Lead-free Copper-based Halides with Bright Emission

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Lead halide perovskites especially for cesium lead halides ($CsPbX_3$, X= Cl, Br, and I) are well known for their outstanding optoelectronic properties. However, the intrinsic toxicity of lead restricts their further applications. Recently, copper has been emerged as a potential candidate for the replacement of lead because of its abundance and low price, and the structural, compositional, and stoichiometric flexibility of the copper-based compounds. Moreover, ternary copper halides have been used to fabricate optoelectronic devices such as light-emitting diodes (LEDs), photodetectors, and X-ray scintillators, which encourages people to further explore the synthesis and applications of copper-based compounds.

Herein, we synthesized a series of all-inorganic and organic-inorganic ternary copper halides as single crystals, nanocrystalline or microcrystalline suspensions with bright emission from deep blue to red as shown in Fig.1.[1,2] $Cs_3Cu_2X_5$ (X = I, Br/I, Br, Br/Cl, and Cl) and $CsCu_2I_3$ nanocrystals were synthesized by the antisolvent method and the hot injection method. They possess composition tunable emission spectra over the spectral region of 440-530 nm, a high photoluminescence quantum yield (PLQY) of ~100% for X = Cl, and large effective Stokes shifts over 100 nm for all species. These NCs can be purified and used as the inkjet printing ink for array patterned film, and the white light can be realized by tuning the ratio of $Cs_3Cu_2Cl_5$, $Cs_3Cu_2Br_5$, and $CsCu_2I_3$.We further explored to replace the alkali atoms in the ternary copper halides. A_2CuX_3 (A = K, Rb; X = Cl, Br) nano/microcrystals were synthesized with deep blue PL emission from 380-400 nm and long PL lifetimes. Phase purity of these crystals can be improved and morphology control can be achieved by using the hot injection method, and a high PLQY of up to ~100% can be obtained for K_2CuCl_3 crystals. White light can be achieved for K_2CuCl_3 or Rb_2CuCl_3 crystals with $CsCu_2I_3$ crystal solutions.

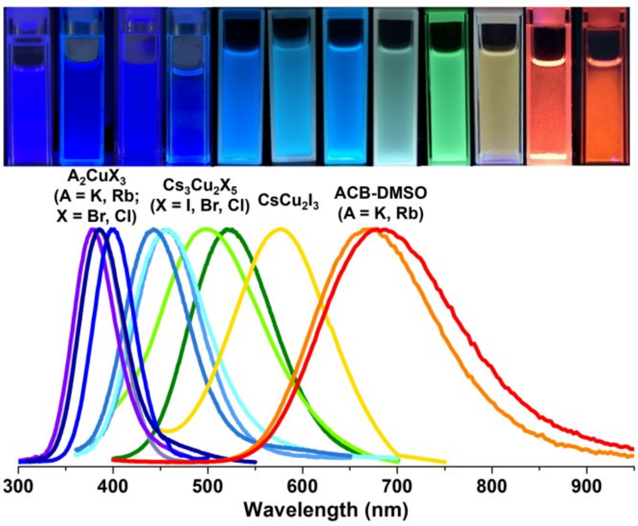

Fig. 1. PL spectra of colloidal solutions of A_2CuX_3 (A = K, Rb; X = Br, Cl), $Cs_3Cu_2X_5$ (X = I, I/Br, Br, Br/ Cl, and Cl), $CsCu_2I_3$, and ACB-DMSO (A = K, Rb).

However, the red emission has not been achieved among these all-inorganic ternary copper halides due to the difficulty in tuning the self-trapped exciton (STE) emission. Thus, we tried to use organic molecules to adjust the structures of the copper-based compounds and tune their optical properties. We successfully achieved red emission for lead-free hybrid organic-inorganic ternary copper halides $A_6(DMSO)_{12}[Cu_8Br_{13}][Cu_4Br_4(OH)(H_2O)]$ (ACB-DMSO, A = K, Rb) synthesized as single crystals and microcrystalline suspensions with a high PLQY of up to 75%. The solvent-induced transformation from A_2CuBr_3 to ACB-DMSO which reversibly transforms blue-emitting 1D copper chains to red-emitting 0D copper clusters. Additionally, KCB-DMSO can be used as the red-emitting phosphor for red light-emitting diodes (LEDs), and an all copper-based white LED with a high color rendering index (CRI) over 97 is achieved.

The optical parameters of the above-mentioned compounds are summarized in Table 1. Our findings demonstrate the great potential of the low-toxicity copper-based halides for applications in optoelectronics and expand the structural possibilities of these compounds.

Table 1. Optical parameters of copper-based halides.

Materials	PL peak (nm)	PLQY (%)
K_2CuBr_3	380	77
K_2CuCl_3	383	100
Rb_2CuBr_3	388	64
Rb_2CuCl_3	396	67
$Cs_3Cu_2I_5$	443	30
$Cs_3Cu_2(Br/I)_5$	457	36
$Cs_3Cu_2Br_5$	458	20
$Cs_3Cu_2(Cl/Br)_5$	508	6
$Cs_3Cu_2Cl_5$	521	100
$CsCu_2I_3$	575	11
KCB-DMSO	670	75
RCB-DMSO	686	75

References

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[2] Y. Li, Z. Zhou, F. K. Sheong, Z. Xing, R. Lortz, K. S. Wong, H. H. Sung, I. D. Williams, J. E. Halpert, *ACS Energy Lett.,* 2021, 6, 4383-43892.