacancy defects and poor crystal quality make them suffer from low PLQYs, usually its PLQY did not exceed 50%.^[19] ii) The insurmountable spectra instability likely caused by defects and poor crystallinity. Therefore, utilizing the ultrafast-thermodynamic control to enhance crystallinity and reduce defects provides an opportunity to address these two challenges simultaneously, but this aspect has not been noticed before. Therefore, at present, it is extremely challenging and urgent for blue emitting perovskite to simultaneously meet the three requirements of high PLQY, spectra stability, and the easily tunable emission color.

In this work, we reported the blue emitting CsPbBr_xCl_{3-x} NCs, which possess near-unity absolute PLQY, stable spectra, and the tunable emission color covering the whole blue spectra range. To achieve this, the UTC strategy was designed by utilizing liquid nitrogen (77 K) to instantaneously freeze the superior crystal lattices of CsPbBr_xCl_{3-x} NCs formed at high temperature (453 K). The ultrafast cooling rate (50 K s⁻¹) can effectively make the reaction thermodynamic energy of the system lower than the threshold very quickly. Therefore, the abrupt termination of further crystal grain growth could be achieved, which also avoids the additional nucleation at low temperature for achieving better crystallinity and grain size uniformity. With the assist of Pb(BrCl)₂ salts defect passivation, there are almost no deep-level defects that can capture carriers, which was confirmed by the femtosecond transient absorption (fs-TA) and time-resolved PL dynamics characterization. As a result, the blue PLQY was boosted to 98%. Especially, they exhibited excellent spectra stability, and there was no spectra shift caused by phase separation after 40 h continuous ultraviolet (UV) irradiation (5 mW cm⁻²) or 8 days storage in atmosphere environment (60% RH). Therefore, we believe that this UTC strategy is of great significance for promoting the further progress of blue emitting perovskite to break the exceedingly unbalanced development of three primary colors.

2. Results

The crystallinity of perovskite is very important in determining their efficiency in LED and solar cell.^[23,32,33] Enhancing its crystal quality has been proven to be effective in eliminating the non-radiative recombination lattice defects^[34–36] and suppressing the lattice distortion, thereby enabling perovskite to have stable lattices to resist external degradation.^[31,37–39] Since the synthesis of CsPbX₃ NCs by high temperature thermal injection was proposed in 2015,^[40] almost all attention has been paid to varying the synthesis temperature, reaction time, surface ligands, or controlling the amount of reactants.^[10,24,41] However, the research on how to stop the high-temperature chemical reaction quickly to obtain high crystallinity and uniform grain size has not been well researched, and the ice-water

is widely used cooling medium at present. While, the lowest temperature of ice-water is only 0 °C and the cooling ratio is limited. Moreover, the ice-water is a strong polar liquid which cannot be directly mixed with the reaction solution.^[42] The high temperature chemical reaction could only be slowly stopped by immersing the flask containing reaction solution into ice-water, which also further greatly inhibits the efficiency of cooling. In addition, cooling with a flask to separate ice-water from the high temperature reaction solution will cause a temperature difference between the wall and the center of the flask, thus resulting in uneven cooling and non-uniform grain sizes. Besides, efficient and uniform cooling is the most critical prerequisite for large-scale industrial production, but this conventional icewater cooling is currently inhibiting it significantly. Although the ice-water could completely stop the synthesis reaction of CsPbX₃ NCs in about 100 s, the grains obtained at high temperature will continue to grow. Besides, the new grains may also be generated during such a long time at low temperature.^[43,44] These inevitable shortcomings will lead to poor crystallinity and non-uniform grain sizes.^[24,41]

Therefore, to obtain blue emitting CsPbBr_xCl_{3-x} NCs with more uniform grain sizes and higher crystal quality, the liquid nitrogen (77 K) was introduced for the first time to instantaneously freeze crystal structure of CsPbBr_xCl_{3-x} NCs formed at high temperature (Figure 1; Videos S1 and S2, Supporting Information). It should be noted that liquid nitrogen is relatively cheap and will not cause a significant increase in synthesis costs. To further demonstrate the superiority of liquid nitrogen, the blue emitting $CsPbBr_{x}Cl_{3-x}$ NCs were obtained by different degrees of cooling ratio as shown in Figure 2. It is noteworthy that intrinsic crystal structure and surface organic ligands will not be affected due to the chemical inertness of liquid nitrogen and gas nitrogen (Figure S4, Supporting Information). The transmission electron microscopy (TEM) images clearly indicate that the slowest thermodynamic control (natural cooling) result in the worst crystal quality, crystallize coverage rate, and a large grain size distribution (Figure 2a,b). While, the ice-water cooling (Figure 2d,e) could mitigate these undesired phenomena. Subsequently, the UTC completely eliminated them and gave CsPbBr_xCl_{3-x} NCs better crystallinity (Figure 2g,h). As shown in Figure 2b,e,h, the slower thermodynamic control results in smaller average grain size, which is the direct evidence that nucleation is still continuing at low temperatures, thus leading to the formation of small grains. In addition, the selected area electron diffraction (SAED) patterns reveal that the obtained CsPbBr_xCl_{3-x} NCs by faster thermodynamic control possess better crystal orientation and crystallinity. (Figure 2c,f,j).^[11,45] It should be noted that the ultra-fast cooling just enhanced the orientation rather than completely changing the random orientation into a unified orientation. The powder X-ray diffraction results also show the stronger and sharper peaks as well as narrower the FWHM based on faster thermodynamic control, corroborating that the better crystallinity (Figure S4b, Supporting Information). Moreover, the formation of "black dots" in TEM images could be effectively suppressed by UTC (Figure S5, Supporting Information), the "black dots" have been frequently found in previous reports.^[46-48] Although it is still controversial about what they are, they have been proven to be non-radiative recombination





Figure 1. The schematic diagram of the synthesis method with liquid nitrogen cooling and the relationship between cooling rate and crystal quality.

centers and detrimental to the PL properties of perovskite NCs, and less "black dots" is a direct proof of better crystal quality and higher PL efficiency. $^{[34]}$

It took about 100 s for conventional ice-water cooling to completely stop the synthesis reaction (average cooling rate is 1.5 K s^{-1}). While, liquid nitrogen cooling could make the

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Figure 2. The characterization of $CsPbBr_xCl_{3-x}$ NCs obtained by different thermodynamic control. The HRTEM patterns, statistical chart of particle size distribution and SAED of a–c) natural cooling, d–f) ice-water cooling, and g–i) liquid nitrogen cooling, the scale bar is 50 nm. j) Comparison of different cooling rates. k) 3 s after adding different amounts of liquid nitrogen to the initial reaction solution, the recorded temperature and PLQY of the corresponding samples. m) The PLQY absorption and PL emission spectra corresponding to three different cooling method.







Figure 3. The photophysical characterization of defect passivation strategy. a) The schematic demonstration of defect passivation strategy. b) The Stokes shift and E_u in whole blue spectra before and after defect passivation. c) The decay dynamics traces and d) PL spectra before and after defect passivation. e) The strong blue emitting CsPbBr_xCl_{3-x} NCs film and colloidal solution under ultraviolet lamp and their corresponding PLQY. f) PLQY statistical histogram of 30 samples.

reaction immediately escape the active stage within 3 s (average cooling rate is as high as 50 K s⁻¹) and quickly freeze the superior crystal lattices formed at high temperatures, greatly elevating grain size uniformity and crystallinity (Figure S6, Supporting Information). The high temperature difference of 373 K in about 6 s can rapidly solidify all the solvents containing the target CsPbBr_xCl_{3-x} NCs into solid state (Figure S7, Supporting Information). To further investigate the effect of thermodynamic control on PLQY, we added different amounts of liquid nitrogen to the initial reaction solution, recorded the temperature after 3 s. As presented in Figure 2k, the temperature of the reaction solution decreased with the increase of liquid nitrogen. As expected, the PLQY of the final $CsPbBr_{x}Cl_{3-x}$ NCs increases almost linearly with increasing liquid nitrogen, indicating that the thermodynamic control has a great influence on luminescence efficiency once again. The Figures 2m and Figure S8, Supporting Information present the absorption, PL emission spectra and decay dynamics traces of CsPbBr_xCl_{3-x} NCs obtained at different degrees of thermodynamic control, it resulted that faster thermodynamic control led to better crystal quality and hence higher PLQYs. Consequently, the PLQY of blue emitting CsPbBr_xCl_{3-x} NCs has been boosted to 90% (video S3, Supporting Information), which is much higher than previous reports.[49-52]

Based on UTC strategy, the obtained blue emitting $CsPbBr_xCl_{3-x}$ NCs possess high crystal quality and PLQY, but a small number of halide vacancy defects still inevitably exist due to its low formation energy,^[45,46,53,54] which will trap carriers and release them through non-radiative recombination. Therefore, passivating these residual defects and repairing

the crystal lattices leaves considerable opportunity to further improve the PLQY. In this regard, we utilized Pb(BrCl)₂ salts to passivate PbX₆⁴⁻ octahedra in situ. As presented in Figure 3a, since the introduced uncoordinated Br and Cl ions have four lone electron pairs, which enable it to be shared by multiple Pb ions simultaneously, thus could effectively passivate these remaining under-coordinated Pb ions dangling bond (halide vacancy defects),^[2,11] which was first proved by XPS results in Figures S9 and S10, Supporting Information. In addition, the passivated CsPbBr_xCl_{3-x} NCs possessed much smaller Stokes shift and Urbach energy (E_{u}) than that of unpassivated samples (Figure 3b), directly validating a lower defect density and more ordered crystal structure.^[2,3,5] Moreover, a slower dynamics decay could be observed with the increasing average lifetime (τ_{ave}) from 14 to 19 ns (Figure 3c). In addition, the non-radiative decay rate ($\Gamma_{\rm non-rad}$) was greatly reduced from 10 to 1 ns⁻¹. Benefiting from UTC and the assistance of defect passivation, the decay behavior changed from double exponential to single exponential function, which means that almost all the remaining halide vacancy defects were effectively eliminated and almost all carriers were released by radiative recombination. However, the similar solution that did not contain Pb(BrCl)₂ salts was also utilized to treat the CsPbBr_xCl_{3-x} NCs and the result turned out that it is ineffective (Figure S11, Supporting Information). After UTC and defect optimization, the near-unity absolute PLQY as well as high blue emitting purity with narrow FWHM of only 15 nm was achieved (Figure 3d and Figure S12, Supporting Information). In addition, the emission color of $CsPbBr_xCl_{3-x}$ NCs could cover the whole blue spectra range easily (Figures S13 and S14; Table S1, Supporting









Figure 4. The dynamics characterization. a) The fs-TA spectra at different delay time of a) unoptimized and b) optimized samples. c,d) The comparison of bleach recovery kinetics monitored at 463 nm. e) The photobleach formation dynamics of unoptimized and optimized samples. f) The bandgap renormalization energy at different delay times. g,h) The temperature-dependent PL spectra of unoptimized and optimized samples films. i) Integrated PL intensity as a function of temperature.

Information) and the high PLQYs were achieved from deep blue to pure blue range for the first time (Figure 3e; Figures S15 and S16, Supporting Information). In Figure 3f, the PLQY statistical distribution histogram of 30 samples shows an average blue PLQY of 94%, reflecting the high repeatability of our strategy.

To sought deeper insight into the carrier dynamics of UTC, the femtosecond transient absorption (fs-TA) measurement was carried out (Figure S17, Supporting Information). The CsPbBr_xCl_{3-x} NCs obtained by conventional ice-water cooling (labeled "unoptimizated") and liquid nitrogen cooling with the assistance of passivation (labeled "optimizated") were excited by a pump pulse with light intensity of 0.009 μ J cm⁻² (365 nm), and then induced optical absorption change (ΔTA), which reflects the carrier population change after pump pulse excitation.^[5] The Δ TA as functions of wavelength at different delay times were recorded in Figure 4a,b, two negative probe bleach (PB) profiles, labeled PB1 and PB2 originate from groundstate bleach and hot-exciton induced bleach. The two positive photoinduced absorption (PA) profiles could be attributed to the excited state absorption (PA1) and hot charge carrier (PA2) absorption, respectively.^[55] Two obvious ground-state bleach signals at 463 nm could be observed in CsPbBr, Cl_{3-x} NCs before and after optimization, coinciding with their exciton absorption position in UV absorption spectra. As presented in Figure 4c,b, both the unoptimized and optimized samples exhibit no obvious difference of bleach recovery dynamics behavior on the short (<50 ps) and long (>1000 ps) time regime (the TA intensity are absolute value), representing the exciton-exciton annihilation process and excitonic recombination, respectively.^[7] While, a distinctly different behavior can be observed in intermediate time regime, which stems from carrier trapping,^[11,56] and the optimized sample has a negligible intermediate decay process. To compare the two shorter decay processes more intuitively, the long time regime was subtracted from the recovery dynamics curves. As shown in Figure 4d, the unoptimized sample exhibits the triexponential bleach recovery dynamics, revealing that a large part of the carriers in unoptimized sample will be lost during this process. Surprisingly, the optimized samples hardly decay within 700 ps, corroborating that the complete elimination of non-radiative recombination defect states and channels of capturing carriers, which is in line with its ultra-high PLQY. Also, this result is consistent with the







Figure 5. The characterization of spectra stability. The PL spectra under UV immersion of a) ice-water cooling (two precursor), b) ice-water cooling (three precursor), c) liquid nitrogen cooling (three precursor), and d) liquid nitrogen cooling with the assist of defect passivation. e) The spectra shift of four samples at different UV immersion time. The PL spectra under atmosphere environment of f) ice-water cooling (three precursor), g) liquid nitrogen cooling, and h) liquid nitrogen cooling with the assist of defect passivation.

previously reported $CsPbCl_3$ and $CsPbI_3$ NCs with near 100% $PLQY.^{[5,57]}$

Carriers thermalization process could be tracked by the PB formation within the beginning 1.5 ps after excitation (Figure 4e). Once the samples were excited by ultrafast pulse laser, the generated carriers with higher energy than bandgap will experience intra-band relaxation and carrier thermalization, accumulating the carriers at the edge of the conduction band.^[52] It could be found that the rise time increases from 0.27 to 0.32 ps after optimization, indicating that the slower carriers thermalization in optimized sample. After the CsPbBr_xCl_{3-x} NCs were excited, the electron density of the conduction band will increase, inherently inducing an increase in the Coulombic interactions between the enhanced electron impurity scattering and the electrons in conduction band, thereby inducing the renormalization of the band gap. This process could decrease the conduction band minimum energy and increase the valence band maximum energy, thus narrow the bandgap.^[52] As presented in Table S2, Supporting Information, the bandgap renormalization energy ($\Delta E_{\rm rn}$) could be calculated by the PB and PA1 peak positions. After optimization, the $\Delta E_{\rm rn}$ increases significantly at different delay times (Figure 4f), which indicates that the exciton in optimized sample possesses stronger Coulombic interactions, thus higher exciton binding energy. According to the temperature-dependent PL spectra in Figures 4g,h and Figure S18, Supporting Information, the exciton binding energy could be extracted (Figure 4i),^[20] the results show that the exciton binding energy was enhanced from 35 to 46 meV after optimization, which means more efficient exciton recombination.

Although the blue emitting $CsPbBr_xCl_{3-x}$ NCs have high color purity, tunability, and relatively higher PLQY, the current research on blue emission mainly focused on Br-based 2D perovskite.^[22] This is due to the recognized challenge of

spectra instability in CsPbBr_xCl_{3-x} NCs, which is a fatal limitation for their application. Therefore, it is very urgent to improve the spectra stability of CsPbBr_xCl_{3-x} NCs. After UTC and the assistance of defect passivation, the optimized blue emitting CsPbBr_xCl_{3-x} NCs possess not only superior PLQY but also crystal quality, which motivates us to further evaluate their spectra stability. The UV immersion can cause the spectra shift according to previous reports.^[2] As shown in Figure 5a,e, after 2 h UV immersion (5 mW cm⁻²), the PL spectra of the CsPbBr_xCl_{3-x} NCs synthesized by the conventional ice-water cooling (two-precursor approach, Supporting Information) exhibited a slight blue shift, but when the immersion time was extended to 40 h, its spectra had an astonishing 30 nm red shift. The cross-section energy-dispersive X-ray spectroscopy (EDS) elemental mapping results also establish that a serious redistribution of halide ions (Figure S19, Supporting Information). Moreover, its PL intensity and PLQY were also sharply weakened to one-twentieth of the original value (Figure S20a,b, Supporting Information), revealing that the mixed halide CsPbBr_xCl_{3-x} NCs obtained by conventional ice-water cooling (two-precursor approach) do have extremely poor spectra stability. As shown in Figure 5b,e, the $CsPbBr_{x}Cl_{3-x}$ NCs obtained by ice-water cooling (three-precursor approach, Supporting Information) also exhibited poor spectral stability with a 15 nm red shift. When ice-water was replaced by liquid nitrogen, the spectral stability was greatly improved, but its PL intensity was obviously decreased (Figure 5c,e). Fortunately, based on liquid nitrogen cooling and the assistance of passivation, there was almost no red shift or blue shift could be observed after 40 h UV immersion (Figure 5d,e), which was also proved by the constant Br:Cl ratio in cross-section EDS elemental mapping (Figure S21, Supporting Information). In addition, its PLQY and PL intensity also remained 90% of the original values (Figure S20, Supporting Information). We further researched







Figure 6. The microscopic mechanism analysis of spectral instability. a–c) The schematic diagram of defect-assisted ion migration, which leads to the formation of Br-rich and Cl-rich domains (marked by solid line circles). d) The carrier transfer between CsPbCl₃, CsPbBr_xCl_{3–x⁰} and CsPbBr₃ phase.

the spectra stability in atmosphere environment (60% RH). After 8 days, the $CsPbBr_{x}Cl_{3-x}$ NCs obtained by ice-water cooling (three-precursor) had a 6 nm red shift (Figure 5f). Such spectra shift could be significantly mitigated when cooling with liquid nitrogen (Figure 5g). While, in sharp contrast, the spectra of sample synthesized by liquid nitrogen cooling and the assistance of passivation remained almost unchanged (Figure 5g).

It is reasonable to draw the following two conclusions from the aforementioned analysis: i) The enhanced crystal quality could alleviate spectra instability. ii) The spectra instability possesses vacancy defect-dependent property and the less vacancy defect density, the more stable the spectra could be obtained. Further, combined with our results and previous reports, we propose a possible model for ion migration and phase separation as presented in Figure 6. The halide ions in $CsPbBr_xCl_{3-x}$ NCs tend to migrate to adjacent vacancy defects under UV irradiation (Figure 6a),^[58,59] which results in redistribution of Br and Cl ions. Besides, the lattice distortion arising from poor crystal quality also could facilitate the ion migration.^[58] The difference in affinity between Br⁻ and Cl⁻ ions toward Pb²⁺ is another important cause of halide ion migration. As a result, Br-rich and Cl-rich domains are formed, which finally leads to the appearance of CsPbBr₃ and CsPbCl₃ phase separately (Figure 6b,c). The phase separation means that there will be two peaks, but since the PL intensity CsPbCl₃ is much weak relative to CsPbBr₃ so that it is difficult to observe the newly appearing CsPbCl₃ peak (Figure S22, Supporting Information). Therefore only the continuous redshift could be found, actually the spectra are constantly approaching the peak of CsPbBr₃. Furthermore, once such phase separation occurs, the band structure change between different phases will further accelerate carriers transfer from higher-bandgap Cl-rich domain to CsPbBr_xCl_{3-x}, and then transfer to lower-bandgap Br-rich domain (Figure 6d).^[59,60] This is another reason why the spectra are red shifted instead of blue. Additionally, due to the stronger complexation affinity of Cl⁻ and Pb²⁺ relative to Br⁻ and Pb^{2+,[58,61]} as ion migration proceeds, more CsPbCl₃ will form, which possesses extremely low luminous efficiency. Once the CsPbCl₃ is dominant in CsPbBr_xCl_{3-x} (Figure 6c), the overall PL intensity will be violently weaken. Therefore, the spectra red shift must be accompanied by a significant decrease in PL intensity. To sum up, in order to overcome the current toughest challenges of spectral instability in blue emitting CsPbBr_xCl_{3-x}, we believe that more attention should be paid to reducing vacancy defects and improving crystal quality.

In summary, thermodynamic control is critical to achieving good crystallinity and high luminous efficiency for perovskite, but this has been ignored in the past. Therefore, we designed an UTC strategy by employing liquid nitrogen to instantaneously freeze the crystal lattices of CsPbBr_xCl_{3-x} NCs formed at high temperature, effectively avoiding the poor crystal quality caused by continuous growth and the additional nucleation at low temperature. With the assist of defect passivation, the final CsPbBr_xCl_{3-x} NCs possess uniform grain size and record absolute blue PLQY of 98%. Unprecedentedly, the optimized CsPbBr_xCl_{3-x} NCs could maintain stable spectra after immersing in UV light for 40 h and storing in atmosphere environment for 8 days. We expect that this successful UTC strategy could exert profound influence on solving the toughest challenge of spectra instability and low PLQY in blue emitting mixed halide CsPbBr_xCl_{3-x} NCs, and promote the development of efficient and stable blue perovskite. In addition, we believe that this UTC strategy can also be widely applied not only to other systems of perovskite, but also to other high temperature heat injection synthesis, such as rare-earth nanoparticles, carbon quantum dots, CdSe, lnP, etc.

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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.

Keywords

blue perovskites, defect passivation, mixed halides, phase separation, thermodynamic control

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- J. Li, L. Xu, T. Wang, J. Song, J. Chen, J. Xue, Y. Dong, B. Cai, Q. Shan, B. Han, H. Zeng, *Adv. Mater.* 2017, *29*, 1603885.
- [2] Y. Wu, C. Wei, X. Li, Y. Li, S. Qiu, W. Shen, B. Cai, Z. Sun, D. Yang, Z. Deng, H. Zeng, ACS Energy Lett. 2018, 3, 2030.
- [3] S. Wang, C. Bi, J. Yuan, L. Zhang, J. Tian, ACS Energy Lett. 2018, 3, 245.
- [4] X. M. Li, Y. Wu, S. L. Zhang, B. Cai, Y. Gu, J. Z. Song, H. B. Zeng, Adv. Funct. Mater. 2016, 26, 2435.
- [5] F. Liu, Y. Zhang, C. Ding, S. Kobayashi, T. Izuishi, N. Nakazawa, T. Toyoda, T. Ohta, S. Hayase, T. Minemoto, K. Yoshino, S. Dai, Q. Shen, ACS Nano 2017, 11, 10373.
- [6] D. Yang, X. Li, Y. Wu, C. Wei, Z. Qin, C. Zhang, Z. Sun, Y. Li, Y. Wang, H. Zeng, Adv. Opt. Mater. 2019, 7, 1900276.
- [7] C. Luo, W. Li, D. Xiong, J. Fu, W. Q. Yang, Nanoscale 2019, 11, 15206.
- [8] S. Peng, S. Wang, D. Zhao, X. Li, C. Liang, J. Xia, T. Zhang, G. Xing, Z. Tang, Small Methods 2019, 3, 1900196.
- [9] S. C. Hou, M. K. Gangishetty, Q. M. Quan, D. N. Congreve, *Joule* 2018, 2, 2421.
- [10] J. Li, L. Gan, Z. Fang, H. He, Z. Ye, J. Phys. Chem. Lett. 2017, 8, 6002.
- B. J. Bohn, Y. Tong, M. Gramlich, M. L. Lai, M. Doblinger, K. Wang, R. L. Z. Hoye, P. Muller-Buschbaum, S. D. Stranks, A. S. Urban, L. Polavarapu, J. Feldmann, *Nano Lett.* 2018, *18*, 5231.
- [12] S. Yuan, Z. K. Wang, L. X. Xiao, C. F. Zhang, S. Y. Yang, B. B. Chen, H. T. Ge, Q. S. Tian, Y. Jin, L. S. Liao, *Adv. Mater.* **2019**, *31*, 1904319.
- [13] S. T. Ochsenbein, F. Krieg, Y. Shynkarenko, G. Raino, M. V. Kovalenko, ACS Appl. Mater. Interfaces 2019, 11, 21655.
- [14] S. X. Wang, Y. Wang, Y. Zhang, X. T. Zhang, X. Y. Shen, X. W. Zhuang, P. Lu, W. W. Yu, S. V. Kershaw, A. L. Rogach, J. Phys. Chem. Lett. 2019, 10, 90.



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- [15] T. Jun, K. Sim, S. limura, M. Sasase, H. Kamioka, J. Kim, H. Hosono, Adv. Mater. 2018, 30, 1804547.
- [16] T. D. Creason, A. Yangui, R. Roccanova, A. Strom, M. H. Du, B. Saparov, Adv. Optical. Mater. 2019, 8, 1901338.
- [17] B. Yang, L. Yin, G. Niu, J. H. Yuan, K. H. Xue, Z. Tan, X. S. Miao, M. Niu, X. Du, H. Song, E. Lifshitz, J. Tang, *Adv. Mater.* **2019**, *31*, 1904711.
- [18] R. Roccanova, A. Yangui, H. Nhalil, H. Shi, M.-H. Du, B. Saparov, ACS Appl. Electron. Mater. 2019, 1, 269.
- [19] C. H. Bi, S. X. Wang, S. V. Kershaw, K. B. Zheng, T. Pullerits, S. Gaponenko, J. J. Tian, A. L. Rogach, *Adv. Sci.* **2019**, *6*, 1900462.
- [20] B. Cai, X. M. Li, Y. Gu, M. Harb, J. H. Li, M. Q. Xie, F. Cao, J. Z. Song, S. L. Zhang, L. Cavallo, H. B. Zeng, *Sci. China Mater.* 2017, 60, 811.
- [21] P. Vashishtha, M. Ng, S. B. Shivarudraiah, J. E. Halpert, Chem. Mater. 2019, 31, 83.
- [22] Y. Liu, J. Cui, K. Du, H. Tian, Z. He, Q. Zhou, Z. Yang, Y. Deng, D. Chen, X. Zuo, Y. Ren, L. Wang, H. Zhu, B. Zhao, D. Di, J. Wang, R. H. Friend, Y. Jin, *Nat. Photonics* **2019**, *13*, 760.
- [23] Z. Li, Z. Chen, Y. Yang, Q. Xue, H. L. Yip, Y. Cao, Nat. Commun. 2019, 10, 1027.
- [24] D. Yang, Y. Zou, P. Li, Q. Liu, L. Wu, H. Hu, Y. Xu, B. Sun, Q. Zhang, S.-T. Lee, *Nano Energy* **2018**, *47*, 235.
- [25] R. L. Z. Hoye, M. L. Lai, M. Anaya, Y. Tong, K. Galkowski, T. Doherty, W. W. Li, T. N. Huq, S. Mackowski, L. Polavarapu, J. Feldmann, J. L. MacManus-Driscoll, R. H. Friend, A. S. Urban, S. D. Stranks, ACS Energy Lett. 2019, 4, 1181.
- [26] Y. Jiang, C. Qin, M. Cui, T. He, K. Liu, Y. Huang, M. Luo, L. Zhang, H. Xu, S. Li, J. Wei, Z. Liu, H. Wang, G. H. Kim, M. Yuan, J. Chen, *Nat. Commun.* **2019**, *10*, 1868.
- [27] W. Zou, R. Z. Li, S. T. Zhang, Y. L. Liu, N. N. Wang, Y. Cao, Y. F. Miao, M. M. Xu, Q. Guo, D. W. Di, L. Zhang, C. Yi, F. Gao, R. H. Friend, J. P. Wang, W. Huang, *Nat. Commun.* **2018**, *9*, 608.
- [28] J. Xing, Y. B. Zhao, M. Askerka, L. N. Quan, X. W. Gong, W. J. Zhao, J. X. Zhao, H. R. Tan, G. K. Long, L. Gao, Z. Y. Yang, O. Voznyy, J. Tang, Z. H. Lu, Q. H. Xiong, E. H. Sargent, *Nat. Commun.* **2018**, *9*, 3541.
- [29] K. H. Wang, Y. D. Peng, J. Ge, S. L. Jiang, B. S. Zhu, J. S. Yao, Y. C. Yin, J. N. Yang, Q. Zhang, H. B. Yao, ACS Photonics 2019, 6, 667.
- [30] C. Yan, Y. Gao, S. Zhao, S. Zhang, Y. Zhou, W. Deng, Z. Li, G. Jiang, L. Jin, G. Tian, T. Yang, X. Chu, D. Xiong, Z. Wang, Y. Li, W. Yang, J. Chen, *Nano Energy* **2019**, *67*, 104235.
- [31] X. H. Yi, Z. M. Zhang, A. L. Chang, Y. C. Mao, Y. G. Luan, T. Lin, Y. Z. Wei, Y. Y. Zhang, F. Y. Wang, S. K. Cao, C. Li, J. Z. Wang, *Adv. Energy Mater.* **2019**, *9*, 1901726.
- [32] S. Ghosh, T. Singh, Nano Energy 2019, 63, 103828.
- [33] Y. G. Tu, X. Y. Yang, R. Su, D. Y. Luo, Y. Cao, L. C. Zhao, T. H. Liu, W. Q. Yang, Y. F. Zhang, Z. J. Xu, Q. Z. Liu, J. H. Wu, Q. H. Gong, F. Y. Mo, R. Zhu, *Adv. Mater.* **2018**, *30*, 1805085.
- [34] F. Li, Y. Liu, H. L. Wang, Q. Zhan, Q. L. Liu, Z. G. Xia, Chem. Mater. 2018, 30, 8546.
- [35] T. Udayabhaskararao, M. Kazes, L. Houben, H. Lin, D. Oron, *Chem. Mater.* 2017, 29, 1302.
- [36] M. Zhang, H. B. Li, Q. Jing, Z. D. Lu, P. Wang, Crystals 2018, 8, 2.
- [37] T. H. Wu, Y. B. Wang, Z. S. Dai, D. Y. Cui, T. Wang, X. Y. Meng, E. B. Bi, X. D. Yang, L. Y. Han, *Adv. Mater.* **2019**, *31*, 1900605.
- [38] B. Chen, P. N. Rudd, S. Yang, Y. B. Yuan, J. S. Huang, Chem. Soc. Rev. 2019, 48, 3842.
- [39] W. J. Hou, Y. M. Xiao, G. Y. Han, C. B. Qin, L. T. Xiao, Y. Z. Chang, H. G. Li, *Mater. Res. Bull.* **2019**, *112*, 165.
- [40] L. Protesescu, S. Yakunin, M. I. Bodnarchuk, F. Krieg, R. Caputo, C. H. Hendon, R. X. Yang, A. Walsh, M. V. Kovalenko, *Nano Lett.* 2015, 15, 3692.
- [41] Y. Bekenstein, B. A. Koscher, S. W. Eaton, P. D. Yang, A. P. Alivisatos, J. Am. Chem. Soc. 2015, 137, 16008.

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- [42] M. L. Xie, H. Liu, F. J. Chun, W. Deng, C. Luo, Z. H. Zhu, M. Yang, Y. M. Li, W. Li, W. Yan, W. Q. Yang, *Small* **2019**, *15*, 1901994.
- [43] I. Lignos, S. Stavrakis, G. Nedelcu, L. Protesescu, A. J. Demello, M. V. Kovalenko, Nano Lett. 2016, 16, 1869.
- [44] M. V. Kovalenko, L. Protesescu, M. I. Bodnarchuk, Science 2017, 358, 745.
- [45] G. H. Ahmed, J. K. El-Demellawi, J. Yin, J. Pan, D. B. Velusamy, M. N. Hedhili, E. Alarousu, O. M. Bakr, H. N. Alshareef, O. F. Mohammed, ACS Energy Lett. 2018, 3, 2301.
- [46] Z. J. Yong, S. Q. Guo, J. P. Ma, J. Y. Zhang, Z. Y. Li, Y. M. Chen, B. B. Zhang, Y. Zhou, J. Shu, J. L. Gu, L. R. Zheng, O. M. Bakr, H. T. Sun, J. Am. Chem. Soc. 2018, 140, 9942.
- [47] J. S. Yao, J. Ge, B. N. Han, K. H. Wang, H. B. Yao, H. L. Yu, J. H. Li, B. S. Zhu, J. Z. Song, C. Chen, Q. Zhang, H. B. Zeng, Y. Luo, S. H. Yu, J. Am. Chem. Soc. 2018, 140, 3626.
- [48] Z. Liang, S. Zhao, Z. Xu, B. Qiao, P. Song, D. Gao, X. Xu, ACS Appl. Mater. Interfaces 2016, 8, 28824.
- [49] Y. Su, X. Chen, W. Ji, Q. Zeng, Z. Ren, Z. Su, L. Liu, ACS Appl. Mater. Interfaces 2017, 9, 33020.
- [50] P. C. Wang, B. H. Dong, Z. J. Cui, R. J. Gao, G. Su, W. Wang, L. X. Cao, RSC Adv. 2018, 8, 1940.

- [51] W. Zheng, P. Huang, Z. L. Gong, D. Tu, J. Xu, Q. L. Zou, R. F. Li, W. W. You, J. C. G. Bunzli, X. Y. Chen, *Nat. Commun.* **2018**, *9*, 3462.
- [52] N. Soetan, A. Puretzky, K. Reid, A. Boulesbaa, H. F. Zarick, A. Hunt, O. Rose, S. Rosenthal, D. B. Geohegan, R. Bardhan, ACS Photonics 2018, 5, 3575.
- [53] S. Seth, T. Ahmed, A. De, A. Samanta, ACS Energy Lett. 2019, 4, 1610.
- [54] J. Kang, L. W. Wang, J. Phys. Chem. Lett. 2017, 8, 489.
- [55] N. Mondal, A. Samanta, Nanoscale 2017, 9, 1878.
- [56] W. F. Yang, F. Igbari, Y. H. Lou, Z. K. Wang, L. S. Liao, Adv. Energy Mater. 2019, https://doi.org/10.1002/aenm.201902584.
- [57] N. Mondal, A. De, A. Samanta, ACS Energy Lett. 2019, 4, 32.
- [58] S. J. Yoon, M. Kuno, P. V. Kamat, ACS Energy Lett. 2017, 2, 1507.
- [59] S. J. Yoon, S. Draguta, J. S. Manser, O. Sharia, W. F. Schneider, M. Kuno, P. V. Kamat, ACS Energy Lett. 2016, 1, 290.
- [60] D. J. Slotcavage, H. I. Karunadasa, M. D. McGehee, ACS Energy Lett. 2016, 1, 1199.
- [61] S. J. Yoon, K. G. Stamplecoskie, P. V. Kamat, J. Phys. Chem. Lett. 2016, 7, 1368.