Supporting Information

Phase Transition and Rapid Temperature Response of Lead-Free Perovskite Cs-Cu-I Nanocrystals Enabled by Their Size

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Experimental section and characterization; TEM images; Size distribution of $Cs_3Cu_2I_5$ NCs; EDS mapping of $Cs_3Cu_2I_5$ NCs; XRD patterns of $Cs_3Cu_2I_5$ NCs, $Cs_3Cu_2Br_5$ and $Cs_3Cu_2Cl_5$; XPS survey spectra; Normalized PL spectra of $Cs_3Cu_2I_5$ NCs with various reaction time; PL spectra under different volumes of Cs-oleate; PL spectra under different reaction temperatures; The images of colloidal solution of $Cs_3Cu_2I_5$ NCs dispersed in n-hexane; Normalized PL spectra of $Cs_3Cu_2Br_5$ NCs and $Cs_3Cu_2Cl_5$ NCs; EDS atomic ratio of $Cs_3Cu_2I_5$ NCs; Fitting parameters of TRPL spectra (PDF)

Supporting Video: demonstration of paper chromatism (MP4)

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1. Synthesis of $Cs_3Cu_2Br_5$ and $Cs_3Cu_2Cl_5$ NCs

0.4 mmol of CuX (X = Br or Cl) and 10 mL of ODE were introduced into a 25 mL three-necked flask and heated to 120 °C for 30 minutes under vacuum. After that, 1 mL of OA and 1 mL of OAm were swiftly injected into the reaction flask. The transparent solution was obtained. Then, the temperature was increased to 150 °C under nitrogen, and x mL (x = 4.0, 0.8, 0.4) of Cs-oleate precursor was immediately injected into the mixture. NCs were grown for 10 s at 150 °C, and then the reaction solution was cooled to room temperature in an ice bath. Finally, the solution was centrifuged at 10,000 rpm for 5 min. The supernatant was discarded, and the solids were dispersed in 5 mL of hexane followed by centrifuging at 10,000 rpm for 5 min. Finally, the supernatant was thrown away and precipitate was retained for the next characterization.

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2. Experimental data

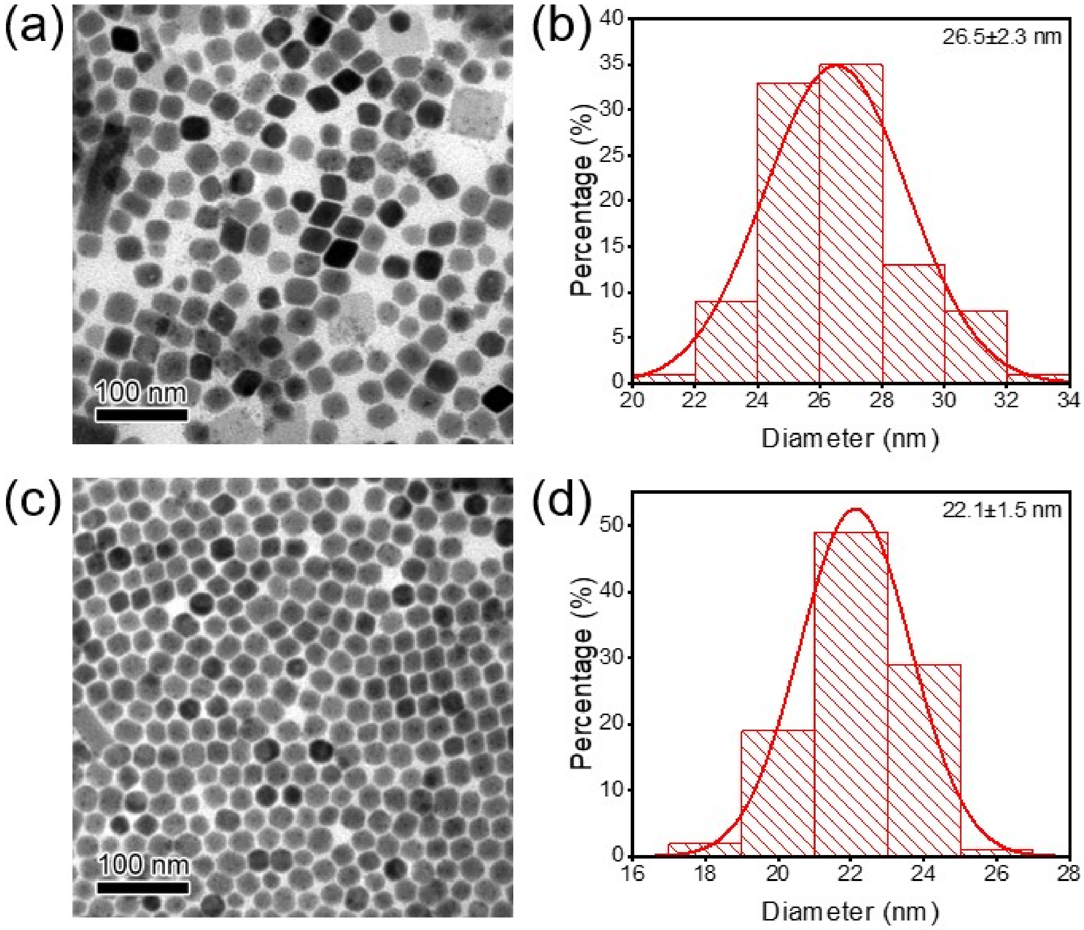

Fig. S1 TEM images and size distribution of $Cs_3Cu_2I_5$ NCs with (a) (b) 0.5 mL and (c) (d) 1.0 mL OA.

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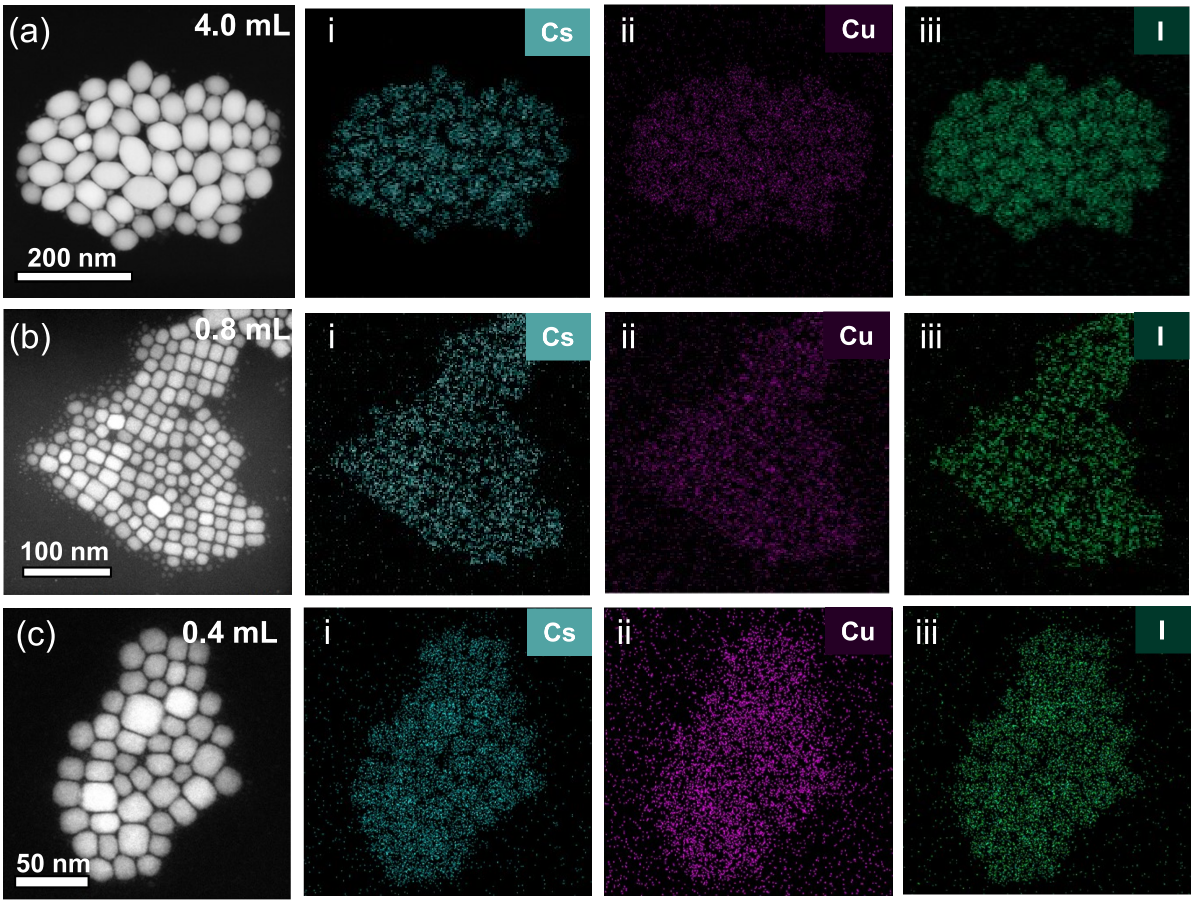

Fig. S2 TEM images and corresponding EDS elemental mapping images of (a) $Cs_3Cu_2I_5$-4.0, (b) $Cs_3Cu_2I_5$-0.8 and (c) $Cs_3Cu_2I_5$-0.4 at 70 °C.

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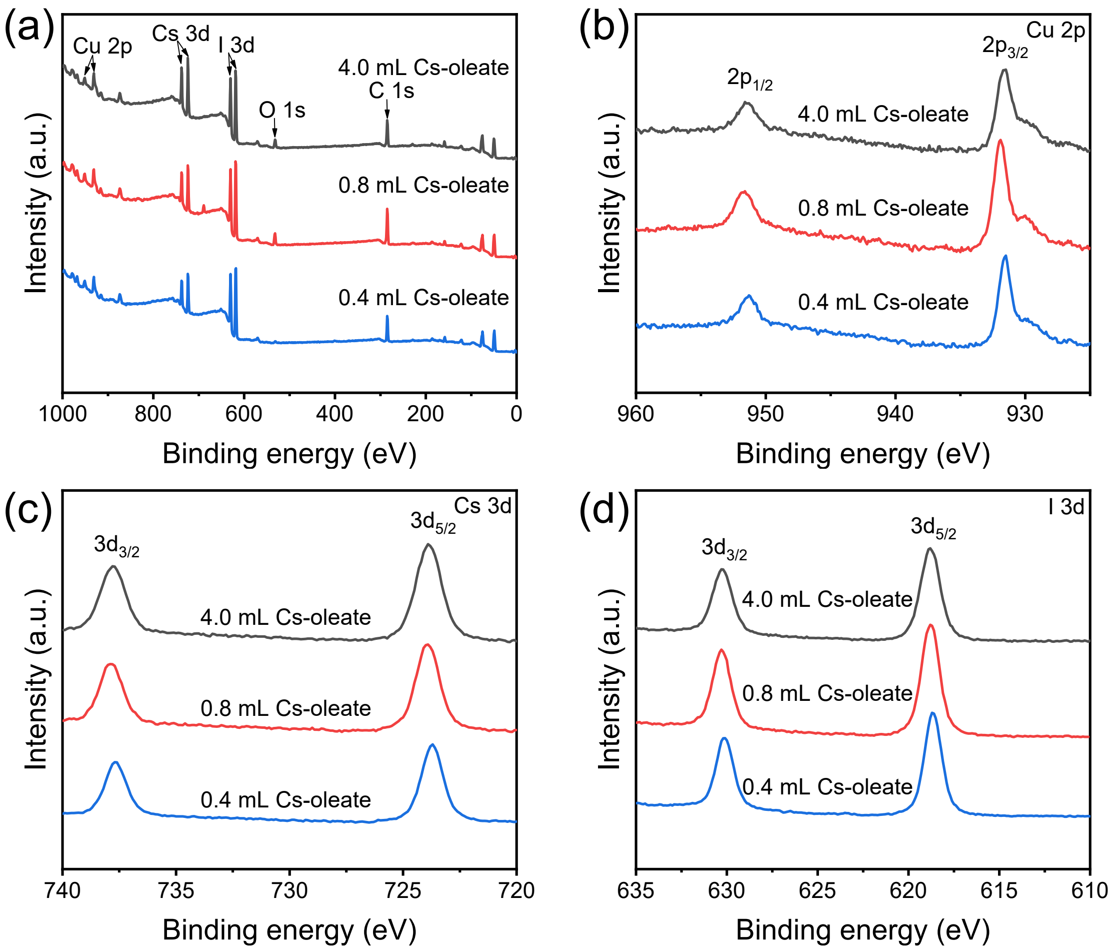

Fig. S3 XPS results of $Cs_3Cu_2I_5$ at 70 °C. (a) XPS survey spectra and curves of (b) Cu 2p, (c) Cs 3d, and (d) I 3d.

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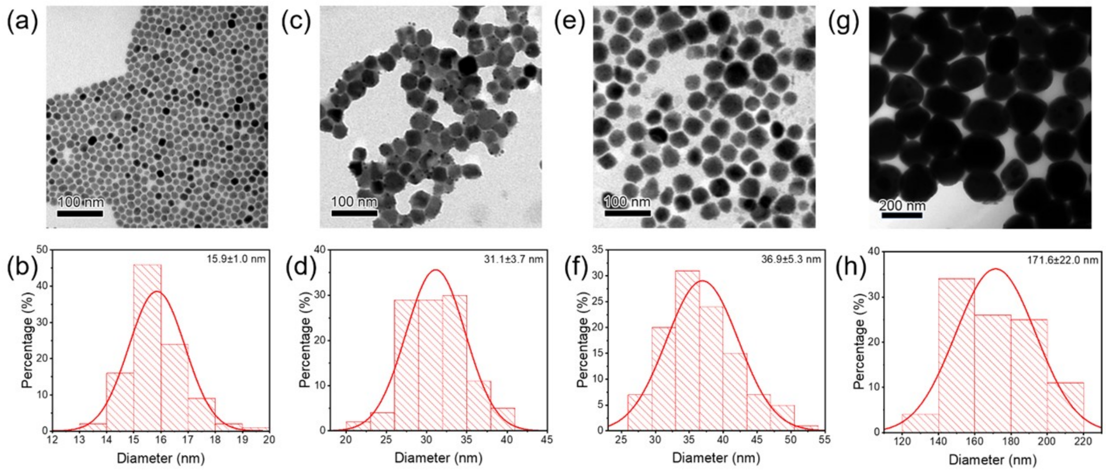

Fig. S4 TEM images and size distribution histograms of (a, b) $Cs_3Cu_2I_5$-2.0, (c, d) $Cs_3Cu_2I_5$-6.0, (e, f) $Cs_3Cu_2I_5$-8.0 and (g, h) $Cs_3Cu_2I_5$-12 at 70 °C.

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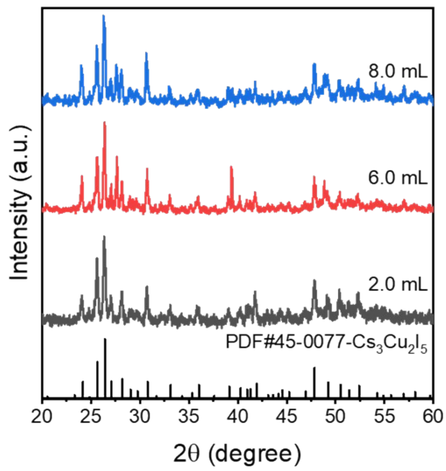

Fig. S5 XRD of $Cs_3Cu_2I_5$-2.0, $Cs_3Cu_2I_5$-6.0 and $Cs_3Cu_2I_5$-8.0 at 70 °C.

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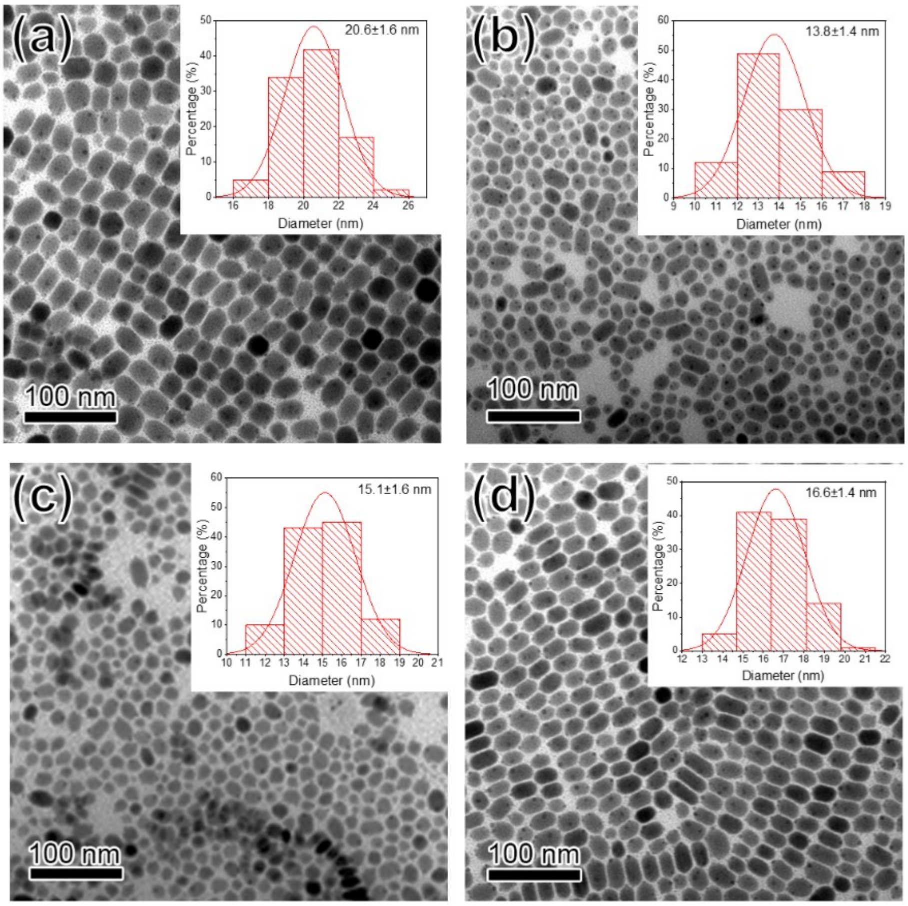

Fig. S6 TEM images and the corresponding size distribution histograms of $Cs_3Cu_2I_5$-0.8 at 70 °C under various reaction time: (a) 10 min, (b) 30 min, (c) 60 min, (d) 120 min.

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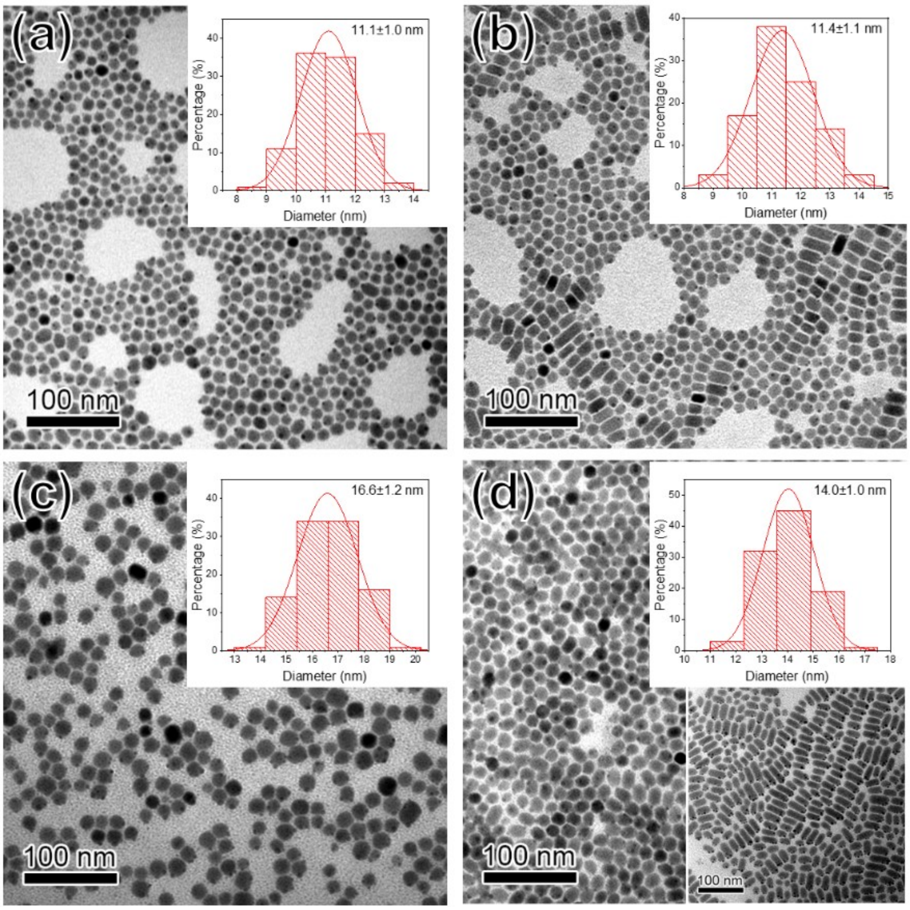

Fig. S7 TEM images and the corresponding size distribution histograms of $Cs_3Cu_2I_5$-0.4 at 70 °C under various reaction time: (a) 10 min, (b) 30 min, (c) 60 min, (d) 120 min.

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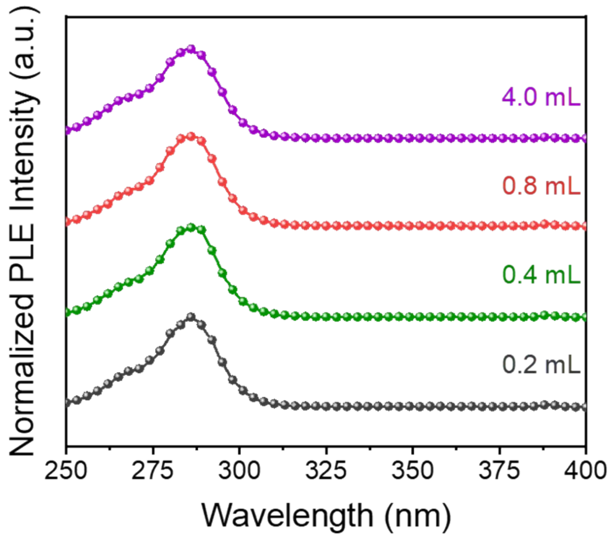

Fig. S8 PLE spectra of $Cs_3Cu_2I_5$ NCs.

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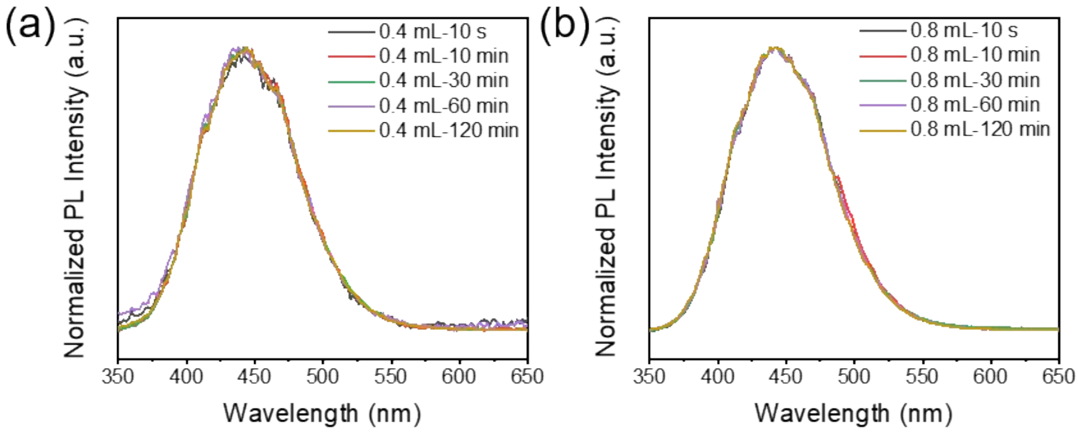

Fig. S9 Normalized PL spectra of (a) $Cs_3Cu_2I_5$-0.4 and (b) $Cs_3Cu_2I_5$-0.8 under various reaction time.

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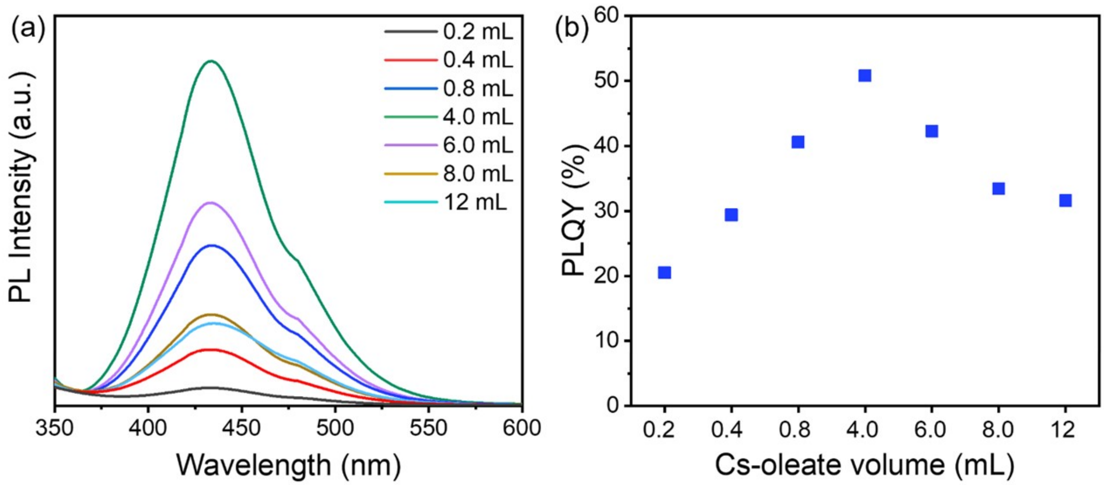

Fig. S10 (a) PL spectra with excitation wavelength of 290 nm and (b) PLQY of $Cs_3Cu_2I_5$ NCs with different Cs-oleate volumes.

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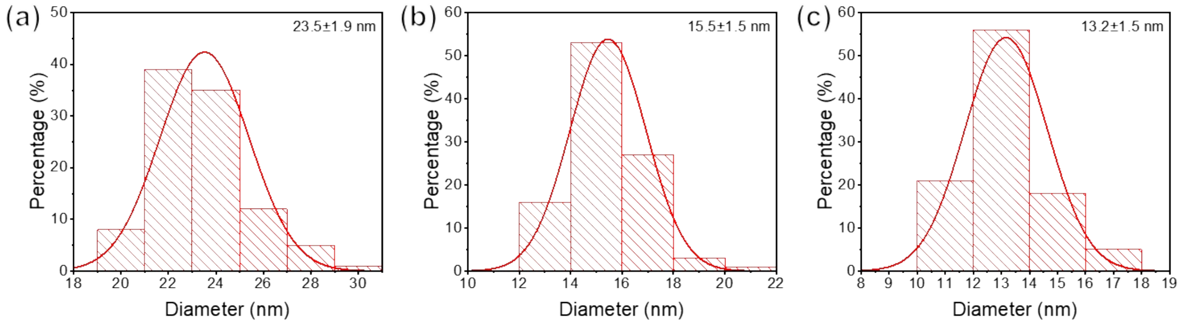

Fig. S11 The size distribution histograms of (a) $Cs_3Cu_2I_5$-4.0, (b) $Cs_3Cu_2I_5$-0.8 and (c) $Cs_3Cu_2I_5$-0.4 at 100 °C.

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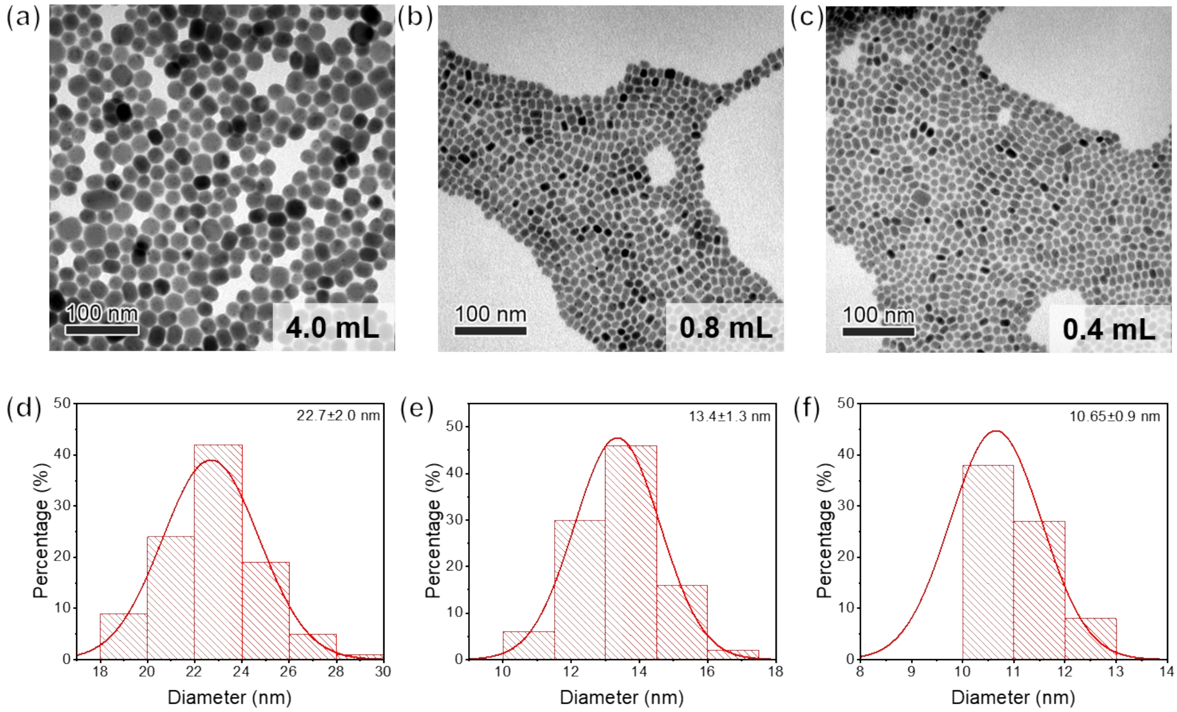

Fig. S12 TEM images and the corresponding size distribution histograms of (a, d) $Cs_3Cu_2I_5$-4.0, (b, e) $Cs_3Cu_2I_5$-0.8 and (c, f) $Cs_3Cu_2I_5$-0.4 at 80 °C.

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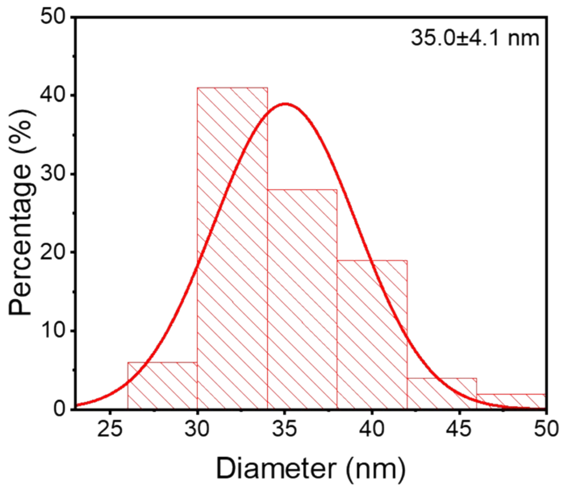

Fig. S13 The size distribution histograms of $Cs_3Cu_2I_5$-4.0 at 120 °C.

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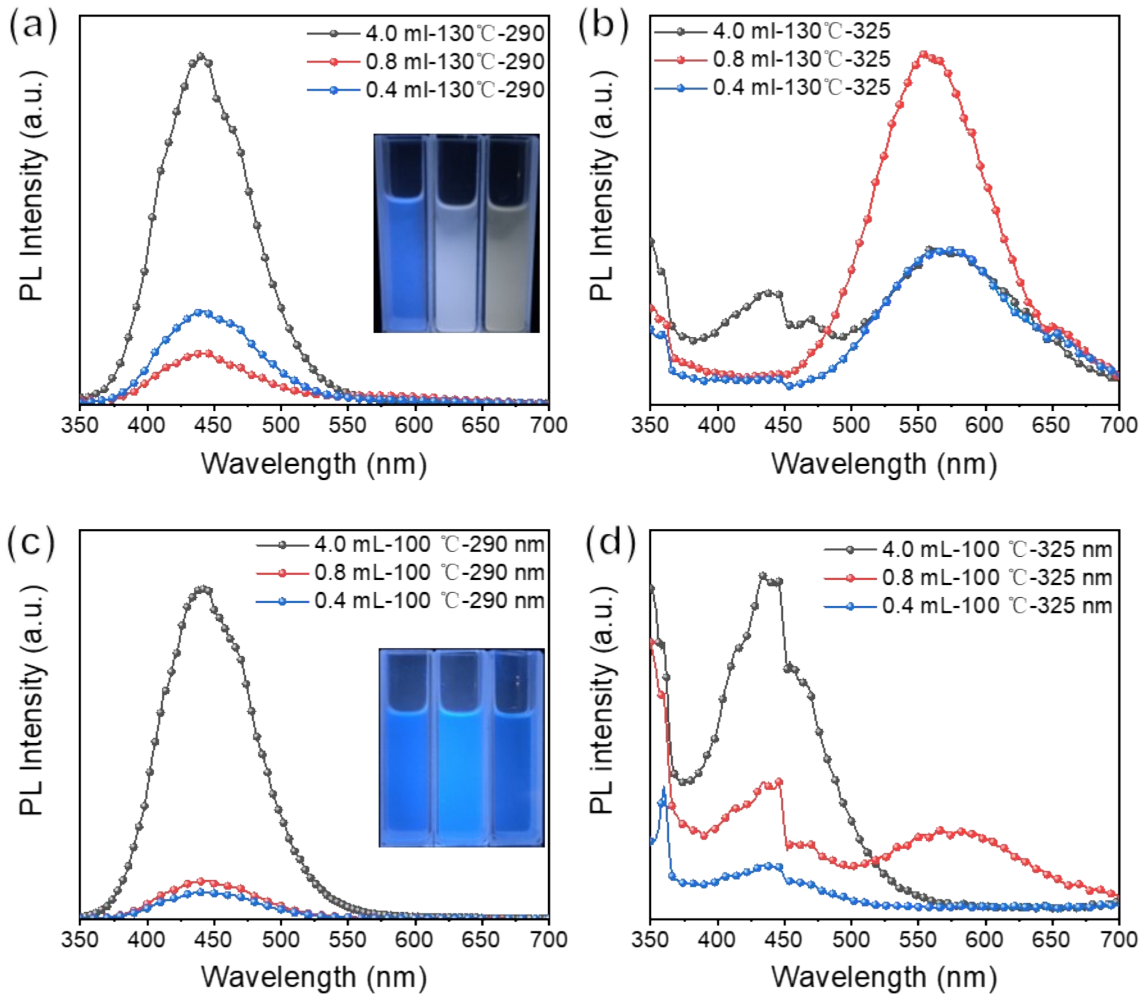

Fig. S14 PL spectra of $Cs_3Cu_2I_5$ NCs with various Cs-oleate volumes and reaction temperatures of (a, b) 130 °C, (c, d) 100 °C (excitation wavelengths are 290 nm and 325 nm). Inset: colloidal solution of NCs in n-hexane under UV light (λ = 295 nm).

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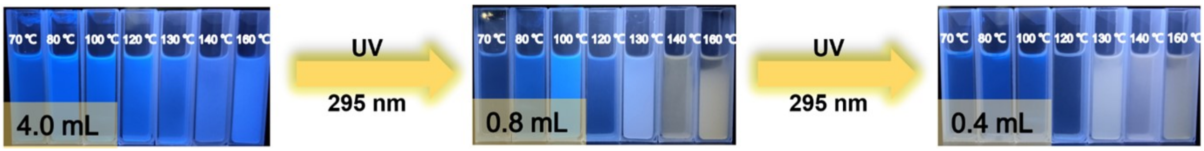

Fig. S15 The images of colloidal solution of $Cs_3Cu_2I_5$ NCs dispersed in n-hexane synthesized at different reaction temperatures under UV light (λ =295 nm).

The images show the colloid solution of $Cs_3Cu_2I_5$ NCs dispersed in n-hexane synthesized at different reaction temperatures under UV irradiation (λ =295 nm). When 4.0 mL of Cs-oleate was injected and the reaction temperature was raised, the synthesized samples showed blue light under 295 nm UV lamp. It further indicates that the content of yellow phase $CsCu_2I_3$ was less. When 0.8 mL and 0.4 mL of Cs-oleate were injected and the reaction temperature was increased, the synthesized samples were converted from blue to yellow under 295 nm UV lamp, indicating that the yellow phase $CsCu_2I_3$ was dominant at a higher temperature.

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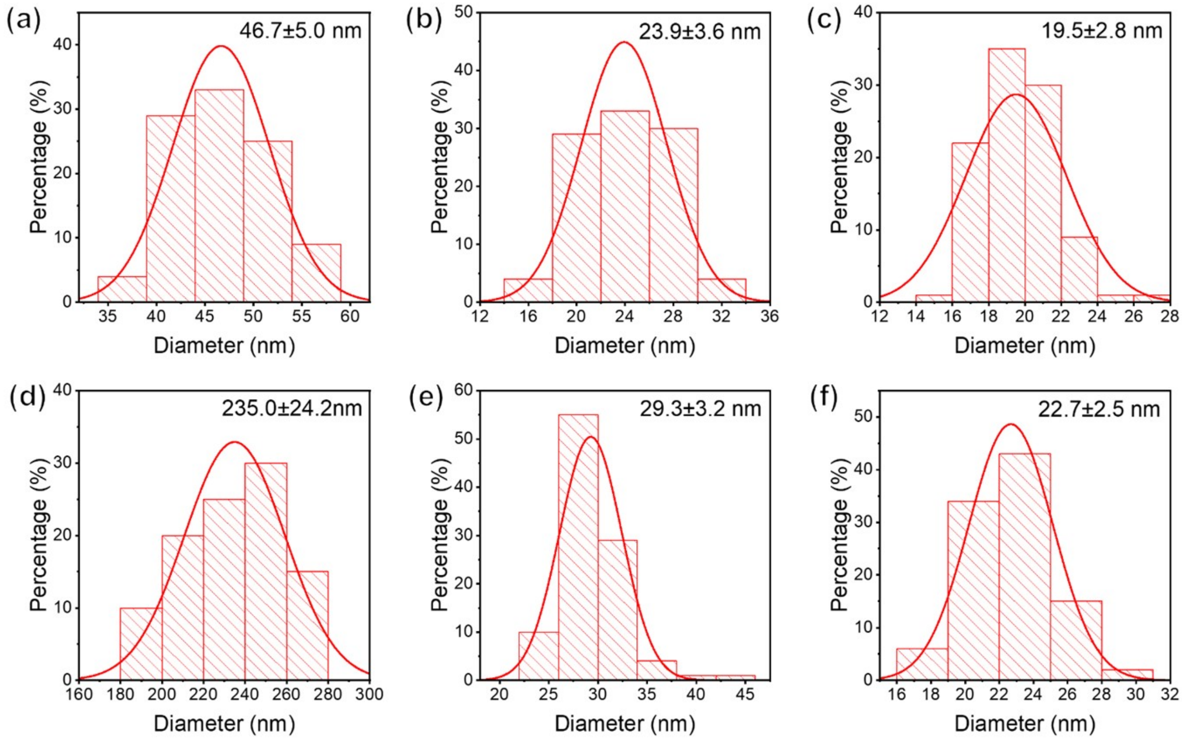

Fig. S16 The size distribution histograms of (a-c) $Cs_3Cu_2Br_5$ NCs and (d-f) $Cs_3Cu_2Cl_5$ NCs with various Cs-oleate volumes at 150 °C.

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Table S1. EDS measured the atomic ratio of $Cs_3Cu_2I_5$ NCs.

Sample	Atomic ratio (%)		
	Cs	Cu	I
$Cs_3Cu_2I_5$-4.0	25.3	25.6	49.1
$Cs_3Cu_2I_5$-0.8	23.5	29.3	47.3
$Cs_3Cu_2I_5$-0.4	23.6	30.3	46.2

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Table S2. Fitting results of TRPL spectra

Sample	τ (ns)
$Cs_3Cu_2I_5$-4.0	1303.2
$Cs_3Cu_2I_5$-0.8	1106.8
$Cs_3Cu_2I_5$-0.4	1113.5
$Cs_3Cu_2I_5$-0.2	952.7

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Table S3. Performance comparison of materials.

Materials	Transition temperature	Transition time	Year	Ref
$CsPbI_{3-x}Br_x$	340 ℃		2022	1
$(CH_2)_2(NH_3)_2CuCl_4$	230 ℃		2022	2
(1,6-HDA)$CuCl_4$	1400 ℃		2021	3
$Cs_2AgBiBr_6$	450 ℃	24 h	2022	4
$(C_6H_4(CH_2NH_3)_2)(CH_3NH_3)[Pb_2I_7]$	60 ℃	A couple of hours	2021	5
$CsPbIBr_2$	240 ℃	17 min	2023	6
$(C(NH_2)_3)PbI_3$	200 ℃	5 min	2021	7
$MA_4PbI_6 \cdot H_2O$	55.7 ℃	4 min	2022	8
$(C_6H_4(CH_2NH_3)_2)(CH_3NH_3)[Pb_2I_7]$	100 ℃	A couple of minutes	2021	5
$(CH_3NH_3)_2CuCl_xBr_{4-x}$	70 ℃	1 min	2021	9
$MAPbBr_{2.7}I_{0.3}$	90 ℃	1 min	2017	10
$MAPbBr_{2.4}I_{0.6}$	120 ℃	30 s	2017	10
$Cs_3Cu_2I_5$	＞120 ℃	3 min	2022	11
$Cs_3Cu_2I_5$	130 ℃	15 s	This work	

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