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Supplementary Information for

Crystalline Phase-Controlled Synthesis of Regular and Stable Endotaxial Cesium Lead Halide Nanocrystals

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Figure S1. Photographs showing the transformation process of Cs_4PbBr_6 NCs to $CsPbBr_3$ NCs. The samples were illuminated with natural light (top) and UV 365nm irradiation (bottom). (1) Water, (2) Cs_4PbBr_6 nanocrystals dispersed in octane. (3) Solution with injecting Cs_4PbBr_6 nanocrystals into water

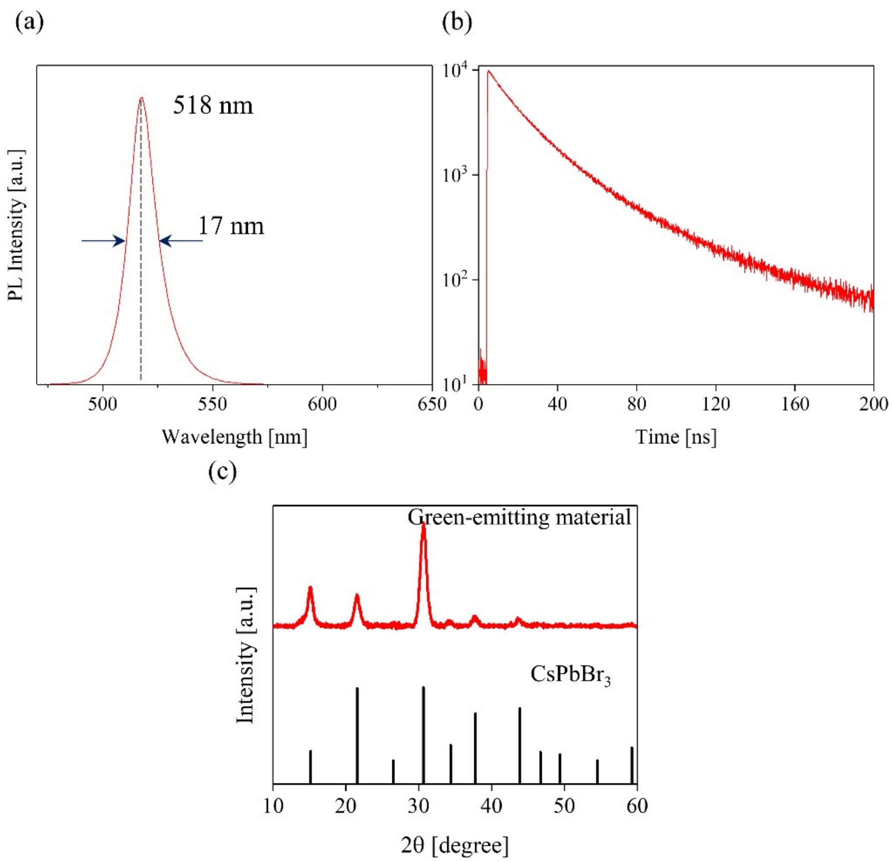

Figure S2. (a) PL emission spectra; (b) Time-resolved PL and (c) XRD patterns of supernatant of the mixture of $C_{S4}PbBr_6$ octane solution and water.

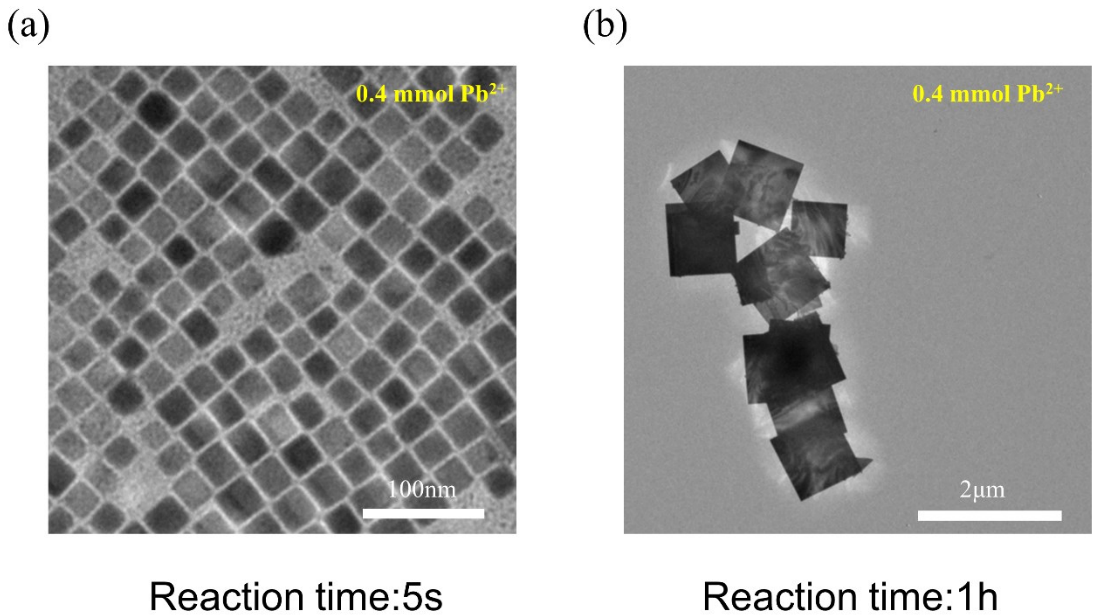

Figure S3. TEM images of nanocrystals synthesized both with 0.4 mmol Pb but different reaction time: (a) 5 s and (b) 1 h

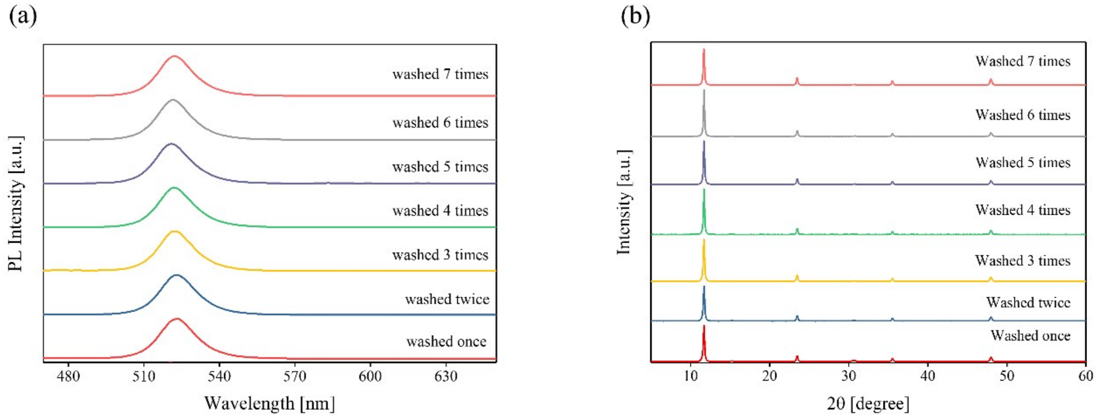

Figure S4. (a) PL emission spectra of $CsPb_2Br_5$ NSs dispersed in toluene with different washing cycles. (b) Corresponding XRD patterns of the samples in (a).

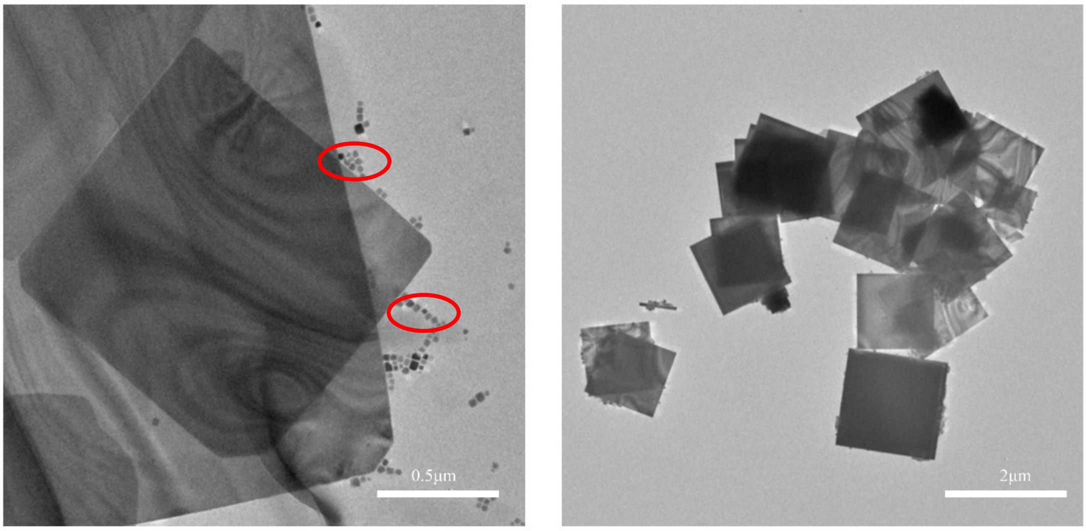

Figure S5. (a) TEM images of NSs synthesized with 0.3mmol Pb^{2+} (left) and 0.4mmol Pb^{2+} (right).

Time-resolved PL decays were fitted to

$$A(t) = A_1 \exp\left(-\frac{\tau}{\tau_1}\right) + A_2 \exp\left(-\frac{\tau}{\tau_2}\right) + A_3 \exp\left(-\frac{\tau}{\tau_3}\right). \quad (1)$$

The average lifetimes were calculated using the intensity-weighted model as

$$\tau = (A_1\tau_1^2 + A_2\tau_2^2 + A_3\tau_3^2)/(A_1\tau_1 + A_2\tau_2 + A_3\tau_3). \quad (2)$$

Table S1. The fitting results of PL decay for nanocrystals synthesized with 0.1mmol, 0.3mmol and 0.4mmol Pb^{2+}, respectively.

	0.1 mmol Pb^{2+}	0.3 mmol Pb^{2+}	0.4 mmol Pb^{2+}
A_1	5005.0	323.9	307.1
τ_1	6.97	149.31	232.55
A_2	3544.0	3135.3	2776.5
τ_2	2.94	30.93	40.76
A_3	412.5	5344.0	5367.0
τ_3	16.67	7.21	9.55
τ_{ave}	7.44	57.10	92.05

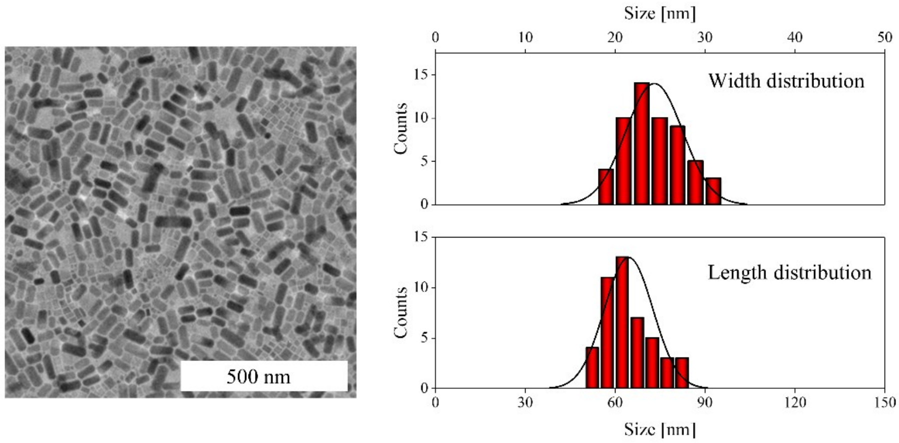

Figure S6. TEM images of hexagonal nanorods and histograms of length and width distributions.

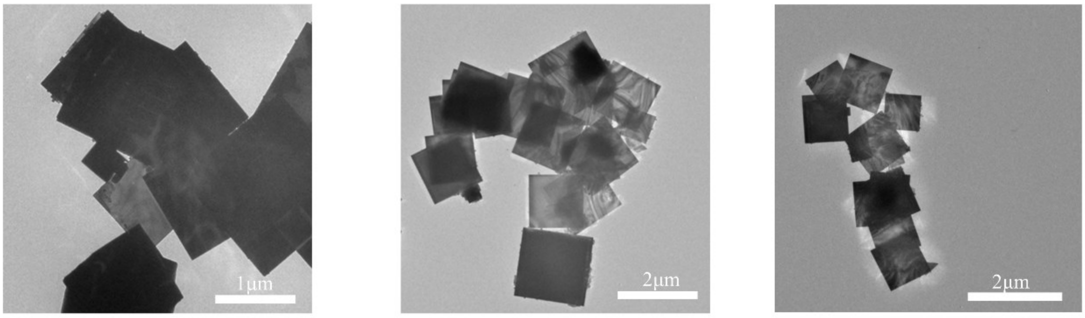

Figure S7. TEM images of pure $CsPb_2Br_5$ NSs with 7 washing cycles showing no obvious $CsPbBr_3$ NCs.

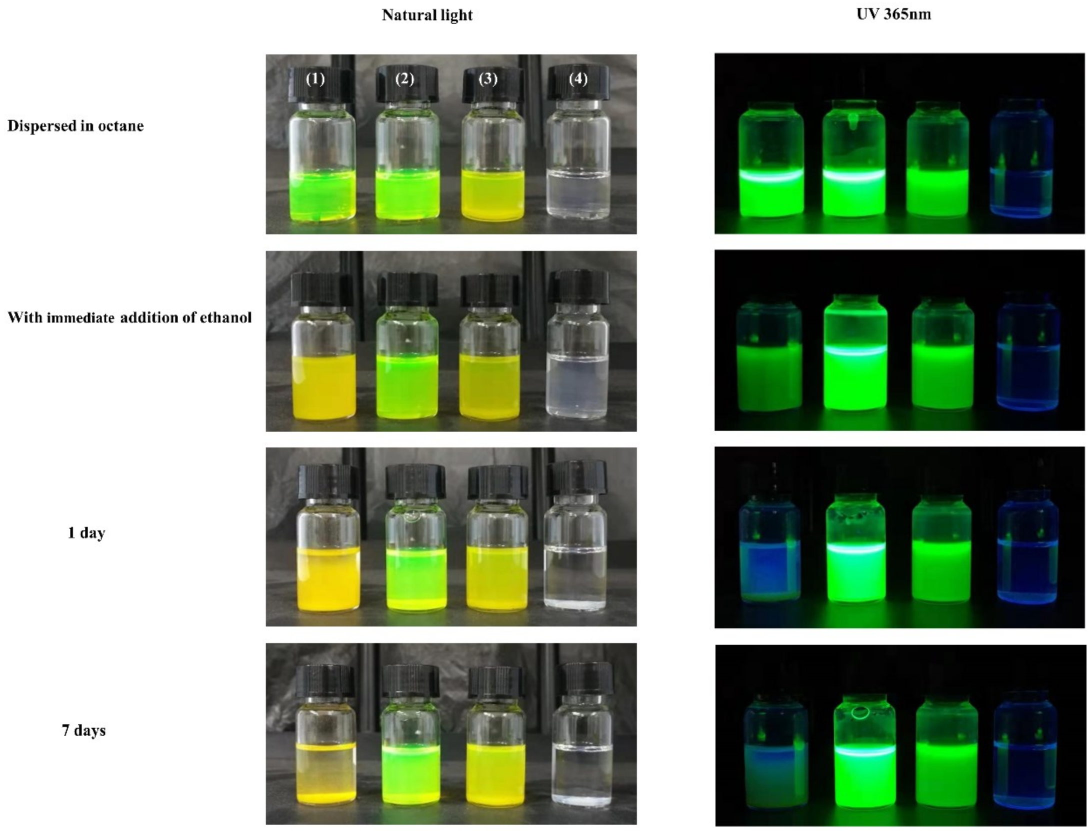

Figure S8. Photographs of (1) OAm-capped $CsPbBr_3$, (2) APTES-capped $CsPbBr_3$, (3) APTES-capped $CsPb_2Br_5$ and (4) APTES-capped Cs_4PbBr_6 nanocrystals under natural light (left) and UV 365nm irradiation (right) without (top) and with (bottom) addition of ethanol

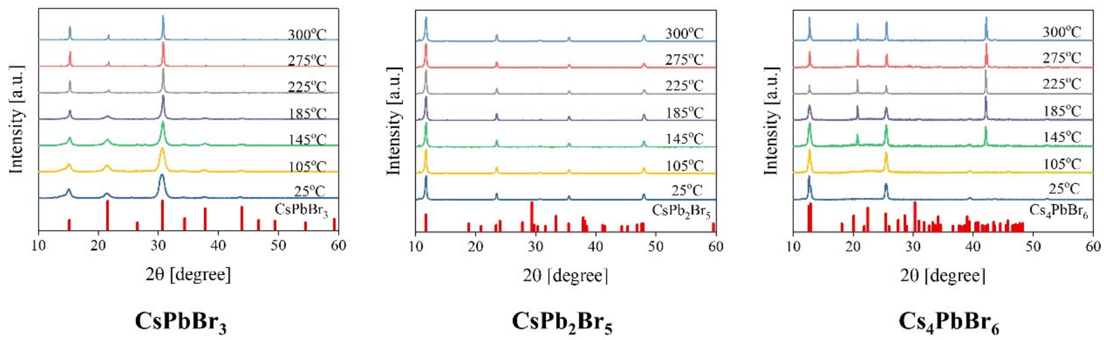

Figure S9. XRD patterns for $CsPbBr_3$, $CsPbBr_5$ and Cs_4PbBr_6 deposited on glass films after a heating process at different temperature.

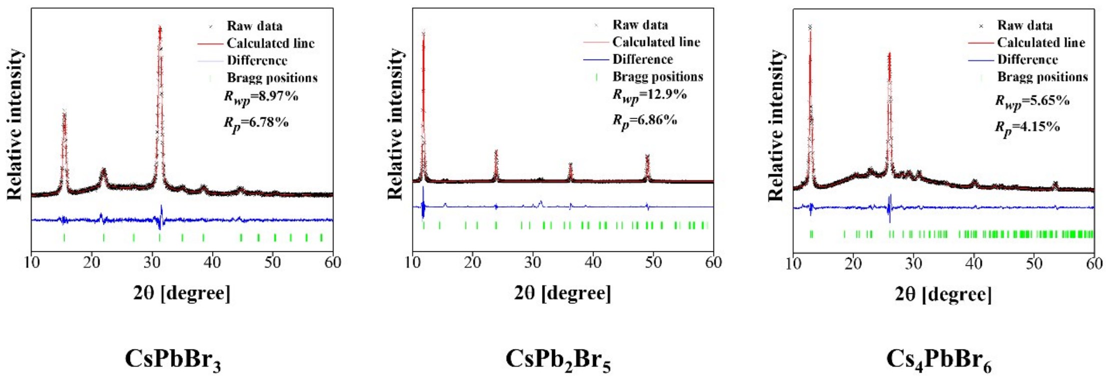

Figure S10. XRD refinement results for $CsPbBr_3$, $CsPb_2Br_5$ and Cs_4PbBr_6 NCs

Table S2. Rietveld refinement and crystal data for $CsPbBr_3$ NCs

Cell parameter	Reliability factors
a=b=c=5.729Å	Rwp(%)=8.97
α=β=γ=90°	Rp(%)=6.98
Cell volume=488.05Å^3	Chi^2=1.30
Radiation(Å): Cu-Kα(λ=1.54056Å)	Density=5.120g/cm^3
Space group: P m -3 m, cubic	Calculated unit cell formula weight: 579.817

Atom	X	Y	Z	Occupancy
Cs	0.0000000	0.0000000	0.000000	1.000
Pb	0.500000	0.500000	0.500000	1.000
Br	0.500000	0.500000	0.000000	1.000

Table S3. Rietveld refinement and crystal data for $CsPb_2Br_5$ NSs

Cell parameter	Reliability factors
a=b=8.589Å,c=14.911Å	Rwp(%)=12.9
α=β=γ=90^o	Rp(%)=6.86
Cell volume=1099.93Å^3	Chi^2=10.67
Radiation(Å): Cu-Kα(λ=1.54056Å)	Density=5.718g/cm^3
Space group: I 4/m c m, tetragonal	Calculated unit cell formula weight: 3787.300

Atom	X	Y	Z	Occupancy
Cs	0.500000	0.500000	0.750000	1.000
Pb	0.308164	0.808164	0.500000	1.000
Br1	0.500000	0.500000	0.500000	1.000
Br2	0.202558	0.702556	0.629432	1.000

Table S4. Rietveld refinement and crystal data for Cs_4PbBr_6 NCs

Cell parameter	Reliability factors
a=b=13.400Å,c=16.936Å	Rwp(%)=5.65
α=β=90^o, γ=120^o	Rp(%)=4.15
Cell volume=2633.662Å^3	Chi^2=0.18
Radiation(Å): Cu-Kα(λ=1.54056Å)	Density=4.609g/cm^3
Space group: R -3 c, hexagonal	Calculated unit cell formula weight: 7309.464

Atom	X	Y	Z	Occupancy
Cs1	0.706000	0.666700	0.916700	1.000
Cs2	0.000000	0.000000	0.250000	1.000
Pb	0.000000	0.000000	0.000000	1.000
Br	0.010603	0.824400	0.891600	1.000