

Supporting Information

Distinct green electroluminescence from lead-free CsCuBr₂ halide microcrosses

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Experimental Section

Sample preparation

Prior to producing CsCuBr₂ MCs, Cs₃Cu₂Br₅ micro-rods (MRs) was firstly synthesized by a one-pot solution method, in which 5 mL of dimethyl sulfoxide (DMSO, >99.8%), 1 mL of oleic acid (OA, 85%), 0.42 mmol of CsBr (99.5%) and 0.4 mmol of CuBr₂ (99%) were loaded into a 50 mL three-neck flask and reacted in a water bath at 70 °C for 5 h. When the reaction was finished, the crude solution was precipitated by 50 mL of dichloromethane (DCM, 99.5%) and the resultant Cs₃Cu₂Br₅ precipitate was separated via centrifugation. After being washed by ethyl acetate (EA, 99.5%) for several times, Cs₃Cu₂Br₅ powder was obtained by drying the Cs₃Cu₂Br₅ precipitate under vacuum at 70 °C for 0.5 h. Afterwards, 0.08 g of Cs₃Cu₂Br₅ and 1 mL of N,N-dimethylformamide (DMF, 99.5%) were mixed in a glass vial. The suspended mixed solution was then spin-casted onto pre-cleaned p-Si substrates under 1500 rpm for 40 s and dried at 90 °C for 20 min to produce a thin CsCuBr₂ MCs film on the p-Si substrates.

Characterization

Scanning electron microscopy (SEM) images of the samples were measured in electron probe microanalyzer (EPMA, JEOL JXA-8230). Energy dispersive X-ray spectrometer (EDS) characterizations were performed by Oxford Instruments X-Max^N that was coupled to the EPMA. X-band (9.44 GHz) electron paramagnetic resonance (EPR) measurements were carried out by using JEOL JES-FA300. X-ray diffraction (XRD) was introduced to characterize the crystal structure (Rigaku MiniFlex600, Cu K α radiation). X-ray photoelectron spectrometer (XPS) analysis was carried out in Thermo Scientific ESCALAB 250Xi.

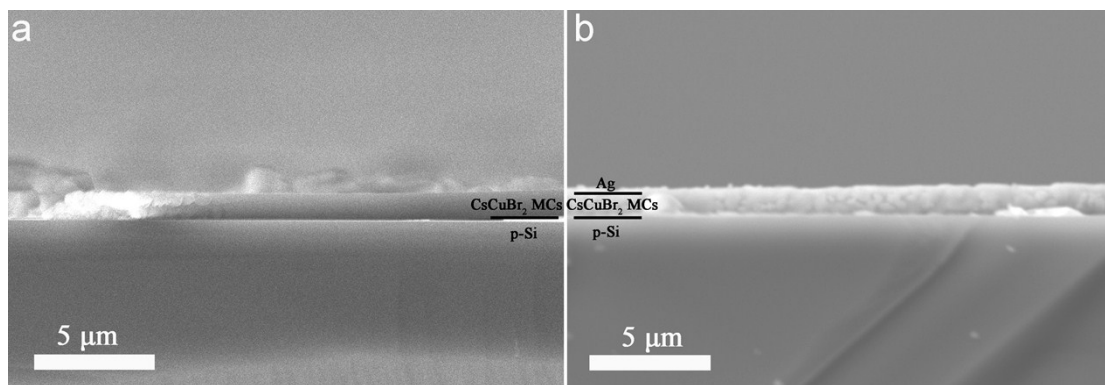


Fig. S1 Cross-sectional images of (a) CsCuBr₂ MCs/p-Si and (b) Ag/CsCuBr₂ MCs/p-Si heterojunctions. The thicknesses of the CsCuBr₂ MCs and the Ag electrode are measured as ~1.1 μm and ~90 nm, respectively.

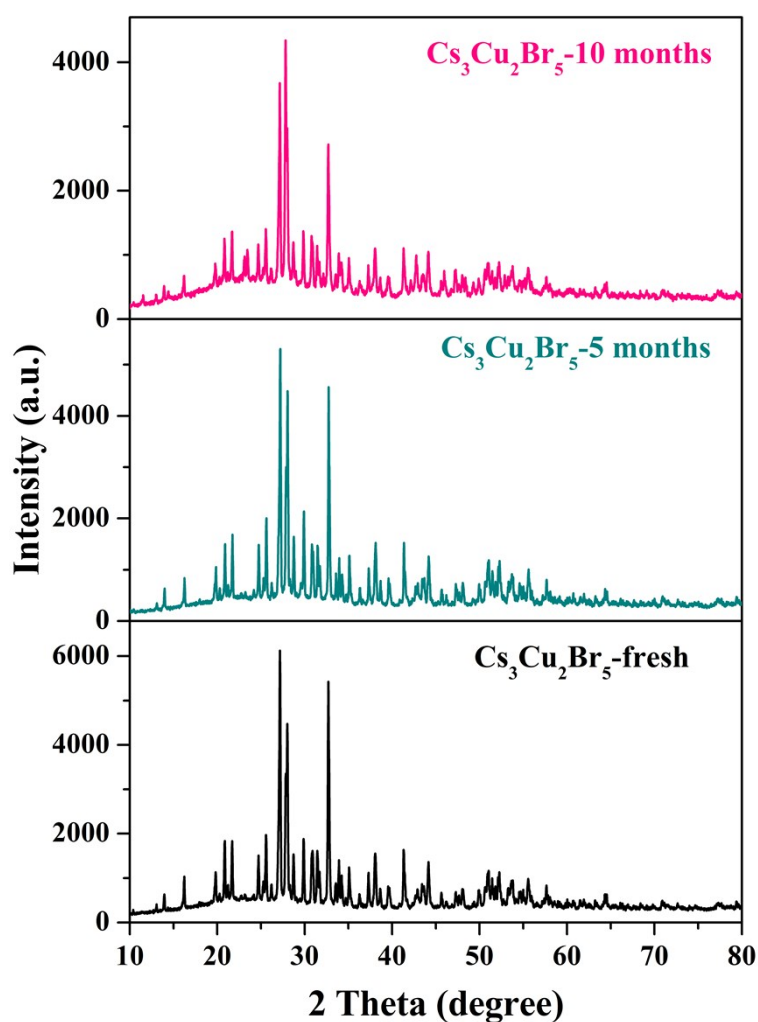


Fig. S2 XRD patterns of Cs₃Cu₂Br₅ MRs with different storage time in air at room temperature (Relative Humidity: ~30%). Preservation of all the diffraction peaks even after 10 months firmly proves the long-term stability of the crystal structure of the Cs₃Cu₂Br₅ MRs in air.

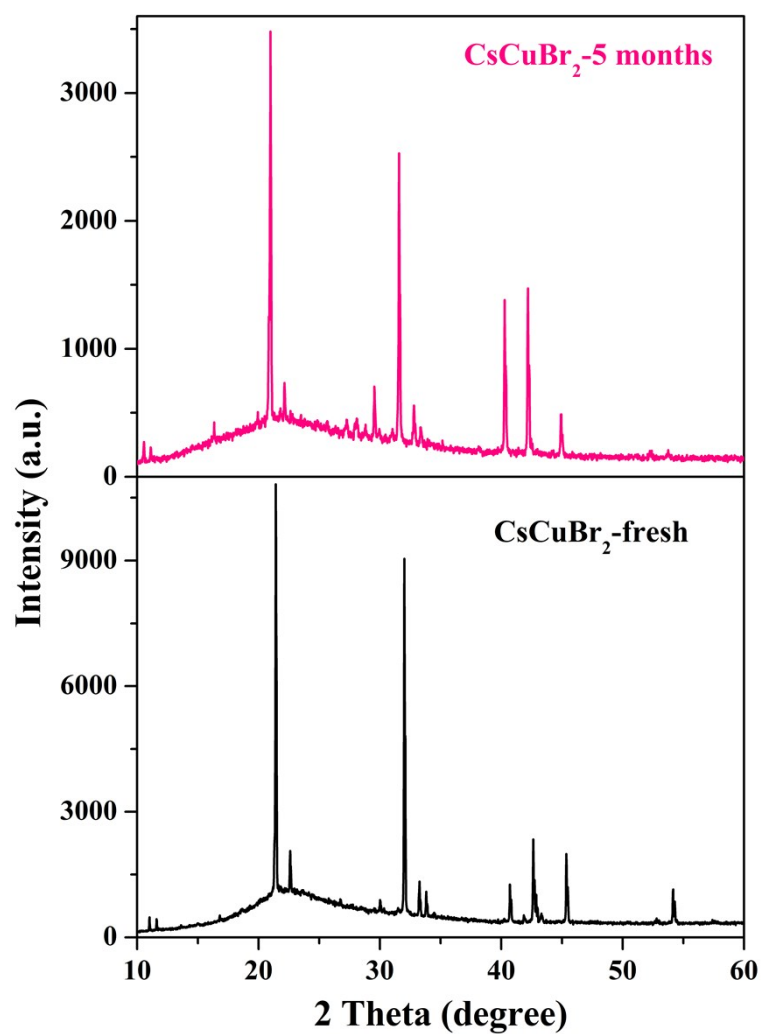


Fig. S3 XRD patterns of CsCuBr₂ MCs with different storage time in air at room temperature (Relative Humidity: ~30%). All the diffraction peaks are preserved after storage in air for 5 months, which strongly proves the long-term stability of the CsCuBr₂ MCs in air.

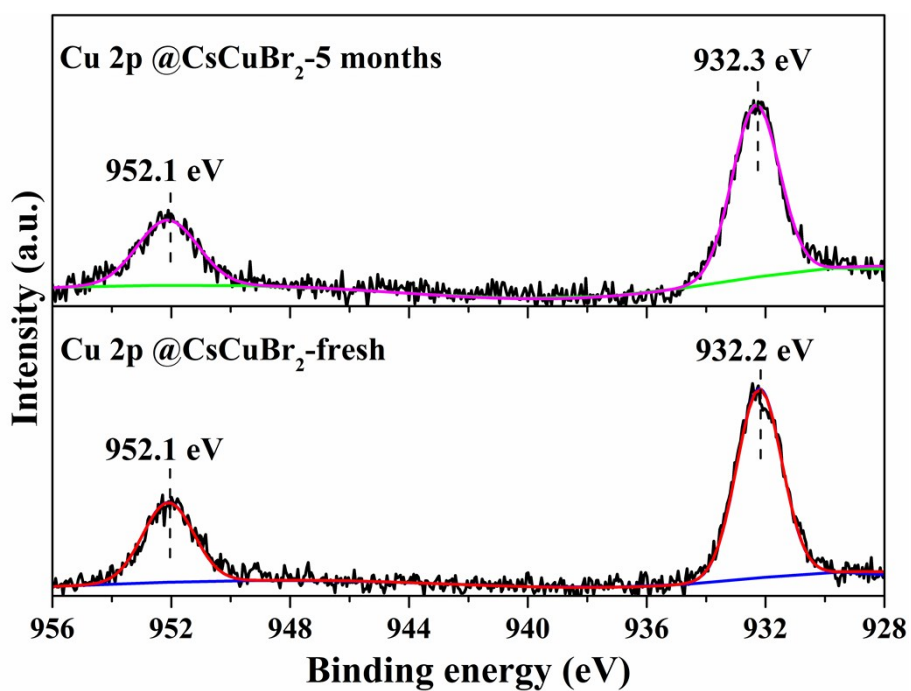


Fig. S4 Cu 2p XPS spectra of the CsCuBr₂ MCs with different storage time in air at room temperature (Relative Humidity: ~30%). Both of the two peaks located around 952.1 and 932.2 eV—assigned to the Cu 2p_{1/2} and Cu 2p_{3/2}, respectively—remain unchanged, strongly verifying the long-term stability of Cu^I in the CsCuBr₂ MCs in air even beyond 5 months.

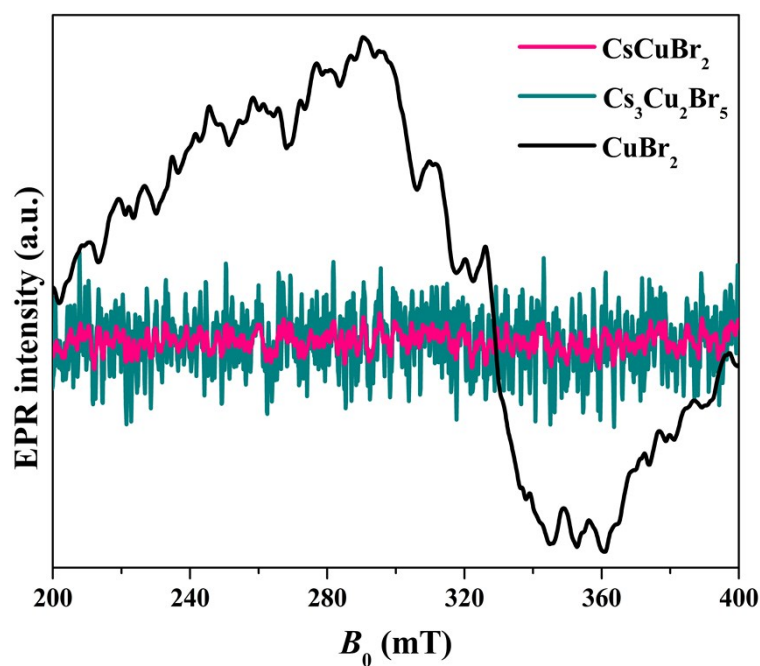


Fig. S5 X-band (9.44 GHz) EPR spectra of $\text{Cs}_3\text{Cu}_2\text{Br}_5$ MRs and CsCuBr_2 MCs at room temperature, with CuBr_2 powder as the reference (the same as those used to synthesize the $\text{Cs}_3\text{Cu}_2\text{Br}_5$ MRs and CsCuBr_2 MCs), for which the value of proportionality factor (g-factor) is 2.045. In comparison with the CuBr_2 , the absence of the EPR signal of Cu^{II} in the $\text{Cs}_3\text{Cu}_2\text{Br}_5$ MRs and CsCuBr_2 MCs samples verifies that Cu^{II} is reduced to Cu^{I} or Cu^0 [1-4]. Since the patterns corresponding to Cu^0 cannot be found in the XRD results (see Fig. 2), it can be concluded that the oxidation of copper in the $\text{Cs}_3\text{Cu}_2\text{Br}_5$ MRs and CsCuBr_2 MCs is Cu^{I} .

Table S1 Chemical composition data from different CsCuBr₂ MCs by EDS that is coupled to the EPMA.

No.	Cs	Cu	Br	Total
1	0.262947	0.281053	0.456	1
2	0.264391	0.269531	0.466077	1
3	0.260038	0.287626	0.452335	1
4	0.262287	0.27782	0.459893	1
5	0.263062	0.280613	0.456324	1
6	0.277256	0.257184	0.46556	1
7	0.255976	0.282269	0.461756	1
8	0.265644	0.265042	0.469314	1
9	0.264026	0.274566	0.461408	1
10	0.258979	0.266065	0.474956	1
11	0.266956	0.245339	0.487704	1
12	0.274813	0.267876	0.457311	1
13	0.248495	0.270306	0.481199	1
14	0.265468	0.27901	0.455522	1
15	0.277185	0.266657	0.456159	1
16	0.247294	0.265333	0.487373	1
17	0.262118	0.278718	0.459163	1
18	0.262566	0.262771	0.474663	1
19	0.250516	0.284331	0.465152	1
20	0.247018	0.276438	0.476544	1
Average	0.261852	0.271927	0.466221	1
Sigma (variance)	0.008866	0.010286	0.010814	

Reference

- [1] A. Aboukaïs, A. Bennani, C. Lamonier-Dulongpont, E. Abi-Aad, and G. Wrobel, Redox behaviour of copper(II) species on CuCe oxide catalysts: electron paramagnetic resonance (EPR) study, *Colloids Surfaces A*, 1996, **115**, 171-177.
- [2] N. Y. Garces, L. Wang, L. Bai, N. C. Giles, and L. E. Halliburton, Role of copper in the green luminescence from ZnO crystals, *Appl. Phys. Lett.*, 2002, **81**, 622.
- [3] R.-A. Eichel, M. D. Drahus, P. Jakes, E. Erünal, E. Erdem, S.K.S. Parashar, H. Kungl, and M. J. Hoffmann, Defect structure and formation of defect complexes in Cu²⁺-modified metal oxides derived from a spin-Hamiltonian parameter analysis, *Mol. Phys.*, 2009, **107**, 1981-1986.
- [4] W. Jo, J.-B. Ollagnier, J.-L. Park, E.-M. Anton, O.-J. Kwon, C. Park, H.-H. Seo, J.-S. Lee, E. Erdem, R.-A. Eichel, and J. Rödel, CuO as a sintering additive for (Bi_{1/2}Na_{1/2})TiO₃-BaTiO₃-(K_{0.5}Na_{0.5})NbO₃ lead-free piezoceramics, *J. Eur. Ceram. Soc.*, 2011, **31**, 2107-2117.