

Copper-doping defect-lowered perovskite nanosheets for deep-blue light-emitting diodes

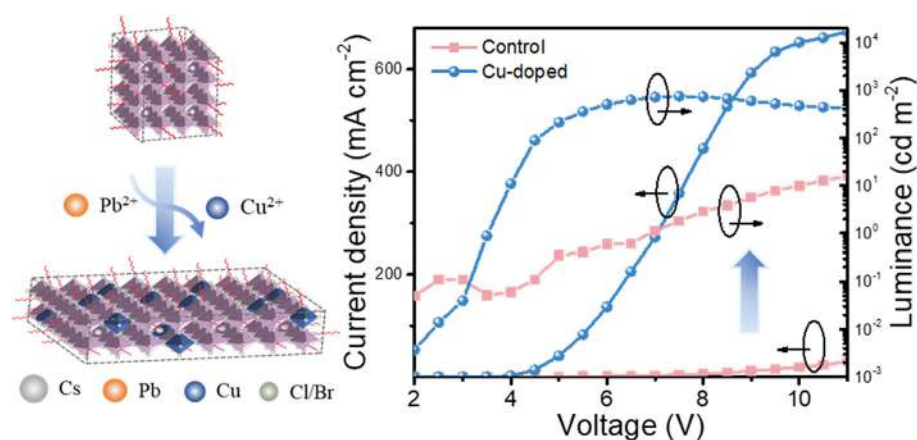
Yue Gao^a, Chao Luo^b, Cheng Yan^a, Wen Li^a, Chuanqi Liu^c, Weiqing Yang^{a,*}

^a Key Laboratory of Advanced Technologies of Materials (Ministry of Education), School of Materials Science and Engineering, State Key Laboratory of Traction Power, Southwest Jiaotong University, Chengdu 610031, PR China

^b State Key Laboratory for Mesoscopic Physics and Frontiers Science Center for Nano-optoelectronics, School of Physics, Peking University, Beijing 100871, PR China

^c College of Optoelectronic Engineering, Chengdu University of Information Technology, Chengdu 610225, PR China

GRAPHICAL ABSTRACT



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ABSTRACT

Mixed-halide blue perovskites $\text{CsPb}(\text{Br}/\text{Cl})_3$ are considered promising candidates for developing efficient deep-blue perovskite light-emitting diodes (PeLEDs), but their low photoluminescence quantum yield (PLQY), environmental instability, and poor device performance gravely inhibit their future development. Here, we employ a heteroatomic Cu^{2+} doping strategy combined with post-treatment Br^- anion exchange to prepare high-performance deep-blue perovskites $\text{CsPb}(\text{Br}/\text{Cl})_3$. The Cu^{2+} doping strategy significantly decreases the intrinsic chlorine defects, ensuring that the inferior CsPbCl_3 quantum dots are transformed into two-dimensional nanosheets with enhanced violet photoluminescence and increased exciton binding energy. Further, with the post-treatment Br^- anion exchange, the as-prepared $\text{CsPb}(\text{Br}/\text{Cl})_3$ nanosheets with more radiation recombination and less ion migration present an enhanced PLQY of 94% and better humidity stability of 30 days. Based on the optimized $\text{CsPb}(\text{Br}/\text{Cl})_3$, we fabricated deep-blue PeLEDs with luminescence emission at 462 nm, a maximum luminance of 761 cd m^{-2} , and a current density of 205 mA cm^{-2} . This work puts forward a feasible synthesis strategy to prepare efficient and stable mixed-halide blue perovskite $\text{CsPb}(\text{Br}/\text{Cl})_3$ and related blue PeLEDs, which may promote the further application of mixed-halide perovskites in the blue light range.

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* Corresponding author.

E-mail address: wqyang@swjtu.edu.cn (W. Yang).

1. Introduction

Recently, all inorganic perovskites, CsPbX_3 ($X = \text{Cl, Br, and I}$), have shown notable achievements in perovskite light-emitting diodes (PeLEDs) owing to their attractive capacities such as low cost, high photoluminescence, and easy bandgap tuning [1–7]. However, CsPbX_3 with different emission colors are evolving at an unbalanced speed. The red and green perovskites possess ultra-high photoluminescence quantum yield (PLQY) that give rise to efficient PeLEDs [3,5,8,9], whereas the blue perovskites present unsatisfactory performance, such as low PLQY, low external quantum efficiency (EQE), impure luminescence, and poor stability against various external fields [1,10–12]. This lagging progress of blue perovskites poses a major hindrance to the extensive development of perovskites in colorful displays and white illumination based on three primary colors (red, green, and blue) [13], therefore it is quite urgent to obtain highly efficient and long-term stable blue perovskites.

Dimensional engineering and component engineering are usually employed to prepare blue perovskites. Dimensional engineering reduces the dimension or size of pure CsPbBr_3 using long-chain ammonium ligands, blueshifts the luminescence peak through a strong quantum confinement effect [14,15], and achieves the highest efficiency of blue PeLEDs [6,16,17]. Moreover, compared with the three-dimensional quantum dots (QDs), these low-dimensional perovskites, featuring suppressed ion migration and higher exciton binding energy (E_b), exhibit better stability under light, heat, and electric fields [10]. However, the difficulty in controlling the accuracy of dimensional engineering causes these low-dimensional perovskites to usually emit sky blue light (>470 nm) and even have multiple emission peaks [15,17], which is far from satisfying the deep-blue light region (~ 460 nm). Fortunately, component engineering provides a more accurate bandgap adjustment by easily changing the Br/Cl ratio, which can be more suitably utilized for preparing blue perovskites, especially for deep-blue perovskites [4,18]. However, this method is critically underestimated and lacking in practical applications on blue perovskites, owing to the low PLQY and poor spectral stability of mixed-halide perovskite $\text{CsPb}(\text{Br/Cl})_3$ [10,19,20]. Deeply analyzing the causes, the intrinsic chlorine defects existing in mixed-halide perovskites should be responsible for these inferior performances [10,21]. These chlorine defects not only capture the photogenerated carriers and initiate nonradiative recombination [21,22] but also induce ion migration to accelerate the separation or decomposition of $\text{CsPb}(\text{Br/Cl})_3$ [23–27]. Therefore, considering the advantages of dimensional engineering and component engineering, low-dimensional mixed-halide perovskites with fewer halide defects and higher E_b can be proposed to achieve both efficient luminescence in the deep-blue light region and good stability against external fields.

Minimizing the abovementioned defects may eliminate the fatal mechanical instability within the lattice of perovskites, which originates from the fragility of the soft ionic lattice [28,29]. In this context, doping smaller divalent metal ions into perovskites could stabilize the lattice structure because of the part substitution of metal ions for Pb^{2+} . This part substitution can induce lattice contraction [30,31], increase the tolerance factor [32–34], and greatly decrease halide defects [35–38] and lattice disorders [12,39,40], which is advantageous to the enhancement of photoluminescence (PL) properties. The metal-doping strategy can also change the morphology of perovskites by optimizing the crystallization, influencing the charge distribution, and competing with surface ligands, which has been successfully applied to the preparation of one-dimensional (1D) nanocubes [22] and two-dimensional (2D) nanosheets [41,42]. Moreover, the metal-doping strategy is

superior in comparison with dimensional engineering in terms of morphology changing because the carrier transport limitation caused by the introduction of excessive long-chain ligands can be effectively sidestepped [43].

Clearly different from previous reports, we combined the advantages of dimensional and component engineering to prepare efficient and stable deep-blue perovskite $\text{CsPb}(\text{Br/Cl})_3$ using a heteroatomic Cu^{2+} doping strategy and post-treatment Br^- anion exchange. Owing to the significantly decreasing chlorine defects after Cu^{2+} doping, the inefficient CsPbCl_3 QDs transformed into 2D nanosheets with enhanced violet photoluminescence and increased E_b energy. Following post- Br^- anion exchange, the deep-blue $\text{CsPb}(\text{Br/Cl})_3$ nanosheets, showing an increase in radiative recombination and inhibition of extra ion migration, showed an ultrahigh PLQY and long-term stability against humidity. Besides, using the efficient $\text{CsPb}(\text{Br/Cl})_3$ nanosheets, we also prepared deep-blue PeLEDs with an electroluminescence (EL) peak at 462 nm, showing a peak luminance of 761 cd m^{-2} and a current density of 205 mA cm^{-2} . This work provides a workable and effective heteroatomic doping strategy to synthesize efficient and stable deep-blue perovskite $\text{CsPb}(\text{Br/Cl})_3$ nanosheets and related blue PeLEDs, enhancing the competitiveness of mixed-halide blue perovskites in the future blue light field.

2. Experimental methods

2.1. Materials

Cesium carbonate (Cs_2CO_3 , 99.9%), lead(II) chloride (PbCl_2 , 99.999%), cupric chloride (CuCl_2 , 99%), lead(II) acetate ($(\text{CH}_3\text{COO})_2\text{Pb}$, 99%), hydrobromic acid (HBr, 99%), octadecene (ODE, 90%), oleic acid (OA, 90%), oleylamine (OAm, 70%), tri-*n*-octylphosphine (TOP, 99%), and toluene (99.9%) were purchased from Aldrich and used without any further purification. Poly(4-butylphenyldiphenylamine) (poly-TPD), 1,3,5-Tris (1-phenyl-1H-benzimidazol-2-yl) benzene (TPBi) and poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate) (PEDOT:PSS) were purchased from Xi'an Baolite Photoelectric Technology Company.

2.2. Preparation of the Cs oleate solution

Cs_2CO_3 (0.2 g), ODE (10 mL), and OA (1.5 mL) were loaded into a 25-mL three-necked flask and stirred under vacuum until the temperature reached 120°C . Then, the mixture was heated for 1 h under N_2 until all Cs_2CO_3 dissolved.

2.3. Preparation of the CuCl_2 solution

X g ($X = 0.04, 0.08$, and 0.12) CuCl_2 , 5 mL ODE, and 1 mL OAm were loaded into a 25-mL three-necked flask, and stirred at 60°C under N_2 .

2.4. Synthesis of CsPbCl_3

PbCl_2 (0.114 g) and ODE (10 mL) were added to a 25-mL three-necked flask and stirred under vacuum until the temperature reached 120°C , and X g ($X = 0.02, 0.04, 0.06, 0.08$, and 0.10) CuCl_2 was added to prepare Cu- CsPbCl_3 . Next, 1 mL OA and 1 mL OAm were added to the flask and stirred for 10 min. Then, 1 mL TOP was added and stirred for 50 min under N_2 . The temperature was raised to 200°C , and 1 mL of the Cs oleate solution was added immediately and reacted for 1 min to obtain the perovskite colloidal solution, followed by cooling with ice water to room temperature immediately. The obtained colloidal solution was centrifuged at 9000 rpm for 10 min. After centrifugation, the supernatant was

discarded and the precipitate was redispersed in toluene and centrifuged twice at 9000 rpm for 10 min. The powder and solution obtained with the last centrifugation were taken for characterization. For preparing the lower-defect CsPbCl₃ nanosheets, named as “the Optimized”, CuCl₂ solution was added to the colloidal solution and stirred under N₂ for 1 h; then, the purification and centrifugation processes were conducted.

2.5. Synthesis of CsPbBr₃

Cs₂CO₃ (0.0326 g), (CH₃COO)₂Pb (0.1625 g), ODE (6 mL), OA (1 mL), OAm (1 mL), and TOP (1 mL) were added to a 25-mL three-necked flask and stirred for 15 min at 120 °C under vacuum. Then, the mixture was stirred for 45 min at 120 °C under N₂. After that, the temperature was increased to 180 °C and stirred for 10 min; then, 0.9 mL HBr was added immediately and reacted for 5 s, followed by cooling with ice water to room temperature immediately. The obtained colloidal solution was further purified and centrifuged in the same way.

2.6. Synthesis of CsPb(Br/Cl)₃

CsPb(Br/Cl)₃ was prepared via the ion exchange method. A CsPbCl₃ toluene solution was first added to a glass bottle; then, a CsPbBr₃ toluene solution of different volumes was added dropwise, and this mixed solution was fully stirred before the further characterizations.

2.7. Device fabrication

The patterned indium tin oxide substrates were successively cleaned with a cleaning agent, ultrapure water, acetone, and isopropanol before a 30-min UV-ozone treatment. Then, the PEDOT:PSS was spin coated (1000 rpm, 3 s, followed by 4500 rpm, 60 s) and was annealed at 130 °C for 30 min. Next, the device was placed in a glove box for further preparation. Poly-TPD (8 mg/mL) was spin coated (3500 rpm, 60 s) and annealed at 110 °C for 30 min. Then, the device was treated with UV-ozone for 20 s. Subsequently, the blue perovskites were further spin coated (1800 rpm, 30 s) and annealed at 40 °C for 10 min. The device was further prepared by successively depositing TPBi (30 nm), LiF (1 nm), and Al (100 nm). The device's active area was 4 mm².

2.8. Characterizations

The transmission electron microscopy (TEM) was determined using an FEI Tecnai G2 F20) with an acceleration voltage of 200 kV. The crystal structure and phase composition were determined using an XPert Pro (The Netherlands) X-ray diffractometer with Cu Kα1 radiation ($\lambda = 0.154$ nm). The UV absorption spectra were obtained using a UV-2500 (Shimadzu Corporation). The PL properties and temperature-dependent PL were investigated at room temperature using an FLS980 (Edinburgh Instruments) spectrometer with a 450-W xenon lamp. The time-resolved PL (TRPL) decay curves were obtained using an FLS980 with a xenon flash lamp as the light source at room temperature ($\lambda = 405$ nm). The PLQY of the samples were measured on the FLS980 spectrometer using an integrating sphere ($\lambda = 365$ nm). The Fourier transform infrared (FTIR) measurements were performed using a Thermo Fisher Nicolet Is10. The ¹H-nuclear magnetic resonance (¹H NMR) spectra were taken on a Bruker Avance III 400 MHz NMR with an autosampler. The femtosecond transient absorption (TA) measurements were performed on a Helios pump-probe system (Ultrafast Systems LLC) combined with an amplified femtosecond laser system (Coherent). All the characterizations of the PeLEDs were

obtained using a QE-Pro spectrometer (Ocean Optics) at room temperature in a glove box, including EQE, EL spectra, and brightness.

3. Results and discussion

The metal-doping strategy for passivating halide defects has proven to be an effective method for preparing high-performance mixed-halide perovskite CsPb(Br/Cl)₃ [10,21,31]. However, conducting the metal-doping process and the preparation of mixed-halide perovskites in one process would lead to an unsatisfactorily low PLQY due to incomplete passivation of defects [31]. Therefore, aiming at more thorough chlorine defect passivation, this work separately achieved the metal-doped passivation process and the preparation of mixed-halide perovskites. First, we used a Cu²⁺ doping strategy to prepare the Optimized, followed by post-Br[−] anion exchange to synthesize mixed-halide blue perovskite CsPb(Br/Cl)₃. The specific synthesis steps of the Optimized are provided in the [Supporting Information](#). For convenient comparison, the system without any Cu²⁺ doping is referred to as “the Pristine.”

The synthesis of CsPbCl₃ nanosheets with fewer defects by Cu²⁺ doping is schematically illustrated in [Fig. 1](#). Benefiting from the stronger interaction force with halide ions, smaller Cu²⁺ ions (73 pm) partially substituted Pb²⁺ ions (113 pm) and formed a shrunk lattice with shorter Cu–halide bonds [31], effectively passivating the intrinsic halide defects and improving the PL performance of the Optimized. The passivation of intrinsic halide defects also increased the content of surface halide ions. During the crystallization of CsPbCl₃, OAm ions compete with Cs⁺ ions, coordinate with surface halide ions to occupy the surface, and further inhibit crystal growth [22,44]. However, Cu²⁺ ions with higher metallicity than OAm ions and double bonding sites [22] can easily coordinate with surface halide ions to form a new perovskite lattice and promote crystal growth. Therefore, in the presence of Cu²⁺ ions, the OAm ions absorbed in the surface were too few to suppress the crystal growth, which is conducive to the formation of nanosheets. However, in the absence of Cu²⁺ ions, the Pristine evenly absorbed the ligands and only formed QDs. To prove this growth model, TEM was used to study the morphology of different Cu–CsPbCl₃ systems, as shown in [Fig. S2a–2d](#). As the amount of Cu²⁺ ions increased, the overall morphology of Cu–CsPbCl₃ gradually changed from QDs to nanosheets, which proves that Cu²⁺ ions competed with OAm ions to promote crystal growth. Besides, both 0.08 Cu (defined in [Supporting Information](#)) and the Optimized showed 2D nanosheets but with different sizes, which demonstrates that the morphology change was more likely to occur in case of hot injection, where Cu²⁺ ions were more effectively doped into the lattice [45] and affected the morphology.

The TEM and HRTEM were further used to analyze the morphologies of the Pristine and the Optimized. As shown in [Fig. 2a](#) and [2b](#), the Pristine comprised uniform QDs with an average size of 7.7 nm. The Optimized showed 2D nanosheets with rough squares ([Fig. 2d](#)), and the nanosheets were either parallel or perpendicular to the substrate. These arrangements benefited the length and thickness estimation [46], and these nanosheets presented a thickness of 2.94 nm and a lateral size of 16.40 nm ([Fig. 2e](#)). The HRTEM images (insets presented in [Fig. 2a](#) and [2d](#)) show that the Pristine had an interplanar distance of 0.375 nm whereas the Optimized possessed a smaller value of 0.368 nm, which implies that lattice shrinkage occurred due to the partial substitution of smaller Cu²⁺ ions for Pb²⁺ ions [36,47]. [Fig. 2c](#) and [2f](#) present the selected area electron diffraction with more specific structural information. The Pristine showing QDs had diffraction rings of diffuse intensity; however, the Optimized showed more obvious diffraction spots, indicating better crystallinity and obvious characteristics of the 2D structure [2,25,48].

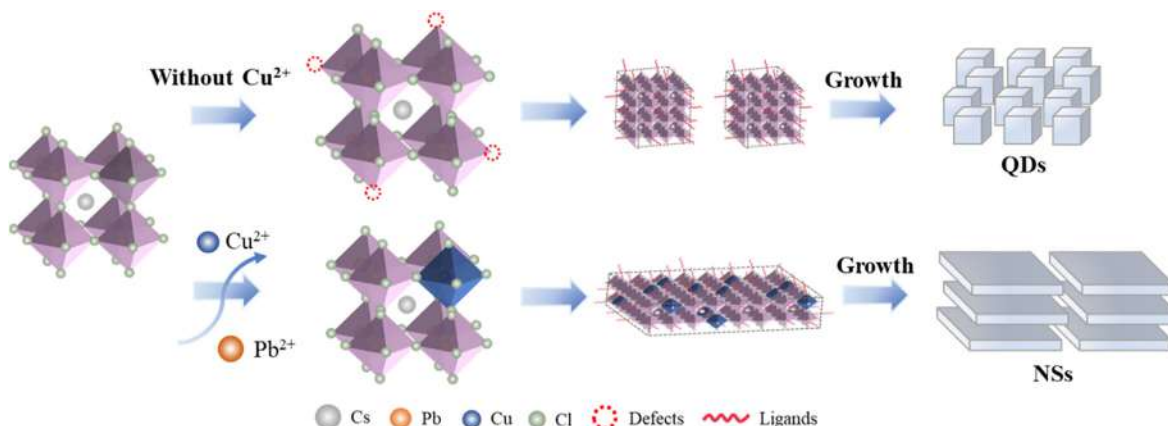


Fig. 1. Schematic for the synthesis of CsPbCl₃ nanosheets with reduced defects after Cu²⁺ doping.

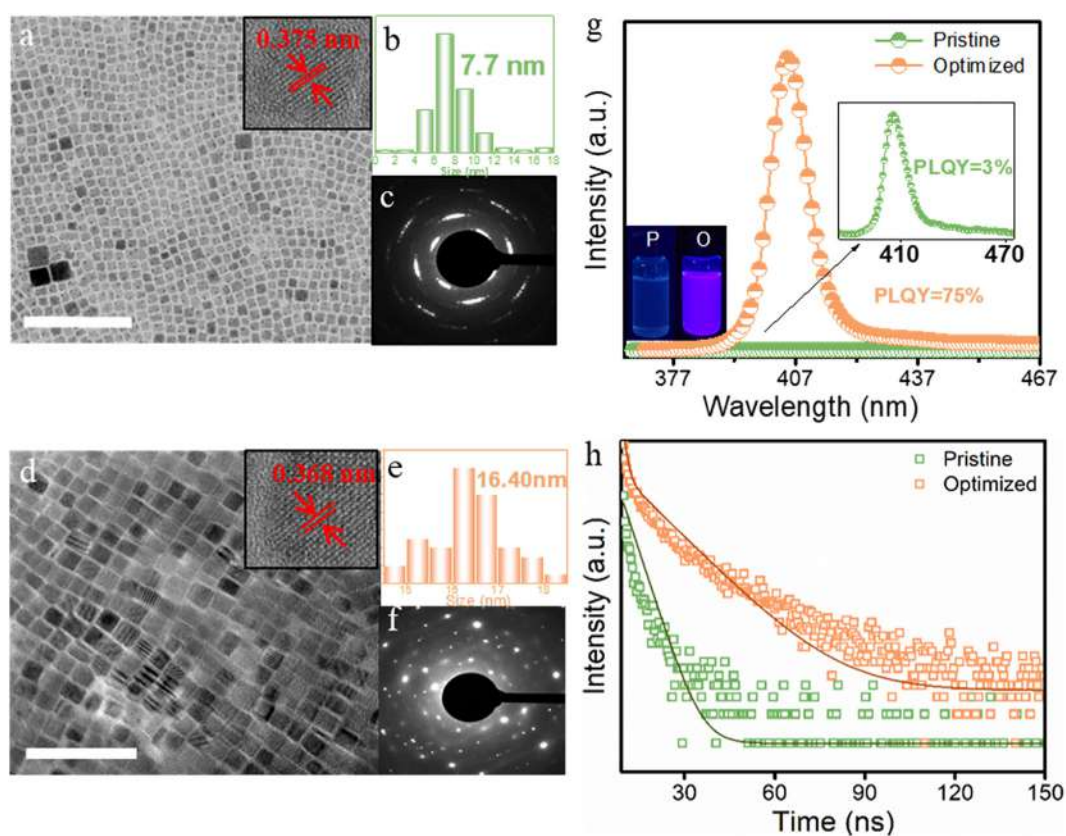


Fig. 2. Characterizations of CsPbCl₃ before and after Cu²⁺ doping. TEM images of the Pristine (a) and the Optimized (d) with related high-resolution TEM (HRTEM) images. Scale bar: 100 nm. Crystal size distribution and selected area electron diffraction of the Pristine (b, c) and the Optimized (e, f). PL spectra (g) and TRPL curves (h) of the Pristine and the Optimized. Inset in (g): pictures of the Pristine (P) and the Optimized (O) irradiated by UV excitation.

The powder X-ray diffraction (XRD) shows that the Optimized still exhibited the same cubic structure (PDF#18–0366) as the Pristine (Fig. S3), proving that Cu²⁺ doping did not influence the lattice structure. Besides, fewer impurity peaks in the XRD of the Optimized indicate that fewer defects and impurities were inside its lattice. The diffraction peak of the (100) plane is slightly shifted to higher angles, further proving that Cu²⁺ doping induced a lattice contraction [33,36]. In Fig. S4, the energy-dispersive X-ray (EDS) images of the Optimized display a homogeneous distribution of Cs, Pb, Cl, and Cu elements as well as successful Cu²⁺ doping.

To explore the influence of Cu²⁺ doping on PL properties, a series of optical characterizations, including PL spectra, TRPL, and UV

absorption were performed. A comparison between the PL intensity, luminous intensity, and PLQY of the Optimized and the Pristine is shown in Fig. 2g. The Optimized had a stronger PL intensity and higher PLQY of 75% with strong violet light whereas the Pristine showed an extremely low PLQY of 3% and weak luminous intensity. The TRPL curves of the Pristine and the Optimized are shown in Fig. 2h. Both the samples were well fitted by biexponential decay, and the Optimized possessed a longer lifetime (τ_{ave}) of 10.49 ns, whereas the Pristine only possessed a lifetime of 4.02 ns. The detailed decay data of the two samples are shown in Table S1. Compared with the Pristine, the Optimized had more a radiative recombination component (Γ_{rad}) of 71.49 μs^{-1} and a less

nonradiative recombination component (Γ_{nonrad}) of $23.8 \mu\text{s}^{-1}$. Evidently, for the Optimized, the defect-induced nonradiative recombination was effectively reduced, which demonstrates that halide defects were greatly passivated after Cu^{2+} doping [12,21,35].

Adding more halide ions to the system for compensating the halide loss could also boost the PL performance [35,49]. Therefore, to determine the origin of this PL enhancement after adding CuCl_2 , three dopants MCl_x ($M = \text{Eu}$, Zn , and Cu) were doped into CsPbCl_3 . The results in Fig. S5 show that the Cu^{2+} -doped CsPbCl_3 showed the best enhancement, which proves that the Cu^{2+} ions played a decisive role in improving the performance.

The UV absorption curves of the Pristine and the Optimized are shown in Fig. 3a. The Pristine presented an absorption peak at $\sim 407 \text{ nm}$, and the Optimized showed a slightly blue-shifted peak at $\sim 406 \text{ nm}$. The bandgaps of the two samples were calculated based on the UV absorption, as shown in Fig. S6a and S6b. The bandgap of the Pristine was 2.98 eV and that of the Optimized was 3.01 eV , which indicates that Cu^{2+} doping slightly changed the electronic state distribution to blue-shift the absorption peak and increase the bandgap [50]. Furthermore, Fig. S7a and S7b com-

pare the Urbach energy (E_u) for studying the degree of lattice disorder. In general, a lower E_u means fewer lattice disorders [9,25]. The Optimized presented lower E_u (1.3 meV) than the Pristine, further revealing that Cu^{2+} doping reduced the halide defects and improved the lattice short-range orders.

XPS was applied to further study the chemical environment and electronic states of the Optimized and the Pristine. As shown in Fig. 3b and S8, the Optimized showed two additional peaks at 931.5 and 956.5 eV , which respectively corresponded to $\text{Cu } 2p_{3/2}$ and $\text{Cu } 2p_{1/2}$ [50], which further demonstrates the successful Cu^{2+} doping. Besides, based on the XPS, the atom ratio of Cl to Pb was calculated and increased from 1.24 to 2.16 after Cu^{2+} doping, illustrating that Cu^{2+} doping greatly increased the Cl^- ions content and reduced halide defects (Fig. 3c).

Usually, OAm ligands combine with halide ions on the surface of perovskites to avoid halide loss and form ligand protective layers [36,49]. Therefore, FTIR and ^1H NMR were used to qualitatively study the change in OAm ligands to indirectly demonstrate the Cl^- change. In Fig. 3d and S9, a small enhancement in the C–H and N–H bonds of the OAm ligands showed a slight increase in the

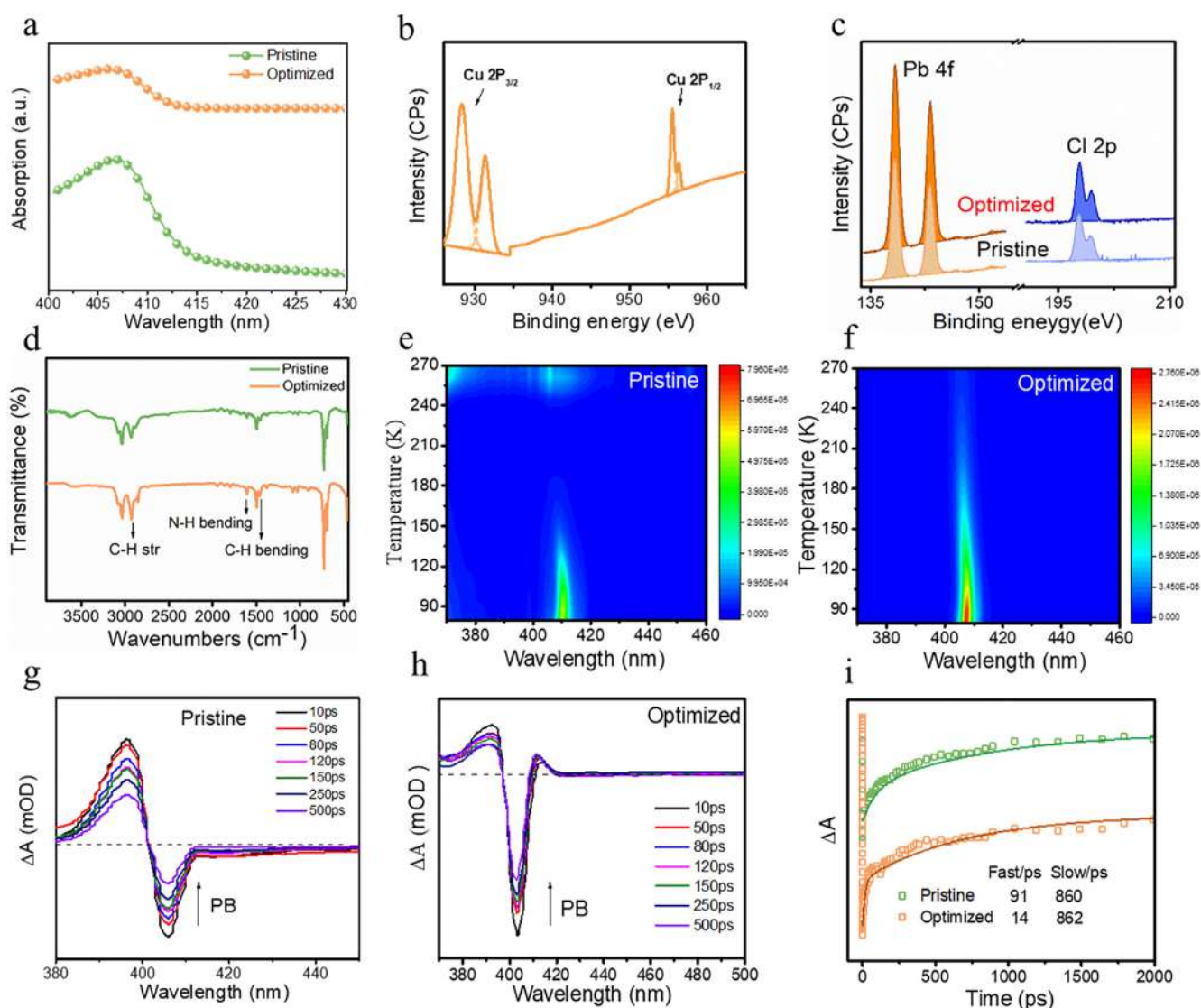


Fig. 3. Photophysical capacities, chemical analysis, and carrier dynamics of CsPbCl_3 before and after Cu^{2+} doping. (a) The UV absorption of the Optimized and the Pristine. (b) X-ray photoelectron spectroscopy (XPS) spectra of $\text{Cu } 2p$ in the Optimized. (c) XPS spectra of $\text{Pb } 4f$ and $\text{Cl } 2p$ in the Optimized and the Pristine. (d) FTIR of the Optimized and the Pristine. Temperature-dependent PL spectrum of the Pristine (e) and the Optimized (f). TA spectra of the Pristine (g) and the Optimized (h). (i) Bleach recovery dynamics of the Pristine and the Optimized.

ligands' contents [36,51], equally testifying to the increase in the Cl^- content and more surface protection after Cu^{2+} doping.

Temperature-dependent PL spectra of the Pristine and the Optimized are shown in Fig. 3e and f. The PL intensities of the two samples both decreased with the increasing temperature, which is attributed to the temperature-activated defects trapping carriers [36]. However, the Optimized presented a slower decreasing process (Fig. 3f), further demonstrating that the intrinsic halide defects were reduced after Cu^{2+} doping. Based on the temperature-dependent PL spectra, the E_B energy of the two samples was fitted by the Arrhenius equation, as shown in Fig. S10. The Optimized, with unique 2D nanosheets, showed a higher E_B of 52.73 meV, proving that it had a more efficient and stable exciton radiation recombination [10,52].

A TA measurement was performed to study the carrier dynamics of the Pristine and the Optimized. As shown in Fig. 3g and h, the Pristine showed a shallower probe bleach (PB) peak at ~ 406 nm, while the Optimized showed a deeper PB peak at ~ 404 nm, which is consistent with the UV absorption curves in Fig. 3a. Moreover, the rise component of the PB peak originates from the dissociation of excitons into free carriers [53]. The PB peak of the Pristine rose faster, but the Optimized had a slower rising process, also indicating that Cu^{2+} doping effectively enhanced the exciton stability and increased the radiation recombination. Fig. 3i compares the bleach recovery dynamics of the Pristine and the Optimized, and both samples were fitted as biexponential decays with fast and slow components, which respectively correspond to carrier trapping and recombination [36,53]. Obviously, the Optimized had less carrier trapping and more radiation recombination, further proving that Cu^{2+} doping greatly suppressed the carrier trapping and eventually provided a more efficient radiation recombination.

After achieving the optimized CsPbCl_3 , Cu^{2+} -doped mixed-halide blue perovskite $\text{CsPb}(\text{Br}/\text{Cl})_3$ with PL peak at ~ 464 nm was prepared via post-treatment Br^- anion exchange. As shown in Fig. 4a, the Pristine blue perovskite (mixing the Pristine and CsPbBr_3 , named as PB) had a weak PL intensity with a low PLQY of 11% whereas the Optimized blue perovskite (mixing the Optimized and CsPbBr_3 , named as OB) presented strong PL intensity and near-unity PLQY of 94% with purer and brighter blue light. Fig. 4b compares the TRPL curves of OB and PB, and the detailed decay-fitting information is shown in Table S2. Both samples were fitted using a biexponential decay. The lifetime, radiative recombination component, and nonradiative recombination component are respectively recorded as τ_{ave} , Γ_{rad} , and Γ_{nonrad} . OB had a longer τ_{ave} of 7.92 ns and more Γ_{rad} of $118.69 \mu\text{s}^{-1}$ than that of PB. The considerable enhancement in the PL intensity, PLQY, and lifetime of OB are attributed to the optimized CsPbCl_3 , with decreased chlorine defects after Cu^{2+} doping. Furthermore, the TEM images in Fig. S11 show that OB and PB exhibited the same morphology as the used CsPbCl_3 but with different sizes.

The long-term stability of mixed-halide blue perovskites was also examined. Fig. 4c and S12 compare the PL intensity of the two samples soaked in UV light (365 nm, 20 W). When the illumination time increased, the PL intensity of PB rapidly weakened and almost disappeared at 105 min. However, OB showed better stability with a slightly decreased intensity under lasting illumination and still showed strong blue light at 120 min, as shown in Fig. S12b and S12d. In addition, Fig. S13 shows the morphology of two samples after illumination. PB was destroyed and became an amorphous mixture, whereas OB still maintained a 2D structure and presented better stability. Fig. 4d and S14 show the PL intensity change in OB and PB in a humid environment. As the time

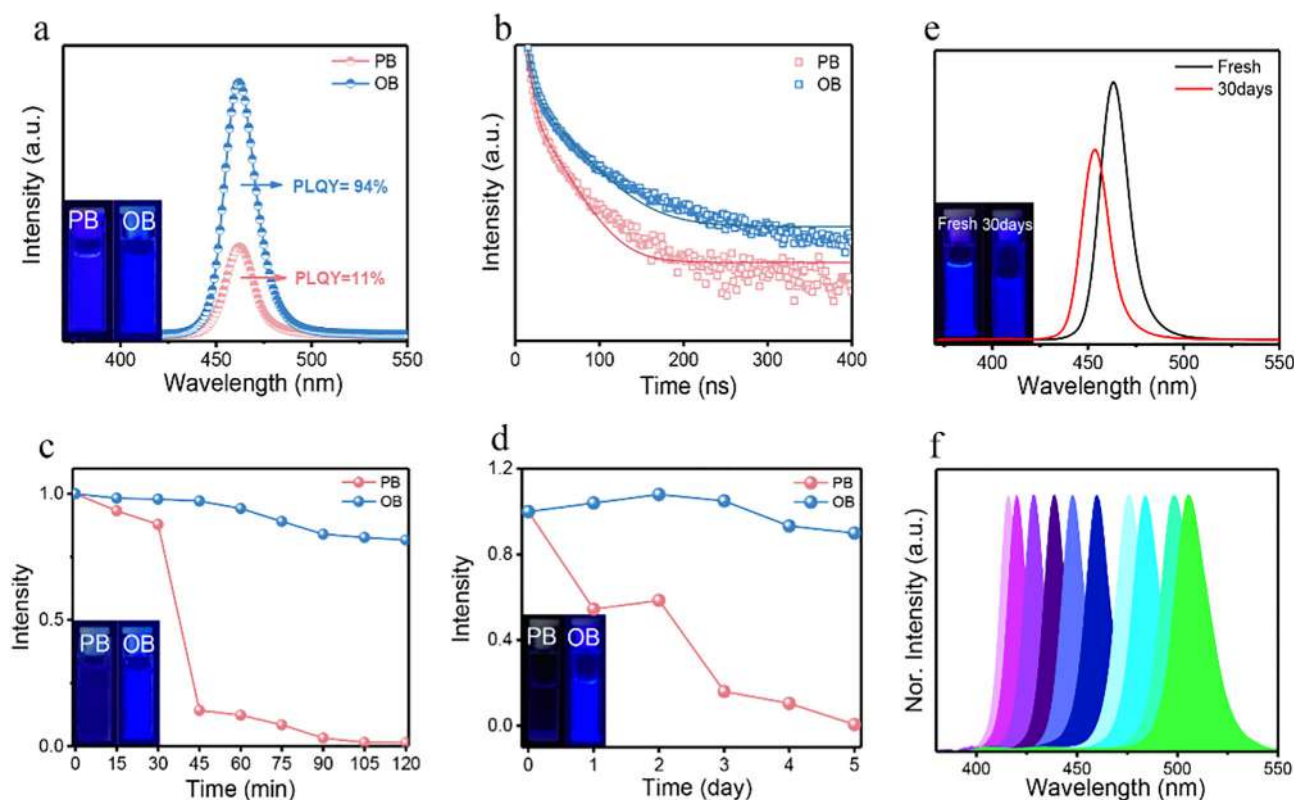


Fig. 4. Photophysical capacities and stability of $\text{CsPb}(\text{Br}/\text{Cl})_3$ before and after Cu^{2+} doping. PL spectra (a) and TRPL curves (b) of OB and PB. PL intensity change of OB and PB under UV light (c) and humid environment (d). (e) PL intensity change of OB and PB after 30 days. Inset: the corresponding photographs of OB and PB under UV illumination. (f) PL spectra of mixed-halide perovskite $\text{CsPb}(\text{Br}/\text{Cl})_3$ via post-treatment Br^- anion exchange.

increased, PB showed an obviously decreased PL intensity and a blue-shifted peak, and it was completely lightless after 5 days, as shown in Fig. S14a and S14c. However, OB still emitted the same strong blue light as that on the first day and only lost a quarter of its emission intensity after being placed in a humid environment for 30 days (Fig. 4e), showing great long-term stability. The E_B of OB and PB was also calculated through the temperature-dependent PL spectra, as shown in Fig. S15. OB with 2D nanosheets had higher E_B (42.22 meV) than PB, proving that it had a more stable excitation and better stability [52]. The improved stability of OB benefited from the suppressed ion migration and reduced chlorine defects after Cu^{2+} doping [26,54]. Besides, the unique 2D structure of OB, endowed by improving the formation energy of the lattice [10,41], also enhanced the resistance to an external force.

Post-treatment Br^- anion exchange was further used to synthesize mixed-halide perovskite $\text{CsPb}(\text{Br/Cl})_3$ with different luminescent colors, and the normalized PL spectra are shown in Fig. 4f. With the increase in the Br^- ion content, the luminescent color of the system gradually turned from purple to green, with the PL peak changing from ~ 410 to ~ 510 nm, which is consistent with previous reports [4,7]. The successful preparation of mixed-halide perovskites with variable luminous color proves that Cu^{2+} -doped perovskites have an easily adjustable PL spectrum, which provides more research direction for the application of metal-doped perovskites.

Finally, deep-blue PeLEDs based on PB and OB (named as P-PeLEDs and O-PeLEDs) were prepared to prove their practical application value and the device structure is shown in Fig. 5a. PEDOT:PSS and poly-TPD were selected as the hole-transporting layer, and TPBi was the electron-transporting layer. In Fig. 5b, the P-PeLEDs showed two split, weak, and wide EL peaks, which is attributed to the severe instability and more nonradiative recombination of the perovskites luminescent layer. According to current density–voltage–luminance (J – V – L) curves, the P-PeLEDs only appeared a lower luminance of 21 cd m^{-2} and a current density of 33 mA cm^{-2} (Fig. 5c). However, because of its rapid decomposi-

tion under electric field, we did not collect any effective EQE. Fortunately, the O-PeLEDs performed better in electric field. They exhibited a clear and bright deep-blue light at 462 nm (Fig. 5b) with a maximum luminance of 761 cd m^{-2} , EQE of 0.12%, and current density of 205 mA cm^{-2} (Fig. 5c and 5d). Moreover, this excellent luminance of the O-PeLEDs is competitive with recent reports on blue PeLEDs [6,55–66], particularly in the deep-blue light range, as illustrated in Fig. 5e. The EL stability of the O-PeLEDs was further measured by observing the EL intensity under different voltages. As shown in Fig. S16, the O-PeLEDs showed great spectrum stability, with no shift in the EL peaks from 5 to 8 V, which benefits from the suppressed ion migration after Cu^{2+} doping. The operational stability of the PeLEDs is also judged by T_{50} (the time taken for the luminance to decrease from 100 to 50). The O-PeLEDs showed a T_{50} of $\sim 57.6 \text{ s}$ (Fig. 5f); however, the P-PeLEDs had no effective T_{50} due to their low brightness and rapid quenching. The O-PeLEDs showed better EL properties and stability under electric field, which indicates that Cu^{2+} doping enhanced the radiation recombination and suppressed the ion migration of its perovskite luminescent layer. Though these blue O-PeLEDs appeared with a relatively low EQE and poor operational stability, the successful preparation of mixed-halide blue PeLEDs with Cu^{2+} doping still proves their practical potential and possible prospects in novel optoelectronic devices.

4. Conclusion

In this work, a heteroatomic Cu^{2+} doping strategy and post-treatment Br^- anion exchange were combined to achieve highly efficient deep-blue $\text{CsPb}(\text{Br/Cl})_3$ nanosheets. Benefiting from the Cu^{2+} doping for obviously passivating the chlorine defects and competing with ligands, we successfully synthesized CsPbCl_3 nanosheets with enhanced PL intensity and increased E_B energy. Further, through the Br^- anion exchange, deep-blue $\text{CsPb}(\text{Br/Cl})_3$ nanosheets exhibiting a high PLQY of 94% and humidity stability for 30 days were prepared. The improved performance profited

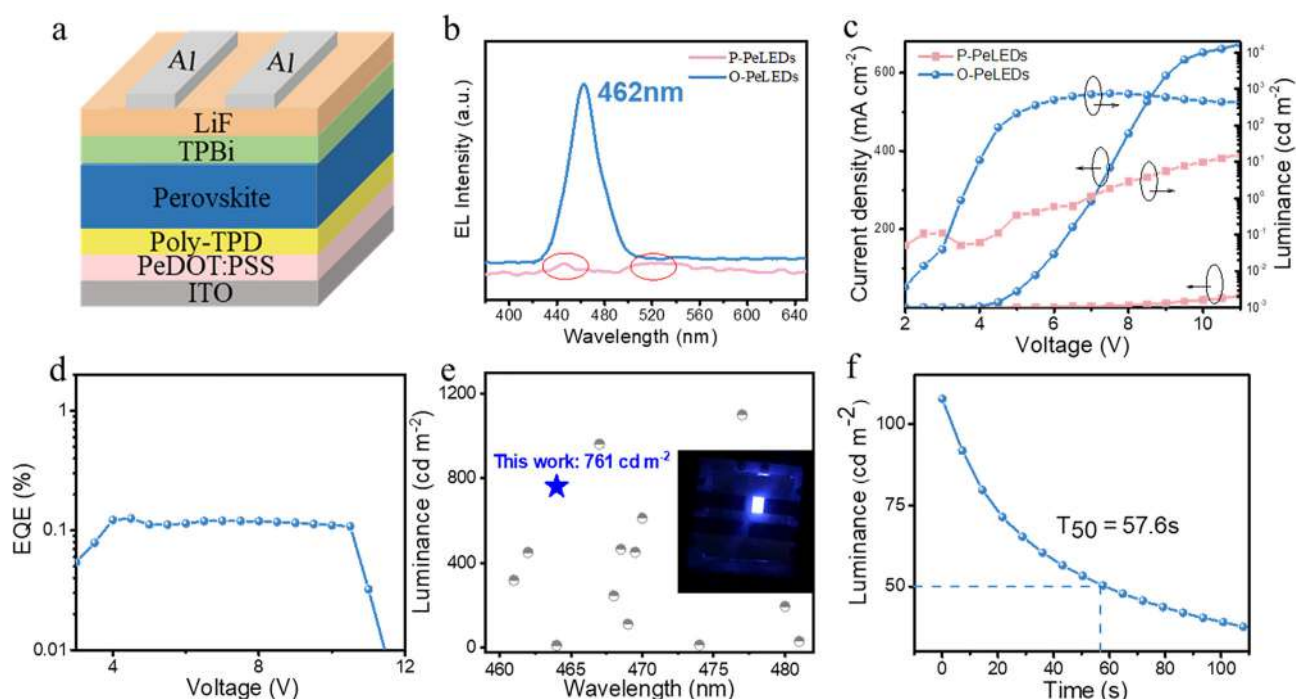


Fig. 5. Capacities of blue PeLEDs. (a) The device structure of the PeLEDs. (b) EL spectra for P-PeLEDs and O-PeLEDs. (c) The J – V – L curves of the blue PeLEDs. (d) EQE versus voltage of the O-PeLEDs. (e) Comparison of the luminance in this work with that in previous reports. Inset: a photo of the O-PeLEDs. (f) Operational stability of the O-PeLEDs.

from an enhanced radiation recombination and inhibited ion migration after Cu^{2+} doping. Based on these modified $\text{CsPb}(\text{Br}/\text{Cl})_3$ nanosheets, we produced blue PeLEDs with an EL peak at 462 nm, maximum luminance of 761 cd m^{-2} , and a current density of 205 mA cm^{-2} , demonstrating great competition with recent reports on deep-blue PeLEDs [62–66]. This work provides an operational preparation strategy for stable and efficient mixed-halide blue perovskites as well as related blue PeLEDs. It also promotes the practical application of mixed-halide blue perovskites in deep-blue high-performance PeLEDs.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jcis.2021.09.061>.

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