Supplementary Information

Synthesis of Lead Halide Perovskite Nanocrystals by Melt Crystallization in Halide Salts

Bo Wang\textsuperscript{a}, Congyang Zhang\textsuperscript{a}, Weilin Zheng\textsuperscript{a}, Qinggang Zhang\textsuperscript{a}, Qun Wan\textsuperscript{a}, Long Kong\textsuperscript{a}, Liang Li\textsuperscript{*;a,b}

\textsuperscript{a} School of Environmental Science and Engineering, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, China

\textsuperscript{b} Shanghai Institute of Pollution Control and Ecological Security, 1239 Siping Road, Shanghai 200092, China

*corresponding author: liangli117@sjtu.edu.cn.
Experimental Section

Chemicals: Lead bromide (PbBr$_2$, 99%), cesium bromide (CsBr, 99.5%), lead chloride (PbCl$_2$, 99.99%), cesium chloride (CsCl, 99.5%) were purchased from Aladdin. Magnesium bromide hexahydrate (MgBr$_2$·6H$_2$O, 98+%), calcium bromide hydrate (CaBr$_2$·xH$_2$O, 95%), strontium bromide hexahydrate (SrBr$_2$·6H$_2$O, 95%), barium bromide dehydrate (BaBr$_2$·2H$_2$O, 98+%), sodium bromide (NaBr, 99+%), potassium bromide (KBr, 99+%), rubidium bromide (RbBr, 99.8%), strontium chloride hexahydrate (SrCl$_2$·6H$_2$O, tech) were purchased from Alfa Aesar. All chemicals were used without further purification.

Preparation of CsPbBr$_3$ NCs by metal halide high temperature melt crystallization. Three raw materials were weighed and mixed thoroughly according to the molar ratio of CsBr:PbBr$_2$:SrBr$_2$·6H$_2$O = 0.05:0.05:1 (named as Cs:Pb:Sr = 0.05:0.05:1). The calcining temperature for the sample was set as 800 ºC at a heating rate of 5 ºC/min, keeping 60 min on 200 ºC and 10 min on 800 ºC, respectively, subsequently cooling down to room temperature. The whole synthetic process performed under a nitrogen atmosphere. CsPbBr$_3$ NCs embedded in SrBr$_2$ matrixes (named as CsPbBr$_3$@SrBr$_2$) were obtained through grinding calcined products at ambient conditions. The products for different molar ratios, temperatures, and time were taken the same procedure by changing the molar ratio, calcining temperature and time, respectively. For CsPbCl$_3$ NCs were just exchanged bromide salts with corresponding chloride salts.

Thermal Stability Test. The CsPbBr$_3$@SrBr$_2$ powders were added into a sample bottle; the CsPbBr$_3$ NCs solution was dropped into a sample bottle to form a film. Then, they were put into an oven with 100 ºC for the thermal stability test, and the photoluminescence (PL) spectra at different time intervals were recorded by using an ocean optical fluorescence spectrometer after the bottles were taken from the oven and cooled down. (The caps were tightened when the bottles taken from the oven.) For data processing, the integral area of PL for the original sample was set as the standard, and the integral areas of PL at different time intervals were compared with that of the original sample; then, the remnant PLQY of these samples were obtained.

Characterization. The UV-vis absorption spectra were recorded on the Lambda 950 UV-vis-NIR spectrophotometer. PL spectra were recorded by Hitachi F-7000 fluorescence spectrometer. X-ray powder diffraction (XRD) patterns were detected by the BrukerD8 Advance X-ray Diffractometer at 40 kV and 30 mA using Cu K$_\alpha$ radiation ($\lambda$=1.5406 Å). The scanning electron
microscope (SEM) images were obtained from the JEOL JSM-7800F field emission scanning electron microscope. The high-resolution transmission electron microscope (HR-TEM) and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images were obtained from the FEI Talos F200X TEM instruments operated at an accelerating voltage of 200 kV. The absolute photoluminescence quantum yields (PLQY) were measured using an Edinburgh Instruments FLS1000 fluorescence spectrometer with an integrating sphere, exciting the powders at 450 nm. Thermogravimetric analysis-differential scanning calorimetry (TGA-DSC) was conducted on a Mettler Toledo analyzer from 30 to 800 °C at a heating rate of 5 °C/min, keeping 60 min on 200 °C and 10 min on 800 °C, respectively, subsequently cooling down to 30 °C at a rate of 5 °C/min, and all test was performed under a nitrogen atmosphere with a flow rate of 30 mL/min.
Figure. S1 The FWHM and the PL peaks position of different molar ratios of CsBr:PbBr$_2$:SrBr$_2$ samples calcined 10 min at 800 °C under a nitrogen atmosphere.

Figure. S2 PL spectra with different molar ratios of CsBr:PbBr$_2$:SrBr$_2$ samples calcined 10 min at 800 °C under a nitrogen atmosphere.
Figure. S3 XRD patterns with different molar ratios of CsBr:PbBr₂: SrBr₂ samples calcined 10 min at 800 °C under a nitrogen atmosphere (a) and the local enlarged CsPbBr₃ diffraction peaks (b,c).

Figure. S4 The SEM images of SrBr₂ (a,b), and CsBr:PbBr₂ = 1:1 (c,d) samples calcined 10 min at 800 °C under a nitrogen atmosphere.
Figure. S5 The size distributions of CsPbBr$_3$ NCs for CsBr:PbBr$_2$:SrBr$_2$ = 0.05:0.05:1 sample calcined 10 min at 800 °C under a nitrogen atmosphere.

Figure. S6 The TEM images of CsBr:PbBr$_2$:SrBr$_2$ = 0.05:0.05:1 sample calcined 10 min at 800 °C under a nitrogen atmosphere (a,b), and the corresponding maps of (c) Sr, (d) Br, (e) Cs, and (f) Pb.
**Figure S7** The TEM and HAADF images of CsBr:PbBr$_2$:SrBr$_2$ = 0.05:0.05:1 sample calcined 10 min at 800 °C under a nitrogen atmosphere (a,b), and the corresponding maps of (c) Sr, (d) Br, (e) Cs, and (f) Pb. (The sample used for TEM was obtained by ultrathin section.)

**Figure S8** The XRD patterns of CsBr:PbBr$_2$:SrBr$_2$ = 0.05:0.05:1 samples calcined 10 min at different temperatures under a nitrogen atmosphere.
**Figure. S9** The absorption (a) and PL (b) spectra, photo images (c) under ambient light (top) and 365 nm lamp (bottom), and XRD patterns (d) of CsBr:PbBr$_2$:SrBr$_2$ = 0.05:0.05:1 sample calcined for different time at different temperatures under a nitrogen atmosphere.

**Figure. S10** The TGA of CsBr:PbBr$_2$ = 1:1 sample.
Figure. S11 The thermal stability of CsPbBr$_3$@SrBr$_2$ powders and CsPbBr$_3$ N Cs film.

![Figure S11](image1.png)

Figure. S12 The absorption and PL spectra (a), and XRD patterns (b) of CsCl:PbCl$_2$:SrCl$_2$ = 0.05:0.05:1 sample calcined 10 min at 800 °C under a nitrogen atmosphere. (red line: SrCl$_2$·2H$_2$O JCPDS 43-1493, black line: SrCl$_2$ JCPDS 72-1537)

![Figure S12](image2.png)

Figure. S13 The absorption (a) and PL (b) spectra of CsBr:PbBr$_2$:NBr$_2$ = 0.05:0.05:1 (N = Mg, Ca, Sr, and Ba) samples calcined 10 min at 800 °C under a nitrogen atmosphere.

![Figure S13](image3.png)
Figure. S14 The XRD patterns (a,b,c), and photo images (d) under ambient light (top) and 365 nm lamp (bottom) of CsBr:PbBr$_2$:NBr$_2$ = 0.05:0.05:1 (N = Mg, Ca, Sr, and Ba) samples calcined 10 min at 800 °C under a nitrogen atmosphere.

Fig. S15 The absorption (a) and PL (b) spectra, and photo images (c) under ambient light (top) and 365 nm lamp (bottom) of CsBr:PbBr$_2$:MBr$_2$ = 0.05:0.05:1 (M = Na, K, Rb, and Cs) samples calcined 10 min at 800 °C under a nitrogen atmosphere.
Fig. S16 The XRD patterns of CsBr:PbBr$_2$:MBr = 0.05:0.05:1 (M = Na, K, Rb, and Cs) samples calcined 10 min at 800 °C under a nitrogen atmosphere.