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Supporting Information

Transition metal halides doped highly stable all-inorganic perovskite nanocrystals for fabrication of white light-emitting diodes

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Experiment Section.

Chemicals. All chemicals, including Cs_2CO_3 (Aladdin, 99.9%), PbO (Sinopharm, >99%), $PbBr_2$ (Aladdin, 99%), $FeBr_3$ (Macklin, 98%), $CoBr_2 \cdot xH_2O$ (Aladdin, 98%), $CuBr_2$ (Aladdin, 99%), $ZnBr_2$ (Aladdin, 99.9%), $NiBr_2$ (Macklin, 96%), ZnI_2 (Aladdin, 99.99%), $NiCl_2 \cdot 6H_2O$ (Aladdin, 99.9%), oleylamine (OLA) (Aladdin, 80-90%), oleic acid (OA, Aladdin, AR), octadecene (ODE, Aladdin, 90%), polyvinyl butyral (PVB, Sinopharm), n-hexane (Sinopharm, AR) and toluene (Sinopharm, AR), chloroform (Sinopharm, AR) were commercially available and used as received without further purification.

Preparation of Cs-oleate and Pb-oleate solution. To obtain Cs-oleate solution, 0.326 g of Cs_2CO_3, 2 mL of OA, and 18 mL of ODE were loaded in a 50 mL 3-neck flask and heated to 150 °C under nitrogen flow until all the powder was dissolved absolutely. Pb-oleate was prepared by a similar method, i.e., 1.786 g of PbO, 2 mL of OA, and 18 mL of ODE were loaded in a 50 mL 3-neck flask and heated to 120 °C until all the powder was dissolved absolutely.

Synthesis of pristine $CsPbBr_3$ NCs. We adopted a synthetic method reported by Protesescu et al. with some modifications.[S1] For the synthesis of pristine-$CsPbBr_3$ NCs, 0.147 g of $PbBr_2$ (0.4 mmol), 1 mL of OA, 1 mL of OLA, and 10 mL of ODE were loaded in a 50 mL 3-neck flask. The mixture was heated to 120 °C until all the powder was dissolved absolutely under nitrogen atmosphere, then the temperature of the solution was increased to 180 °C, and 1 mL of Cs-oleate solution was swiftly injected into the optically transparent precursor solution. After 10-30 s from the injection, the heating mantle was removed and the flask was rapidly cooled down in a water bath.

Synthesis of metal halides assisted $CsPbX_3$ NCs. For the $FeBr_3$ assisted synthesis of $CsPbBr_3$ NCs, 10 mL ODE was heated to 120 °C in a 50 mL 3-neck flask under nitrogen atmosphere. Then, 1 mL OLA and 0.09 g of $FeBr_3$ were added into the flask until all the powder was dissolved absolutely. Then 1 mL Pb-oleate solution and 1 mL OA were added into the flask and the temperature of the solution was increased to 180 °C, and 1 mL of Cs-oleate solution was swiftly injected into the solution. After 10-30 s from the injection, the flask was rapidly cooled down in a water bath. For the $CoBr_2$, $ZnBr_2$ $NiBr_2$ or $CuBr_2$ assisted synthesis of $CsPbBr_3$ NCs, 0.095 g of $CoBr_2$ (0.4 mmol), 0.09 g of $ZnBr_2$ (0.4 mmol), 0.087 g of $NiBr_2$ (0.4 mmol) or 0.089 g of $CuBr_2$ (0.4 mmol) was loaded instead of $FeBr_3$ and other procedures were performed similarly except that the reaction temperature reduced to 120 °C when $CuBr_2$ was used. For the synthesis of blue-emitting NCs or red-emitting NCs, 0.059 g of $FeBr_3$ and 0.048 g of $NiCl_2$ or 0.029 g of $FeBr_3$ and 0.096 g of ZnI_2 were added instead of $FeBr_3$ based on above procedure.

Purification of $CsPbBr_3$ NCs. $CsPbBr_3$ NCs were extracted by high-speed centrifugation. After the reaction, crude reaction solution was centrifuged for 5 min at 6000 rpm. After the centrifugation, the supernatant was discarded and the precipitates were redispersed in 10 mL of n-hexane. After the NCs were completely dispersed in n-hexane, the solution was centrifuged for 10 min at 12000 rpm. After that, the supernatant was discarded and the NC precipitates were redispersed in toluene, which was used for further characterization.

Fabrication of nanocrystal films. For the preparation of nanocrystal film, the NCs (about 20 mg/mL) and PVB (10mg/mL) were dissolved in chloroform. Then, the mixture was ultrasound for 5 min and spin-coated on the glass substrate at low speed 800 rpm for 10 s and high speed 3000 rpm for 20 s.

Fabrication of WLEDs. A certain amount of as prepared green-emitting $FeBr_3$-assisted $CsPbBr_3$ NCs, red-emitting KSF phosphor (purchased from Shenzhen Looking Long Technology Co. Ltd., China), and LTD (mass ratio 3:1) were mixed with 0.1 g of silicone resin OE-6550A (Dow Corning, USA) under vigorous stirring. Subsequently, the hardener (OE-6550B, 0.1 g) was added to form a paste. After bubbles were removed, the paste was dropped onto a blue-LED chip (Ding yuan technology, Taiwan, China).

Characterization.

The fluorescence and UV−vis spectra were recorded using a Shimadzu RF-5301PC fluoremeter (Japan) and a Biomate 3S spectrophotometer (Thermo Fisher, USA), respectively. The time-resolved PL measurements were performed using a time-correlated single photon counting setup (TCSPC) (HORIBA, France) utilizing FluoroHub counting module and NanoLED-340 picosecond laser, as an excitation source, with pulse duration < 1 ns, at a wavelength of 339 nm. The X-ray photoelectron spectra (XPS) were measured on a PHI 5000 VersaProbe XPS (ULVAC-PHI, Japan). The samples were fabricated via drop coating the NCs on silicon wafers. The transmission electron microscope (TEM) images and energy dispersive spectrometer (EDS) were acquired with a JEM-2100 TEM (JEOL, Japan) and a Zeiss Ultra Plus SEM (Zeiss, Germany). Powder X-ray diffraction (XRD) patterns were recorded with a D8-ADVANCE diffractometer (Cu Ka radiation; 40 kV, 60 mA) and the samples were prepared by drop casting the NC solutions on glass substrates. The emission spectra and the photometric characteristics of WLEDs were measured on a high accuracy array rapid spectroradiometer (HAAS-2000).

Photoluminescence quantum yield (PL QY) measurements. The relative PLQY of green-emitting NCs was measured by using quinine sulfate as standard reference according to the literature.[S2]

Stability test under ambient condition. NCs were deposited on glass substrates or TEM grids. After initial characterizations, the samples were stored under ambient condition with relative humidity of 70-80%. Characterizations (PL and TEM) were conducted as a function of exposure time to ambient condition.

Thermal stability test. NCs were deposited on glass substrates or TEM grids and the solvent was naturally dried. After initial characterizations, the films were placed in a hot oven under 120 °C for 30 min. Then the characterizations of PL spectra and TEM were conducted again.

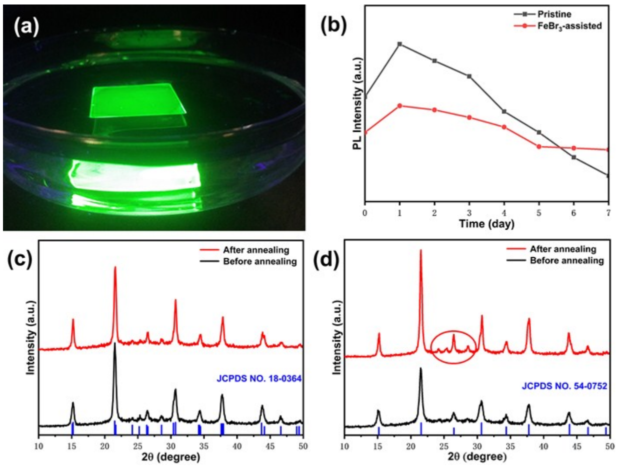

Fig. S1 The photo of NCs@PVB film immersed in water under UV light (a); The changes of PL intensity pristine NCs and $FeBr_3$-assisted NCs films' in water during one week; The variation in XRD pattern of $FeBr_3$-assisted NCs (c) and pristine NCs (d) after annealing at 150 °C for 15 min.

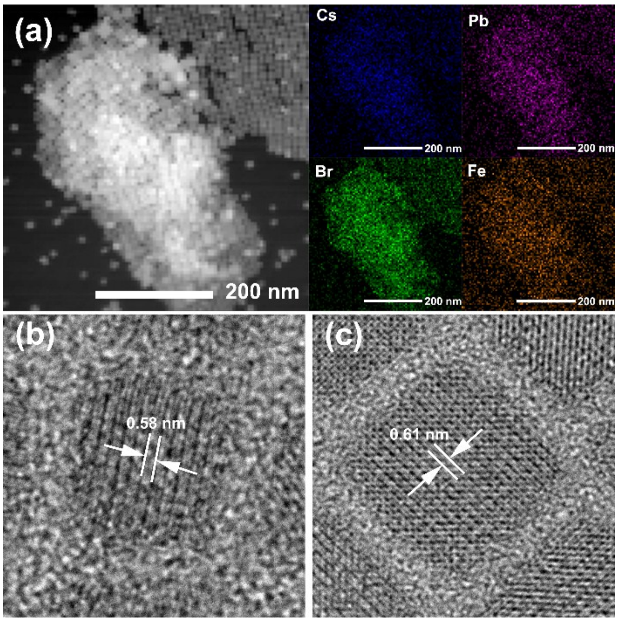

Fig. S2 HAADF-STEM image of $FeBr_3$-assisted NCs and the corresponding energy dispersive X-ray spectroscopy mapping of Cs, Pb, Br, and Fe, demonstrating the presence of Fe in the perovskite NCs (a); HRTEM images of pristine NCs (b) and $FeBr_3$-assisted NCs (c).

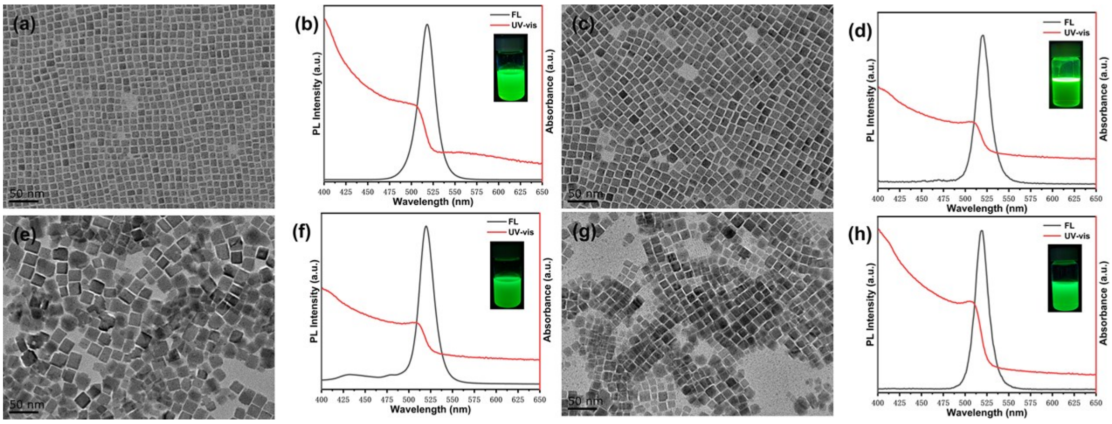

Fig. S3 TEM image of $CoBr_2$-assisted NCs (a), $NiBr_2$-assisted NCs (c), $CuBr_2$-assisted NCs (e) and $ZnBr_2$-assisted NCs (g); Absorbance and emission spectra of $CoBr_2$-assisted NCs (b), $NiBr_2$-assisted NCs (d), $CuBr_2$-assisted NCs (f) and $ZnBr_2$-assisted NCs (h) and the corresponding pictures of NCs solution under UV light were shown as inset.

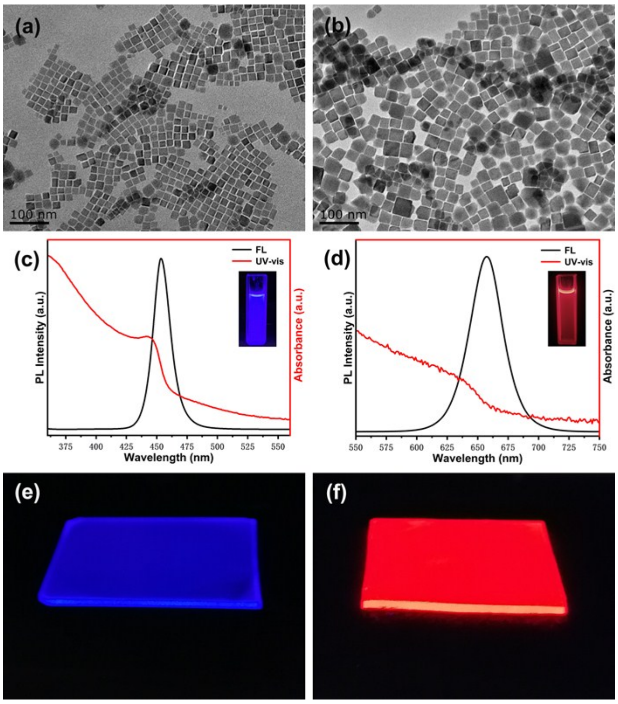

Fig. S4 TEM image of blue-emitting NCs (a), red-emitting NCs (b); The PL spectra of blue-emitting NCs (c) and red-emitting NCs (d), and the corresponding pictures of NCs solution under UV light were shown as inset; Pictures of blue film and red film of as prepared NCs (e, f)

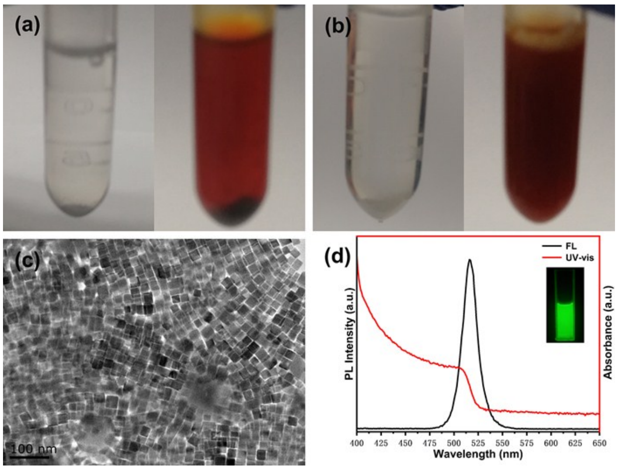

Fig. S5 Photos of $PbBr_2$ and $FeBr_3$ in hot OA, left is $PbBr_2$ and right is $FeBr_3$ (a); Photos of $PbBr_2$ and $FeBr_3$ in hot OLA, left is $PbBr_2$ and right is $FeBr_3$ (b); TEM image (c), Absorbance and emission spectra (d) of $CsPbBr_3$ NCs prepared without additional OA. The pictures of NCs solution under UV light were shown as (c) inset.

Table S1 Optical properties of different transition metal bromides doped NCs

	Emission Wavelength (nm)	FWHM (nm)	PL Lifetime (ns)	PLQY
$CoBr_2$ doped NCs	518	23	3.7	51%
$NiBr_2$ doped NCs	520	19	7.8	84%
$CuBr_2$ doped NCs	520	21	0.8	10%
$ZnBr_2$ doped NCs	519	19	7.3	76%

References

S1 L. Protesescu, S. Yakunin, M. I. Bodnarchuk, F. Krieg, R. Caputo, C. H. Hendon, R. X. Yang, A. Walsh and M. V. Kovalenko, *Nano Lett.*, 2015, **15**, 3692-3696.

S2 A. M. Brouwer, *Pure Appl. Chem.*, 2011, **83**, 2213-2228.