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Supporting Information

Enhancement of Photoluminescence Quantum Yield in Lead-Free Inorganic Copper Based Halide Perovskite by Zinc Doping

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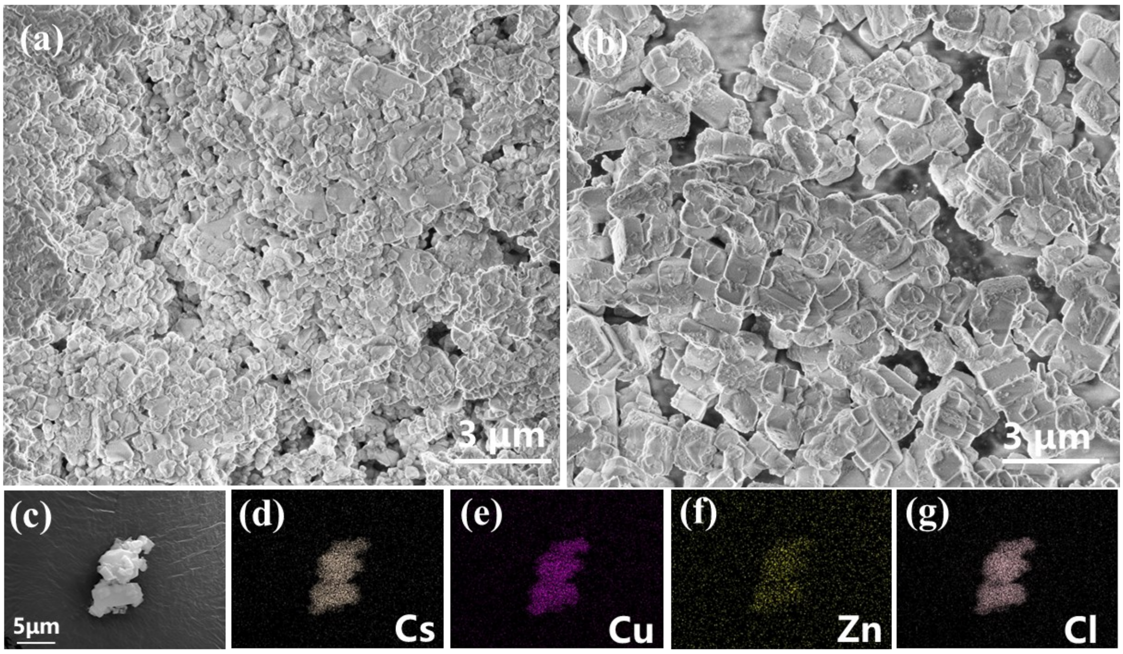

Figure S1. SEM images of (a) $Cs_3Cu_2Cl_5$ and (b) $Cs_3Cu_2Cl_5$: 0.20 Zn^{2+}, (c) $Cs_3Cu_2Cl_5$: 0.20 Zn^{2+} particles in (b). (d)-(g) Elemental mapping of (c).

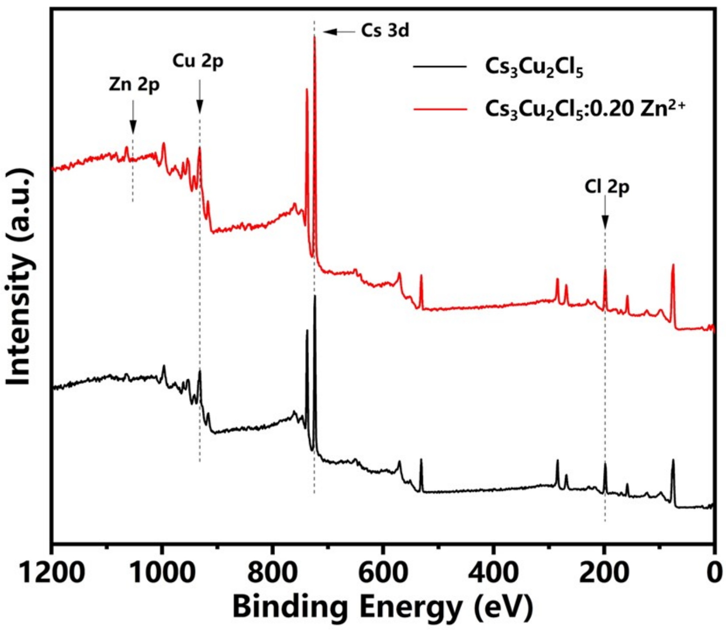

Figure S2. XPS overall spectrum of $Cs_3Cu_2Cl_5$ and $Cs_3Cu_2Cl_5$: 0.20 Zn^{2+}

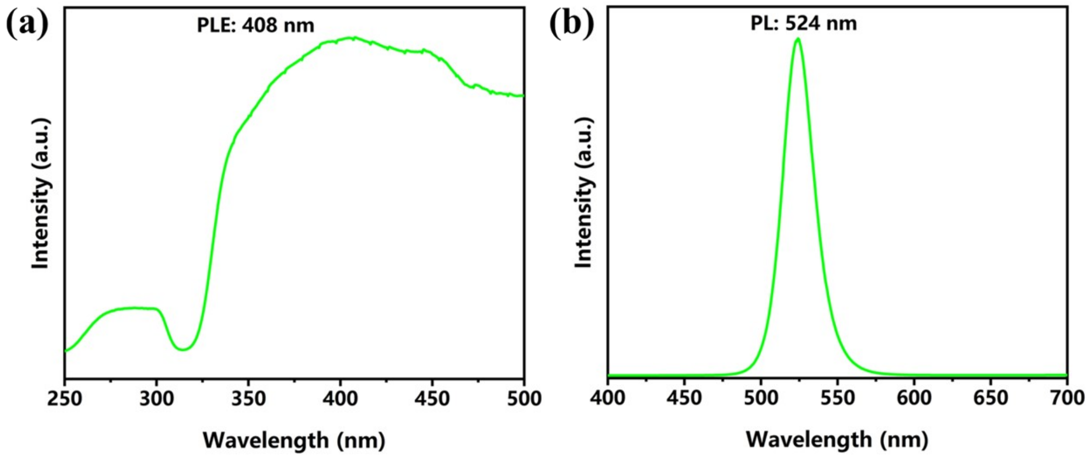

Figure S3. (a) PLE and (b) PL of $CsPbBr_3$ for comparison.

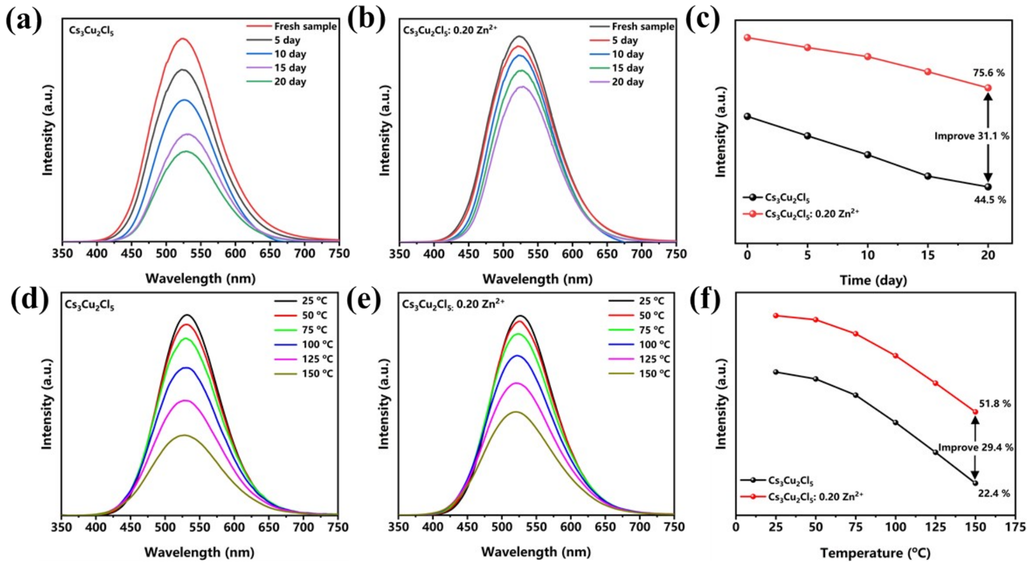

Figure S4. The storage stability of different samples: PL spectra change of (a) $Cs_3Cu_2Cl_5$ and (b) $Cs_3Cu_2Cl_5$: 0.20 Zn^{2+}, (c) the corresponding change tendency form a-b; The thermal stability of different samples: PL spectra change of (d) $Cs_3Cu_2Cl_5$ and (e) $Cs_3Cu_2Cl_5$: 0.20 Zn^{2+}, (f) the corresponding change tendency form d-e.

The storage stability was test to place the samples in air at room temperature. Figure S4 (a-b) are the luminescence cures and S4 (c) summarizes the intensity. Obviously, with time prolong, the intensity of both $Cs_3Cu_2Cl_5$ and $Cs_3Cu_2Cl_5$: 0.20 Zn^{2+} decrease while the Zn doped sample is consistently higher than that of $Cs_3Cu_2Cl_5$. 20 days later, $Cs_3Cu_2Cl_5$: 0.20 Zn^{2+} is 75.6 % left while $Cs_3Cu_2Cl_5$ is only 44.5 %. Figure S4 (d-e) are the temperature-dependent fluorescence cures of the samples varies from 25 ^oC to 150 ^oC with an interval of 25 ^oC and S4 (f) is rollup of intensity. It decreases with temperature increasing and the intensity of $Cs_3Cu_2Cl_5$: 0.20 Zn^{2+} is 51.8 % retain and $Cs_3Cu_2Cl_5$ is 22.4 % at 150 ^oC, nearly 29.4 % improvement obtained after doping with Zn^{2+}. It is clear doping with Zn^{2+} largely improved the thermal and storage stability of $Cs_3Cu_2Cl_5$.

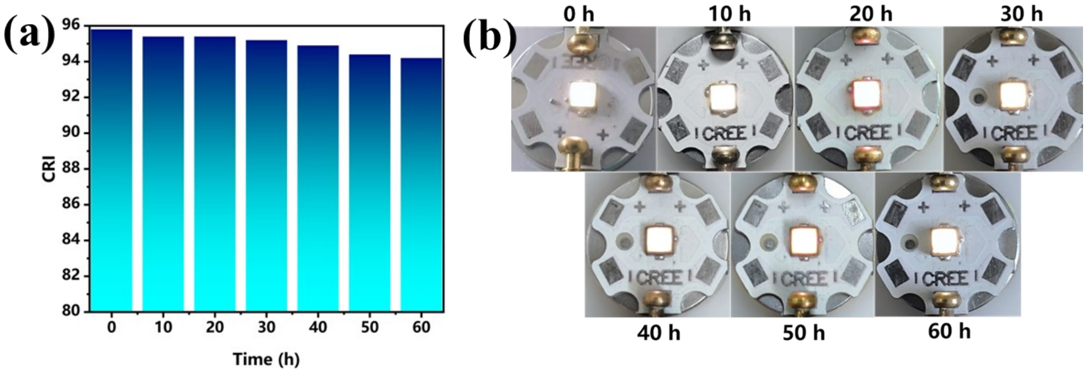

Figure S5. (a) The CRI of WLED was tested intermittently for 60 h. (b) Record WLED photos for 60 h

Moreover, the working stability of the WLED under a prolonged operation should be tested in figure S5 (a). Fortunately, after 60 h lighting, the CRI is 94.2, keeping 98.33 %. The white LED prepared with other-related perovskite materials have been cited [S1, S2] in Table S3, meaning that the WLED with Zn-doped $Cs_3Cu_2Cl_5$ green light materials have comparable or superior property in the stability.

Table S1 ICP-OES results of $Cs_3Cu_2Cl_5$: x Zn^{2+}(x represents the molar ratios between Zn^{2+} and Cu^{+}).

Sample: (ZnCl$_2$ addition)	Cu (mg/L)	Zn (mg/L)	Ratio between Zn and Cu (mol)	Sample (ture)
$Cs_3Cu_2Cl_5$:0.1 mmol $ZnCl_2$	**55.2705**	**5.3347**	**0.09:1**	**$Cs_3Cu_2Cl_5$: 0.09 Zn^{2+}**
$Cs_3Cu_2Cl_5$:0.2 mmol $ZnCl_2$	**55.5556**	**11.2893**	**0.20:1**	**$Cs_3Cu_2Cl_5$: 0.20 Zn^{2+}**
$Cs_3Cu_2Cl_5$:0.4 mmol $ZnCl_2$	**57.5286**	**20.4135**	**0.35:1**	**$Cs_3Cu_2Cl_5$: 0.35 Zn^{2+}**
$Cs_3Cu_2Cl_5$:0.6 mmol $ZnCl_2$	**57.3393**	**33.3479**	**0.57:1**	**$Cs_3Cu_2Cl_5$: 0.57 Zn^{2+}**

Details of the experiment method for the PLQY measurements: In detail, the F-7000 spectrometer equipped with an integrating sphere was used to measure the relevant parameters of direct and indirect excitation of $BaSO_4$ at excitation wavelength (here 310 nm for $Cs_3Cu_2Cl_5$ and $Cs_3Cu_2Cl_5$: 0.20 Zn^{2+}, 408 nm for $CsPbBr_3$), and then the $BaSO_4$ was replaced with test samples. When measuring direct excitation, the sample was placed in the groove facing the xenon lamp light source, and the barium sulfate was placed in the side groove. When measuring indirect excitation, the positions of sample and barium sulfate are interchanged. Relevant parameters were obtained through the measurement before, the quantum efficiency of samples is calculated by formula (2).

Table S2 Parameters and values required for calculating PLQY.

Sample	φ_d	φ_i	A_d
$Cs_3Cu_2Cl_5$	**0.37**	**0.16**	**0.75**
$Cs_3Cu_2Cl_5$: 0.20 Zn^{2+}	**0.78**	**0.32**	**0.76**

Table S3 Stability comparison of WLED devices.

Sample	Initial R_a	Working time/h	eventual R_a	Retention rate%	Reference
$Cs_3Cu_2Cl_5$: $0.20Zn^{2+}$	95.8	60	94.2	98.33	this work
$Cs_3Cu_2Cl_5@SiO_x$	94	380	88	93.62	S1
$C_4H_{12}N_2ZnBr_4$	83.3	4464	78.3	94.00	S2

References:

S1. S. Zhao, C. Chen, W. Cai, R. Li, H. Li, S. Jiang, M. Liu and Z. Zang, *Adv. Opt. Mater.,* 2021, **9**, 2100307.

S2. Y.-P. Lin, S. Hu, J. Xu, Z. Zhang, X. Qi, X. Lu, J. Jin, X.-Y. Huang, Q. Xu, Z. Deng, Z. Xiao and K.-Z. Du, *Chem. Eng. J.,* 2023, **468**, 143818.