Highly Efficient and Stable Eu$^{3+}$-Doped CsPbBr$_3$/Cs$_4$PbBr$_6$ Perovskites for White Light-Emitting Diodes

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1. Introduction

All-inorganic lead halide perovskites (CsPbX$_3$, X = Cl, Br, and I) nanocrystals (PeNCs) are useful materials for optoelectronic devices because of their simple synthesis process, low cost, high photoluminescence quantum yield (PLQY), wide wavelength tunability, and narrow emission bandwidth [1–4]. However, several limitations affect the use of these materials in practical applications: (i) sharply decreased efficiency in solid-states; (ii) poor stability when exposed to water, air, heat, or light; and (iii) the lack of scale preparation materials in practical applications: (i) sharply decreased efficiency in solid-states; (ii) poor stability when exposed to water, air, heat, or light; and (iii) the lack of scale preparation.

Recently, researchers have become interested in a zero-dimensional Cs$_4$PbBr$_6$ perovskite composed of Cs$^+$ and [PbBr$_4$]$^{4-}$ that has a large forbidden band width, emits invisible light in the ultraviolet range, and exhibits extremely high lattice compatibility with CsPbBr$_3$ [8–13]. Therefore, Cs$_4$PbBr$_6$ can be used as a matrix material to improve the fluorescence performance of CsPbBr$_3$ nanocrystals (NCs). For example, Zhong et al. adopted a core/shell structure of CsPbBr$_3$/Cs$_4$PbBr$_6$ and obtained a composite single crystal with a PLQY of up to 90% [14]. Hu et al. used ligand-assisted recrystallization (LARP) to achieve large-scale preparation of Cs$_4$PbBr$_6$/CsPbBr$_3$ microcrystals with a high quantum yield (48.78%) [15]. Although the PLQY of the CsPbBr$_3$/Cs$_4$PbBr$_6$ composites was considerably enhanced, the lack of significant improvement in the optical and thermal stabilities [8,16,17] prevents the composites from meeting practical application requirements.
Doping impurity ions into crystals has been confirmed as an effective and common way to enhance the photoluminescence (PL) stability of traditional colloidal II-VI and III-V semiconductor materials [18]. This strategy is also effective for improving the stability of PeNCs. Zou et al. reported that doping CsPbBr$_3$ NCs with Mn$^{2+}$ ions can stabilize exciton emissions and improve thermal stability. Moreover, first-principles calculations have confirmed that Mn$^{2+}$, Sr$^{2+}$, Sn$^{2+}$, Co$^{2+}$, Zn$^{2+}$, and Cd$^{2+}$-ion-doped CsPbBr$_3$ perovskites have enhanced thermodynamic stability [19–21]. Doping various lanthanide ions (Sm$^{3+}$, Yb$^{3+}$, Ce$^{3+}$, Eu$^{3+}$, Tb$^{3+}$, Er$^{3+}$, and Dy$^{3+}$) into CsPbX$_3$ NCs also enhances PL properties and stability [22,23]. Although doping engineering is an effective way to improve the stability and PL performance of PeNCs, the PLQYs of doped PeNCs are considerably reduced when transformed into solid-states for photoelectric device applications [18,24]. Therefore, synchronously improving the photoluminescence (PL) properties and stability of PeNCs in the solid-state remains a considerable challenge.

Herein, we synthesized green Eu$^{3+}$-doped CsPbBr$_3$/Cs$_4$PbBr$_6$ perovskite composites by a simple recrystallization method at room temperature [25]. The as-prepared composites exhibit a high PLQY of 87%, a narrow full-width-at-half-maximum (FWHM) of 20 nm, and a high product yield of 80%. The doping of Eu$^{3+}$ ions both effectively improves the PL performance of the CsPbBr$_3$/Cs$_4$PbBr$_6$ composite and enhances the water and thermal stabilities. Furthermore, high-efficiency and wide-color-gamut WLEDs were fabricated using this green perovskite composite.

2. Experimental Section

Chemicals: PbBr$_2$ (98%), CsBr (99.9%), oleylamine (OAM, 70%), oleic acid (OA, 90%), and 1-octadecene (ODE, 90%) were purchased from Merck Ltd. Eu(NO$_3$)$_3$·6H$_2$O (98%) and N,N-dimethylformamide (DMF, 99.8%) were obtained from Shanghai Aladdin Biochemical Technology Co., Ltd. (Shanghai, China) Toluene (99.5%) was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China)

Synthesis CsPbBr$_3$/Cs$_4$PbBr$_6$ composite: First, 0.0848 g of CsBr and 0.0369 g of PbBr$_2$ were dissolved in 10 mL of DMF to form a precursor solution. The solution was stirred for 30 min, after which 1 mL of OA and 1 mL OAm were added and continuously stirred for 4 h to ensure that the precursor had completely dissolved. Second, 10 mL of toluene were injected into the precursor solution under vigorous stirring. Third, the solution was centrifuged at 11,000 r·p·m for 10 min to remove impurities. Finally, the purification process was repeated twice to yield a green precipitate that was then dried under vacuum at 50 °C for 12 h to obtain a bright green solid powder.

Eu$^{3+}$-doped CsPbBr$_3$/Cs$_4$PbBr$_6$ perovskite composites: A similar synthesis was performed as for the CsPbBr$_3$/Cs$_4$PbBr$_6$ composite material. First, 0 (0%), 0.2 (9%), 0.4 (16.7%), and 0.6 (23.1%) mmol Eu(NO$_3$)$_3$·6H$_2$O were dissolved in 10 mL of DMF solution and stirred for 10 min. Then, 0.0848 g of CsBr and 0.0369 g of PbBr$_2$ were added to the resulting solution, and stirring was continued for 30 min to form a body solution. The subsequent steps were similar to those used to synthesize the abovementioned CsPbBr$_3$/Cs$_4$PbBr$_6$ perovskite composites.

Fabrication of WLEDs: Green Eu$^{3+}$-doped CsPbBr$_3$/Cs$_4$PbBr$_6$ perovskite composites (16.7%), red K$_2$SiF$_6$:Mn$^{4+}$ phosphor, and AB organic silicone (in an A-to-B mass ratio of 1:2) were added to a mortar and stirred well until all bubbles disappeared completely, after which the obtained product was spread evenly. Next, the product was coated onto a blue InGaN LED chip and heated and cured in an oven at 120 °C for 2 h. A WLED for optical performance testing was thus successfully fabricated.

Characterization: PL spectra were measured by a spectrofluorophotometer (Horiba Jobin Yvon, FluoroMax-4). The photoluminescence quantum yield (PLQY) is defined as the fraction of absorbed photons that are emitted [26]. In this study, the integrating sphere
(Horiba Jobin Yvon, F3029) was used to measure and calculate the PLQY. The following formula was used to calculate the PLQY:

\[ PLQY = \frac{E_a - E_b}{L_a - L_b} \]

where \( E_a \) is the fluorescence emission of the sample, \( L_a \) is the scattering of the sample, \( E_b \) is the fluorescence emission of the background and \( L_b \) is the scattering of the background.

UV/vis absorption spectra of the as-prepared composites were measured by using a spectrophotometer (Hitachi U-3900, Tokyo, Japan). The phase of the material was qualitatively and quantitatively analyzed by a D-MAX 2200 VPC ray diffractometer from Rigaku, Tokyo, Japan. TEM data of the composites were obtained by a JEM-2100 high-resolution transmission electron microscope (HRTEM, JEOL, Tokyo, Japan). The performance parameters (the luminous efficiency, color rendering index, color coordinates, spectrum, color temperature, etc.) of the WLED devices were investigated by using a small uniform light source system (USS-600C, American Bluefield Optics, Sutton, NH, USA).

3. Results and Discussion

3.1. Morphology and Structure

Figure 1a shows the XRD patterns of undoped and Eu\(^{3+}\)-doped CsPbBr\(_3\)/Cs\(_4\)PbBr\(_6\) perovskite composites with different doping concentrations of Eu\(^{3+}\) ions. The diffraction peaks correspond to the hexagonal Cs\(_4\)PbBr\(_6\) perovskite (JCPDS No. PDF#73-2478) and the cubic CsPbBr\(_3\) perovskite (JCPDS No. PDF#54-0752), which confirms the formation of CsPbBr\(_3\)/Cs\(_4\)PbBr\(_6\) perovskite composites. Due to the limited X-ray penetration depth of the XRD diffractometer and the low proportion of CsPbBr\(_3\) in the composite, diffraction peaks of CsPbBr\(_3\) were not detected in the XRD pattern [27]. Doping with Eu\(^{3+}\) resulted in significant changes in the peak positions and intensities of the perovskite diffractogram. The enlargement of the XRD peaks at approximately 34.2° (Figure 1b) shows a clear redshift as the Eu\(^{3+}\) doping concentration increases. This result can be attributed to the partial replacement of Pb\(^{2+}\) (119 pm) in the composites by Eu\(^{3+}\) with a smaller ion radius (94.7 pm), leading to lattice shrinkage. The decrease in the intensity of the diffraction peaks at approximately 39° may be attributed to the decrease in crystallinity caused by Eu\(^{3+}\) doping [28–30].

![Figure 1](image_url) (a) XRD patterns and (b) magnified XRD patterns of CsPbBr\(_3\)/Cs\(_4\)PbBr\(_6\) and CsPbBr\(_3\)/Cs\(_4\)PbBr\(_6\):Eu\(^{3+}\) with different Eu\(^{3+}\) doping concentrations.

Transmission electron microscopy (TEM) was carried out to determine the morphological characteristics of the undoped and Eu\(^{3+}\)-doped perovskite composites. Figure 2a shows that the CsPbBr\(_3\)/Cs\(_4\)PbBr\(_6\) composites are ball-shaped with poor size distribu-
These results can be explained in terms of the successful doping of Eu\(^{3+}\) ions. The enlarged TEM image (Figure 2e) shows many smaller particles embedded into the composites. The high-resolution TEM (HR-TEM) image (Figure 2f) shows lattice spacings of 0.346 and 0.290 nm that correspond to the (111) plane of cubic-phase CsPbBr\(_6\) and the (223) plane of hexagonal-phase Cs\(_4\)PbBr\(_6\), respectively, confirming the coexistence of CsPbBr\(_3\) and Cs\(_4\)PbBr\(_6\) [31].

Figure 2. TEM images of (a) Undoped CsPbBr\(_3\)/Cs\(_4\)PbBr\(_6\) and (b–d) CsPbBr\(_3\)/Cs\(_4\)PbBr\(_6\):Eu\(^{3+}\) composite with different Eu\(^{3+}\) doping concentrations (e) Enlarged TEM image of the CsPbBr\(_3\)/Cs\(_4\)PbBr\(_6\):Eu\(^{3+}\) composites with an Eu\(^{3+}\) doping concentration of 16.7% (f) HR-TEM image of CsPbBr\(_3\)/Cs\(_4\)PbBr\(_6\):Eu\(^{3+}\) composites with an Eu\(^{3+}\) doping concentration of 16.7%.

Figure 3a shows the XPS spectra of the CsPbBr\(_3\)/Cs\(_4\)PbBr\(_6\) and CsPbBr\(_3\)/Cs\(_4\)PbBr\(_6\):Eu\(^{3+}\) perovskite composites. Compared with the undoped CsPbBr\(_3\)/Cs\(_4\)PbBr\(_6\) composite (black curve), the spectrum of the CsPbBr\(_3\)/Cs\(_4\)PbBr\(_6\):Eu\(^{3+}\) composites (red curve) exhibits a new peak at 1135 eV (the high-resolution Eu 3d XPS spectrum is shown in Figure 3b), corresponding to 3d\(_{5/2}\) Eu\(^{3+}\) [28]. Furthermore, the incorporation of Eu\(^{3+}\) ions (Figure 3c–e) results in significantly reduced binding energies of the 4f\(_{5/2}\) and 4d\(_{7/2}\) orbitals of Pb\(^{2+}\). These results can be explained in terms of the successful doping of Eu\(^{3+}\) ions that replace Pb\(^{2+}\) in the CsPbBr\(_3\)/Cs\(_4\)PbBr\(_6\) perovskite composites [28]. To determine the actual doping concentration of Eu\(^{3+}\) in the perovskite composites, energy dispersion spectroscopy (EDS) and inductively coupled plasma atomic emission spectrometry (ICP–AES) tests were performed, and the results are shown in Figure S1 and Table S1. The actual atomic ratios of Eu/Pb in the composites were 0%, 0.084%, 0.117%, and 0.065% for the 0%, 9%, 16.7%, and 28.6% Eu\(^{3+}\) doping concentrations, respectively, which confirms the successful doping of Eu\(^{3+}\) into the CsPbBr\(_3\)/Cs\(_4\)PbBr\(_6\) composites.
The effect of Eu$^{3+}$ doping on the fluorescence kinetics of the CsPbBr$_3$/Cs$_4$PbBr$_6$ composites was investigated. In this study, the time-resolved PL decay (excitation wavelength of 445 nm) was measured for pure CsPbBr$_3$/Cs$_4$PbBr$_6$ composites and CsPbBr$_3$/Cs$_4$PbBr$_6$:Eu$^{3+}$ composites with different doping concentrations. Figure 4d shows the PL decay curves of pure CsPbBr$_3$/Cs$_4$PbBr$_6$ composites and CsPbBr$_3$/Cs$_4$PbBr$_6$:Eu$^{3+}$ composites with different doping concentrations monitored at 520 nm. All the decay curves of the CsPbBr$_3$/Cs$_4$PbBr$_6$:Eu$^{3+}$ composites with different Eu$^{3+}$ doping concentrations could be fitted by a biexponen-
tial function. The decay lifetimes could be divided into a fast component $\tau_1$ (nonradiative recombination) and a slow component $\tau_2$ (radiative recombination) [31]. As the Eu$^{3+}$ doping concentration increased from 0% to 16.7%, the average lifetime of the composites increased from 9.49 ns to 24.31 ns (Table S2). However, as more Eu$^{3+}$ ions were doped into the composite, the average lifetime decreased to 17.39 ns, indicating an increase in nonradiative recombination. Thus, an appropriate quantity of an Eu$^{3+}$ dopant can increase the PLQY of the composites because of an increase in the defect formation energy. However, overdoping increases the number of defects introduced into the composites, reducing the PLQY [28].

![Figure 4. CsPbBr$_3$/Cs$_4$PbBr$_6$:Eu$^{3+}$ composites with different Eu$^{3+}$ doping concentrations: (a) absorption spectra, (b) PL spectra, (c) PL peak position and intensities, and (d) PL decay curves.](image)

### 3.3. Stability of CsPbBr$_3$/Cs$_4$PbBr$_6$:Eu$^{3+}$ Composites

To test the thermal stability of the Eu$^{3+}$-doped perovskite composites, the pure and Eu$^{3+}$-doped CsPbBr$_3$/Cs$_4$PbBr$_6$ composites were heated from 280 K to 430 K. Figure 5a,b show the temperature-dependent PL spectra of the CsPbBr$_3$/Cs$_4$PbBr$_6$ composites and CsPbBr$_3$/Cs$_4$PbBr$_6$:16.7% Eu$^{3+}$ composites, respectively. Interestingly, approximately 81% of the initial relative PL intensity (Figure 5c) of the Eu$^{3+}$-doped perovskite composites was preserved when the temperature increased to 305 K, indicating the doped composite exhibited higher thermal stability than that of the pure perovskite composites (66%).

Moreover, the doped composites maintained 30% of the initial PL intensity when the temperature increased to 430 K. The water stability of the CsPbBr$_3$/Cs$_4$PbBr$_6$@PMMA and CsPbBr$_3$/Cs$_4$PbBr$_6$:Eu$^{3+}$@PMMA composites was tested by immersing the composites in water for different periods of time (Figure 5d,e). The relative PL intensity (Figure 5f) of the Eu$^{3+}$-doped CsPbBr$_3$/Cs$_4$PbBr$_6$@PMMA composites that had been immersed in water for five days remained at 94% of the initial intensity, which was much higher than that of the CsPbBr$_3$/Cs$_4$PbBr$_6$@PMMA composites (27%). The long-term water stability of the doped composites was also evaluated. The relative PL intensity of the doped composites remained at 64% of the initial value after 30 days, whereas the undoped sample exhibited almost no fluorescence. These results demonstrate that Eu$^{3+}$-doped CsPbBr$_3$/Cs$_4$PbBr$_6$ composites exhibit superior thermal and water stabilities to those of the pure CsPbBr$_3$/Cs$_4$PbBr$_6$ composites. Figure S2 shows the light stability of CsPbBr$_3$/Cs$_4$PbBr$_6$ and CsPbBr$_3$/Cs$_4$PbBr$_6$:Eu$^{3+}$
under the illumination of a 365-nm LED lamp with a power density of 175 mW/cm². The doped composites are clearly more stable than the pure composites. Irradiation for 2 h caused the PL intensity of CsPbBr₃/Cs₄PbBr₆ to almost vanish, whereas the luminescence intensity of CsPbBr₃/Cs₄PbBr₆:Eu³⁺ remained at approximately 30% of the initial value. The increase in the crystal formation energy after doping Eu³⁺ into the CsPbBr₃/Cs₄PbBr₆ composites may explain the enhanced stability of the CsPbBr₃/Cs₄PbBr₆:Eu³⁺ composites over that of the pure composites [22,34–37].

Figure 5. Temperature-dependent (280 K–430 K) PL spectra of (a) CsPbBr₃/Cs₄PbBr₆ composites and (b) CsPbBr₃/Cs₄PbBr₆: Eu³⁺ composites. (c) Relative PL intensity of undoped and Eu³⁺-doped CsPbBr₃/Cs₄PbBr₆ composites as a function of temperature. PL spectra of (d) CsPbBr₃/Cs₄PbBr₆@PMMA composites and (e) CsPbBr₃/Cs₄PbBr₆: Eu³⁺@PMMA composites immersed in water for different times. (f) Relative PL intensity of undoped and Eu³⁺-doped CsPbBr₃/Cs₄PbBr₆@PMMA composites as a function of the time immersed in water.
3.4. WLED Applications

A white light-emitting diode (WLED, Figure 6a) was fabricated by combining green CsPbBr\(_3\)/Cs\(_4\)PbBr\(_6\):Eu\(^{3+}\) with a commercial red K\(_2\)SiF\(_6\):Mn\(^{4+}\) phosphor and blue InGaN chips. Figure 6b,c shows the electroluminescence spectrum of the device driven at a current of 20 mA, which exhibits three emission bands centered at 460 nm (blue), 521 nm (green), and 631 nm (red), corresponding to the blue chip, CsPbBr\(_3\)/Cs\(_4\)PbBr\(_6\):Eu\(^{3+}\), and KSF phosphors, respectively. The WLED exhibits a bright emission with a high luminous efficiency of 43.06 lm/W and color coordinates of (0.3345,0.3276). Figure 6d shows the triangle region generated by plotting the RGB chromaticity coordinates as (0.635,0.325), (0.091,0.803), and (0.144,0.030) on the CIE 1931 chromaticity diagram. The calculated color gamut is 125% of that of the National Television System Committee (NTSC) color gamut. This result is higher than those of conventional phosphor-based WLEDs (86% of the NTSC color gamut) and Cd-based quantum dot-based WLEDs (115% of the NTSC color gamut) [38–43]. These results indicate the potential of green CsPbBr\(_3\)/Cs\(_4\)PbBr\(_6\):Eu\(^{3+}\) perovskite composites for use in LCD displays.

![Image](image-url)

**Figure 6.** (a) Photograph of a WLED based on green CsPbBr\(_3\)/Cs\(_4\)PbBr\(_6\):Eu\(^{3+}\), red KSF phosphors, and a blue LED chip. (b) Photograph and (c) EL spectrum of the WLED driven at 20 mA. (d) The color coordinates of the WLEDs and the NTSC are shown in a CIE 1931 diagram.

4. Conclusions

In summary, green Eu\(^{3+}\)-doped CsPbBr\(_3\)/Cs\(_4\)PbBr\(_6\) perovskite composites were successfully synthesized by a recrystallization method at room temperature. These composites show bright green emission centered at 520 nm with a FWHM of 21 nm and a high PLQY of 87%. The doped perovskite composites exhibit enhanced water and thermal stability over those of undoped composites, while exhibiting excellent optical properties. Consequently, the green composites were used to fabricate WLEDs with a high luminous efficacy of 43.06 lm/W and a wide color gamut (124% of the NTSC standard).
Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/coatings12040512/s1, Figure S1: The ratio of the concentration of Eu³⁺ to Pb²⁺ corresponds to the actual doping concentration of Eu³⁺ ions measured by ICP-AES. Figure S2: Photostability of the CsPbBr₃/Cs₂PbBr₆, CsPbBr₃/Cs₄PbBr₆:Eu³⁺. Table S1: CsPbBr₃/Cs₂PbBr₆:Eu³⁺: The addition content of Eu/Pb molar ratio and Eu in precursor synthesis and actual Eu³⁺ content tested by ICP and EDS measurement., Table S2: Average lifetimes of CsPbBr₃/Cs₄PbBr₆ and CsPbBr₃/Cs₂PbBr₆:Eu³⁺ composites.

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