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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(Br₁₋ₓIₓ)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 CsPbBr₁ (α) and CsPbI₃ (δ) and other decomposition products. On the other hand, highly stable and luminescent red perovskite CsPbBr₁ 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 CsPbBr₁ NCs with higher luminescence were synthesized in a halide-rich passivation method. The highly stable and luminescent Cu²⁺-substituted CsPbBr₁ NCs can function well as efficient light emitters toward the fabrication of high-performance red perovskite LEDs.

Keywords: CsPbBr₁, 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(Br₁₋ₓIₓ)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(Br₁₋ₓIₓ)₃ NCs, we found that the instability of pristine CsPbBr₁₂ 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 CsPbBr₁₂ NCs spontaneously forms CsPbBr₁ (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-CsPbBr₁₂ 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 CsPbBr₁₂ NCs, which is beneficial to the stability of CsPbBr₁₂ NCs. Moreover, halide-rich passivation Cu²⁺-substituted CsPbBr₁₂ NCs were synthesized with higher luminescence. Benefiting from such greatly improved stability and optical performance, these halide-rich Cu²⁺-substituted CsPbBr₁₂ 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 CsPbBr₁₂ 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
Intensity can be observed for all Cu-degradation rate of red PL brightness with a further increase in the exposure time. The PL emission intensity results and pervious report, we can conclude that the instability of pristine CsPbBrI NCs may mainly result from the lower band strength of Pb-I, in other words, the band of Pb-I in the pristine CsPbBrI NCs will collapse firstly in the presence of moisture, resulting in a serious phase separation. From above discussions, pristine CsPbBrI NCs may suffer from severe degradation by the following decomposition pathway:

$$3\text{CsPbBr}_I + \text{H}_2\text{O} = \text{CsPbBr}_I(\alpha) + \text{CsOH} + 2\text{PbI}_2 + \text{CsI} + \text{HI}$$

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 CsPbBrI(α). Meanwhile, the absolute value of formation energy $\Delta E_{\text{form}}$ of the samples calculated from Density functional theory (DFT) analyses increased in the content of Cu$^{2+}$ at CsPbBrI NCs films even after 15 days storage (Fig. 2b), suggesting that the Cu$^{2+}$-substituted CsPbBrI NCs are very stable. The corresponding XRD patterns revealed that the degraded products of pristine CsPbBrI NCs, as displayed in Fig. 2c. Notably, the peak at 15.2° indicated the existence of a small amount of CsPbBrI after aging 2 days, and other decomposition products, including PbX$_2$, CsX, PbO, CsOH and yellow-phase CsPbI$_3$ (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 CsPbBrI(α), which means that CsPbBrI NCs will decompose to CsPbBr$_3$ and other decomposition products when stored in a humid environment. For the all-inorganic perovskite CsPbBrI NCs, the pathways for moisture-induced degradation are not well-defined, but from our XRD and PL emission intensity results and pervious report, we can conclude that the instability of pristine CsPbBrI NCs may mainly result from the lower band strength of Pb-I, in other words, the band of Pb-I in the pristine CsPbBrI NCs will collapse firstly in the presence of moisture, resulting in a serious phase separation. From above discussions, pristine CsPbBrI NCs may suffer from severe degradation by the following decomposition pathway:

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3.7 mol % but decreased in the content of Cu$^{2+}$ at 5.56 mol %, indicating that Cu$^{2+}$ cations partly replacing the Pb$^{2+}$ ions in the lattice structure of CsPbBrI$_2$ NCs can stabilize the α-CsPbBrI$_2$ NCs. From the above discussion, it is easy to draw a conclusion that the reason for highly stable of Cu$^{2+}$-substituted CsPbBrI$_2$ NCs is the comprehensive effect of Cu$^{2+}$ and Br$^{-}$ ion.

The pristine CsPbBrI$_2$ NCs and Cu$^{2+}$-substituted CsPbBrI$_2$ NCs (Cu/Pb practical ratio: 3.15%) and halide rich Cu$^{2+}$-substituted CsPbBrI$_2$ NCs were adopted as light emitters for PeLED fabrication. The as-fabricated PeLEDs structures are ITO/ZnO/PEI/NCs/TCTA/MoO$_3$/Al. Fig. 3a shows the normalized device electroluminescence (EL) and device PL spectra of pristine CsPbBrI$_2$ and Cu$^{2+}$-substituted CsPbBrI$_2$ NCs based PeLEDs. The EL of Cu$^{2+}$-substituted CsPbBrI$_2$ NCs based PeLEDs device were narrow 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 Cu$^{2+}$-substituted CsPbBrI$_2$ NCs based PeLEDs device have better luminance than that of the unsubstituted ones. In addition, the turn-on voltage required for the Cu$^{2+}$-substituted CsPbBrI$_2$ NCs based PeLEDs device (2.2 V) is lower than that of the PeLED based on unsubstituted CsPbBrI$_2$ 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 CsPbBrI$_2$ 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 Cu$^{2+}$-substituted CsPbBrI$_2$ NCs based PeLEDs, and 2.2 cd A$^{-1}$ and 5.1% for halide rich Cu$^{2+}$-substituted CsPbBrI$_2$ NCs. In addition, the operation stability of Cu$^{2+}$-substituted CsPbBrI$_2$ NCs based PeLEDs was improved. This is clearly manifesting the advantages of Cu$^{2+}$-substituted CsPbBrI$_2$ NCs and halide rich Cu$^{2+}$-substituted CsPbBrI$_2$ NCs against the pristine ones for high-performance red PeLEDs.

3. CONCLUSIONS

In summary, the moisture-induced degradation pathways of these red-Emitting perovskite CsPbBrI$_2$ NCs were discussed. Highly stable and luminescent red perovskite Cu$^{2+}$-substituted CsPbBrI$_2$ NCs were prepared through a simple hot injection method. The Pb-halide bonds strength and stability of CsPbBrI$_2$ NCs are increased after copper(I) substitution. Moreover, halide-rich passivation Cu$^{2+}$-substituted CsPbBrI$_2$ NCs were synthesized to improve PL QY. As a result, these high-quality perovskite Cu:CsPbBrI$_2$ NCs help us to fabricate efficient red perovskite light-emitting diodes. The PeLEDs utilizing these halide-rich Cu:CsPbBrI$_2$ NCs as emissive layers showed a promoted performance with the maximum EQE of 5.1%.

4. ACKNOWLEDGMENTS

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5. REFERENCES


