Electronic Supplementary Information

Colloidal Syntheses of Zero-Dimensional Cs_4SnX_6 (X = Br, I) Nanocrystals with High Emission Efficiencies

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Part I: Materials and Sample Preparation

Chemicals

1-octadecene (ODE, 90%), tri-*n*-octylphosphine (TOP), oleylamine (OLA, >70%), oleic acid (OA, 90%) were purchased from Sigma-Aldrich. Tin (II) bromide ($SnBr_2$, 99.2 %) and Tin (II) iodide (SnI_2, 99+ %) were purchased from Alfa. Cesium carbonate (Cs_2CO_3, 99.99%) was purchased from Aladdin. All chemicals were stored in an air-free, Ar-filled glovebox with O_2 and H_2O level < 0.5 ppm, and were used as received without any further purification.

Syntheses of phase-pure Cs_4SnX_6 (X = Br, I) NCs

8 mg of Cs_2CO_3 was loaded in a three-necked Schlenk flask and sealed in a glovebox, and then 5 mL of ODE was injected into the flask, followed by the addition of 0.1 mL of OA and 0.1 mL of OLA. The flask was then degassed under vacuum for 1 h at 115 ^{o}C. Subsequently, the reaction was heated to the chosen reaction temperature before the desired amount of SnX_2 dissolved in 0.5 mL of TOP was swiftly injected into the prepared Cs-precursor. The reaction vessel was kept at the injection temperature for appropriate time, followed by cooling down to room temperature by using a water bath. Finally, NCs were collected via centrifugation at 10000 rpm for 5 min, and then the samples were immediately stored in glovebox.

For the preparation of Cs_4SnBr_6 NCs, 60 mg of $SnBr_2$ was used, and the reaction was conducted at 210 ^{o}C for 1 min. For the mixed halide NCs, 45 mg of $SnBr_2$ and 17.5 mg of SnI_2 were used to initiate the reaction, and the reaction was performed at 210 ^{o}C for 1 min. To synthesize Cs_4SnI_6 NCs, 70 mg of SnI_2 was dissolved in TOP, and the reaction temperature was set to 250 ^{o}C to obtain a pure phase. Instead of 1 min reaction, 15 s was used to obtain monodisperse Cs_4SnI_6 NCs.

Part II: Characterizations Methods and Calculation Details

Characterizations

Transmission electron microscopy (TEM) measurement was performed in Hitachi HT7700 microscope operated at 100 kV to investigate the sizes and morphologies of Cs_4SnX_6 NCs. The

microstructures of the Cs_4SnX_6 samples were characterized by high-resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED), and their chemical composition were analyzed by energy dispersive X-ray spectroscopy (EDX) under scanning transmission electron microscopy (STEM) mode using the Super-X EDS detector in a double Cs-corrected FEI Themis G2 60-300 microscope operated at 60 kV. Analyses of STEM-EDX images were carried out by using the Velox software. The sizes of the Cs_4SnX_6 NCs were estimated from TEM images using Nano Measurer software with ~200 particles statistics.

X-ray diffraction (XRD) patterns were recorded on an X-ray diffractometer (Rigaku SmartLab) with Cu Kα radiation (λ = 0.15418 nm) at a voltage of 45 kV and a current of 200 mA.

X-ray photoelectron spectroscopy (XPS) analyses were carried out on a PHI 5000 VersaProbe Ⅲ spectrometer using monochromatic Al K(alpha) X-ray source. XPS samples were prepared in an argon filled glove box (O_2, H_2O < 0.5 ppm) and transferred to an ultrahigh vacuum chamber.

Raman spectra were measured by using the Raman spectrometer of HORIBA iHR550 with 532 nm laser.

The UV-Vis absorption spectra were measured with Agilent Technologies Cary Series UV-Vis-NIR Spectrophotometer in the range of 200-800 nm. The Photoluminescence (PL) and PL excitation spectra were taken by HORIBA Scientific FluoroMax-4 Spectrofluorometer. For Cs_4SnBr_6 NCs and $Cs_4SnBr_xI_{6-x}$ NCs, the excitation wavelength was 320 nm, and the excitation wavelength for Cs_4SnI_6 NCs was 360 nm. PL lifetime measurements were performed by using the Edinburgh Instruments FLS 980-Laser Flash Photolysis Spectrometer correlated single photo counting method with a μF2 light source. The PL decay curves were fitted by using U11487 Software from Hamamatsu Photonics, and the average radiative lifetimes were determined by

$$\tau_{avg} = \left(\sum_{i=1}^{2} \tau_i^2 A_i \right) / \left(\sum_{i=1}^{2} \tau_i A_i \right),$$

where A_i and τ_i are the corresponding amplitudes and exponential decay parameters in a bi-exponential analysis. The absolute luminescent quantum yields (PLQY) were recorded with Hamamatsu absolute PL quantum yield spectrometer C11347.

First-Principle Calculations

Theoretical calculations of band structure and partial density of state (PDOS) were performed using Materials Studio 5.5 program, with generalized gradient approximation (GGA)-perdew-burke-ernzerhof (PBE) functions as implemented in the CASTEP package.[1] During calculation, the plane waves kinetic energy cut off and grid density were chosen as 280 eV and 48 × 48 × 48, respectively, and the convergence tolerance between optimization cycles was set as energy change with 5.0×10^{-7} eV/atm. Meanwhile, the ion-electron interactions were modeled by the ultrasoft pseudopotential for all the elements.

Part III: Supplementary Figures and Tables

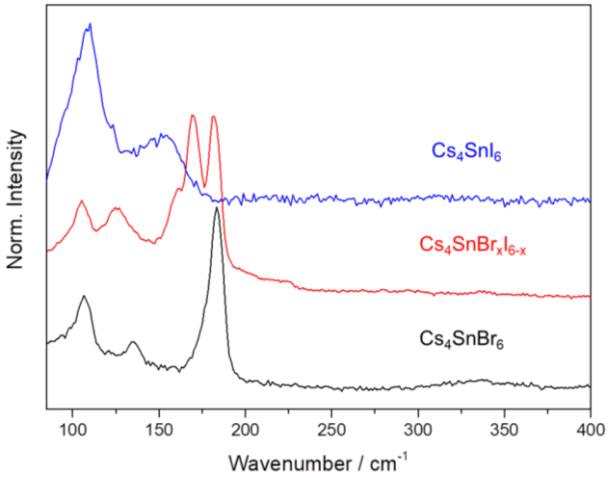

Fig. S1 Raman spectra of as-prepared Cs_4SnBr_6 NCs, $Cs_4SnBr_xI_{6-x}$ NCs and Cs_4SnI_6 NCs, showing Sn-X vibrations of $[SnX_6]^{4-}$ octahedra.

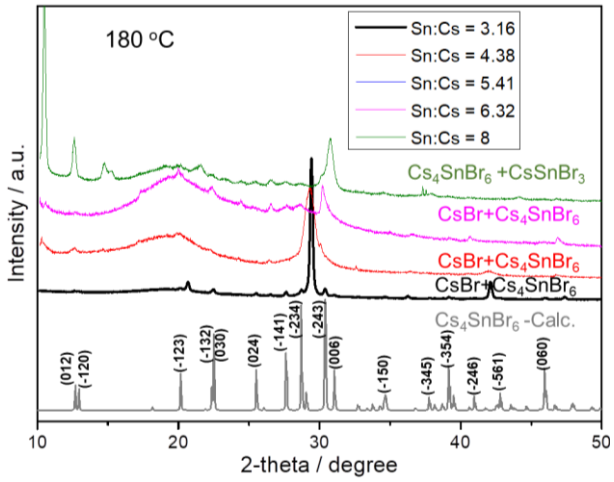

Fig. S2 XRD patterns of Cs_4SnBr_6 NCs synthesized at 180 °C with different Sn/Cs ratios. Note: CsBr and $CsSnBr_3$ impurities are observed.

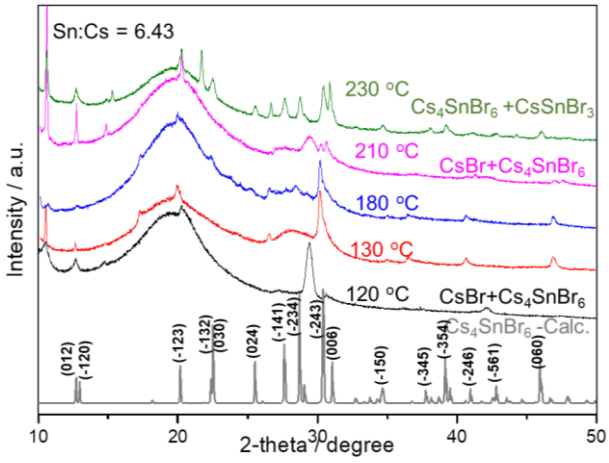

Fig. S3 XRD patterns of Cs_4SnBr_6 NCs synthesized at different temperatures with the Sn/Cs ratio of 6.43. Note: CsBr and $CsSnBr_3$ impurities are observed.

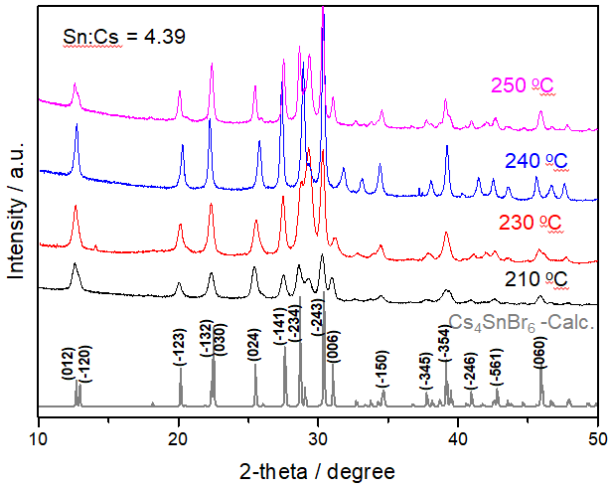

Fig. S4 XRD patterns of Cs_4SnBr_6 NCs synthesized at different temperatures with the Sn/Cs ratio of 4.39.

Table S1 Cs_4SnX_6 (X= Br, I) NC compositions obtained from the quantification of STEM-EDX mapping results.

	Cs_4SnBr_6	$Cs_4SnBr_xI_{6-x}$	Cs_4SnI_6
Cs	33.3 ± 4.7 at.%	28.2 ± 3.8 at.%	38.1 ± 6.2 at.%
Sn	10.2 ± 1.5 at.%	10.5 ± 1.5 at.%	10.9 ± 1.4 at.%
Br	56.6 ± 5.8 at.%	54.6 ± 5.2 at.%	—
I	—	6.6 ± 0.9 at.%	51.0 ± 8.2 at.%

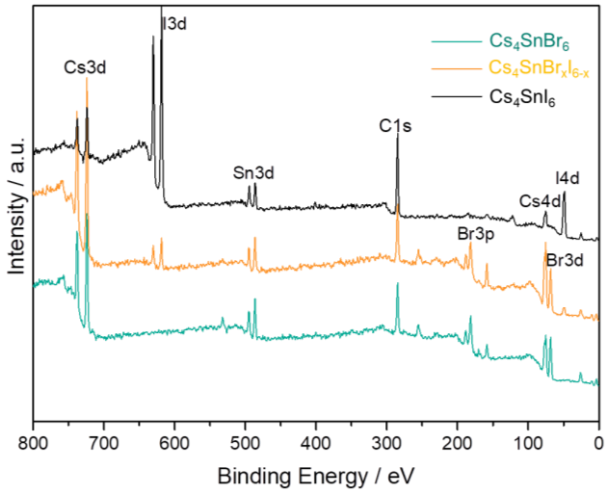

Fig. S5 XPS survey spectra of Cs_4SnX_6 (X = Br, I) NCs.

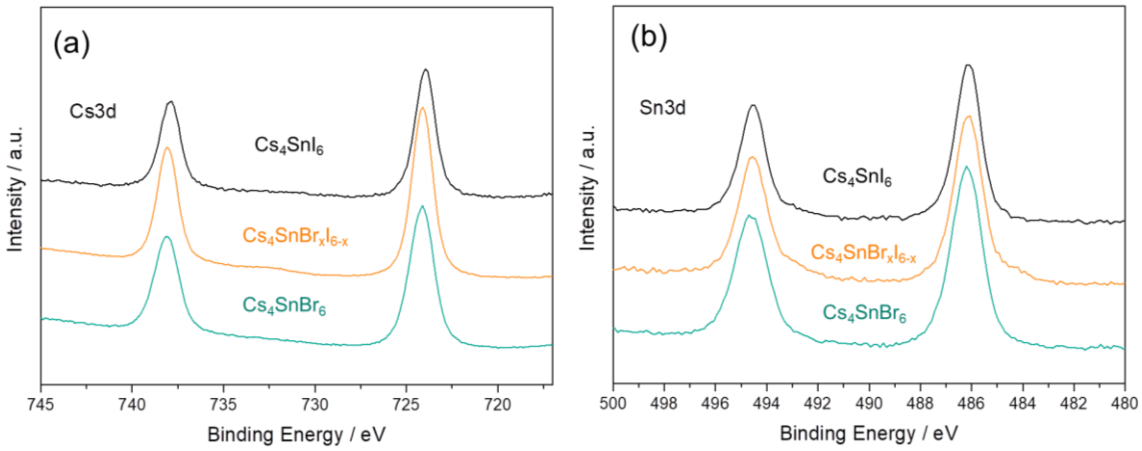

Fig. S6 XPS spectra of Cs3d (a) and Sn3d (b) of Cs_4SnX_6 (X = Br, I) NCs.

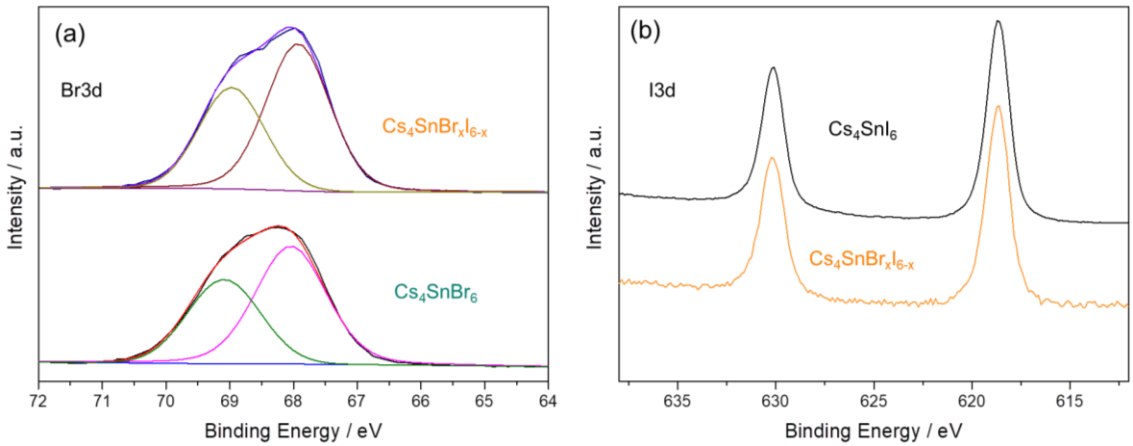

Fig. S7 XPS spectra of Br3d (a) and I3d (b) of Cs_4SnX_6 (X = Br, I) NCs.

Table S2 Cs_4SnX_6 (X= Br, I) NC compositions from the quantification of XPS.

	Cs_4SnBr_6	$Cs_4SnBr_xI_{6-x}$	Cs_4SnI_6
Cs	9.8 at.%	11.98 at.%	4.37 at.%
Sn	2.62 at.%	3.36 at.%	1.39 at.%
Br	14.0 at.%	15.15 at.%	—
I	—	1.77 at.%	7.12 at.%

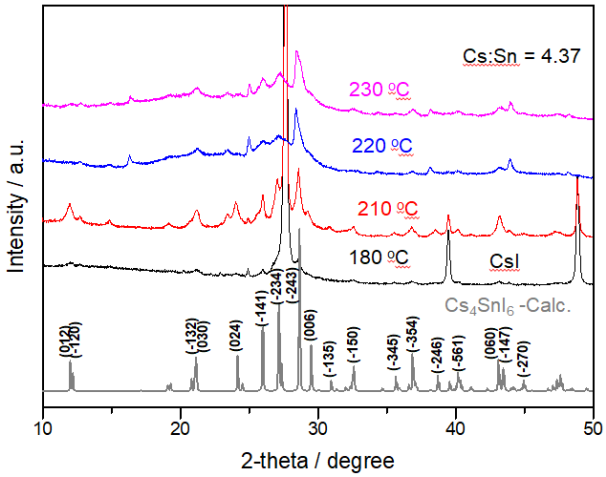

Fig. S8 XRD patterns of Cs_4SnI_6 NCs synthesized at different temperatures with the Sn/Cs ratio of 4.37.

Note: CsI is observed.

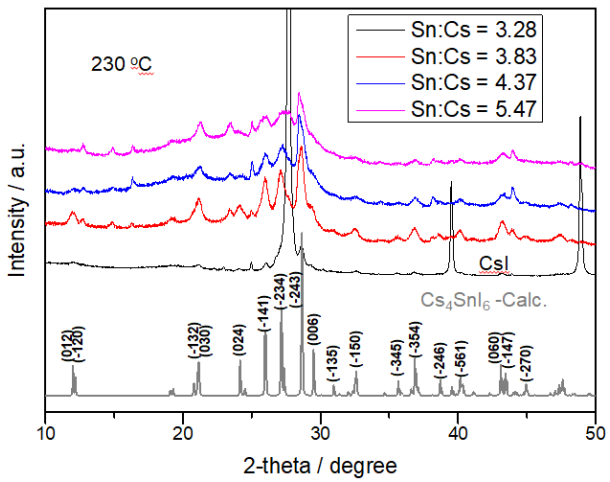

Fig. S9 XRD patterns of Cs_4SnI_6 NCs synthesized at different temperatures with the Sn/Cs ratio of 3.83.

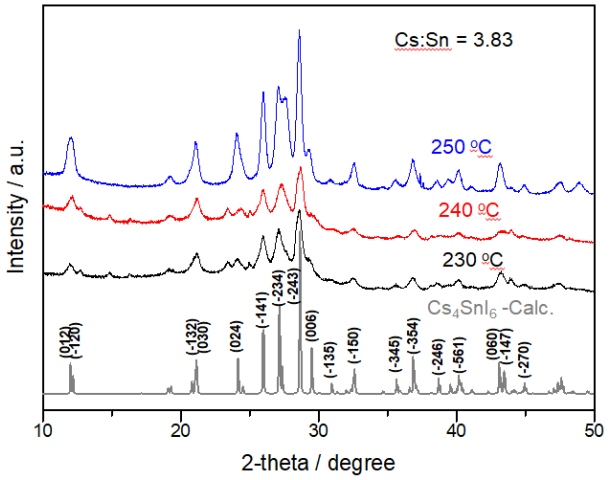

Fig. S10 XRD patterns of Cs_4SnI_6 NCs synthesized at 230 ^{o}C with different Sn/Cs ratios. Note: CsI is observed.

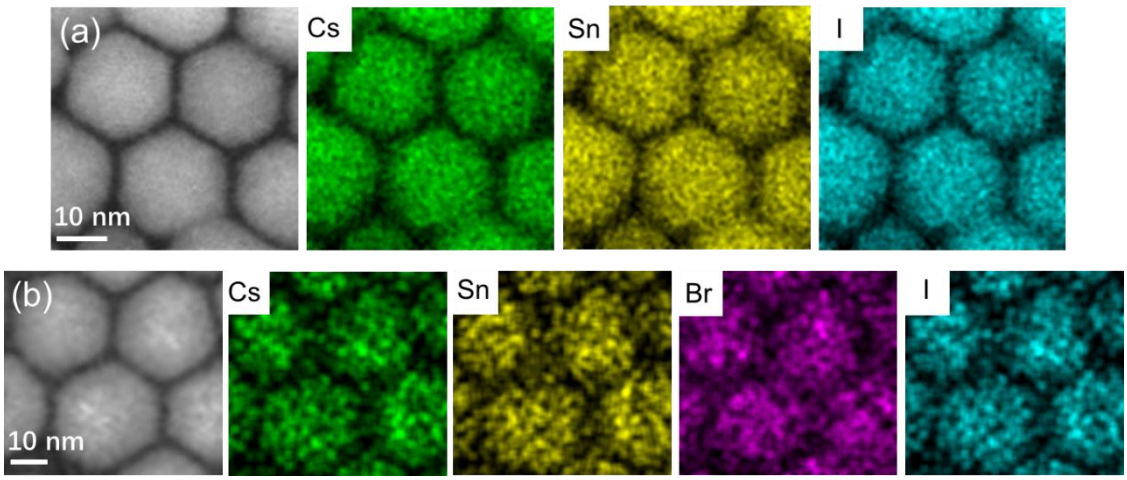

Fig. S11 STEM-EDX mapping results of Cs_4SnI_6 NCs (a) and $Cs_4SnBr_xI_{6-x}$ NCs (b).

Table S3 Overview of optical characterizations of Cs_4SnX_6 (X = Br, I) NCs, including PLQYs, PL emission peaks, FWHM values, Stokes shifts and PL lifetimes. Note: all the values are the average of three measurements from three individual samples.

	PLQY (%)	**PL peak (nm)**	**FWHM (nm)**	**Stokes Shift (nm)**	**PL Lifetime (ns)**
Cs_4SnBr_6	21	534	119	215	737
$Cs_4SnBr_xI_{6-x}$	6.6	546	121	227	253
Cs_4SnI_6	0.7	578	121	215	13

Table S4 PLQY comparisons of all-inorganic tin-halide NCs.

	PLQYs
Cs_2SnI_6 [2]	0.48 % (quantum dots), 0.11 % (nanorods), 0.08% (nanowire), 0.054 % (nanobelts), 0.046 % (nanoplates)
$CsSn(Br_{0.5}I_{0.5})_3$ [3]	0.05 % (nanocubes)
$CsSnBr_3$ [3, 4]	2.1 % (nanocages), 0.14 % (nanocubes)
$CsSnI_3$ [3]	0.06 % (nanocubes)
Cs_4SnX_6 (This work)	21.4 % (Cs_4SnBr_6), 6.6 % ($Cs_4SnBr_xI_{6-x}$), 0.7 % (Cs_4SnI_6)

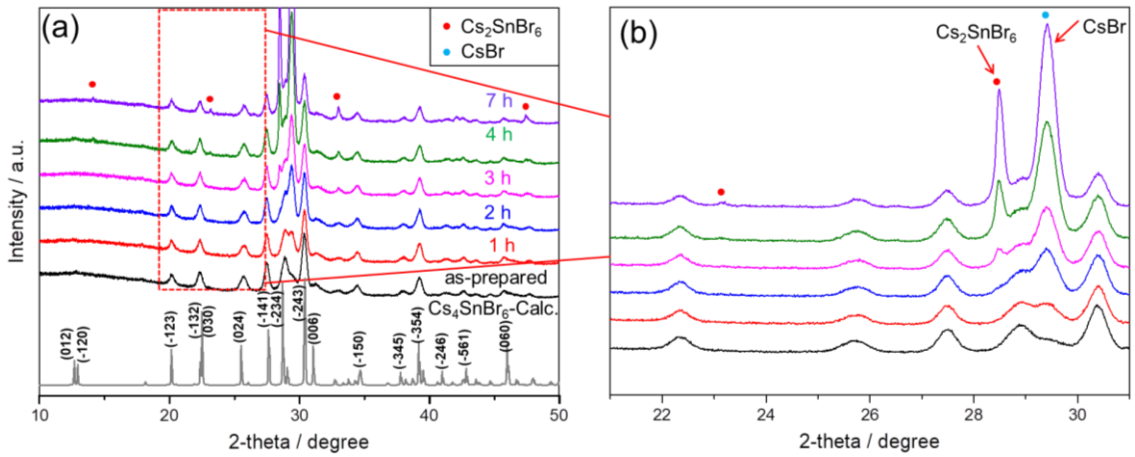

Fig. S12 XRD patterns of Cs_4SnBr_6 NCs after storage in air. (a) The XRD evolutions of Cs_4SnBr_6 NCs after storage in air for 1 h, 2 h, 3 h, 4 h and 7 h, showing that Cs_4SnBr_6 phase gradually changes into Cs_2SnBr_6 and CsBr. (b) Enlarged-view of the XRD patterns, indicating the formation of CsBr within 1 h and the formation of Cs_2SnBr_6 after 2 h.

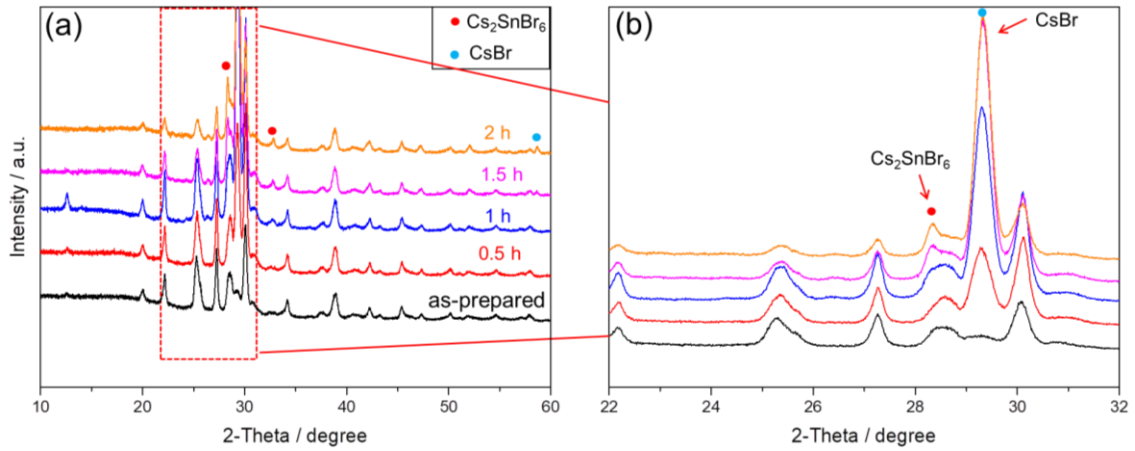

Fig. S13 XRD patterns of $Cs_4SnBr_xI_{6-x}$ NCs after storage in air. (a) The XRD evolutions of $Cs_4SnBr_xI_{6-x}$ NCs after storage in air for 0.5 h, 1 h, 1.5 h and 2 h, showing that $Cs_4SnBr_xI_{6-x}$ phase gradually changes into Cs_2SnBr_6 and CsBr. (b) Enlarged-view of the XRD patterns, indicating the formation of CsBr and Cs_2SnBr_6 within 1 h. Note: the Br/I ratio in $Cs_4SnBr_xI_{6-x}$ NCs is around 9:1, and thus Cs_2SnBr_6 and CsBr compounds are easily observed.

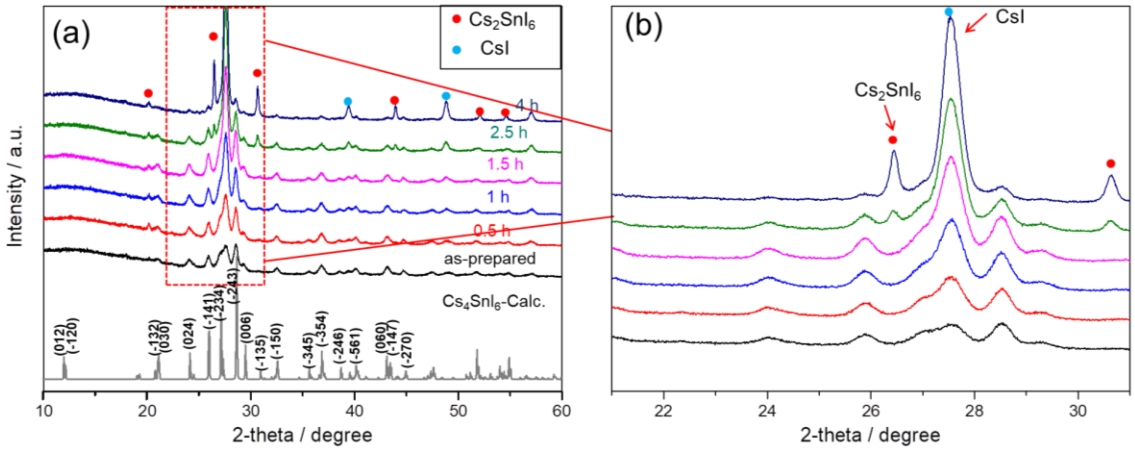

Fig. S14 XRD patterns of Cs_4SnI_6 NCs after storage in air. (a) The XRD evolutions of Cs_4SnI_6 NCs after storage in air for 0.5 h, 1 h, 1.5 h, 2.5 h, and 4 h, showing that Cs_4SnI_6 phase gradually changes into Cs_2SnI_6 and CsI. (b) Enlarged-view of the XRD patterns, indicating the formation of CsI and Cs_2SnI_6 within half an hour.

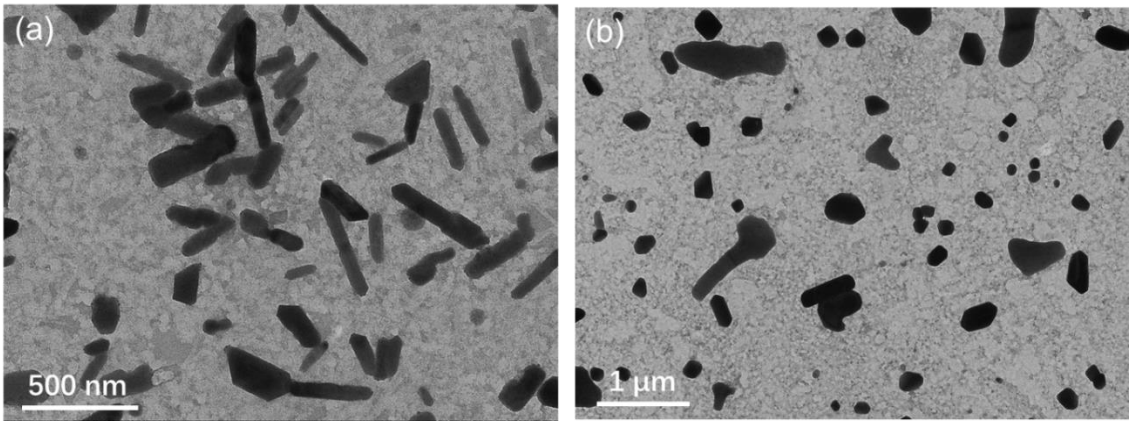

Fig. S15 TEM images of (a) Cs_4SnBr_6 NCs and (b) Cs_4SnI_6 NCs after storage in air for 1 week.

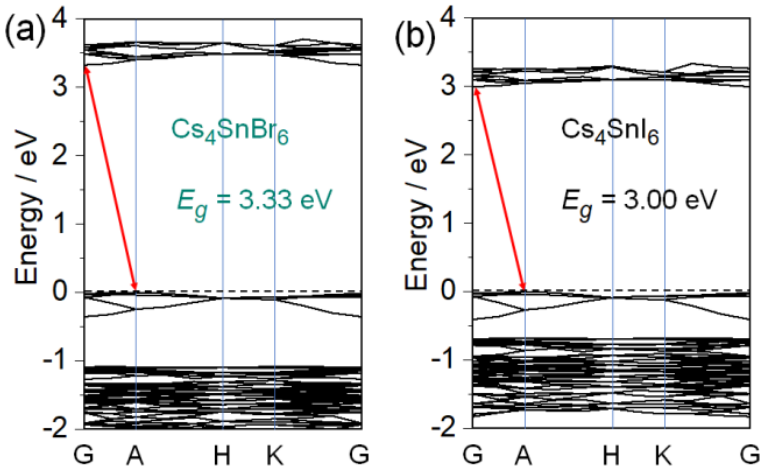

Fig. S16 Electronic band structures of (a) Cs_4SnBr_6 and (b) Cs_4SnI_6 calculated based on the PBE functions (E_g, bandgap energy).

References

1. J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865-3868.
2. A. Wang, X. Yan, M. Zhang, S. Sun, M. Yang, W. Shen, X. Pan, P. Wang and Z. Deng, *Chem. Materi.*, 2016, **28**, 8132-8140.
3. T. C. Jellicoe, J. M. Richter, H. F. J. Glass, M. Tabachnyk, R. Brady, S. E. Dutton, A. Rao, R. H. Friend, D. Credgington, N. C. Greenham and M. L. Böhm, *J. Am. Chem. Soc.*, 2016, **138**, 2941-2944.
4. A. Wang, Y. Guo, F. Muhammad and Z. Deng, *Chem. Mater.*, 2017, **29**, 6493-6501.