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Synthesis of stable and phase-adjustable $\text{CsPbBr}_3@ \text{Cs}_4\text{PbBr}_6$ nanocrystals *via* novel anion–cation reactions†

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All-inorganic cesium lead halide perovskites have emerged as promising semiconductor materials due to their preeminent performance in lighting, display, light detecting, and laser fields. However, the applications of lead halide perovskites are limited by the dissatisfactory stability owing to their fragile ionic crystal characteristics and highly dynamic surface-coordinated states. The *in situ* diphasic structure passivation possessing the same chemical constituents (such as passivating CsPbBr_3 with Cs_4PbBr_6) has been proven to be an effective way to improve the stabilities and simultaneously maintain the highly efficient luminescence properties. Herein, for the first time, we report a novel anion–cation reaction method to synthesize the lead halide perovskite NCs with diphasic $\text{CsPbBr}_3@ \text{Cs}_4\text{PbBr}_6$ structure. Moreover, we have found that the phase transformation between CsPbBr_3 and Cs_4PbBr_6 is temperature dependent. Thus, we could control the relative composition of the diphasic $\text{CsPbBr}_3@ \text{Cs}_4\text{PbBr}_6$ composite by adjusting the temperature. The optimized $\text{CsPbBr}_3@ \text{Cs}_4\text{PbBr}_6$ composite NCs achieve highly light emissive performance and stabilities against atmosphere, moisture and heating. Furthermore, we could obtain 135% of the NTSC color gamut through anion exchange. These highly emissive composite NCs with improved stabilities exhibit great potential in future optoelectronic fields.

Introduction

Lead halide perovskites gained increasing attention in light-emitting diodes (LED),^{1–8} photodetectors,^{9–12} and lasers¹³ in recent years due to their ultrahigh photoluminescence quantum yields (PLQYs), good carrier mobility, multicolor electroluminescence, and low-threshold lasing. The high-performance halide perovskite is commonly used in the form of three-dimensional (3D) cubic or monoclinic phase,^{14–18} CsPbX_3 ($X = \text{Cl}, \text{Br}, \text{I}$), which is known to be composed of corner-shared

PbX_6^{4-} octahedron and filling Cs^+ ions.¹⁴ However, this structure is affected by its fragility against moisture, illumination, and heating for its intrinsic ionic characteristics and easy-lost halide atoms.^{19,20} Agglomeration of NCs,²¹ polar solvents²² or even the ultraviolet light²³ can easily degrade the luminescence or damage the structure, which restricts further application in photonics and optoelectronics. To overcome the above-mentioned concerns, a lot of strategies have been designed to improve the stability of perovskite NCs, for example, Sun *et al.* wrapped halide perovskite QDs in a cross-linked silica matrix,²⁴ Guarnera *et al.* improved the stabilities *via* perovskites coating with Al_2O_3 ,²⁵ and some other studies obtained water-resistant CsPbX_3 NCs *via* embedding NCs into polymer materials.^{26,27} In general, it seems to be an effective strategy that we package the perovskite NCs into tough encapsulations to resist the harsh conditions outside. However, the introduced additive may affect the original luminescence of NCs, and also increase the complexity of the process.

Recently, the zero-dimensional (0D) Cs_4PbBr_6 , another derived phase of CsPbBr_3 NCs,^{28–31} could provide *in situ* passivation for CsPbBr_3 NCs.^{15,32–34} Cs_4PbBr_6 has been reported to be a natural insulator possessing air-stable and robust properties,^{29,35,36} which shares the same components with CsPbBr_3 . In addition, Quan *et al.*²⁹ has proven that the lattice of Cs_4PbBr_6 matches with that of CsPbBr_3 in one direction, which protects a CsPbBr_3 NC growing inside a Cs_4PbBr_6 matrix. The PbBr_6^{4-} octahedra of Cs_4PbBr_6 are separated by corner Cs^+ without sharing Br^- with each other, and the individual PbBr_6^{4-} octahedron is not connected to the adjacent octahedron leading to the localized excitons in an isolated octahedron, the so-called 0D perovskites. 0D Cs_4PbBr_6 NCs are generally obtained by adjusting the components or regulating the surface ligands, for instance, the high ratio of Cs/Pb environment was favorable to form Cs_4PbBr_6 ,^{29,37} or directly transforming from CsPbBr_3 NCs in a rich Cs^+ condition,³⁵ and mediating the surface ligands with more oleylamine could stimulate the formation of Cs_4PbBr_6 .^{38,39} However, there are only few studies reporting the synthesis of component-controllable $\text{CsPbBr}_3@ \text{Cs}_4\text{PbBr}_6$ composite NCs.

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Moreover, all these syntheses are based on the re-precipitation method, which is conducted by injecting dimethylformamide (DMF) solution containing CsBr and PbBr₂ into the poor solvent. Thus, the production of CsPbBr₃@Cs₄PbBr₆ NCs is limited by the low solubility of CsBr in DMF, particularly for the method needing rich-Cs⁺ environment. Therefore, exploring a new approach to simultaneously obtain high-yield and phase-adjustable CsPbBr₃@Cs₄PbBr₆ NCs is of great importance for industrialization.

Herein, for the first time, we developed a novel anion-cation method to synthesize phase-adjustable CsPbBr₃@Cs₄PbBr₆ composite NCs under atmospheric conditions. In this method, an active brominated agent, pyridinium tribromide (PDBr), was used as the source of bromine; however, cesium acetate and lead acetate with higher solubility were used to replace CsBr and PbBr₂. Besides being used as the source of bromine, PDBr provided highly Br[−]-rich conditions for the growth of perovskites to obtain high-quality crystalline structures with few surface defects. Furthermore, we found that the phase transformation between CsPbBr₃ and Cs₄PbBr₆ was temperature dependent. Cs₄PbBr₆ NCs were preferred to be formed at lower temperatures, while increasing the temperature gave rise to more CsPbBr₃ NCs. Relative proportions of CsPbBr₃ and Cs₄PbBr₆ were calculated from the XRD pattern at different temperatures and the corresponding optical properties were discussed. The optimized sample showed strong green PL emission with a full width at half maximum (FWHM) of 19 nm. PL attenuation curves and PL lifetime demonstrate the greatly improved stabilities and efficient trap-passivation of CsPbBr₃@Cs₄PbBr₆ NCs compared to naked CsPbBr₃ NCs with cubic or monoclinic phase. Furthermore, a wide color gamut of 135% of the NTSC standard was obtained *via* anion exchange. The as-proposed novel anion-cation method paves the way for the mass production of stable and highly emissive perovskite NCs, which have a huge potential application in lightings, displays, and lasers.

Results and discussion

Emissive 3D CsPbBr₃ NCs are usually used in the form of cubic and monoclinic phases, whose structures are presented in

Fig. 1a and b, respectively. Cubic and monoclinic CsPbBr₃ NCs possess similar lattice arrangements, the difference being that the latter has tilting octahedra compared to the former.⁴⁰ Cubic and monoclinic CsPbBr₃ NCs also exhibit similar optical properties and structural characteristics⁴⁶ facing the same stability issue. Well, compared to CsPbBr₃ with cubic or monoclinic structure, the octahedra of rhombohedral Cs₄PbBr₆ were decoupled completely (Fig. 1c), making it a 0D structure. Thus, Cs₄PbBr₆ NCs have quite different properties,^{41,42} such as colorless crystals with wider band gap (3.95 eV)⁴³ and better environmental tolerance,^{29,38} which make it perfect for capsulation.

Cubic NCs are usually synthesized by hot-injection (HI),^{17,44} and by injecting oleic cesium precursors into high-temperature solvents containing PbBr₂ and ligands under inert environments, as shown in Fig. 2. Monoclinic CsPbBr₃ NCs (PDF#18-0346) are widely obtained *via* room-temperature re-precipitation (RP)¹⁶ that is conducted by adding the as-prepared CsBr/PbBr₂ precursors into poor solvents (Fig. 2) under atmospheric environment. Previous reports^{30,39} have demonstrated that CsPbBr₃ could be converted into Cs₄PbBr₆, and Cs₄PbBr₆ could also be converted into CsPbBr₃ with excess PbBr₂, proving the feasibility of passivating CsPbBr₃ with Cs₄PbBr₆. Now, Cs₄PbBr₆ NCs are generally obtained *via* modified RP by using excess Cs⁺ (ref. 35 and 45) or ligand-mediating method.^{38,39} Herein, we put forward a novel anion-cation reaction method without forming PbBr₆^{4−} octahedral precursors in advance to prepare perovskite NCs. The schematic of the anion-cation reaction is shown in Fig. 2, wherein an active brominated agent, pyridinium tribromide (PDBr), was introduced to act as a halogen source. In a typical synthesis, the *N,N*-dimethyl formamide (DMF) solutions of Pb(Ac)₂ and Cs(Ac) were added to toluene containing organic ligands and then, bromine-rich pyridinium tribromide was swiftly added at an appropriate temperature to form perovskite NCs. The adequate Br[−] of PDBr provides a Br[−]-rich condition for perovskites to obtain high-quality NCs with less bromine vacancies.⁴⁶

Through this novel anion-cation reaction method, a typical solution sample of CsPbBr₃@Cs₄PbBr₆ NCs was obtained (shown in Fig. 3a), which exhibited bright photoluminescence

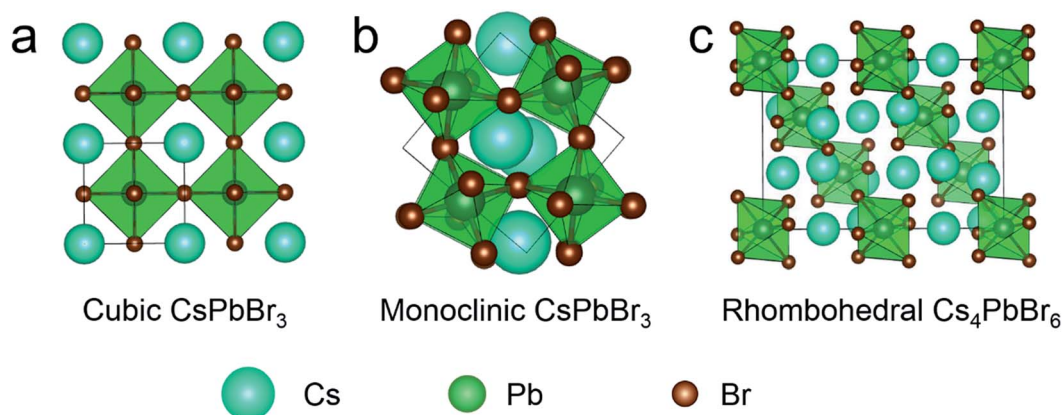


Fig. 1 Simulated crystal structure of (a) cubic CsPbBr₃, (b) monoclinic CsPbBr₃ and (c) rhombohedral Cs₄PbBr₆.





from 25 °C to 80 °C (Fig. 5) with a Cs⁺/Pb²⁺ ratio of 1. The bottom of the abscissa in Fig. 5e shows the standard peaks of dominant rhombohedral phase (PDF#73-2478), while the opposite shows the standard peaks of cubic phase (PDF#54-0752). At a temperature of 25 °C, the XRD pattern (Fig. 5e) shows that the main peaks all from the rhombohedral and cubic phases are un conspicuous. The corresponding SEM image in Fig. 5a also presents consistent morphological features. With the temperature increasing to 40 °C and 60 °C, new peaks at 15.1°, 21.5°, 30.6°, 37.8°, and 46.7° enhanced gradually, which corresponds to the (100), (110), (200), (211), and (300) lattice planes of cubic CsPbBr₃ NCs. Simultaneously, the peak intensities of Cs₄PbBr₆ become weaker, while view of SEM (Fig. 5b and c) images maintains a uniform rhombic shape without impurities at 40 °C and 60 °C, which demonstrate the effective embedding of cubic CsPbBr₃ NCs in Cs₄PbBr₆. We calculate the relative content of CsPbBr₃ and Cs₄PbBr₆ phases by the area method. Only a tiny amount (2.4%) of cubic phase could be obtained at room temperature and higher proportion of CsPbBr₃ (15.4% and 44.5%, respectively) came into being with the increase in temperature. The productions of 44.5% CsPbBr₃ under 60 °C almost resulted in the diamond shape without cubes, as shown in Fig. 5c, which confirmed the formation of CsPbBr₃@Cs₄-PbBr₆ composite NCs. While with the temperature increasing to 80 °C, CsPbBr₃ NCs began to nucleate and grow separated from Cs₄PbBr₆ matrix into independent bulk alone, as seen from the typical cuboidal NC marked in Fig. 5d. In addition, the XRD pattern in Fig. 5e reveals that only a fraction of Cs₄PbBr₆ existed in the composites. When the temperature was higher than 100 °C, the cubic phase accounted for the vast majority (more than 90%). The relation between the proportions of these two phases and the temperature is listed in Table 1. Cs₄PbBr₆ NCs were preferred to form at lower temperature, while higher temperature conditions were more conducive to the formation of cubic phase, and higher temperature also created a more

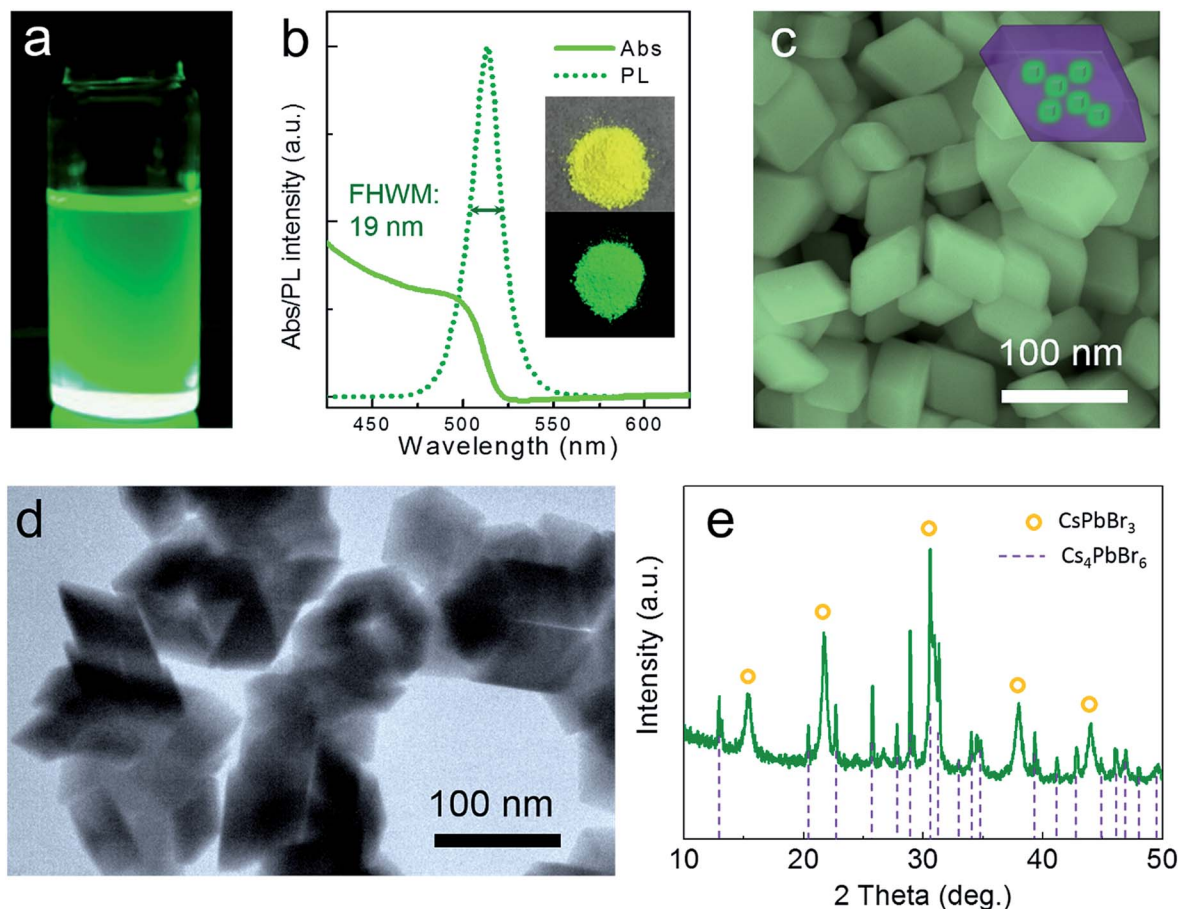


Fig. 3 Typical $\text{CsPbBr}_3@ \text{Cs}_4\text{PbBr}_6$ sample: (a) toluene dispersion under UV light. (b) PL and absorption spectrum. Inset: photographs of powder sample under day light and UV light, respectively. (c) SEM image of typical $\text{CsPbBr}_3@ \text{Cs}_4\text{PbBr}_6$. Inset: schematics of the microstructure. (d) TEM image of the typical $\text{CsPbBr}_3@ \text{Cs}_4\text{PbBr}_6$. (e) XRD pattern of the typical $\text{CsPbBr}_3@ \text{Cs}_4\text{PbBr}_6$.

violent reactivity, thereby leading to independent nucleation and growth of CsPbBr_3 NCs.

Temperature could not only adjust the phase composition but also influence the optical properties. Fig. 6a exhibits solution samples synthesized at different temperatures and their corresponding PL spectra. Blue emission (480 nm) is observed

when reaction temperature is 20 °C, which could be explained by the dimensionality reduction of embedded CsPbBr_3 NCs resulted from lower temperature.^{48,49} With the increase in temperature, the spectra reveal a slight redshift due to the aggregation and size of CsPbBr_3 NCs with the increasing proportion. The broader FWHM at 20 °C and 40 °C maybe the

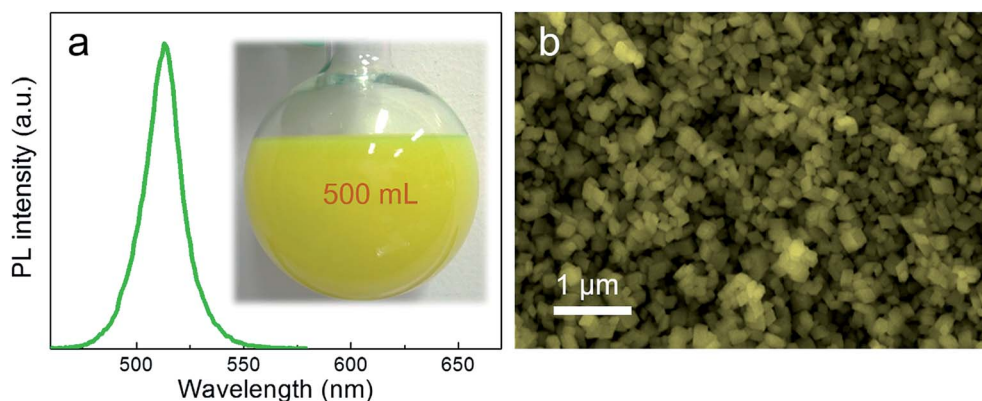


Fig. 4 (a) PL spectrum of large-yield $\text{CsPbBr}_3@ \text{Cs}_4\text{PbBr}_6$ NCs, inset is the photograph of large-yield reaction product. (b) Large-scale SEM image of high yields of $\text{CsPbBr}_3@ \text{Cs}_4\text{PbBr}_6$ NCs.



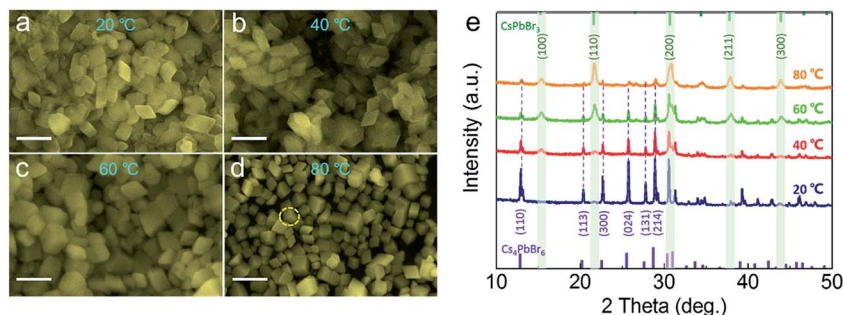


Fig. 5 SEM images of products prepared at different temperatures: (a) 20 °C, (b) 40 °C, (c) 60 °C and (d) 80 °C. (e) The corresponding XRD patterns of products prepared at different temperatures.

Table 1 The corresponding proportion of CsPbBr₃ controlled by different temperatures

T/°C	20	40	60	80
Ratio/CsPbBr ₃	2.4%	15.4%	44.5%	80.5%
Ratio/Cs ₄ PbBr ₆	97.6%	84.6%	55.5%	19.5%

Table 2 PL lifetime parameters of CsPbBr₃@Cs₄PbBr₆ NCs prepared at different temperatures

T/°C	20	40	60	80
τ_1 /ns	6.77	5.83	4.5	2.71
τ_2 /ns	22.1	28.36	18.6	14.3
τ_{aver} /ns	23.1	22.3	17.7	15.6

result of uneven size of dysgonic CsPbBr₃ NCs. The absorption spectra (Fig. S1†) also exhibited the same trend. PLQY gradually improved with the increasing proportion of CsPbBr₃ NCs in the system as shown in Fig. 6b. However, owing to the dissociative CsPbBr₃ NCs, the PL lifetime of composites obtained at 80 °C was sharply decreased (Fig. 6c). Longer lifetime was detected as the Cs₄PbBr₆ matrix increased, which is consistent with the previous reports. Detailed parameters of the PL lifetime are listed in Table 2. CsPbBr₃@Cs₄PbBr₆ synthesized at 60 °C (with 44.5% CsPbBr₃) shows the best excitons combination performance, which was chosen to conduct the following stability tests.

We compared CsPbBr₃@Cs₄PbBr₆ composite NCs with monoclinic CsPbBr₃ and cubic CsPbBr₃ NCs separately to verify its improved stabilities. The cubic CsPbBr₃ NCs were synthesized by traditional hot-injection, whereas the monoclinic CsPbBr₃ NCs were synthesized by re-precipitation (see ESI†). For better comparison tests, we mixed the NCs

(CsPbBr₃@Cs₄PbBr₆, monoclinic CsPbBr₃ and cubic CsPbBr₃) with polydimethylsiloxane (PDMS) to form films, respectively, as shown in the inset photographs of Fig. 7a. It could be seen that CsPbBr₃@Cs₄PbBr₆ NCs maintained the best photoluminescence, while severe quenching occurred on both cubic and monoclinic CsPbBr₃ NCs. The certain arrangement of CsPbBr₃ NCs in Cs₄PbBr₆ made CsPbBr₃@Cs₄PbBr₆ NCs have a narrower FWHM compared to HI cubic CsPbBr₃ NCs. The slight differences in PL spectra (Fig. 7a) were probably caused by the size effect. The PL decay curves of the three are presented in Fig. 7b. The average lifetime of cubic and monoclinic CsPbBr₃ were 5.7 ns and 5.5 ns, while an increasing radiative lifetime of 17.7 ns was evidenced in CsPbBr₃@Cs₄PbBr₆ compounds (Table 3). In order to further prove the improving stability of CsPbBr₃@Cs₄PbBr₆ NCs, the storage stability test and thermal stability test were designed based on the luminescence degradation. Fig. 7c shows the PL intensity decays of

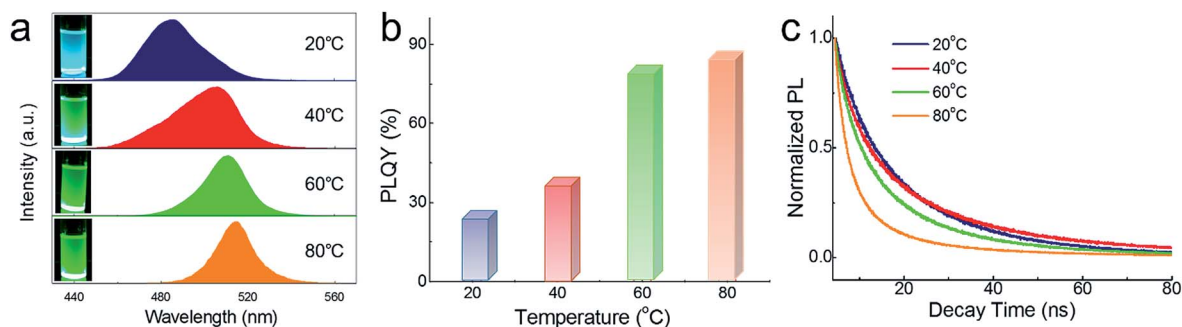


Fig. 6 (a) PL spectra of CsPbBr₃@Cs₄PbBr₆ NCs prepared at 20 °C, 40 °C, 60 °C and 80 °C, respectively. Inset: the corresponding photographs of the CsPbBr₃@Cs₄PbBr₆ NC samples prepared at different temperatures. (b) PLQY of CsPbBr₃@Cs₄PbBr₆ NCs synthesized at 20 °C, 40 °C, 60 °C and 80 °C. (c) PL decay of CsPbBr₃@Cs₄PbBr₆ NCs synthesized at 20 °C, 40 °C, 60 °C and 80 °C.



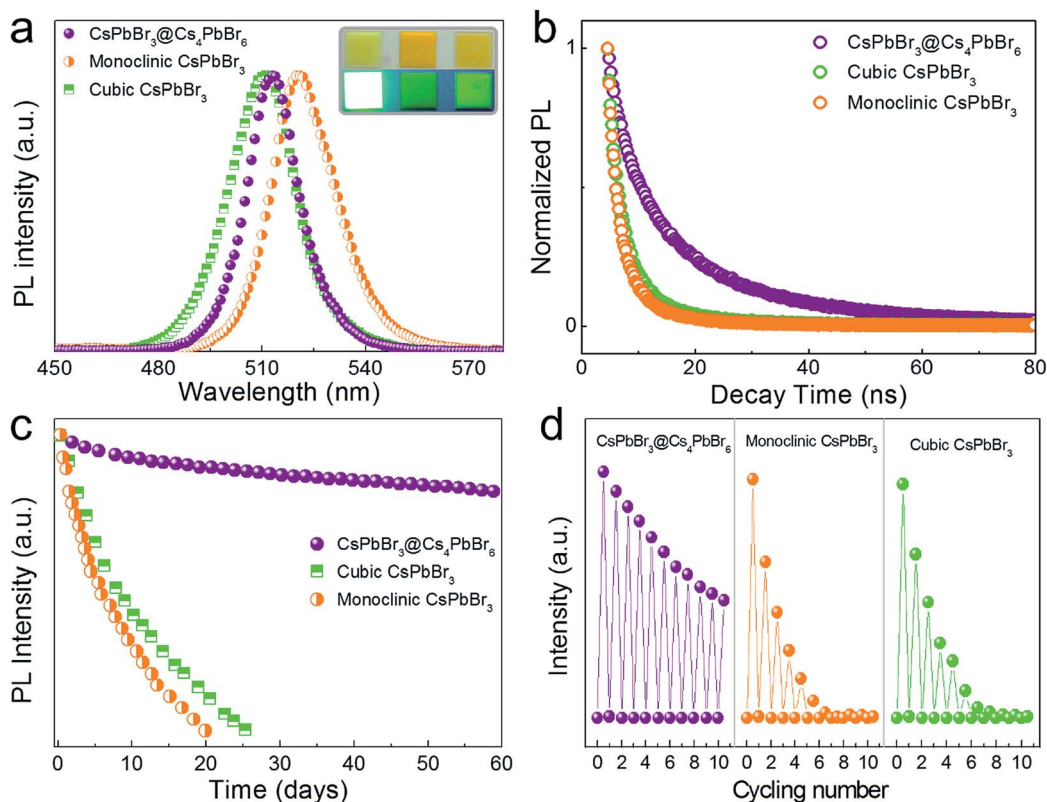


Fig. 7 (a) PL spectra and inset photographs (from left to right) of CsPbBr₃@Cs₄PbBr₆, monoclinic CsPbBr₃ and cubic CsPbBr₃ films (mixing with PDMS). (b) PL decays of CsPbBr₃@Cs₄PbBr₆, monoclinic CsPbBr₃ and cubic CsPbBr₃ films. (c) Storage stability tests of CsPbBr₃@Cs₄PbBr₆, monoclinic CsPbBr₃ and cubic CsPbBr₃ under ambient conditions with RH 50% for two months. (d) Thermal stability tests of CsPbBr₃@Cs₄PbBr₆, monoclinic CsPbBr₃ and cubic CsPbBr₃ heated from RT to 150 °C for ten cycles under ambient conditions.

Table 3 PL lifetime parameters of CsPbBr₃@Cs₄PbBr₆ NCs, cubic CsPbBr₃ NCs and monoclinic CsPbBr₃ NCs, respectively

T/°C	CsPbBr ₃ @Cs ₄ PbBr ₆	Cubic CsPbBr ₃	Monoclinic CsPbBr ₃
τ ₁ /ns	4.5	1.83	1.62
τ ₂ /ns	18.6	7.37	6.33
τ _{aver} /ns	17.7	5.7	5.48

the three films shown in Fig. 7a under ambient storage conditions with RH 50% for two months. The CsPbBr₃@Cs₄PbBr₆ film showed a decrease of 19%, while cubic and monoclinic CsPbBr₃ films completely lost their emission within one month. The thermal cycling tests (Fig. 7d) were performed from room temperature to 150 °C with RH 50% under ambient conditions. After 10 cycles, CsPbBr₃@Cs₄PbBr₆ remained approximately half of the original PL intensity, whereas the cubic CsPbBr₃ without Cs₄PbBr₆ passivation degenerated sharply to baseline only for 6 cycles, and monoclinic CsPbBr₃ was even worse. In conclusion, CsPbBr₃@Cs₄PbBr₆ NCs exhibited improved stability, indicating the effective protection of Cs₄PbBr₆, and this new method will take perovskite NCs towards practical applications in optical and photoelectric fields.

We could obtain blue- and red-emitting NCs based on green emitting CsPbBr₃@Cs₄PbBr₆ NCs *via* anion exchange. Didodecyltrimethylammonium chloride (DDA-Cl) was used for the (Cl/Br)-based blue NCs, and oleylamine iodine (OAm-I) was chosen for red NCs. The schematic of the anion exchange is presented in Fig. 8a, and the amount of DDA-Cl and OAm-I affected the light emissive colors. The photograph of the obtained solution samples under daylight and ultraviolet light is presented in Fig. 8a. Fig. 8b exhibits the corresponding PL spectra, blue to 437 nm and red to 630 nm. We mark the commission Internationale de l'Eclairage (CIE) of our spectra using solid line in Fig. 8b; the dashed line area is NTSC standard. It could be seen that our CIE encompasses 135% of the NTSC standard.

A backlit LED was assembled using the as-prepared CsPbBr₃@Cs₄PbBr₆ powder and a 450 nm blue chip as shown in the insert photograph of Fig. 9a, which showed the EL spectra of the LED under increasing current (2–12 mA). The EL intensity gradually increased with the increase in current. We continuously light the LED for 10 days in ambient environment (under 8 mA), and no obvious attenuation was observed on the LED (Fig. 9b). All these results imply the huge applicable value of CsPbBr₃@Cs₄PbBr₆ NCs in display and lighting fields.

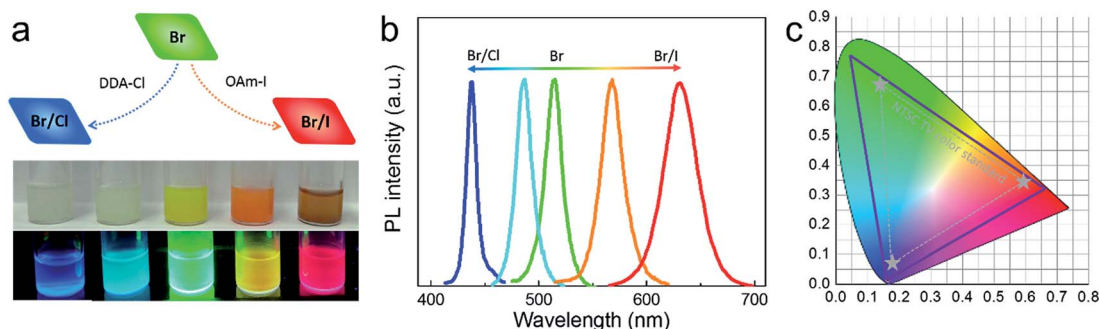


Fig. 8 (a) Schematic of anion exchange with DDACl and OAmI for blue and red spectra, and the corresponding solution samples after anion exchange (blue to red from left to right). (b) The PL spectra of typical samples from blue to red. (c) Solid line area is CIE coordinates of NCs after anion exchange, and the dashed area is the standard NTSC TV color.

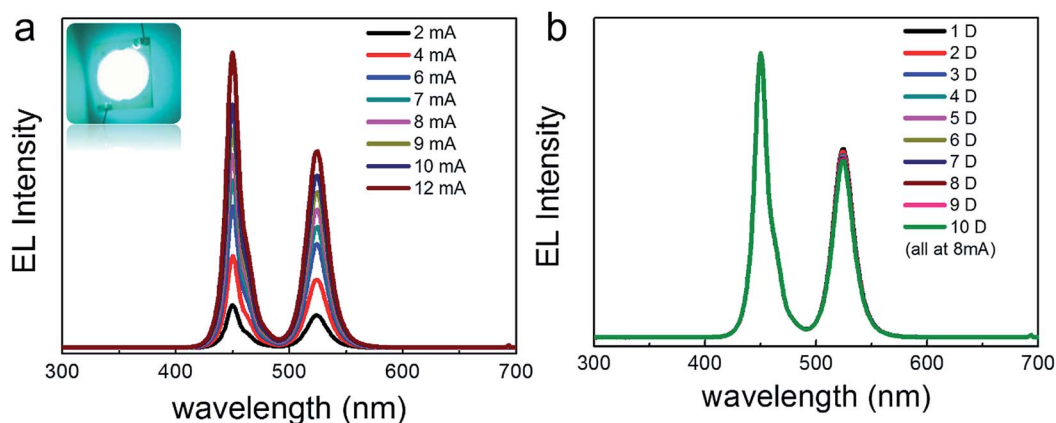


Fig. 9 (a) EL spectra of the CsPbBr₃@Cs₄PbBr₆ NC powder-based backlit LED under different currents; inset is the photograph of the backlit LED. (b) EL spectra of the CsPbBr₃@Cs₄PbBr₆-based backlit LED lighted for 10 days under ambient conditions.

Conclusion

In summary, a novel anion–cation reaction method was proposed to synthesize the highly emissive CsPbBr₃ NCs embedded in the air-stable and crystalline Cs₄PbBr₆ matrix. In this method, temperature was used to adjust the relative proportions of CsPbBr₃ and Cs₄PbBr₆. Besides narrower FWHM and higher PLQY, the as-prepared CsPbBr₃@Cs₄PbBr₆ compound possessed higher optical stability resisting moist ambient condition and heating. The contrast experiments of storage and thermal stability were designed to compare CsPbBr₃@Cs₄PbBr₆ with conventional cubic CsPbBr₃ and monoclinic CsPbBr₃. Furthermore, the mixed halogen perovskite compound with wide color gamut could be obtained *via* simple anion exchange. In conclusion, the compound of CsPbX₃@Cs₄PbX₆ provided a new passage to improve the stability of perovskite, which would be of great significance in lightings, displays, backlights, and other optoelectronic applications.

Experiment section

Synthesis of CsPbBr₃@Cs₄PbBr₆ nanocrystals

The anion–cation reaction procedure of Cs₄PbBr₆@CsPbBr₃ was conducted by adding the brominating agent into the precursor solution with the presence of cesium ion and lead ion. Typically,

the Cs and Pb precursors were formed by dissolving 0.1 mmol cesium acetate and 0.1 mmol lead acetate into 1 mL *N,N*-dimethyl formamide (DMF), and the brominating agent was prepared by dissolving PDBr into DMF at 0.3 mol L^{−1}. 1 mL PDBr/DMF bromide solution was added into 20 mL toluene with 0.5 mL oleyl amine (OAm), 0.5 mL oleic acid (OA) and 1 mL (Cs, Pb)/DMF precursor under atmospheric conditions; the reaction solution was further stirred for 10 min.

Purification of Cs₄PbBr₆@CsPbBr₃ nanocrystals

The as-prepared Cs₄PbBr₆@CsPbBr₃ nanocrystals were collected by adding 20 mL acetonitrile and 10 mL toluene into the original solution, and then centrifuging at 8000 rpm for 3 min. The liquid sample was obtained by dispersing the precipitate into 5 mL toluene, and the powder sample was obtained by vacuum drying.

Anion exchange reactions

Different amounts of OAm-I dispersed in toluene (0.1 mol L^{−1}) were dropped into 1 mL as-obtained Cs₄PbBr₆@CsPbBr₃ NC solution for red PL emission, while different amounts of DDACl were added for blue emission. The concrete proposal is listed in Table S2.†



Characterization

Powder X-ray diffraction (XRD) patterns were recorded using a Bruker D8 Advance X-ray Diffractometer at 40 kV and 40 mA using Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). The morphologies were investigated using the JEOL JSM-7800F field emission scanning electron microscope (FESEM), and the JEM-2100F and JEM-ARM200F transmission electron microscope (TEM) instruments. PL spectra were recorded using an FLS920P fluorescence spectrometer (Edinburgh Instruments) equipped with a photomultiplier in a thermoelectrically cooled housing (R928P, Hamamatsu) with a 450 W xenon arc lamp used as the excitation source for steady-state spectra. The absolute PL quantum yields were detected using a fluorescence spectrometer with an integrated sphere (Hamamatsu Photonics). The photo-stability measurements were analyzed in a temperature and humidity chamber (25 °C, RH 50%) using a 454 nm LED light (21 mW cm $^{-2}$) provided by Ocean Optics LS-450.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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