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Unraveling the Moisture-induced Decomposition Mechanism of Red-Emitting Perovskite CsPbBrI₂ Nanocrystals and Enhancing their Stability through Copper(II) Substitution

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ABSTRACT

The implementation of red-emitting perovskite CsPb(Br_xI_{1-x})₃ (0 < x < 1) nanocrystals (NCs) is hindered because of their low structural stability, and the moisture-induced degradation pathways of these red-emitting perovskite are not well-defined. In the present work, we show that the moisture-induced degradation of CsPbBrI₂ NCs spontaneously forms CsPbBr₃ (α) and CsPbI₃(δ) and other decomposition products. On the other hand, highly stable and luminescent red perovskite CsPbBrI₂ NCs were achieved through copper substitution and halide rich passivation strategy. We demonstrated that the incorporation of Cu²⁺ ions can enhance formation energy, causing a slight lattice contraction, and hence stabilize the cubic phase of these NCs. Cu²⁺-substituted CsPbBrI₂ NCs with higher luminescence were synthesized in a halide-rich passivation method. The highly stable and luminescent Cu²⁺-substituted CsPbBrI₂ NCs can function well as efficient light emitters toward the fabrication of high-performance red perovskite LEDs.

Keywords: CsPbBrI₂, perovskite nanocrystals, copper-substitution, stability, light-emitting diodes

1. INTRODUCTION

Lead halide perovskites exhibit significant potential for light-emitting diodes (LEDs) because of their high photoluminescence quantum yields (PLQYs), high colour purity and a narrow full-width at half-maximum (FWHM) over the entire visible spectrum[1, 2]. Among various CsPbX₃ NCs, achieving highly stable and luminescent red perovskite NCs whose emission peak wavelength is centered at 630 nm is a key target for present research (Rec. 2020)[3]. Red-emitting perovskite nanocrystals can be achieved by mixed-halide of bromine and iodine, but the mixed-halide will lower stability of the NCs because of soft basic nature of I⁻ as well as weaker bond strength of Pb-I. And the rapid drop of photoluminescence quantum yield (PL QY), shape transformation, and phase transition of CsPb(Br_xI_{1-x})₃ NCs will limit their

practical use[4]. More recently, Pb-site doping or alloying with other metal ions has been demonstrated to be another means to improve the stability of perovskite NCs because of influencing the formation energy and the Goldschmidt's tolerance factor[5].

In this study, we report for the first time on the moisture-induced degradation pathways of these red-emitting perovskite CsPb(Br_xI_{1-x})₃ NCs, we found that the instability of pristine CsPbBrI₂ NCs may mainly result from the lower band strength of Pb-I. From the XRD patterns and PL emission intensity results, we found that the moisture-induced degradation of CsPbBrI₂ NCs spontaneously forms CsPbBr₃ (α) and CsPbI₃(δ) and other decomposition products. On the other hand, we present highly effective copper(II) substitution and halide rich passivation strategy to obtain highly stable and luminescent red perovskite α-CsPbBrI₂ NCs whose emission peak wavelength is centered at ~630 nm. Density functional theory (DFT) analyses reveal that the substitution of Pb²⁺ by Cu²⁺ can enhance formation energy of CsPbBrI₂ NCs, which is beneficial to the stability of CsPbBrI₂ NCs. Moreover, halide-rich passivation Cu²⁺-substituted CsPbBrI₂ NCs were synthesized with higher luminescence. Benefiting from such greatly improved stability and optical performance, these halide-rich Cu²⁺-substituted CsPbBrI₂ NCs can be used as efficient light emitters to fabricate PeLEDs with higher optical performance.

2. RESULTS AND DISCUSSION

The PL spectra also shown that with increasing the incorporation amount of Cu²⁺ dopant, the PL emission peak of NCs underwent a blue-shift from 630 to 621 nm (**Fig. 1a**). The PL spectra was observed to rise first and then decrease with increasing the substituted concentration of Cu²⁺-ion, and the PLQY increased from 70.5% for pristine NCs to 81.3% for Cu²⁺-substituted NCs and then decreased to 42.5% with further increase in the amount of Cu²⁺, suggesting that the Cu²⁺ ion has a significant impact on the optical properties of the NCs. The PL QY of halide-rich Cu²⁺-substituted CsPbBrI₂ NCs can reach up to 94.8% when the ratio of Pb:X is 1:5 in the precursors (**Fig. 1b**), and the stabilities of these halide rich Cu²⁺-substituted

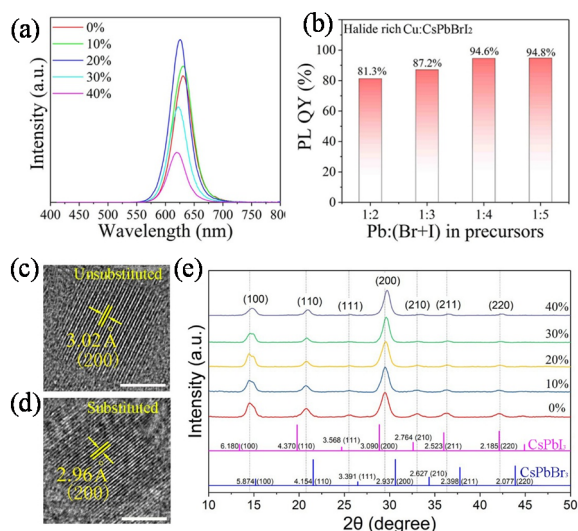
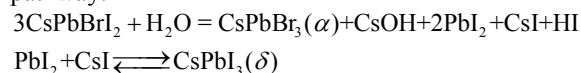


Figure. 1 (a) PL spectra (excitation at 365 nm) of pristine and substituted CsPbBr₂ NCs with different Cu/Pb ratios; (b) PL QY values of halide rich Cu²⁺-substituted CsPbBr₂ NCs; (c) and (d) HR-TEM images of unsubstituted CsPbBr₂ and Cu²⁺-substituted CsPbBr₂ NCs (scale bars: 5 nm); (e) PXRD patterns of Cu²⁺-substituted CsPbBr₂ NCs with different Cu²⁺ concentrations.

CsPbBr₂ NCs were also excellent. High resolution transmission electron microscopy (HR-TEM) images for pristine and Cu²⁺-substituted CsPbBr₂ NCs are presented in **Fig. 1c-d**. The interplanar distances of (200) plane of unsubstituted and substituted CsPbBr₂ NCs are determined to be 3.02 and 2.96 Å respectively, lattice contraction of Cu²⁺-substituted CsPbBr₂ NCs can be seen due to the smaller ionic radius of Cu²⁺ than that of Pb²⁺. X-ray diffraction (XRD) was measured to identify the crystal structure of pristine CsPbBr₂ NCs and Cu²⁺-substituted CsPbBr₂ NCs, and the results are shown in **Fig. 1e**. All of the samples possess same crystalline structure of cubic phase and no overall structural change, indicating that the Cu²⁺-substituted would retain the structure of the perovskite host. Moreover, the peak position of (200) of as-synthesized CsPbBr₂ NCs slightly shifted toward higher angle with increasing the Cu²⁺ concentration, implying that the amount of Cu²⁺ dopants in the CsPbBr₂ NCs is increased, which provides a solid evidence to manifest the successful substituted of Cu²⁺ ion in the lattices of CsPbBr₂ NCs.

The humidity stability for NCs was investigated by coating them on the surface of a glass slide, and the glasses were placed into a temperature and humidity chamber at 25 °C and 85% relative humidity (RH). The inset figure in **Fig. 2a** shows that the red PL brightness for pristine CsPbBr₂ NCs underwent a striking degradation to be nonluminescent within 2 days and translated to green PL brightness with a further increase in the exposure time. **Fig. 2a** shows that the PL emission intensity of pristine CsPbBr₂ NCs decreased distinctly after aging 1 day, and a PL emission peak at 520 nm appeared at 2 days, the PL emission intensity of 520 nm initially increased and then decreased with the aging time going on. By contrast, a much slower degradation rate of red PL brightness and PL emission intensity can be observed for all Cu²⁺-substituted

CsPbBr₂ NCs films even after 15 days storage (**Fig. 2b**), suggesting that the Cu²⁺-substituted CsPbBr₂ NCs are very stable. The corresponding XRD patterns revealed that the degraded products of pristine CsPbBr₂ NCs, as displayed in **Fig. 2c**. Notably, the peak at 15.2° indicated the existence of a small amount of CsPbBr₃ after aging 2 days, and other decomposition products, including PbX₂, CsX, PbO_x, CsOH and yellow-phase CsPbI₃ (δ), can also be observed from the XRD patterns. So, the green emission and the PL emission peak at 520 nm may originate from the CsPbBr₃(α), which means that CsPbBr₂ NCs will decompose to CsPbBr₃ and other decomposition products when stored in a humid environment. For the all-inorganic perovskite CsPbBr₂ NCs, the pathways for moisture-induced degradation are not well-defined, but from our XRD and PL emission intensity results and previous report, we can conclude that the instability of pristine CsPbBr₂ NCs may mainly result from the lower band strength of Pb-I, in other words, the band of Pb-I in the pristine CsPbBr₂ NCs will collapse firstly in the presence of moisture, resulting in a serious phase separation. From above discussions, pristine CsPbBr₂ NCs may suffer from severe degradation by the following decomposition pathway:



With the aging time going on, a slower degradation rate of green PL brightness can be seen, this is because the band strength of Pb-Br is stronger and the decomposition products can act as a buffer layer between water and CsPbBr₃(α). Meanwhile, the absolute value of formation energy ΔE_{form} of the samples calculated from Density functional theory (DFT) analyses increased in the content of Cu²⁺ at

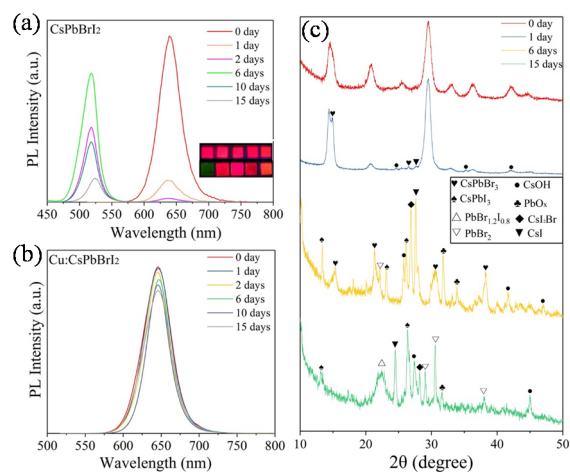


Figure. 2 The PL spectra (excitation at 365 nm) of (a) the pristine CsPbBr₂ and (b) nominal 20% Cu²⁺-substituted CsPbBr₂ NCs films with different aging times under a temperature and humidity chamber with 25 °C and 85% relative humidity (RH); (c) XRD spectra of unsubstituted CsPbBr₂ NCs films with different aging times under a temperature and humidity chamber with 25 °C and 85% relative humidity (RH). The inset in (a) shows photograph of the films under the 365 nm excitation aging at different time (up: day 0 and below: day 15).

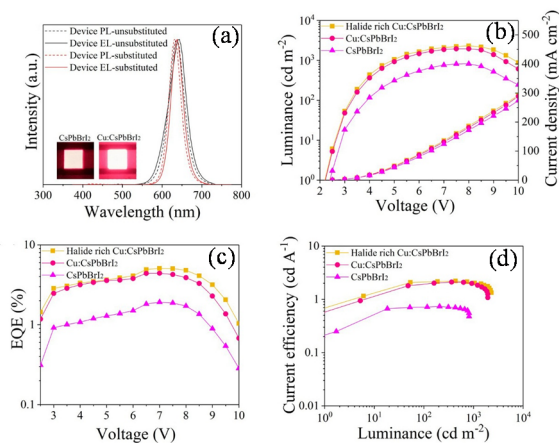


Figure 3 (a) EL spectrum at an applied voltage of 4 V and their corresponding PL emission spectra for unsubstituted and Cu²⁺-substituted CsPbBr₂ based PeLED devices. Inset shows the photo of the corresponding devices at an applied voltage of 4 V; (b) current density and luminance as a function of voltage; (c) EQE of these devices as a function of driving voltage (V); (d) Current efficiency of these devices as a function of luminance.

3.7 mol % but decreased in the content of Cu²⁺ at 5.56 mol %, indicating that Cu²⁺ cations partly replacing the Pb²⁺ ions in the lattice structure of CsPbBr₂ NCs can stabilize the α -CsPbBr₂ NCs. From the above discussion, it is easy to draw a conclusion that the reason for highly stable of Cu²⁺-substituted CsPbBr₂ NCs is the comprehensive effect of Cu²⁺ and Br⁻ ion.

The pristine CsPbBr₂ NCs and Cu²⁺-substituted CsPbBr₂ NCs (Cu/Pb practical ratio: 3.15%) and halide rich Cu²⁺-substituted CsPbBr₂ NCs were adopted as light emitters for PeLED fabrication. The as-fabricated PeLEDs structures are ITO/ZnO/PEI/NCs/TCTA/MoO₃/Al. **Fig. 3a** shows the normalized device electroluminescence (EL) and device PL spectra of pristine CsPbBr₂ and Cu²⁺-substituted CsPbBr₂ NCs based PeLEDs. The EL of Cu²⁺-substituted CsPbBr₂ NCs based PeLEDs device were narrower than that of unsubstituted device, suggesting a high color purity. Voltage–luminance and voltage–current density curves of PeLEDs are presented in **Fig. 3b**. Obviously, in the whole voltage range, the Cu²⁺-substituted CsPbBr₂ NCs based PeLEDs have better luminance than that of the unsubstituted ones. In addition, the turn-on voltage required for the Cu²⁺-substituted CsPbBr₂ NCs based PeLEDs device (2.2 V) is lower than that of the PeLED based on unsubstituted CsPbBr₂ NCs (2.4 V), indicating that an efficient, barrier-free charge injection into the NCs emitters was achieved. Meanwhile, the EQE and current efficiency (CE) as a function for typical CsPbBr₂ NCs based PeLEDs are also shown in **Fig. 3c-d**, respectively. The luminosity characteristics of unsubstituted NCs based LEDs were poorer, in which the maximum CE and EQE were only 0.73 cd A⁻¹ and 1.9%, respectively, while the maximum CE and EQE were 2.1 cd A⁻¹ and 4.4% for Cu²⁺-substituted CsPbBr₂ NCs based PeLEDs, and 2.2 cd A⁻¹ and 5.1%

for halide rich Cu²⁺-substituted CsPbBr₂ NCs. In addition, the operation stability of Cu²⁺-substituted CsPbBr₂ NCs based PeLEDs was improved. This is clearly manifesting the advantages of Cu²⁺-substituted CsPbBr₂ NCs and halide rich Cu²⁺-substituted CsPbBr₂ NCs against the pristine ones for high-performance red PeLEDs.

3. CONCLUSIONS

In summary, the moisture-induced degradation pathways of these red-emitting perovskite CsPbBr₂ NCs were discussed. Highly stable and luminescent red perovskite Cu²⁺-substituted CsPbBr₂ NCs were prepared through a simple hot injection method. The Pb-halide bonds strength and stability of CsPbBr₂ NCs are increased after copper(II) substitution. Moreover, halide-rich passivation Cu²⁺-substituted CsPbBr₂ NCs were synthesized to improve PL QY. As a result, these high-quality perovskite Cu:CsPbBr₂ NCs help us to fabricate efficient red perovskite light-emitting diodes. The PeLEDs utilizing these halide-rich Cu:CsPbBr₂ NCs as emissive layers showed a promoted performance with the maximum EQE of 5.1%.

4. ACKNOWLEDGMENTS

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