Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Ultrasonication-Prepared Copper-Doped Cesium Halide Nanocrystals with Bright and Stable Emission

Jingkun Xu,[a] Shiming Guo,[a] Junfeng Qu,[a] Shuhong Xu,[a] Chunlei Wang[a*], Dayan Ban[b*], and Yiping Cui[a]

a. Advanced Photonics Center, School of Electronic Science and Engineering, Southeast University, Nanjing, 210096, Jiangsu, P. R. China

b. Department of Electrical and Computer Engineering, University of Waterloo, 200 University Ave, Waterloo, ON, Canada

Email: wangchl@seu.edu.cn, dban@uwaterloo.ca

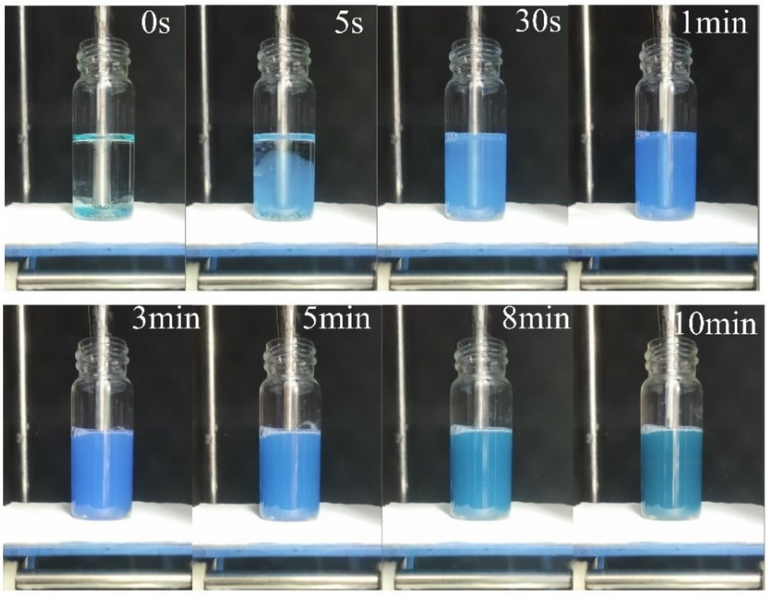


Fig. S1 Photographs of the reaction medium were obtained during the synthesis of Cu:CsBr NCs at 30 W. The color was gradually changed with the increase of reaction time. The NCs need to be purified and redispersed in hexane.

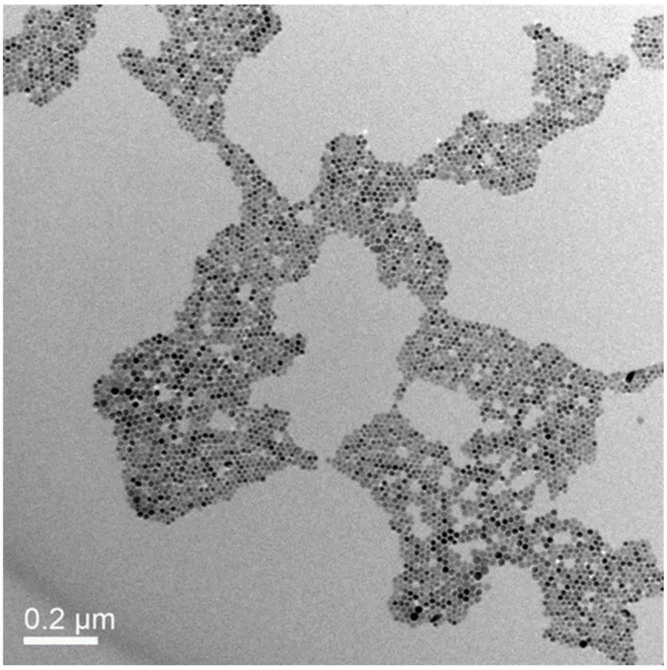
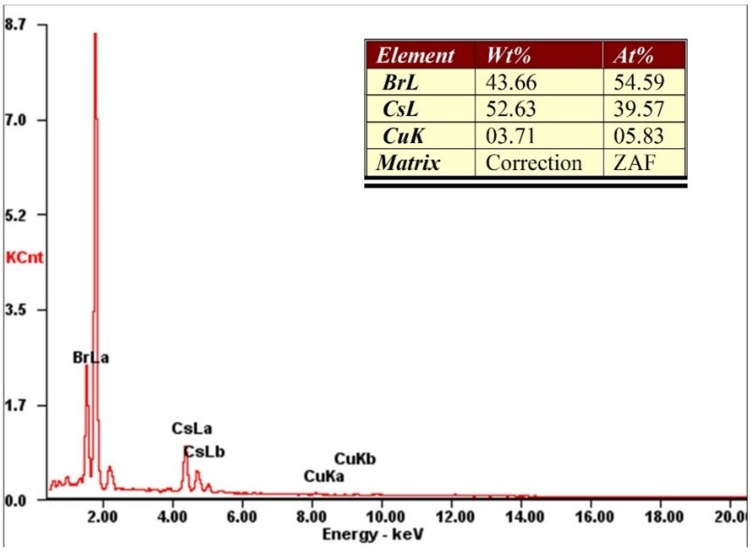


Fig. S2. a-c) TEM image under lower magnification of Cu:CsBr NCs.



Element	*Wt%*	*At%*
BrL	43.66	54.59
CsL	52.63	39.57
CuK	03.71	05.83
Matrix	Correction	ZAF

Fig. S3 EDAX spectra of Cu:CsBr NCs thin film. Inset is the weight ratio and atomic ratio of elements Br, Cs, and Cu.

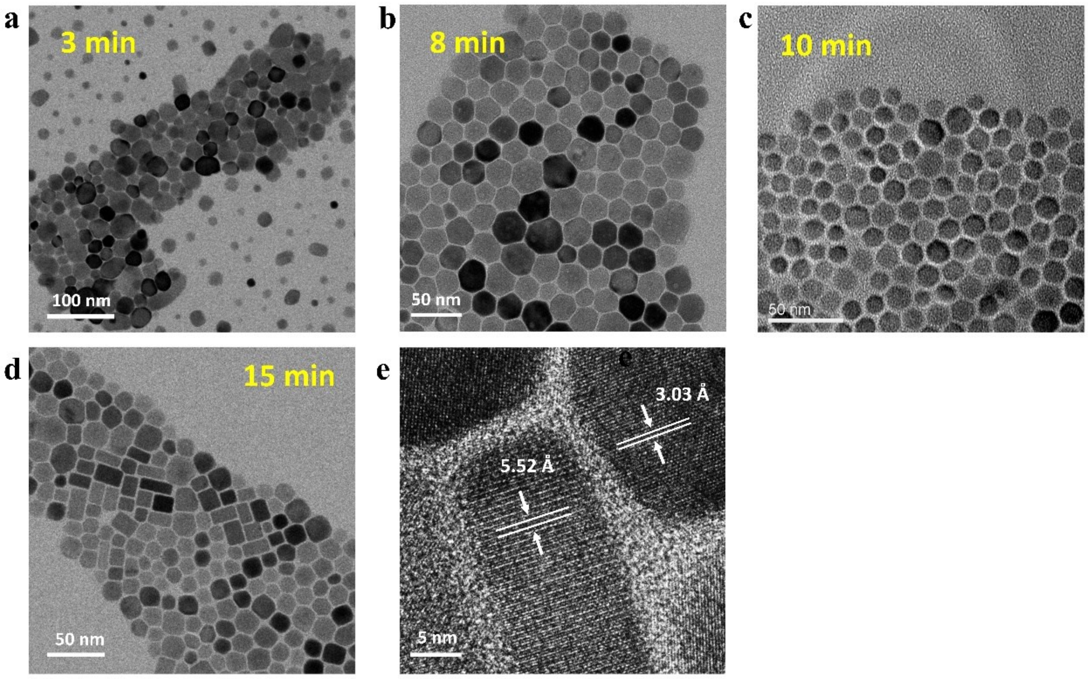


Fig. S4 TEM image of Cu:CsBr NCs prepared with different ultrasonic time: (a) 3 min; (b) 8 min; (c) 10 min; (d) 15 min. (e) HR-TEM image of Cu:CsBr NCs prepared with the ultrasonic of 15 min.

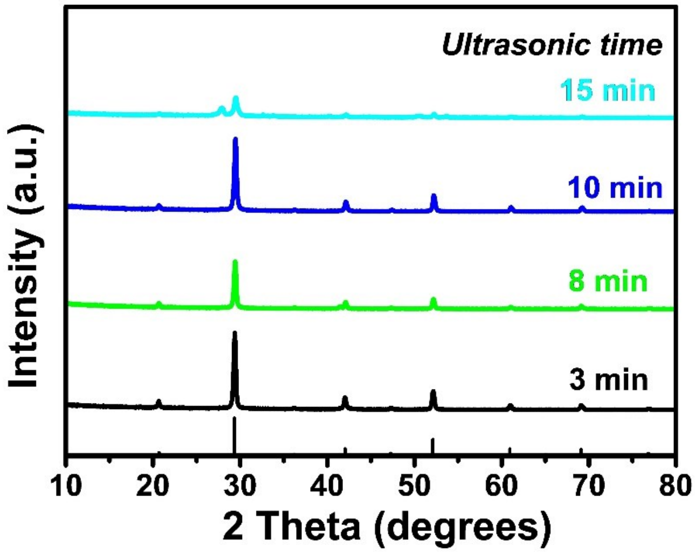


Fig. S5 XRD patterns of the Cu:CsBr NCs prepared with different ultrasonic time. The reference diffractogram of pure CsBr is shown at the bottom as vertical lines.

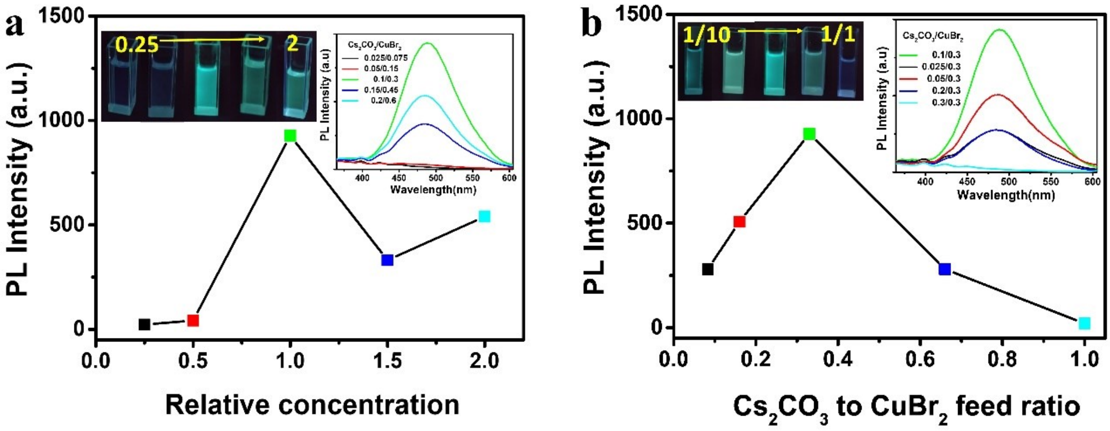


Fig. S6 PL results of Cu:CsBr NCs prepared with (a) different reactant concentration and (b) different feed ratio. The excitation wavelengths is 310 nm. Inset shows the PL spectra and photographs of the NCs dispersed in hexane under UV-LED illumination ($\lambda = 310$ nm). The absorption of all samples at the excitation wavelength is diluted to almost the same to ensure the comparability of PL intensity. Set the reactant concentration in bracket is 1 (0.1 mmol Cs_2CO_3 and 0.3 mmol $CuBr_2$ in 10 mL ODE). Similarly, the relative reactant concentration in bracket is 0.5 (0.05 mmol Cs_2CO_3 and 0.15 mmol $CuBr_2$ in 10 mL ODE). The miscellaneous peaks around 400 nm are from the solvent, and the reason why these peaks become obvious is that the fluorescence of the Cu:CsBr NCs is weak after being diluted.

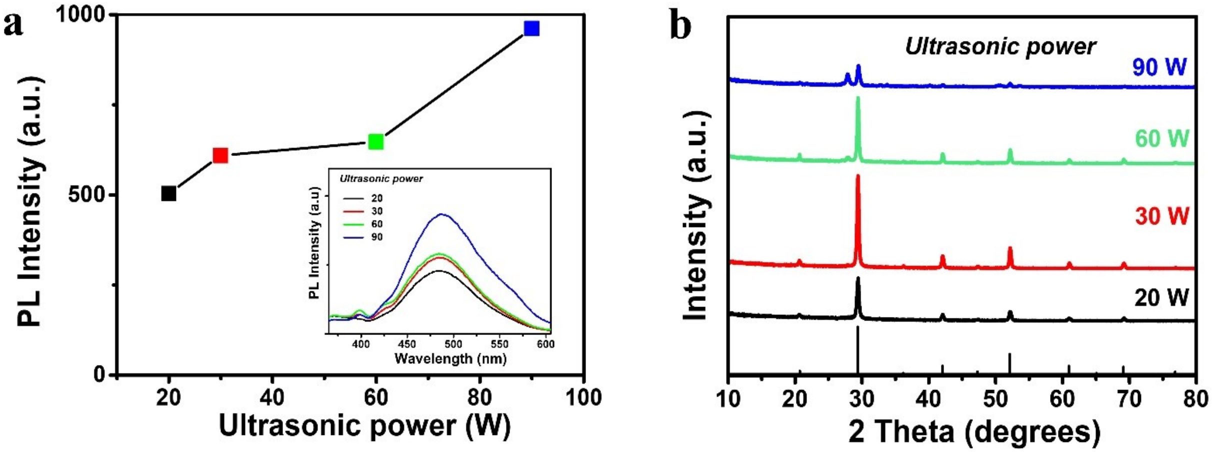


Fig. S7 (a) PL results and (b) XRD patterns of Cu:CsBr NCs prepared under different ultrasonic power with a reaction time of 10 minutes. The excitation wavelengths is 310 nm. Inset shows the PL spectra of the NCs dispersed in hexane under UV-LED illumination (λ = 310 nm). The absorption of all samples at the excitation wavelength is diluted to almost the same to ensure the comparability of PL intensity.

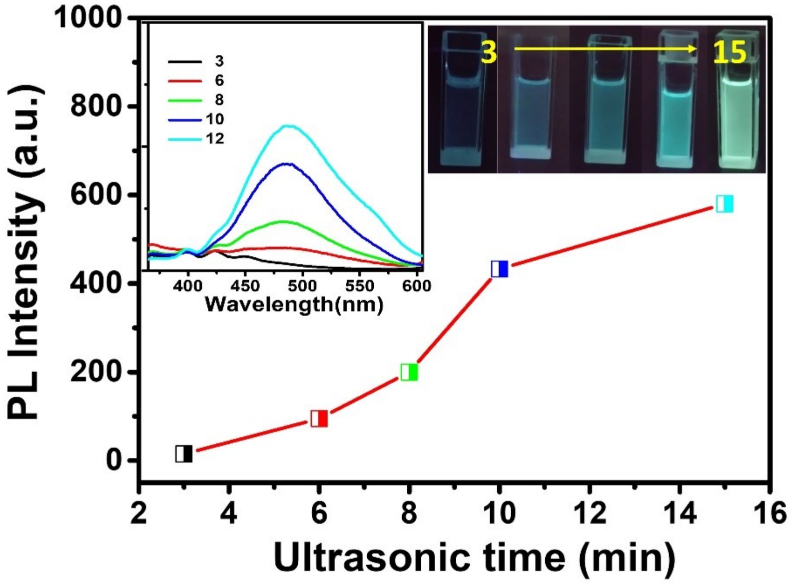


Fig. S8 PL intensity of Cu:CsBr NCs prepared with different ultrasonic time. The excitation wavelengths is 310 nm. Inset shows the PL spectra and photographs of the NCs dispersed in hexane under UV-LED illumination (λ = 310 nm). The absorption of all samples at the excitation wavelength is diluted to almost the same to ensure the comparability of PL intensity.

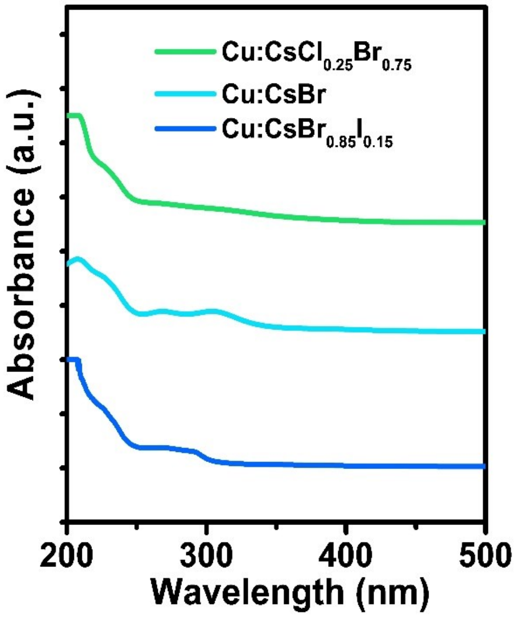


Fig. S9 UV-vis absorption spectra of Cu:CsBr, Cu:CsCl$_{0.25}$Br$_{0.75}$ to Cu:CsBr$_{0.85}$I$_{0.15}$ NCs.

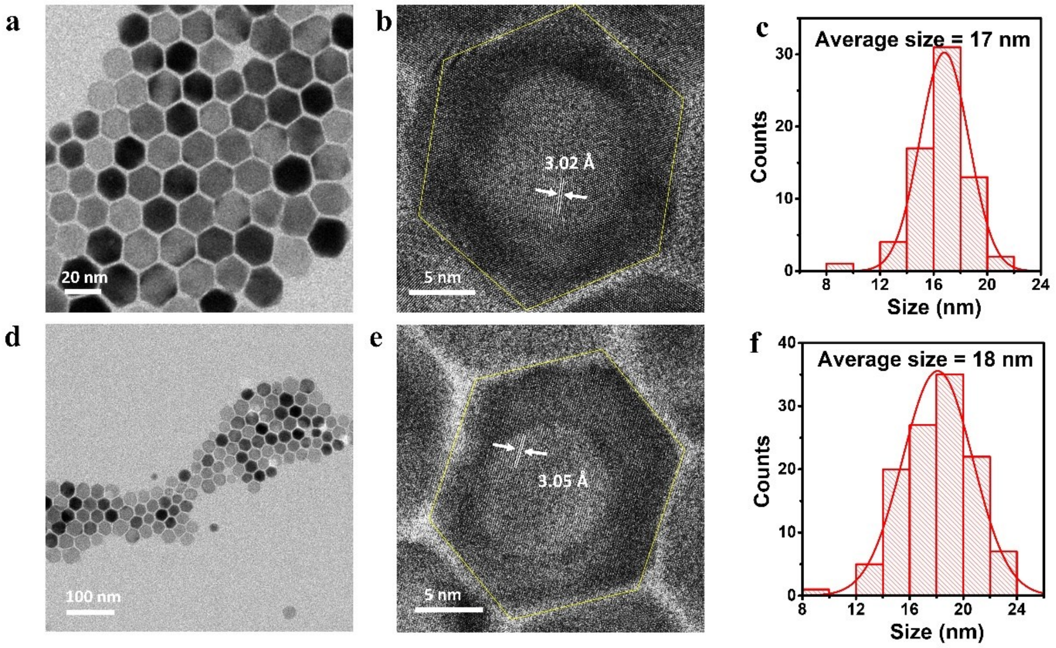


Fig. S10 (a, d)TEM images (b, e) HR-TEM images, and (c, f) size distribution histogram of Cu:CsCl$_{0.25}$Br$_{0.75}$ and Cu:CsBr$_{0.85}$I$_{0.15}$, respectively.

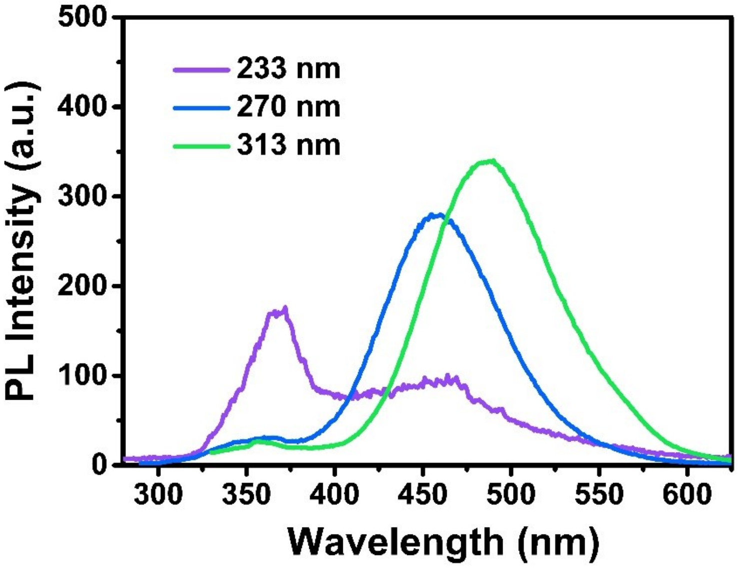


Fig. S11 PL spectra of the Cu:CsBr NCs were recorded at different excitation wavelengths (233, 270, and 313 nm) that correspond to the three band peaks shown in PLE spectra.

As for the emission band at 363 nm, work by Tolmachev et al. described the nature of the broad recombination bands, which originate from direct recombination of the electron (F-center) and the hole (VK-center) radiation defects in the CsBr matrix.[1]

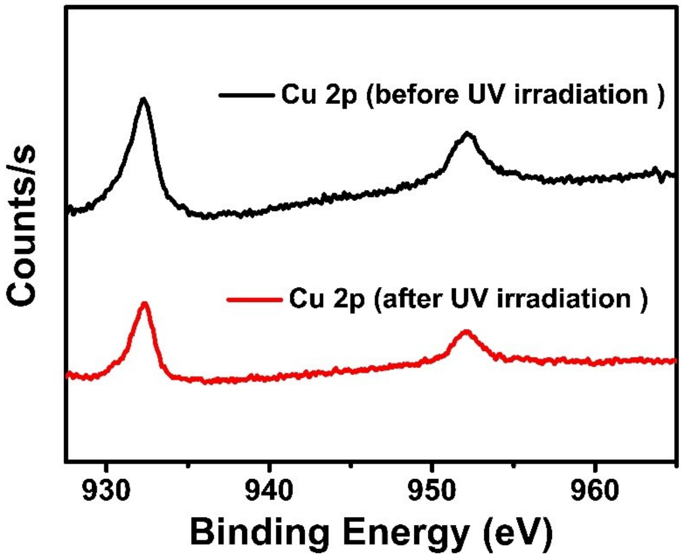


Fig. S12 Narrow-scan XPS results for Cu 2p of Cu:CsBr NCs before and after UV irradiation (254 nm).

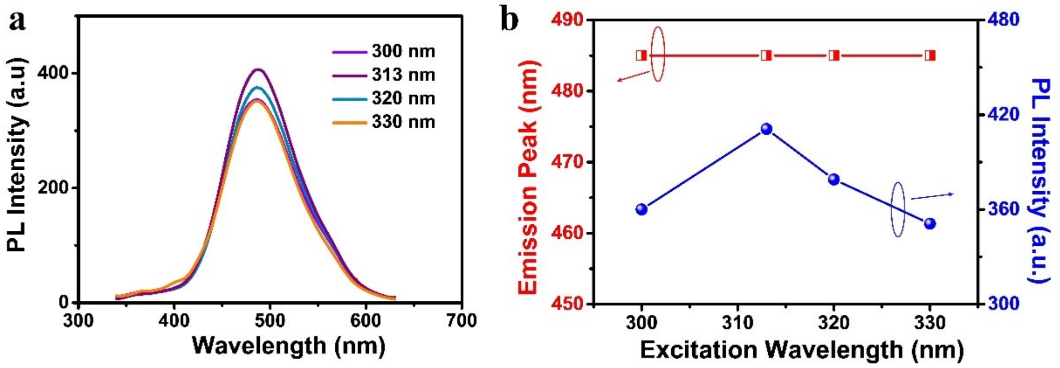


Fig. S13 (a) PL spectra of the Cu:CsBr NCs were recorded at different excitation wavelengths around 313 nm. (b) Emission peak and PL intensity values as a function of excitation wavelengths.

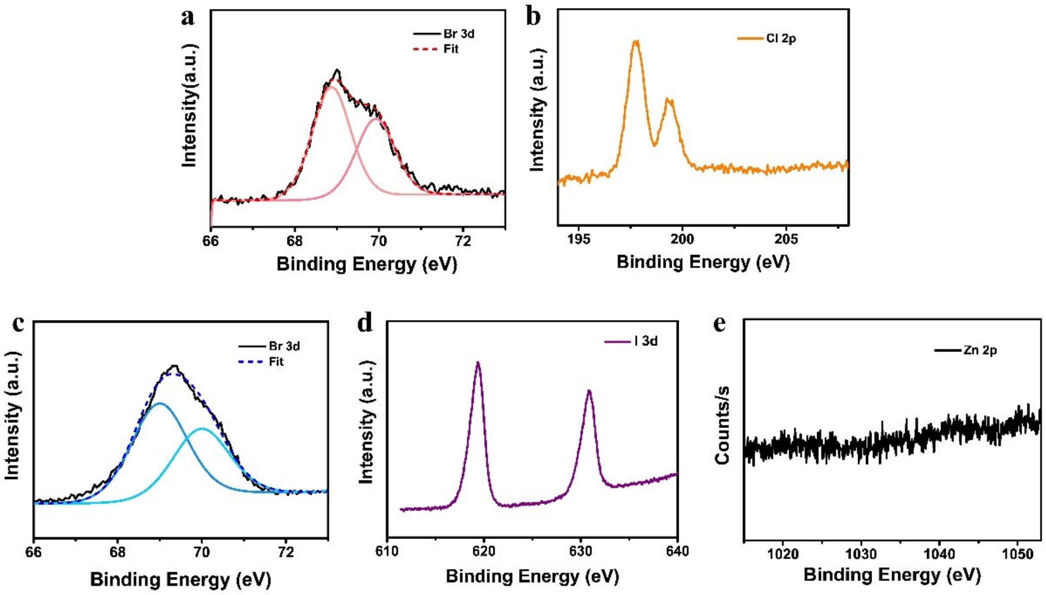


Fig. S14 Narrow-scan XPS results for (a) Br 3d and (b) Cl 2p of Cu:CsCl$_{0.25}$Br$_{0.75}$ NCs; (c) Br 3d, (d) I 3d, and (e) Zn 2p of Cu:CsBr$_{0.85}$I$_{0.15}$ NCs.

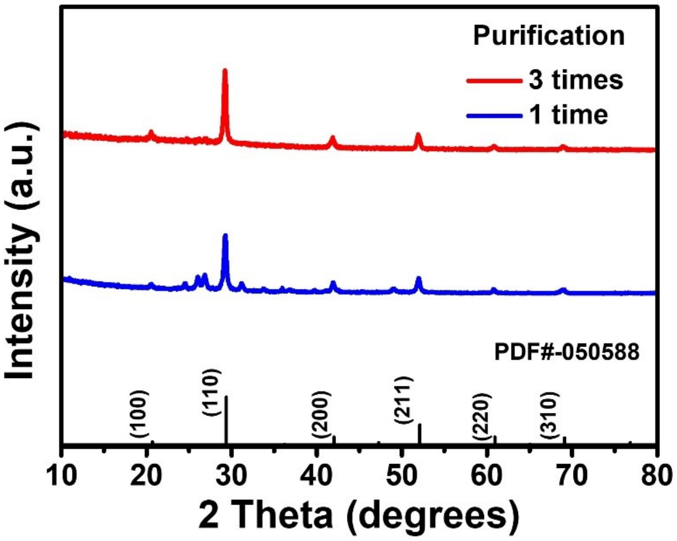


Fig. S15 XRD patterns of the Cu:$CsBr_{0.85}I_{0.15}$ NCs with 1 time and 3 times purification. The reference diffractogram of pure CsBr is shown at the bottom as vertical lines.

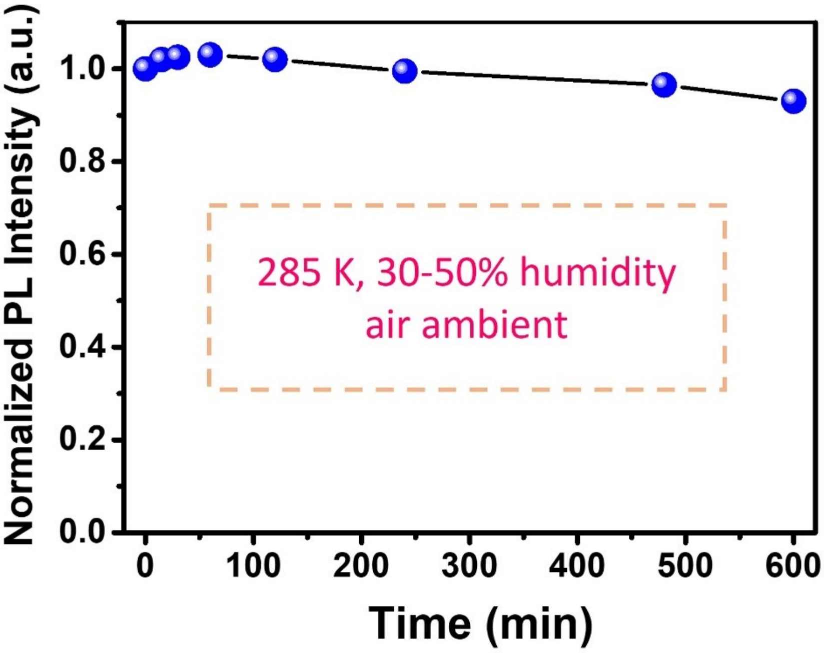


Fig. S16 The PL intensity of Cu:CsBr NCs hexane solution under continuous UV light irradiation (254 nm, 8W). The distance between the sample and the UV lamp is 3 cm.

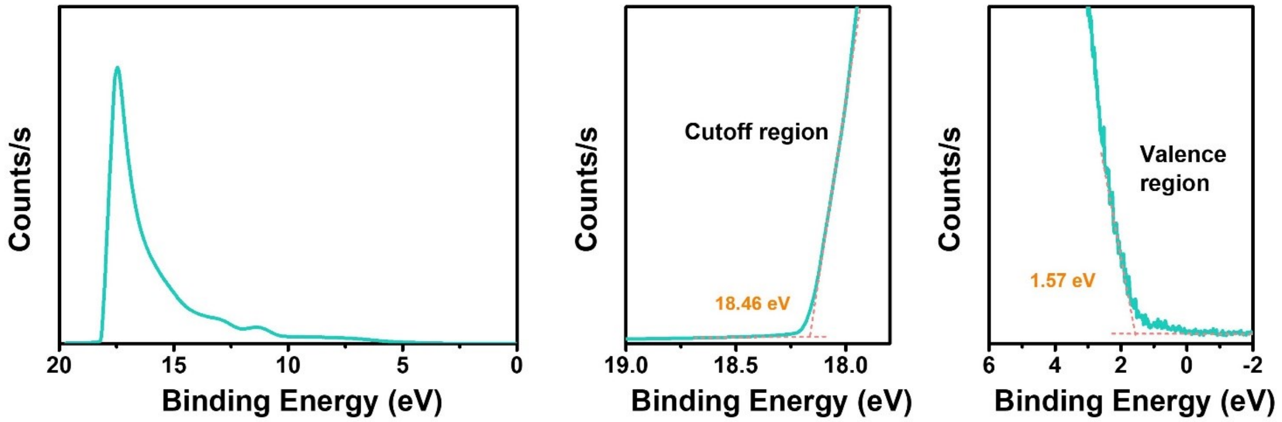


Fig. S17 UPS data of the Cu:CsBr NCs films.

The work functions (WFs) and valance band maximum (E_{VBM}) levels of the Cu: CsX NCs films was calculated as follows: WF = 21.22 eV – E_{cutoff} and E_{VBM} = WF + E_{Fermi}.

E_{VBM} level was calculated to be -4.63 eV.

Table S1 Summary of atomic ratio obtained from EDAX results of Cu:CsBr NCs prepared with different ultrasonic time.

Ultrasonic time (min)	**8**	**10**	**12**
Cs_At%	40.8	39.6	27.3
Br_At%	55.8	54.6	56.6
Cu_At%	3.4	5.8	16.1

Table S2 The feeding ratio of three different NCs synthesized by single-step ultrasonic method at a power of 30 W for 10 minutes with the typical volume of solvent and ligands (10 mL ODE, 0.5 mL OA, and 0.5 mL OAm).

Nanocrystals	Cs_2CO_3 [mmol]	$CuBr_2$ [mmol]	Other [mmol]
Cu:CsBr	0.1	0.3	/
Cu:$CsBr_{0.85}I_{0.15}$	0.1	0.2	0.1 (ZnI_2)
Cu:$CsCl_{0.25}Br_{0.75}$	0.1	0.2	0.1 ($CuCl_2$)

Table S3 Detailed **biexponential** fitting parameters of TRPL profiles of three kinds of Cu:CsX NCs, including the excitation wavelength (λ_{ex}), detection wavelength (λ_{de}), different components of PL lifetimes (τ_n), their weighting (A_n), average PL lifetime τ_{ave}, and R-Square.

Nanocrystals	**λ_{ex} (nm)**	**λ_{de} (nm)**	**τ_1 (μs)**	**A_1**	**τ_2 (μs)**	**A_2**	**τ_{avg} (μs)**	**R-Square**
Cu:CsBr	330	485	87.54	4760.87	31.35	5394.42	71.32	0.99971
Cu:$CsCl_{0.25}Br_{0.75}$	330	505	80.86	4796.51	29.38	5250.10	67.88	0.99973
Cu:$CsBr_{0.85}I_{0.15}$	280	450	18.72	3077.82	3.85	7259.52	16.95	0.99864

Table S4 Detailed **monoexponential** and **triexponential** fitting parameters of TRPL profiles of three kinds of Cu:CsX NCs.

Nanocrystals	**τ_1 (μs)**	**A_1**	**R-Square**
Cu:CsBr	55.70	9472.40	0.98581
Cu:CsCl$_{0.25}$Br$_{0.75}$	53.5	9414.63	0.98635
Cu:CsBr$_{0.85}$I$_{0.15}$	7.93	9322.72	0.97971

Nanocrystals	**τ_1 (μs)**	**A_1**	**τ_2 (μs)**	**A_2**	**τ_3 (μs)**	**A_3**	**τ_{avg} (μs)**	**R-Square**
Cu:CsBr	83.58	4884.08	29.68	5239.57	256.41	46.02	72.56	0.99971
Cu:CsCl$_{0.25}$Br$_{0.75}$	73.28	5158.84	27.71	4672.49	171.46	232.63	69.65	0.99973
Cu:CsBr$_{0.85}$I$_{0.15}$	11.02	4081.13	3.09	5672.12	37.98	690.75	17.42	0.99909

The PL lifetime was fitted using the following equation:

$$I(t) = A_1 e^{\frac{-t}{\tau_1}} + A_2 e^{\frac{-t}{\tau_2}} + A_3 e^{\frac{-t}{\tau_3}} + b$$

where b is the background intensity due to the instrument noise.

The average PL lifetime was calculated using the following equation:

$$\tau_{avg} = \frac{A_1\tau_1^2 + A_2\tau_2^2 + A_3\tau_3^2}{A_1\tau_1 + A_2\tau_2 + A_3\tau_3}$$

As can be seen in Table S3 and S4, compared with biexponential model as the fitting function, the additional components in the triexponential fitting result only account for a negligible proportion. In addition, the R-Square and average PL lifetime of the two fitting methods are almost the same. Besides, the R-Square of the monoexponential fitting method is far inferior to that of biexponential. Therefore, the biexponential model was chosen as the fitting function of the PL lifetime.

Table S5 The crystallite size corresponding to the (110) lattice plane of the three kinds of NCs calculated by using Scherrer equation.

Nanocrystals	**D_{110} (nm)**
Cu:CsBr	22.9
Cu:$CsCl_{0.25}Br_{0.75}$	23.4
Cu:$CsBr_{0.85}I_{0.15}$	22.3

The crystallite size is calculated by using Scherrer equation:

$$D = \frac{K\lambda}{\beta \cos \theta}$$

Where D is crystallites size, K is Scherrer constant (0.9), λ is wavelength of the x-ray sources, β is the FWHM (radians), θ is the peak position (radians).

References

1. D. O. Tolmachev, A. G. Badalyan, R. A. Babunts, V. A. Khramtsov, N. G. Romanov, P. G. Baranov, V. V. Dyakonov, *J. Phys.: Condens. Matter* 2010, **22**, 295306.