

Supporting Information

All inorganic cesium lead halide perovskite nanocrystals for photodetector applications

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Experimental Section

Materials: Cesium carbonate (Cs_2CO_3 , 99.9%), Lead(II) bromide (PbBr_2 , 99.999%), Lithium iodide (LiI , 99%) were all used as received from Sigma Aldrich. Lithium bromide (LiBr , 99.998%), Lithium chloride (LiCl , 99.995%) were purchased from Alfa Aesar and used as received. 1-octadecene (ODE, 90%), Hexane (95%, anhydrous grade) and Ethanol (anhydrous grade, 99.5%) were purchased from Sigma-Aldrich and used without further purification. Oleic acid (OA, 90%) and Oleylamine (OAm, 70%) were purchased from Sigma-Aldrich and dried under vacuum.

Preparation of Cs-oleate: 0.207 g of Cs_2CO_3 was mixed with 10 mL of ODE and 625 μL of OA in a three neck flask. The mixture was dried under vacuum at 120 °C for 1 h. Then the mixture was heated to 150 °C under N_2 until all Cs_2CO_3 reacted with OA and kept at 100 °C.

Synthesis of CsPbBr_3 NCs: 0.069 g of PbBr_2 and 5 mL of ODE were loaded into 25 mL 3-neck flask and dried under vacuum for 1h at 120 °C. Dried OAm (0.5 mL) and dried OA (0.5 mL) were injected at 120 °C under N_2 . After complete solubilisation of a PbBr_2 salt, the temperature was raised to 160 °C. Then 0.4 mL of above mentioned Cs-oleate solution was injected quickly

and 5s later, the reaction mixture was cooled by the ice-water bath. The NCs were precipitated using ethanol, re-dispersed in 30 mL of hexane and filtered through 0.2 μm PTFE filter.

Anion exchange reactions: All the exchange reactions were carried out at room temperature in air. Typically, 10 μL of ethanol solution of LiI or LiCl was added to 1 mL of above prepared CsPbBr₃ NCs in hexane (~2 mg/mL). Then the mixture was shaken vigorously which produced a color change from green to red for LiI and colorless for LiCl. The whole exchange reaction was completed in less than 5 seconds. Then the mixture was filtered through 0.2 μm PTFE filter and taken for analysis.

Reverse anion exchange reactions: For the reverse anion exchange, first the CsPbBr₃ NCs were exchanged with LiI or LiCl to CsPbI₃ or CsPbCl₃ NCs. Then 10 μL of ethanol solution of LiBr was added to 1 mL of above prepared CsPbI₃ or CsPbCl₃ NCs. Then the mixture was shaken vigorously which produced a color change from red to green for CsPbI₃ NCs and colorless to green for CsPbCl₃ NCs. Then the mixture was filtered through 0.2 μm PTFE filter and taken for analysis.

The position of absorption and emission peaks with different concentration of lithium halides are listed in **Table S2**.

Characterization:

X-Ray Diffraction (XRD). X-ray diffractograms were obtained by using a Rigaku MiniFlex 600 diffractometer, equipped with a Cu K α X-ray source ($\lambda=1.5418$ Å). Samples for XRD analysis were prepared by depositing a hexane dispersions NCs on a microscopic glass substrate.

Transmission Electron Microscopy (TEM). TEM, High-resolution TEM (HRTEM) images, STEM Energy Dispersive X-ray Spectroscopy (EDS) spectra were performed on a JEOL-2100F

microscope operating at 200 KeV. Samples were prepared by dropping diluted nanocrystals colloidal suspensions onto a carbon-coated 200 mesh copper grids.

UV-vis Absorption Spectroscopy. Absorption spectra of NCs dispersed in hexane were measured in 1 cm path length quartz cuvettes using a Cary 5000 UV-vis-NIR (Agilent Technologies) spectrophotometer.

Photoluminescence Spectroscopy. PL spectra of NCs dispersed in hexane were measured using Cary Eclipse fluorescence spectrophotometer. (λ_{exc} = 400 nm for all samples but 350 nm for blue emitting CsPbCl₃ samples).

Time resolved PL spectra. The Time-resolved PL spectra was measured using time-correlated single photon counting system (Picoquant, Fluotime 200). The PL emission from the samples was collected by a pair of lenses into the concave holographic grating of 1200g/mm and detected by photomultiplier tube (PMT). The temporal resolution, repetition rate are 80 ps, 10 MHz, respectively. The samples were excited by with 375 nm pulses (LDH-P-C-375, 3 μ W) at room temperature. PL decay curves were fitted by a biexponential decay function (1)

$$I_{PL}(t) = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2} \quad (1)$$

Photocurrent measurements. To evaluate the photoresponse of the CsPbI₃ NCs, two parallel gold electrodes pre-patterned on highly doped silicon wafers with a 100 nm thermal oxide layer was used. The samples were prepared by drop-casting purified colloidal nanostructures in hexane solution onto the substrate. The devices were annealed at 200 °C for 30 min under nitrogen atmosphere. The current–voltage characteristics were recorded using a Keithley 2636A Source Meter with or without illumination under 405nm laser diode with the light intensity from 0.01mw/cm² to 1.38mw/cm². The scan voltage was tuned from –3V to 3 V.

For measurements of the photocurrent action spectra. The photocurrents were measured under monochromatic illumination from a 150W Xenonarc lamp (Oriel #67005) dispersed with the motorized monochromator (Oriel Cornerstone 130 1/8m) with the grating artifacts filtered out. The light intensity at each wavelength was measured with calibrated Si detector (Merlin, 10x10mm, 200-1100nm), mounted exactly in place of the NC samples. The photocurrent response at each wavelength was measured using a Keithley 2400 source meter controlled by home-written Labview program. The action spectra were typically measured by scanning the wavelengths from 750 nm to 450 nm.

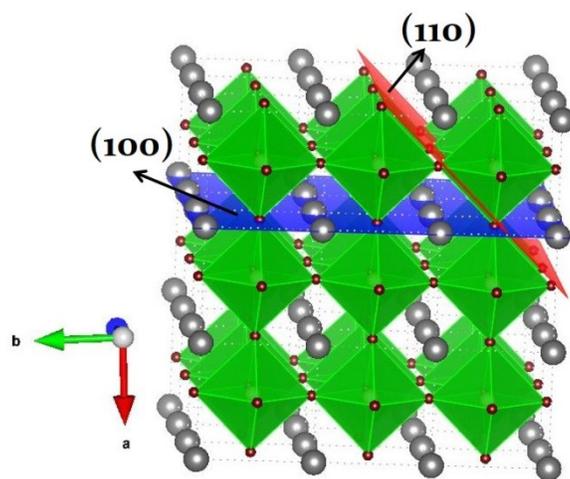


Fig. S1 Crystal structure of CsPbBr₃ with (100) and (110) planes.

Table S1. EDS data of CsPbBr₃ and CsPbI₃ NCs. Due to the very thin nature of CsPbCl₃ NCs we couldn't get any quantitative data.

	CsPbBr ₃ (at %)			CsPbI ₃ (at %)		
	Cs	Pb	Br	Cs	Pb	I
1	21.3	22.6	56.1	21.0	19.3	59.5
2	22.4	22.9	54.7	21.4	19.0	59.6
3	15.5	20.4	64.1	21.6	20.7	57.7
Average ratio	19.7	21.96	58.3	21.3	19.6	58.93

Table S2. The position of absorption and emission peaks of CsPbBr₃ NCs exchange reactions with different concentration of lithium halides.

Lithium halide	Concentration (M)	Volume (μL)	Absorbance (nm)	Emission (nm)
CsPbBr ₃ to CsPbI ₃ (CsPbBr ₃ NCs emission – 508 nm)				
LiI	0.16	10	510	532
LiI	0.32	10	544	570
LiI	0.64	10	589	615
LiI	1.28	10	634	654
CsPbBr ₃ to CsPbCl ₃ (CsPbBr ₃ NCs emission – 508 nm)				
LiCl	0.16	10	452	483
LiCl	0.32	10	430	459
LiCl	0.64	10	405	425

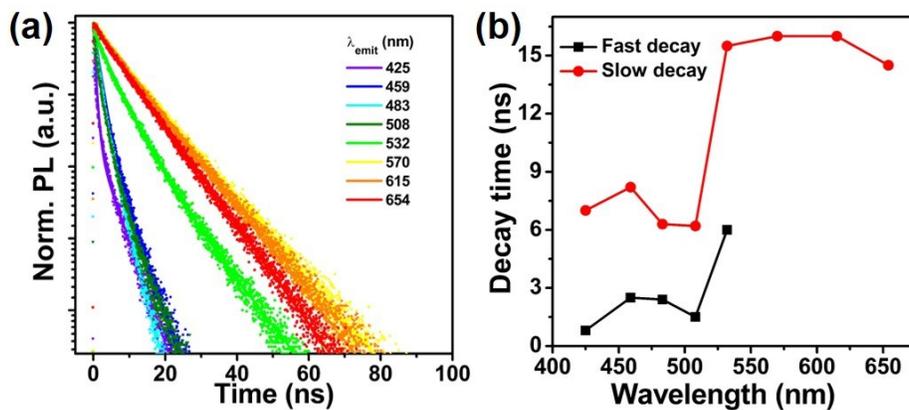


Fig. S2 Time-resolved PL decays and radiative lifetimes of parent CsPbBr₃ and all the anion exchange synthesized samples.

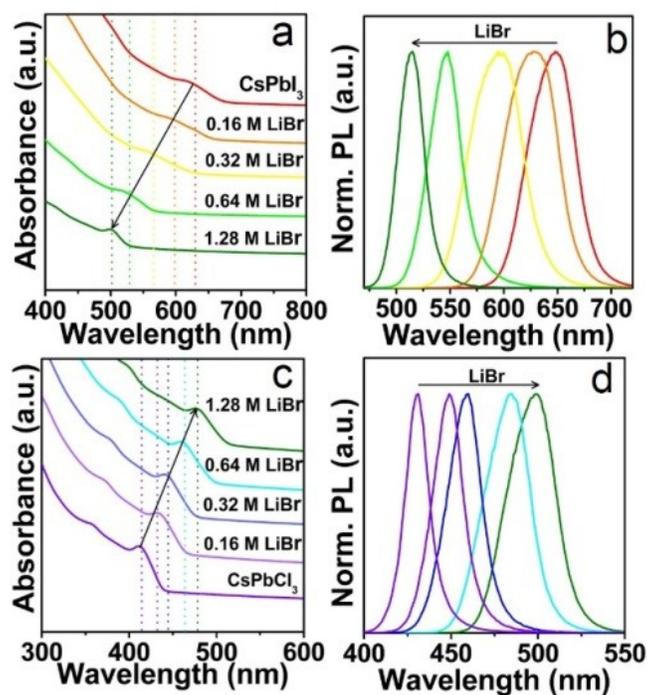


Fig. S3 Absorption and PL spectra of the (a,b) CsPbI₃-CsPbBr₃ and (c,d) CsPbCl₃-CsPbBr₃ reverse halide exchange reactions.

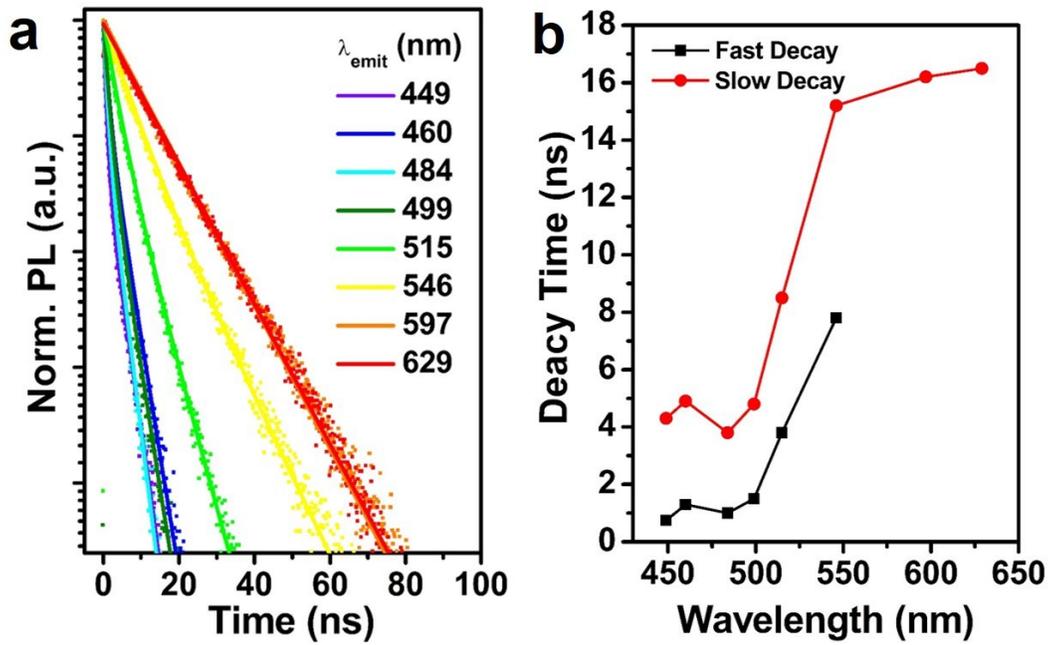


Fig. S4 Time-resolved PL decays and radiative lifetimes of CsPbX₃ nanocrystals synthesized by reverse halide exchange.

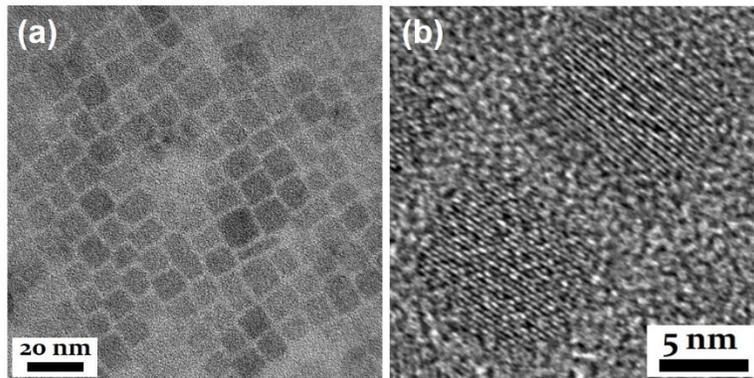


Fig. S5 TEM images of CsPbBr₃ NCs synthesized from reverse exchange reactions of CsPbI₃.

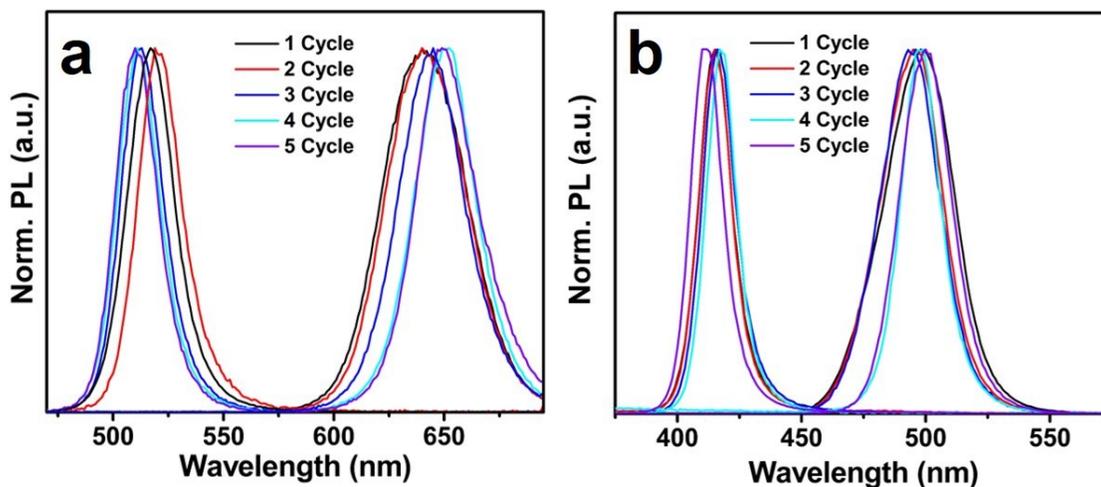


Fig. S6 PL spectra of complete exchange cycles for (a) CsPbI₃ to CsPbBr₃ and (b) CsPbCl₃ to CsPbBr₃ conversion.

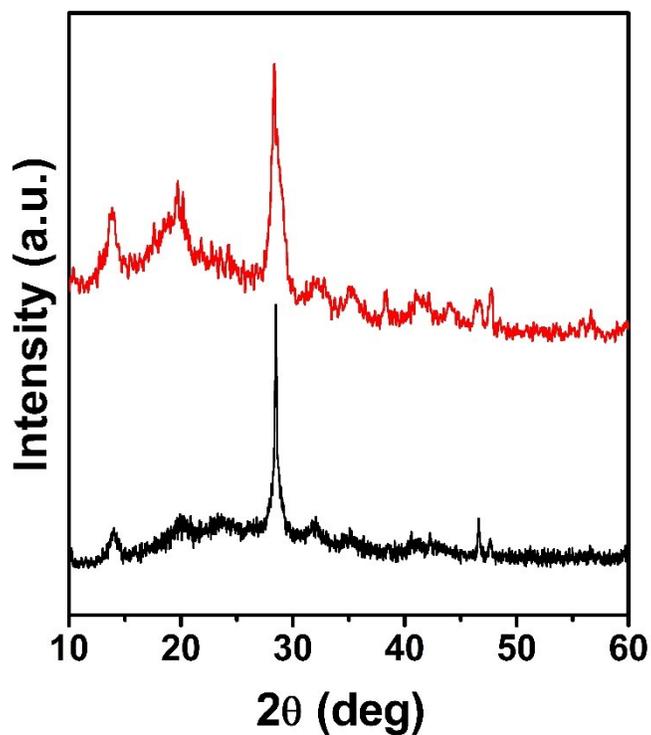


Fig. S7 XRD patterns of as prepared (black) and 200 °C annealed (red) CsPbI₃ nanocrystals films.

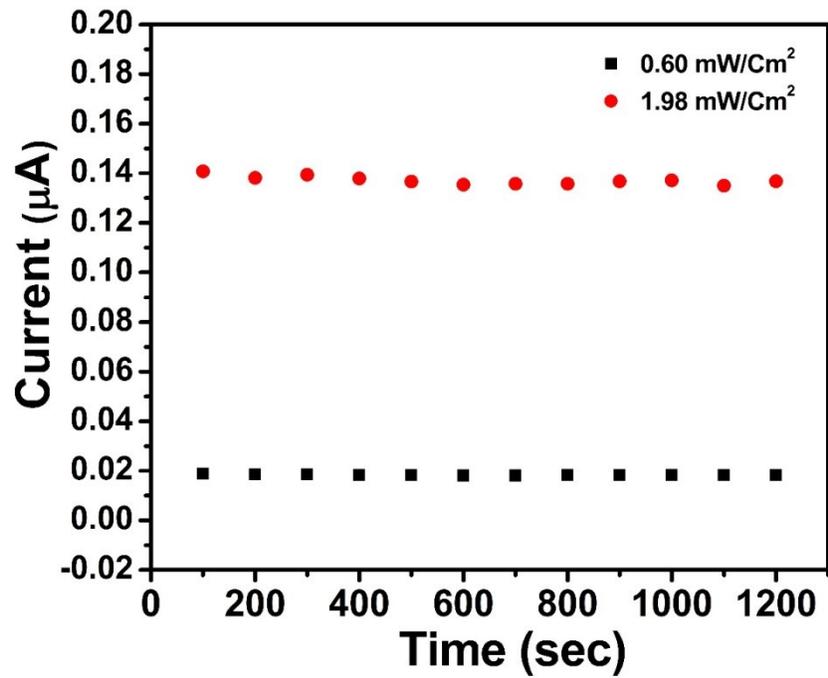


Fig. S8 Photocurrent of CsPbI₃ NCs photodetector measured under continuous illumination using a 405 nm laser diode ($V_{DS} = 1V$).