# Highly Stable Na: CsPb(Br, I)3@Al2O3 Nanocomposites Prepared by

## **Pre-protection Strategy**

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#### Materials and chemicals

The cesium carbonate ( $Cs_2CO_3$ , 99.99%), sodium carbonate ( $Na_2CO_3$ , 99.99%), oleic acid (OA, 85%), oleylamine (OLA, 80-90%),1-octadecene (ODE, >90%), Aluminum sec-butoxide (90%) (ASB), were purchased from Aladdin. The lead(II) bromide (PbBr<sub>2</sub>, 99.999%) and lead(II) iodide (PbI<sub>2</sub>, 99.999%) were purchased from Xi'an Polymer Light Technology Corp, and the toluene and ethyl acetate purchased from Shanghai Chemical Industrial Company. All the reagents were used without further purification.

### Preparation of Cs<sub>x</sub>Na<sub>1-x</sub>OA precursor.

The synthesis procedures were carried out by following a published method.<sup>1</sup> A 100 mL 3-neck flask containing1.22 mmol (X Cs<sub>2</sub>CO<sub>3</sub> and (1-X) Na<sub>2</sub>CO<sub>3</sub> (X=1, 0.9, 0.25, 0.5, 0.75)), 15 mL of ODE, and 1.25 mL of OA was dried for 1 h at 120 °C under N<sub>2</sub>. After that, with the protection of N<sub>2</sub>, the temperature was increased to 150 °C until Cs<sub>2</sub>CO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub> had reacted with OA sufficiently.

### Synthesis and purification of Na: CsPb(Br, I)<sub>3</sub> PQDs

0.188 mmol PbX<sub>2</sub> (in detail, 0.138 g PbBr<sub>2</sub> for CsPbBr<sub>3</sub> PQDs, 0.115 g PbI<sub>2</sub> and 0.046 g PbBr<sub>2</sub> for CsPbBrI<sub>2</sub> PQDs) and 10 mL ODE were loaded into a 100 mL threeneck flask, and dried under N<sub>2</sub> for 1 h at 120 °C. Then, 1.0 mL OLA and 1.0 mL OA were injected to the flask at this temperature. After the solution became clear, the temperature raised to 170 °C, followed by a quick injection of 0.8 mL of Cs<sub>x</sub>Na<sub>1-x</sub>OA precursor. After 5 s, the reaction product was cooled down to room temperature by an ice-water bath. Then, equal volume ethyl acetate was added to the crude solution of PQDs. The solutions were centrifuged at 5000 rpm for 5 min to remove excess byproducts. Then, the supernatant was discarded and the aggregated PQDs were redispersed in toluene.

### Preparation of Na: CsPb(Br, I)<sub>3</sub>@Al<sub>2</sub>O<sub>3</sub> nanocomposites

We choose ASB as the aluminum precursor because it has high reactivity and can hydrolyze at low temperature when exposed to air. Subsequently,  $10 \mu L$ ,  $20 \mu L$  and  $30 \mu L$  ASB were separately dissolved in 1 mL of toluene and then added dropwise to a 15 mL wide-mouth mason jar containing 5 mL of the colloidal Na: CsPb(Br,I)<sub>3</sub> PQDs toluene solution ( $\approx$ 1 mg/mL). The solutions were placed at temperature and humidity chamber with 25 °C and 50%-60% relative humidity without stirring for hydrolysis, and the sol-gel reaction was completed when the toluene evaporated and the mixed solution turned into a solid. After that, Na: CsPb(Br, I)<sub>3</sub>@Al<sub>2</sub>O<sub>3</sub> nanocomposites were annealed at 50 °C for 60 min under vacuum.

#### **Measurement and characterization**

Morphologies and elements of the samples were investigated by field emission scanning electron microscopy (SEM, FEI Quatan FEG 250) equipped with an energy dispersive spectrometer (EDS) and transmission electron microscopy (TEM, JEOL JEM-2100 (morphology) and Tecnai F30 (mapping)). The photoluminescence (PL) spectra, PL quantum yields (PLQYs) and time-resolved PL (TRPL) decay curves were recorded on an Edinburgh Instruments FLS9 spectrometer. The ultraviolet-visible (UV-Vis) absorption spectra were recorded by PE Lambda 950. The x-ray diffraction (XRD) patterns were obtained using the DB-ADVANCE X-ray diffraction analyzer diffractometer. The particle size distribution studies were carried out using Zetasizer Nano ZSE. Attenuated total reflectance Fourier transform infrared (FTIR) spectroscopy was performed using a Bruker VERTEX70. X-ray photoelectron spectroscopy (XPS) spectra were measured by a Thermo Fisher ESCALAB Xi<sup>+</sup>.

Introduce and discuss tri-exponential fitting function, which can be written as

$$I = A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right) + A_3 \exp\left(-\frac{t}{\tau_3}\right)$$

Where  $A_1$ ,  $A_2$  and  $A_3$  are constants, t is time, and  $\tau_1$ ,  $\tau_2$ ,  $\tau_3$  represent the decay lifetimes. The average lifetime ( $\tau_{ave}$ ) can be calculated as follows

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

Table 1 The tri-exponential fitting parameters of time-resolved PL decay curves for different samples.

	A <sub>1(%)</sub>	$\tau_{1(ns)}$	A <sub>2(%)</sub>	$\tau_{2(ns)}$	A <sub>3(%)</sub>	$\tau_{3}$ (ns)	$\tau_{avg(ns)}$
Cs	25.69	19.18	57.25	101.31	17.06	489.79	149.51
Cs: Na = $3:1$	5.65	65.03	31.10	330.92	63.25	915.98	685.33



Figure S1. (a-e) TEM images of Na: CsPbBr<sub>3</sub> PQDs. (f-j) The corresponding size distribution histograms of Na: CsPbBr<sub>3</sub> PQDs. (a, f) Cs: Na= 1:0. (b, g) Cs: Na= 9:1. (c, h) Cs: Na= 3:1. (d, i) Cs: Na= 1:1. (e, j) Cs: Na= 1:3.



Figure S2. (a, b) TEM images of Na: CsPbBr<sub>3</sub> cubic nanocages. (c, d) High resolution TEM (HRTEM) images of Na: CsPbBr<sub>3</sub> cubic nanocage. Cs: Na=1:3.



Figure S3. (a) STEM-HAADF image of Na: CsPbBr<sub>3</sub> PQDs. (b) EDS spectra of the Na: CsPbBr<sub>3</sub> PQDs. (c-f) EDS mapping of Na: CsPbBr<sub>3</sub> PQDs and their atomic percentage. (Na/Cs=1:3).



Figure S4. Na: CsPbBr<sub>3</sub> PQDs with different Na/Cs atom ratios. (a) XRD. (b) PL and absorption spectra. (c) PL spectra of the samples with variation of intensity. (d) PLQYs. Na: CsPbBrI<sub>2</sub> PQDs with different Na/Cs atom ratios. (e) PLQYs. (f) Absorption spectra.



Figure S5. The observed "black dots" lead to the rupture of the periodic lattice.



Figure S6. (a) TEM image of pristine CsPbBr<sub>3</sub> QDs. (b) TEM image of the area upon electron irradiation for 300 s. (c) Enlarged image of the area framed by the yellow frame. (d) HRTEM image of "black dots".



Figure S7. TEM images of particle obtained by precursor of  $PbBr_2$ . (a) Low magnification. (b) High magnification.



Figure S8. (a) XPS spectra of CsPbBrI<sub>2</sub> PQDs synthesized with and without sodium. (b-d) High-resolution XPS spectrum of Na 1s, I 3d and Cs 3d. XPS spectra of pristine (black) and Na: CsPbBr<sub>1</sub>I<sub>2</sub> (red) PQDs. (Na/Cs ratio is 0.33).



Figure. S9 (a) Low- and high-(c) magnification TEM images of pristine  $Cs_4PbBr_6$  PQDs. (b) Low- and high- (d) magnification TEM images of Na:  $Cs_4PbBr_6$  PQDs. (Na/Cs ratio is 0.33).



Figure S10. In situ PL spectra of (a) and (b) were collected every 10 min during the continuous irradiation for mixed solution. In situ absorbance spectra of (c) and (d) were collected every 5 min for mixed PQDs solution. (a) and (c) The mixed of optimum sample Na: CsPbBrI<sub>2</sub> and Na: CsPbBr<sub>3</sub> PQDs. (Na/Cs ratio is 0.33). (b) and (d) The mixed of pristine CsPbBrI<sub>2</sub> and CsPbBr<sub>3</sub> PQDs.



Figure S11. 1024 mg of highly fluorescent Na: CsPbBr<sub>3</sub>@Al<sub>2</sub>O<sub>3</sub> PQDs powder. (ASB=20  $\mu$ L).



Figure S12. Schematic illustration of the formation process. Na: CsPbBr<sub>3</sub> @Al<sub>2</sub>O<sub>3</sub> PQDs (top). Na: CsPbBrI<sub>2</sub> @Al<sub>2</sub>O<sub>3</sub> PQDs (bottom).



Figure S13. Morphology-dependent HRTEM images illustration of the formation process of Na: CsPbBr<sub>3</sub>@Al<sub>2</sub>O<sub>3</sub> PQDs. (ASB=20 µL).



Figure S14. (a) Absorption and PL spectra. (b) XRD patterns. (c) FTIR spectra. (d) EDS patterns. Al<sub>2</sub>O<sub>3</sub> (black), CsPbBr<sub>3</sub> PQDs (green) and Na: CsPbBr<sub>3</sub>@Al<sub>2</sub>O<sub>3</sub> PQDs (olive). (ASB=20 μL).



Figure S15. Digital images of Na: CsPbBrI<sub>2</sub> PQDs solutions with different ASB were illuminated with a 365 nm UV source.



Figure S16. HRTEM images of single nanorods. Inside the yellow frame is an isolated particle within the nanorods. Inside the red frame is the lattice matched particles within the nanorods.



Figure S17. (a) Digital image of paper mulberry in the macro world. (b) SEM image of superstructure analogous to the paper mulberry.



Figure S18. TEM and SEM images of nanorods and their self-assembled superstructures.

5.85K	Si	Element1	Cs	Na	Pb	Br	Ι	0	A1	Si
5.20K		Atomtic %	6.24	7.23	5.82	6.32	11.25	15.23	6.23	41.68
4.55K										
3.90K										
3.25K										
2.60K O K										
1.95K			1182							PhiRs
1.30K	Na K Al K						P	μρο τρο		
0.65K	BrL	Pb M	Cs L Cs	Lβ2						Pb Lβ4 Br Kβ1
Si L Cs	MAA		Γ Lα Cs Lβ					Pb L	α Bri	Κα ΡЬ Lβ Β
0.0	1.3	2.6	3.9	5.2	6.5	7.8	9.1	10.4	11.7	13.0
Lsec: 24.4 0 Cnts 0.000 keV Det: Apollo XL-SDD Det Reso										

Figure S19. EDS spectrum of paper mulberry superstructure.



Figure S20. XPS spectra of  $CsPbBr_1I_2$  (red), Na:  $CsPbBr_1I_2$  (green) and Na:  $CsPbBr_1I_2@Al_2O_3$  (blue). (a) XPS survey spectra. (b) O 1s. (c) Al 2p. (d)Na 1s. (e) I 3d. (f) Br 3d. (Na/Cs ratio is 0.33). (ASB=20  $\mu$ L).



Figure S21. XPS spectra of Na: CsPbBr<sub>1</sub>I<sub>2</sub>@Al<sub>2</sub>O<sub>3</sub> nanocomposites after annealing at 50°C. (a) O 1s, (b) A1 2p. (ASB=20  $\mu$ L).



Figure S22. ASB-induced self-assembly superstructure of CsPbBrI<sub>2</sub> PQDs. (a) Morphology of superstructure. (b-f) Elemental mapping images showing the element distributions. an Si mapping provided as an inset. (g) EDS spectrum of superstructure. (ASB=20  $\mu$ L).



Figure S23. Digital images showing the stability against water. CsPbBr<sub>3</sub> PQDs (top). Na: CsPbBr<sub>3</sub>@Al<sub>2</sub>O<sub>3</sub> PQDs (bottom). Ten milligram samples were dispersed in 2 mL of deionized water by ultrasonication.



Figure S24. Samples were stimulated through illuminating the solution with a 365 nm UV source. (a) The fluorescence intensity of the powder sample changes with the irradiation time. (b) The fluorescence intensity of the solution sample changes with the irradiation time after the addition of water. (ASB=20  $\mu$ L).



Figure S25. Digital images showing the stability against UV source. CsPbBrI<sub>2</sub> PQDs (top). Na: CsPbBrI<sub>2</sub>@Al<sub>2</sub>O<sub>3</sub> nanocomposites (bottom).

## References

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