Growth Kinetics Controlling of $CsPbX_3$ Nanocrystals through Spatial Confinement Effect

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Experimental Section

Materials: Cesium acetate (CsAc, $C_2H_3CsO_2$, 99.9% metals basis), lead acetate trihydrate ($PbAc_2{\cdot}3H_2O$, $C_4H_6O_4Pb{\cdot}3H_2O$, 99.99%), magnesium iodide hydrate ($MgI_2{\cdot}xH_2O$, 98%), magnesium bromide ($MgBr_2$, 98%), hydroiodic acid (HI, 55-58%), hydrobromic acid (HBr, 48 wt. % in H_2O, 99.99%) oleic acid (OA, $C_{18}H_{34}O_2$, AR), oleylamine (OAm, $C_{18}H_{37}N$, 80-90%), acetonitrile (C_2H_3N, HPLC), n-hexane (C_6H_{14}, 98%). The above chemicals are all purchased from Aladdin and can be used directly without any purification.

Preparation of Cs/Pb-OA precursor solution: CsAc (0.5 mmol) and $PbAc_2$ (0.5 mmol) were added into oleic acid (1 mL). The mixture was then stirred and heated at 120 °C for 30 min to dissolve the salts.

Synthesis of $CsPbBr_3$ or $CsPbI_3$ NCs: MgX_2-HX solution (100 μL, 2 M or 1 M for $CsPbBr_3$ or $CsPbI_3$, respectively) was mixed with acetonitrile (5 mL) to receive the solution **A**. OAm (100 μL) and Cs/Pb-OA (100 μL) were added into 10 mL of hexane to get the solution **B**. Under continuing stirring, a certain amount of solution **B** was injected into solution **A**, the reaction was stopped after 1 min. Then, the crude solution was centrifugated at 9000 rpm for 5 min, and the NCs dispersed in the upper layer (hexane) was collected. More details can be found in **Table S2**.

Characterization: Powder XRD patterns were recorded using a Bruker D8 Advance X-ray diffractometer (Cu Ka, l = 1.5406 Å). TEM analysis was carried out with an FEI Talos F200X microscope at an operating voltage of 200 kV. UV-vis absorption spectra were obtained using a Specord 200 Plus spectrophotometer. PL and PL lifetimes were obtained by using an EI-FLS1000 fluorescence spectrometer (Edinburgh Instruments) equipped with an integrating sphere. By using atomic forcemicroscopy in ScanAsyst-Air mode (AFM, Multi Mode 8, Bruker).

Computational methods: Density-functional theory (DFT) calculations were

performed using the Device studio program (from HZWTECH). The generalized gradient approximation with the Perdew–Burke–Ernzerhof functional was employed for geometric optimization. A grid with 3 × 3 × 1 k-points was used for Brillouinzone integration. In addition, the inner electrons of Cs, Pb, and I atoms were kept frozen and substituted by effective core potentials; this approximation was not applied to the other atoms during these calculations. A Fermi smearing of 0.005 Hartree was used to accelerate convergence, and the real-space cutoff was set to 6.2 Å in order to improve the computational performance. In addition, the tolerances on energy, force, and displacement convergence were set to 1×10^{-5} Hartree, 2×10^{-3} Hartree $Å^{-1}$, and 5×10^{-3} Å, respectively.

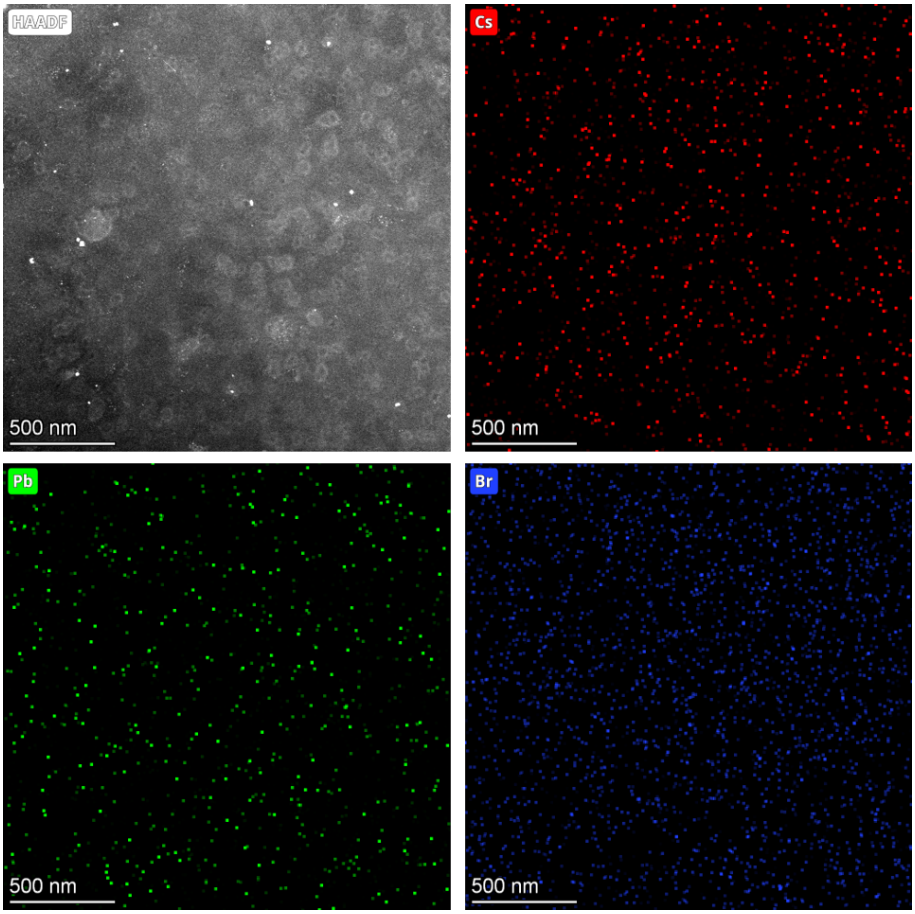

Figure S1. HAADF-STEM and STEM-EDX images of $CsPbBr_3$ NCs.

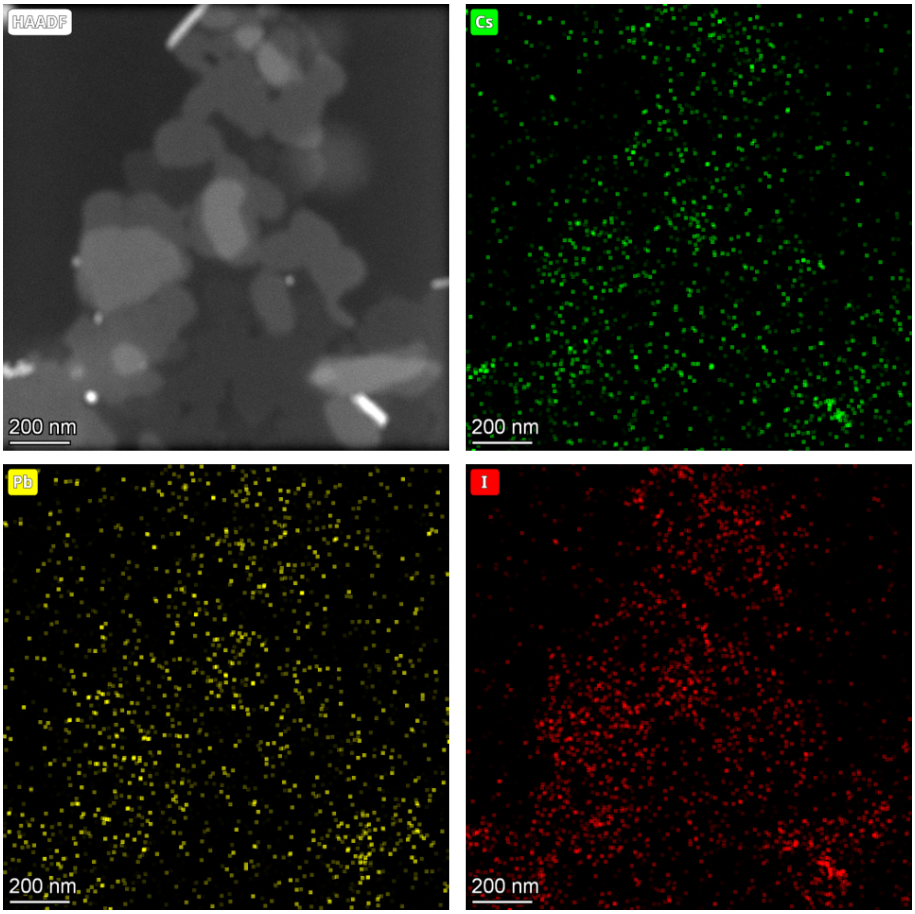

Figure S2. HAADF-STEM and STEM-EDX images of $CsPbI_3$ NCs.

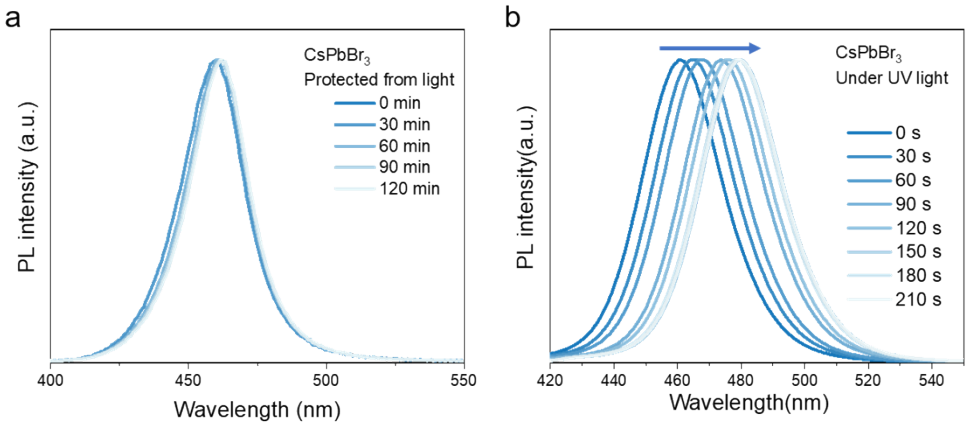

Figure S3. PL spectra of $CsPbBr_3$ NCs protected from light (a) or under UV lamp irradiation (b).

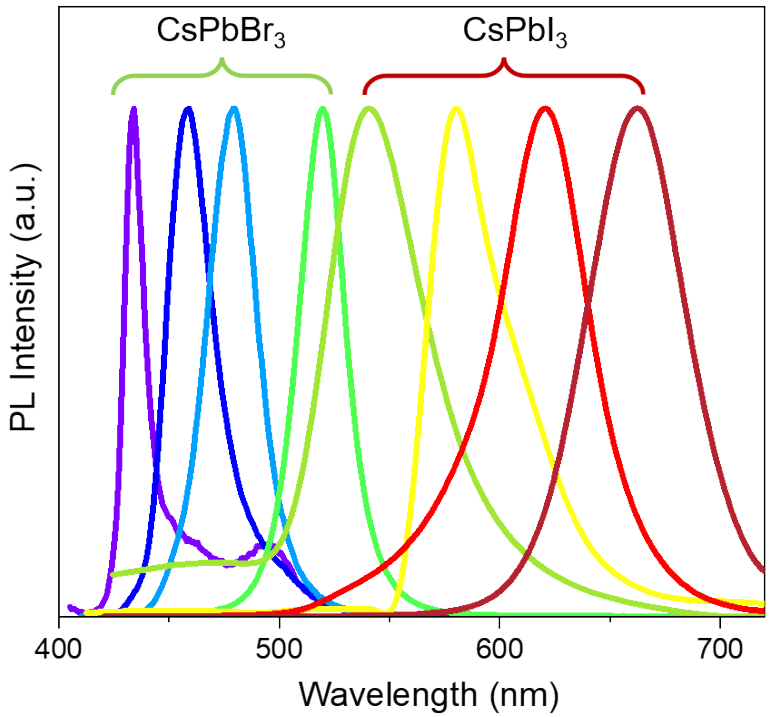

Figure S4. PL spectra of $CsPbX_3$ NCs ultra-wide spectral ranges.

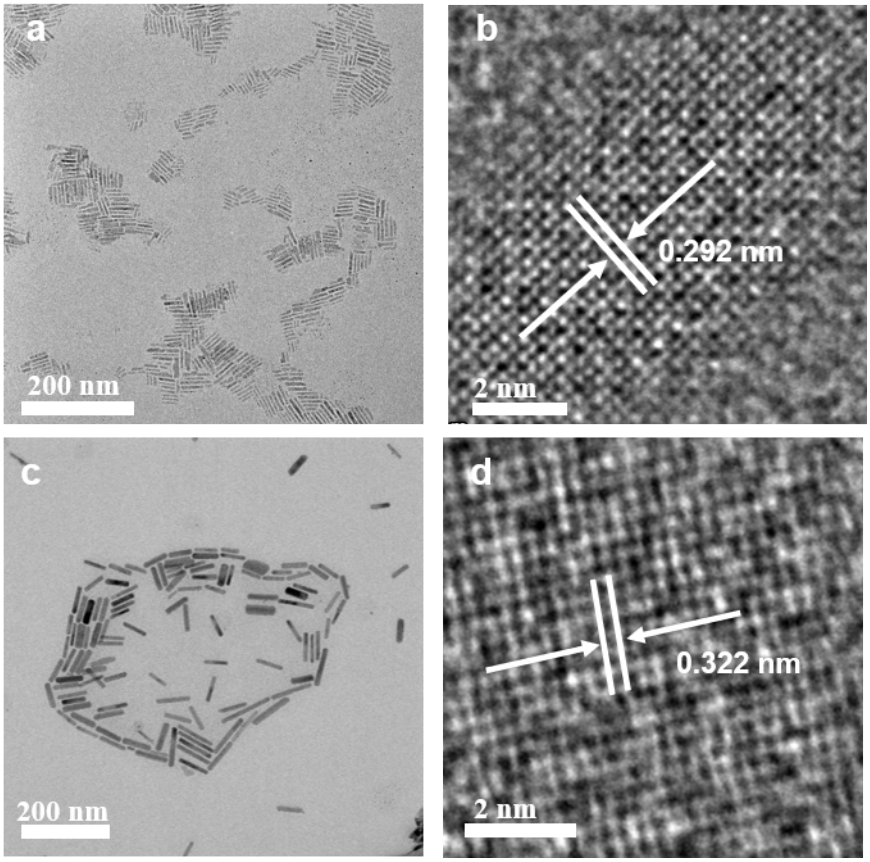

Figure S5. TEM and HRTEM image of $CsPbBr_3$ (a,b) and $CsPbI_3$ (c,d) NCs

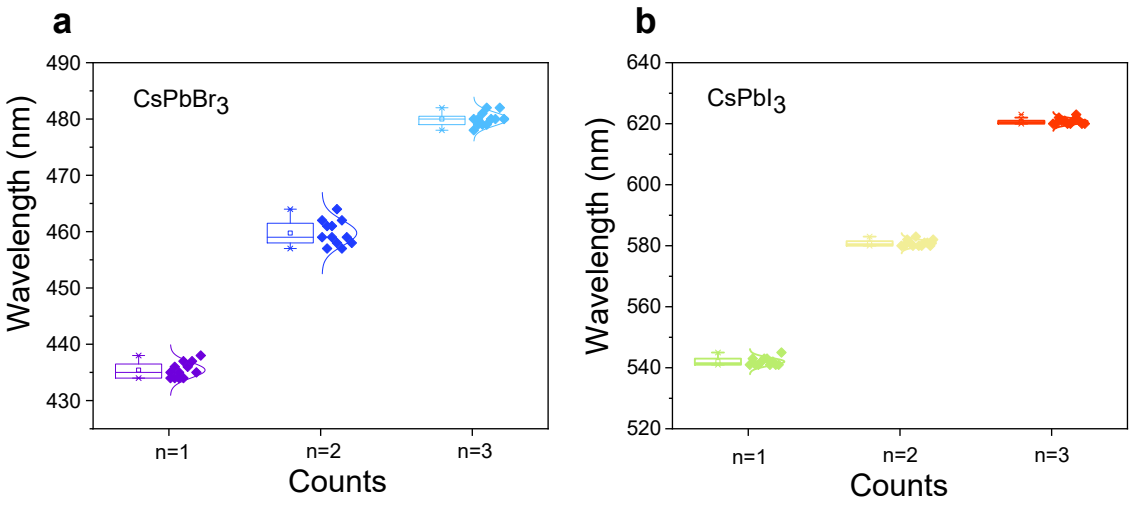

Figure S6. PL spectra of perovskite quantum dots from different batches (a) $CsPbBr_3$, (b) $CsPbI_3$.

Table S1. PL lifetimes of the different samples.

Sample		τ_1 (ns)	A_1 (%)	τ_2 (ns)	A_2 (%)	τ_{ave} (ns)
$CsPbBr_3$	n=1	5.9	46.2	14.5	46.4	9.4
	n=2	7.4	18.8	14.2	10.4	11.0
	n=3	6.3	35.7	19.2	50.1	14.5
$CsPbI_3$	n=1	4.5	32.2	14.1	13.1	13.6
	n=2	11.3	22.3	20.2	22.1	14.9
	n=3	12.2	0.02	43.4	0.01	16.5

Table S2. Detailed information for the synthesis of $CsPbX_3$ NCs.

OAm (μL)	Cs/Pb-OA (μL)	MgX_2-HI (μL)	Temperature (℃)	PL peaks (nm)
160	80	100	0	435
160	80	150	0	459
160	80	200	0	480
160	80	100	60	519
120	80	100	0	541
120	80	150	0	580
120	80	200	20	620
120	80	100	60	662

Table S3. PLQY of $CsPbX_3$ NCs.

Sample		PL peaks (nm)	PLQY (%)
$CsPbBr_3$	n=1	435	52
	n=2	459	72
	n=3	480	85
	n=∞	519	95
$CsPbI_3$	n=1	541	55
	n=2	580	70
	n=3	620	72
	n=∞	662	95