Electronic Supplementary Information (ESI)

Ultra-stable CsPbBr₃ nanocrystals with near-unity photoluminescence quantum yield via postsynthetic surface

engineering

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Experimental Section

1.1 Chemicals.

Cs₂CO₃ (99.99%), PbBr₂ (99.999%) and ZnBr₂ (99.999%) were purchased from Alfa Aesar. 1,3-dicarboxyadamantane (ADA, 97%) was obtained from Aladdin. Oleylamine (OLAM, 80-90%), N,N-Dimethylformamide (DMF, anhydrous, 99.9%), propionic acid (PAD, \geq 99.5%), hexane (HEX, 99.5%), isopropanol (IPrOH, anhydrous, 99.5%) were purchased from Sigma-Aldrich. All chemicals were used without any further purification.

1.2 Synthesis and purification of CsPbBr₃ NCs.

Shape-controlled CsPbBr₃ NCs were successfully synthesized via a ligand-resisted reprecipitation method at room temperature in open air. The detained steps are as followed below: firstly, 3 ml HEX, 3 ml IPrOH and 10 μ l ml Cs-PAD (1.8 M Cs₂CO₃ was dissolved in pure PAD) were thoroughly mixed. Secondly, 200 μ l PbBr₂ precursor (0.5 M PbBr₂ dissolved in total volume of (0.75 ml, V_{PrAc}:V_{DMF}:V_{OLAM}, 1:1:1) was quickly injected under vigorous stirring for about 10 s. The transparent solution instantly turned green and then yellow within seconds (Video. S1). The CsPbBr₃ crude solution was centrifuged at 6000 rpm for 4 min for the removal of unreacted precursors, and the precipitates were dispersed in 5 mL hexane solution.

1.3 Sequential dual-surface passivation of CsPbBr₃ NCs

2 mL CsPbBr₃ NC hexane solution was taken, and divided into two vials. One was used as a control sample, while another one was treated as the sequential dual-surface passivation sample by adding excess ADA powder, followed by slow stirring for a period of time and high-speed centrifugation. Subsequently, 1 ml ZnBr₂ hexane solution (dissolving 0.133 mmol ZnBr₂ in the mixture of 10 ml hexane and 200 μ l OLAM was added and slowly stirred at 160 rpm for another 2 min. To be noted, ZnBr₂ is easier to dissolve in hexane in the presence of OLAM at room temperature, but OLAM almost no impact on the improvement of PLQY. The resultant solution is collected for further characterization. For comparison, the simultaneous dual-surface passivation sample of CsPbBr₃ NCs was also obtained.

1.4 Fabrication of CsPbBr₃ composite films

The detailed procedure for white light-emitting diodes (WLEDs) fabrication is as followed below: firstly, the red-emitting K₂SF₆:Mn⁴⁺ phosphors and poly(dimethylsiloxane) (PDMS) were dropped onto the blue LED chip ($\lambda = 460$ nm). Secondly, the green-emitting CsPbBr₃ NC and PDMS were then dropped on the above layer. Lastly, the mixed composite films were solidified at 100 °C for 2 h, and then left for 12 h at room temperature, forming a down-conversion layer.

1.5 Measurement and characteristic

UV-Vis absorption spectra were measured using a Varian Cary 5 spectrophotometer at room temperature. Photoluminescence quantum yield and photoluminescence lifetime was tested using an FLS920 spectrometer from Edinburgh Instruments. Transmission electron microscopy was carried out with a JEM-2100F TEM (JEOL, Japan) operating at a beam energy of 200 keV. X-ray diffraction patterns were measured with a X-ray diffractometer (D/MAX-2400, Rigaku, Japan) with Cu K α radiation (λ =1.54178 Å). Proton nuclear magnetic resonance spectroscopy was tested using a 400 MHz NMR (Bruker, CH). XPS spectra were collected on an Thermo Fisher ESCALAB Xi+. The photoelectric analysis and measurement system (ATA-500) with an integrating sphere was used to characterize the electroluminescence (EL) spectrum, CIE color coordinates, luminous efficiency of the fabricated devices.

1.6 Computational Methods

All first-principles computations are performed based on density-functional theory (DFT) methods as implemented in the Vienna ab initio simulation package (VASP 5.4)¹. An energy cutoff of 520 eV is employed, and the atomic positions are optimized using the conjugate gradient scheme without any symmetric restrictions until the maximum force on each atom is less than 0.02 eVÅ⁻¹. The ion cores are described by using the projector augmented wave (PAW) method. Grimme's DFT-D3 correction is adopted to describe the long-range van der Waals interaction². A Γ and $5 \times 5 \times 1$ k-point grid are respectively used for optimizations of the models of surface treatments of ADA and ZnBr₂. The electronic structures are computed using PBE0 + SOC functional with

energy cutoff of 400 eV³. A Γ and 3×3×1 k-point grid are respectively used for electronic structures of the models of surface treatments of ADA and ZnBr₂.



Fig. S1 Charge density calculations at the PBE0+SOC level of theory for (a) CsPbBr₃ with a surface bromide vacancy (CsPbBr₃+V_{Br}) and (b) CsPbBr₃ with two surface bromide vacancy (CsPbBr₃ + V_{2Br}). The top surface of the crystal slab is halide-deficient, while the bottom surface is pristine.



Fig. S2 (a) Electronic charge density for the VBM and CBM for an ideal CsPbBr₃ slab, and projected density of states (b) an ideal CsPbBr₃ slab, (c) with a removed Pb-Br ion pair, and (d) with a filled Zn-Br ion pair.



Fig. S3 (a) Snapshot from supplementary "Video S1". Process of CsPbBr₃ NC synthesis. (b) The sequential passivation process for NCs with ADA and ZnBr₂.



Fig. S4 PL spectra of CsPbBr₃ pristine solution, different addition of ZnBr₂ hexane solution and the inset showing their photographs of colloid NCs. The results reveal the increased PLQY of CsPbBr₃ NCs depends on the addition of ZnBr₂ hexane solution, but it doesn't have an obvious change after 1000 μ L ZnBr₂ hexane solution.



Fig. S5 PL spectra of untreated NCs, $PbBr_2$ -treated NCs and $ZnBr_2$ -treated NCs and the inset showing their photographs of colloidal NCs, indicating the postsynthetic modification with $ZnBr_2$ shows more enhancement in PLQY than that of PbBr_2.



Fig. S6 PL spectra of untreated NCs, sequential ADA/ZnBr₂ treated NCs and sequential $ZnBr_2/ADA$ treated NCs, indicating the order of sequential addition with ADA and ZnBr₂ has no obvious effect on the improvement of PLQY.



Fig. S7 PL spectra of untreated NCs, simultaneously $(ADA/ZnBr_2)$ -treated NCs and sequentially $(ADA+ZnBr_2)$ -treated NCs and the inset showing their photographs of colloidal NCs, indicating the sequential post-treatment presents higher PLQY than their simultaneous post-treatment.



Fig. S8 The evidence for the interaction between the carboxyl groups from ADA and Zn²⁺. Digital photos for ZnBr₂ solution, ADA solution and ZnBr₂:ADA solution before and after 6 days. The formation of white precipitation after ZnBr₂:ADA solution aged for 6 days, further indicating the interaction between ZnBr₂ and ADA.



Fig. S9 PL spectra of untreated NCs and $(ADA+ZnBr_2)$ -treated NCs powder with addition of water after stirring 15 min.



Fig. S10 (a) PL spectra of (a) untreated CsPbBr₃ NCs (b) ADA+ZnBr₂ untreated CsPbBr₃ NCs before and after thermal treatment at 80 °C for 2 h.



Fig. S11 TEM images of (a) the untreated NCs and (b) ADA+ZnBr₂ treated NCs after thermal treatment at 80 °C for 2 h.



Fig. S12 TEM images of (a) 1-fold, (b) 60-folds of ADA+ZnBr₂ treated CsPbBr₃ NCs solution.



Fig. S13 PL spectra of untreated NCs film, ADA-treated NCs film, ZnBr₂-treated NCs film and (ADA+ZnBr₂)-treated NCs film, and the inset showing their photographs of colloid NCs, demonstrating the (ADA+ZnBr₂)-treated samples exhibits the highest PLQY among them.



Fig. S14 XPS spectra of (a) Cs 3d, (b) O 1s for both untreated and ADA+ZnBr₂ treated samples.



Fig. S15 XPS spectra of (a) Br 3d for both untreated and ADA+ZnBr₂ treated samples.



Fig. S16 PL spectra of CsPbBr₃ colloid solution synthesized at different HEX:IPrOH ratios and the inset showing their photographs of colloid NCs, indicating the obvious red shift of PL emission peak as the increasing addition of IPrOH.

Materials	Procedure	PLQY	Stability	Date	Reference
CsPbBr ₃	ADA and ZnBr ₂ post- treatment	97.1%	65 days	_	This work
CsPbBr ₃	DDDMAB post- treatment	100+5%	21 days	2019	Ref. 4
CsPbBr ₃	In situ passivated with TOAB	95%	-	2019	Ref. 5
CsPbBr ₃	OA/OAm ligand exchange	91%	-	2019	Ref. 6
CsPbBr ₃	In situ passivated with oleamine bromide	97%	_	2019	Ref. 7
CsPbBr ₃	DDAB and PbBr ₂ post-treatment	90-100 %	_	2019	Ref. 8
CsPbBr ₃	In situ passivated with zwitterionic capping	>90%	28 days	2018	Ref. 9
CsPbBr ₃	Ag-TOP post-treatment	90.1%	5 days	2018	Ref. 10
CsPbBr ₃	DDAB post-treatment	85%	_	2018	Ref. 11
CsPbBr ₃	DDAB post-treatment	93 ± 2.5%	_	2018	Ref. 12
CsPbBr ₃	DDAB, TOAB and ZnBr ₂ post-treatment	79%	_	2018	Ref. 13
CsPbBr ₃	S ⁻² -DDA ⁺ and metal ions post-treatment	80%	_	2018	Ref. 14
CsPbBr ₃	ZnBr ₂ -hexane post- treatment	93%	-	2018	Ref. 15
CsPbBr ₃	NaBF ₄ or NH ₄ BF ₄ post- treatment	≥95%	-	2018	Ref. 16

Table S1. The PLQY and stability of CsPbBr₃ NCs in this work compared with other literature values.

Table S1	. Continued
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Materials	Procedure	PLQY	Stability	Date	Reference
CsPbBr ₃	H ₂ O post-treatment	95.5%	_	2018	Ref. 17
CsPbBr ₃	In situ passivated with benzyl bromide	92%	_	2018	Ref. 18
CsPbBr ₃	APTES and HBr post- treatment	73%	_	2018	Ref. 19
CsPbBr ₃	Hexaphosphonate ion post-treatment	98 %	_	2018	Ref. 20
CsPbBr ₃	Potassium oleate post- treatment	83%	_	2018	Ref. 21
CsPbBr ₃	PEA ligand exchange and PEABr post- treatment	93%	_	2018	Ref. 22
CsPbBr ₃	In situ passivated with $ZnBr_2$	78%	_	2017	Ref. 23
CsPbBr ₃	NaSCN or NH ₄ SCN post-treatment	100 ± 3%	_	2017	Ref. 24
CsPbBr ₃	PbBr ₂ post-treatment	>95%	_	2017	Ref. 25
CsPbBr ₃	DDAB post-treatment	90%	_	2017	Ref. 26
CsPbBr ₃	DDAB post-treatment	71%	_	2016	Ref. 27
CsPbBr ₃	S ⁻² -DDA ⁺ post-treatment	$60 \pm 5\%$	_	2015	Ref. 28

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