

SUPPORTING INFORMATION

Study of the Partial Substitution of Pb by Sn in Cs-Pb-Sn-Br Nanoparticles Owing to Obtain Stable Nanoparticles with Excellent Optical Properties

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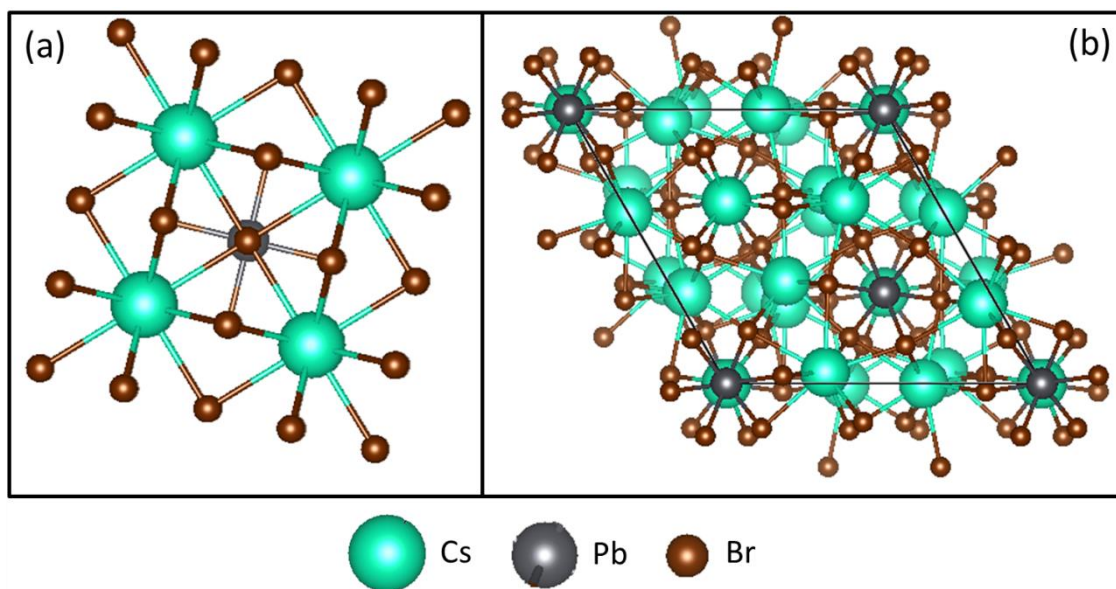


Figure S1: Crystalline structure of (a) CsPbBr_3 cubic phase and (b) Cs_4PbBr_6 tetragonal phase.

S1 Analysis of the results with other synthesis conditions than the ones reported in the main text

Preparation of CsPbBr₃ by Kovalenko's Method

Cesium-oleate solution was prepared according to the approach reported by Kovalenko and coworkers.¹ In brief, 0.4 g of Cs₂CO₃, 1.2 mL of OA and 15 mL of ODE were loaded in a three-neck flask and degassed under vacuum at 120 °C for 1 h, followed by heating at 150 °C under N₂ atmosphere until all Cs₂CO₃ reacted with OA.

CsPbBr₃ nanocrystals was prepared using 0.069 g of PbBr₂ and 5 mL of ODE were loaded in three-neck flask and dried under vacuum for 1 h at 120 °C. 0.5 ml of dried OLEA and 0.5 mL of dried OA were injected at 120 °C under N₂. After the complete dissolution of PbBr₂, the temperature was increased to 150 °C. Finally, 0.4 mL of hot Cs-oleate solution was quickly injected and the reaction mixture was cooled by ice-bath after 5 seconds.

Preparation of Cs-Pb-Sn-Br Nanocrystals – Kovalenko's Method + Sn

Based on Kovalenko's Method, we adapted this procedure to Sn incorporation on CsPbBr₃ NPs. Briefly, 0.069 g of PbBr₂ and 0.131 g of SnBr₂ (molar ratio Pb:Sn = 1:2.5) were mixed with 5 mL of ODE and 1 mL of TOP in a three-neck flask and dried under vacuum for 1 h at 120 °C. 0.5 mL of dried OLEA and 0.5 mL of dried OA were injected at 120 °C under N₂. After the complete dissolution of PbBr₂ and SnBr₂, the temperature was at 150 °C. Then, 0.4 mL of hot (150 °C) Cs-oleate solution was quickly injected and the reaction mixture was cooled by ice-bath after 5 seconds.

Preparation of Cs-Pb-Sn-Br Nanocrystals – Kovalenko's Method (modified) + Sn

We did some modifications on the procedure above mentioned. We kept the amounts of PbBr₂, SnBr₂, TOP, and ODE equals the previous method. The main difference was that we added more amounts of OA and OLEA, that is; before we added 0.5 mL each one and now we used 2.0 mL each one. Then, 0.4 mL of hot (150 °C) Cs-oleate solution was quickly injected and the reaction mixture was cooled by ice-bath after 5 seconds.

Cleaning Nanocrystals

Cs-Pb-Br and Cs-Pb-Sn-Br NPs were extracted from the crude solution after synthesis by centrifugation at 4700 rpm for 10 min and the colored supernatant was discarded. Then, 1 mL of hexane was added, and the NPs were dispersed by shaking. Then, the suspension was centrifuged at 4000 rpm for 3 min to precipitate the larger NPs and agglomerates that were discarded. In the supernatant there were only the NPs dispersed in hexane.

Supporting Figures and Tables

The main differences between the methods previously reported in the literature and the one here reported are the ratios among the precursors and the ligands, as it can be visualized in Table S1 in the Supporting Information. The samples that were done at high-moderate synthesis temperature (150 °C), following the method here presented, showed two kind of nanoparticles matching tetragonal Cs₄PbBr₆ structure (ICDS 162158) and cubic perovskite CsPbBr₃ structure (ICDS 109295) as visualized in Figure S2a, and these both compounds can coexist from 150 °C to 350 °C.²

Table S1: Experimental details and parameters of different synthesis method: Kovalenko's method and our method with and without Sn-replacing.

Methods	Kovalenko's Method	Our Method	Kovalenko's Method + Sn	Our Method + Sn
[Pb] / mmol	0.188	0.166	0.188	0.166
Pb:Sn	1:0	1:0	1:2.5	1:2.5
Cs-oleate / ml	0.4	0.6	0.4	0.6
OLEA – OA / ml	0.5 – 0.5	2 - 2	0.5 – 0.5	2 - 2
[Cs] : [Pb] (Pb+Sn)	1 : 8	1 : 2.8	1 : 28	1 : 9.8
[Pb] (Pb+Sn) : [OA]	1 : 8.4	1 : 12.4	1 : 2.4	1 : 3.5
[Pb] (Pb+Sn) : [OLEA]	1 : 8.1	1 : 12	1 : 2.3	1 : 3.4
Temperature / °C	150	150	150	150
Time / sec	5	5	5	5
PL / nm	507	513	456	503
Bandgap / eV	2.39	^	^	2.43
Stokes Shift	12 nm / 59.3 meV	^	^	10 nm / 50.0 meV
PLQY / %	40.9	7.3	0.4	73.4
FWHM	21.2	22.0	49.1	21.2
Phase	#	*	# / *	# / *

= CsPbBr₃ (ICDS 109295) and * = Cs₄PbBr₆ (ICDS 162158) ^ For the Pb:Sn 1:0 sample the absorption band edge was not easy to determine from the experimental results and consequently the bandgap and the Stokes Shift cannot be calculated without a big error.

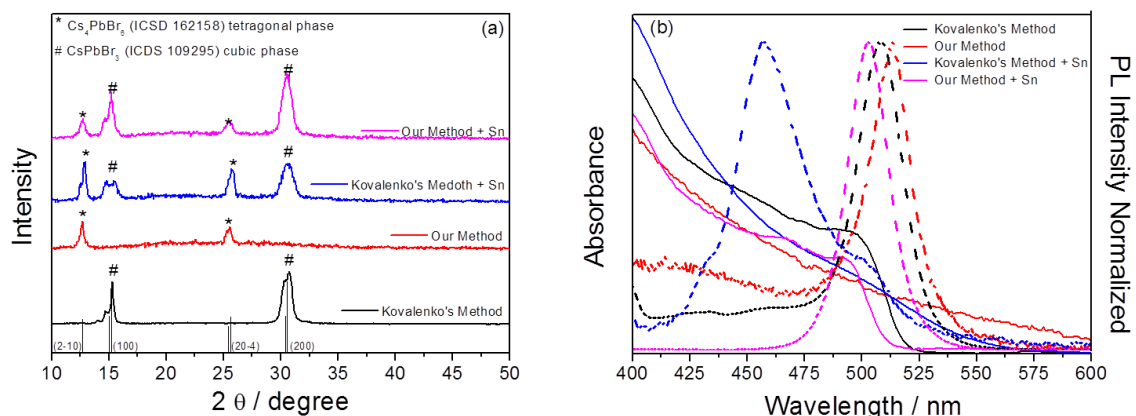


Figure S2: Comparative among different synthesis method: Kovalenko's method and our method with and without Sn-replaced. (a) X-ray diffractograms and (b) Absorption and PL emission spectra.

NPs obtained following the standard Kovalenko's synthesis are only cubic perovskite phase nanocrystals (ICDS 109295), with green emission at 503 nm, as it was expected.³ Nevertheless see the discussion in the main text about the cubic and orthorhombic phases of CsPbBr₃ perovskite NPs. When compared both methodologies, we worked under Cs-rich reaction

conditions and under these conditions, the Cs_4PbBr_6 nanocrystals are favored.⁴ In the literature there are different points view about the optical properties of Cs_4PbBr_6 and the main controversial point is if this material has or not a strong PL emission.^{2, 5-9} In our case, the samples showed a green emission (around 513 nm), but this emission was not a strong emission (see in Figure S2). On the other hand, we could not determinate in this case if this emission is from pure Cs_4PbBr_6 or CsPbBr_3 coexisting compounds (see Figure S1 for more details of the different crystalline structure), as mentioned above. However, the low PLQY could be justified by the presence of Cs_4PbBr_6 NPs in the samples whose crystalline phase was dominant. This hypothesis is confirmed by the low PLQY observed for synthesis where just Cs_4PbBr_6 NPs were obtained, see below.

The NPs with mixed-cation Pb and Sn were prepared modifying the literature methods.^{3, 10} When Sn is introduced to partially replace Pb, the replacing precursors were introduced together with the Pb precursors, at the beginning of the reaction.¹⁰⁻¹² In Kovalenko's synthesis with Sn-replacing, the Pb is greatly substituted by Sn, characterized by a strong blue-shift (with a PL maxima from 507 nm for Sn-free to 456 nm when Sn is introduced, see Figure S2b). Initially, a cubic CsPbBr_3 perovskite is formed, but some PbBr_2 is extracted from CsPbBr_3 to Sn-replacing inside the CsPbBr_3 , forming $\text{CsPb}_{1-x}\text{Sn}_x\text{Br}_3$. This PbBr_2 extraction from CsPbBr_3 perovskite resulted in Cs_4PbBr_6 NPs, as Manna reported.² On the other hand, in our replaced method, we have more ligands (OA and OLEA) and in this case, the precursors keep less available, resulting in a high difficulty to create a rich- PbBr_2 condition. However, we keep using higher Cs concentration than Kovalenko's replaced method, which makes the Cs_4PbBr_6 phase also appears (Figure S2a), but in a less extension. The replacement of Pb by Sn using our method produces just a slight blue-shift of the PL maxima (from 513 nm to 503 nm), see Figure S2b, indicating a lower incorporation of Sn in substitution of Pb.

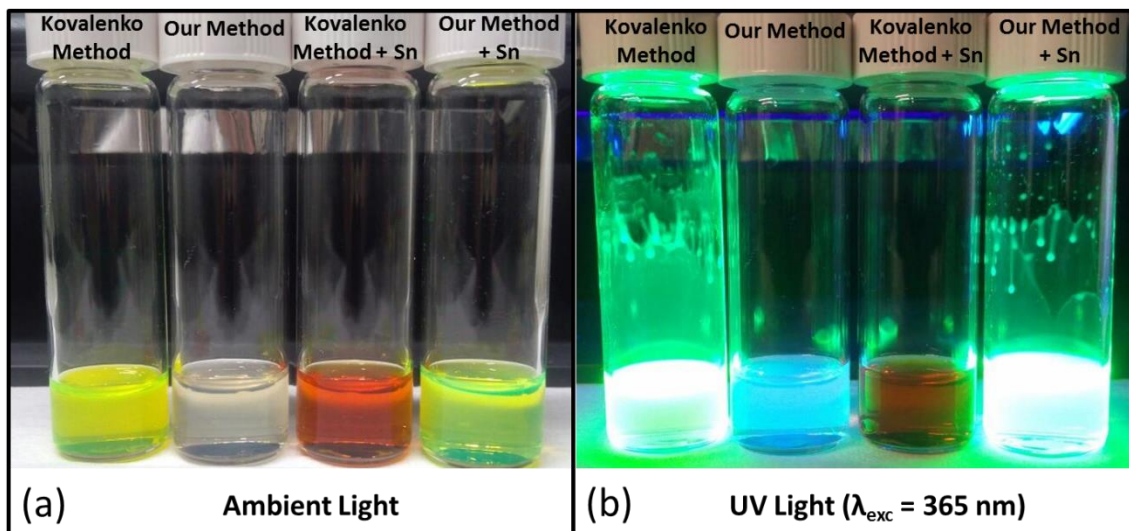


Figure S3: Pictures of different synthesis method: Kovalenko's method and our method with and without Sn-replacing. (a) Under ambient light and (b) under UV light.

By comparing both methods of Sn-replacing, the one based on the standard method produces a higher Sn incorporation as detected by the stronger blue-shift, but resulting in a weak PL emission, and a Photoluminescence Quantum Yield (PLQY) of 0.4%, significantly lower than the 73.4% PLQY obtained for samples produced with the modified method reported here. This huge difference in the sample properties highlight the strong effect that ligands play in

formation and stabilization of NPs,¹³ as the ligand concentration is one of the main differences between both synthesis methods. Because of that, we have performed a new small modification in Kovalenko synthesis with Sn-replacing (for details see Table S2), adding more amounts of ligands, equal to our method (from 0.5 ml to 2 ml). From this modification, the dominant NPs changes to CsPbBr₃ perovskite cubic phase (see Figure S4), showing a much higher PLQY of 56.8%, which is lower than the one obtained with the new method reported here, but increasing significantly the PLQY of the Kovalenko method with lower ligand concentration, that was 0.4% (see Figure S4 and S5).

Table S2: Experimental details and parameters of different synthesis method: Kovalenko method, Kovalenko modified method and our method with Sn-replacing.

Method	Our Method + Sn	Kovalenko's Method + Sn	Kovalenko's Method + Sn (modified)
[Pb] / mmol	0.166	0.188	0.188
Pb : Sn	1 : 2.5	1 : 2.5	1 : 2.5
Cs-oleate / ml	0.6	0.4	0.4
OLEA – OA / ml	2 – 2	0.5 – 0.5	2 – 2
Temperature / °C	150	150	150
Time / sec	5	5	5
PL / nm	503	456	500
Bandgap / eV	2.43	^	2.44
Stokes Shift	10nm / 50.0 meV	^	5nm / 25.0 meV
PLQY / %	73.4	0.4	56.8
FWHM	21.2	49.1	30.8
Phase	# / *	# / *	# / *

= CsPbBr₃ cubic phase (ICDS 109295) and * = Cs₄PbBr₆ tetragonal phase (ICDS 162158)

^=For the Pb:Sn 1:0 sample the absorption band edge was not easy to determine from the experimental results and consequently the bandgap and the Stokes Shift cannot be calculated without a big error.

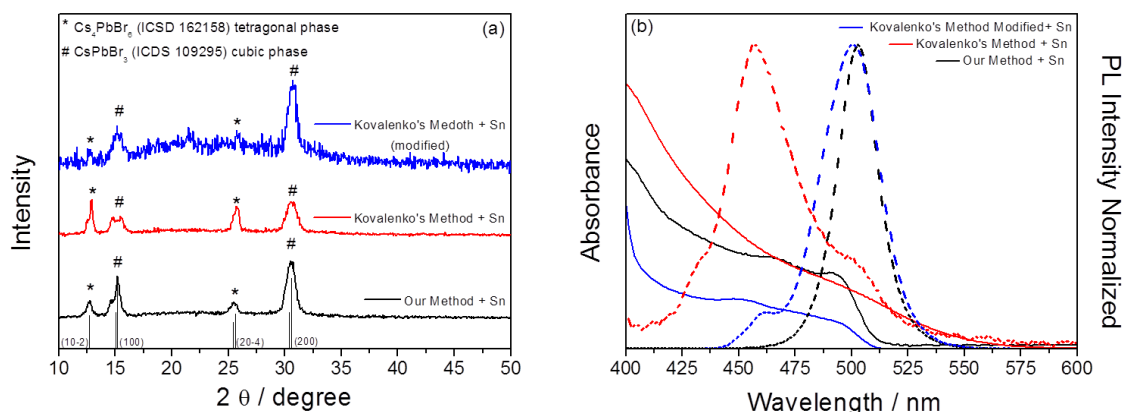


Figure S4: Different synthesis method: Kovalenko's method, Kovalenko's modified method and our method with Sn-replacing. (a) X-ray diffractograms and (b) Absorption and PL emission spectra.

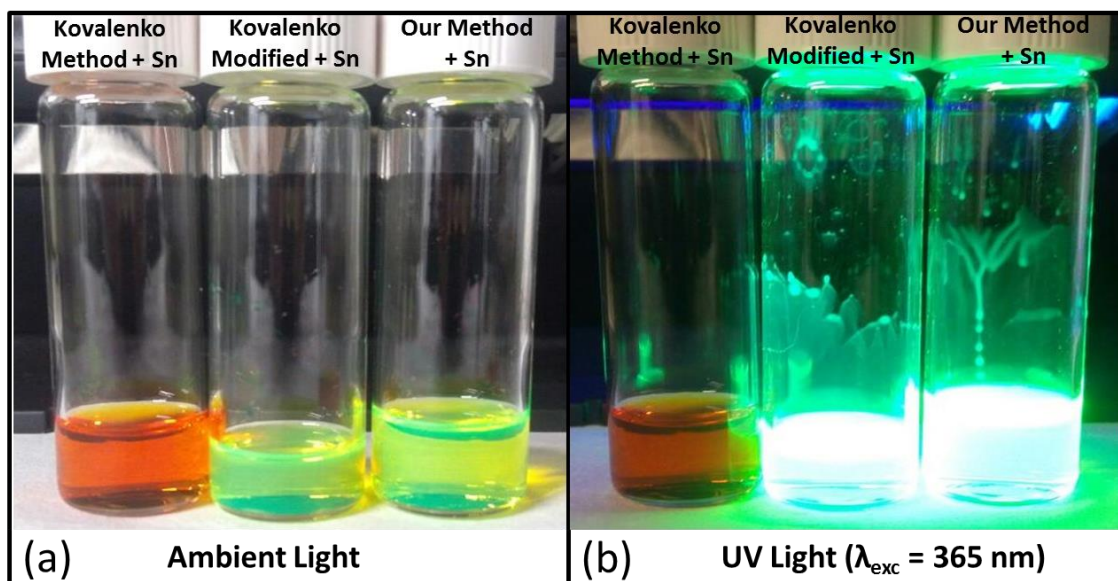


Figure S5: Pictures of different synthesis method: Kovalenko’s method, Kovalenko’s modified method and our method with Sn-replacing. (a) Under ambient light and (b) under UV light.

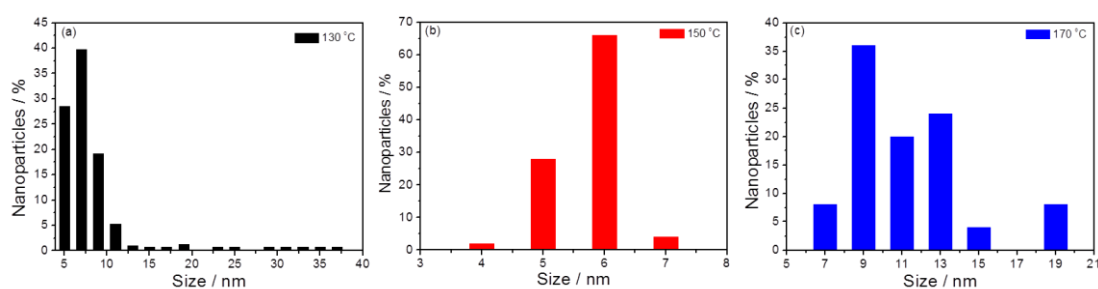


Figure S6: Size distribution of samples with different synthesis temperature. (a) 130 °C, (b) 150 °C and (c) 170 °C.

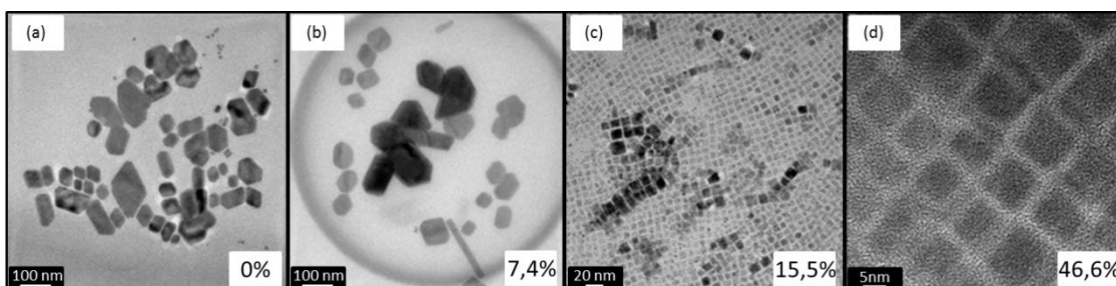


Figure S7: TEM images of Cs-Pb-Sn-Br perovskite nanocrystals synthesized at 130°C reaction temperature. In percentage the Sn amount measured from EDX. (a) Big and small trapezoidal NPs, (b) big particles, (c) more representative particles, and (d) small particles.

Table S3: Average a-lattice parameter obtained from the interplane distance obtained from HRTEM. The distances have been measured in cubic-shaped NPs, at least in 5 different points. Reference values extracted from Joint Committee on Powder Diffraction Standards (JCPDS) data are also indicated for comparison. Both CsPbBr₃ and CsSnBr₃ compounds have cubic structure and the lattice parameter of CsSnBr₃ is higher than that of CsPbBr₃ so an increase in a-lattice parameter of CsPbBr₃ is probable when Pb is substituted by Sn. In fact, this is the trend observed for samples in which Sn has been detected (T=130 and 150°C) that present a larger a parameter than sample without Sn, pointing to an incorporation of Sn into the CsPbBr₃ crystalline structure. We observe an a-lattice parameter closer to CsSnBr₃ than to CsPbBr₃. However EDX and XPS measurements points that the NPs are mainly formed by Pb.

T (°C)	a-lattice parameter (Å)	Sn %
130	5.82 ± 0.03	18.8
150	5.83 ± 0.04	7
170	5.80 ± 0.03	0
CsPbBr ₃ JCPDS: 01-075-0412	5.60	0
CsSnBr ₃ JCPDS: 022-0199	5.82	100

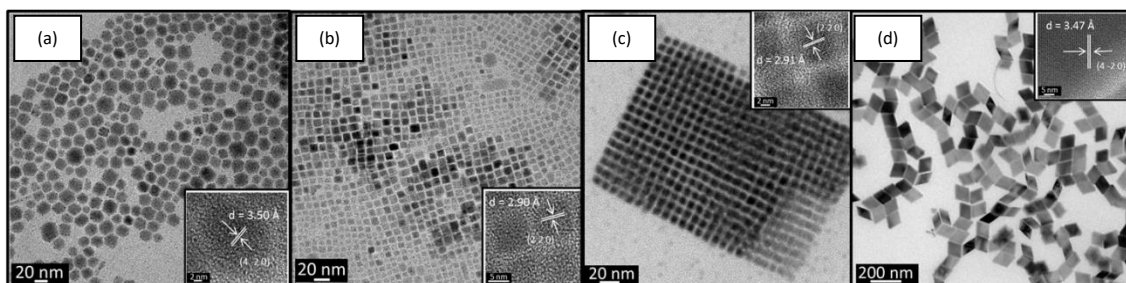


Figure S8: Comparative among different molar ratio (Pb:Sn) synthesis. (a-d) TEM images of Cs-Pb-Sn-Br NPs with different molar ratio synthesis (Pb:Sn): 1:0, 1:1, 1:2.5 and 1:5, respectively. The insert are the HRTEM images.

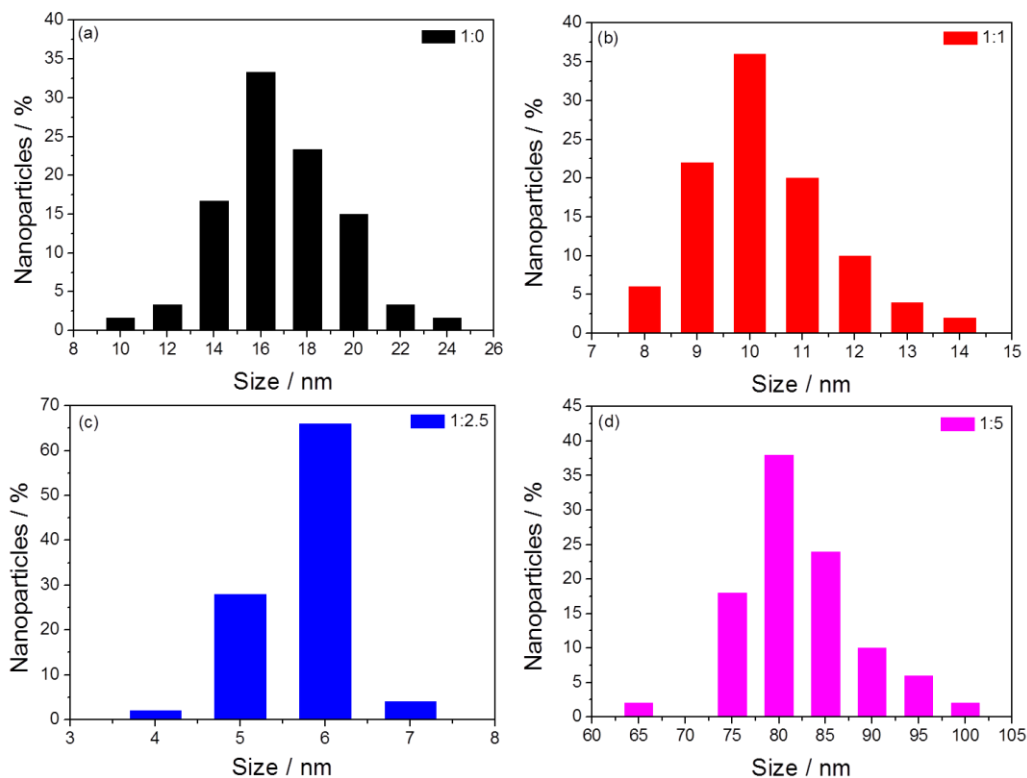


Figure S9: Size distribution of samples with molar ratio (Pb:Sn). (a) 1:0, (b) 1:1, (c) 1:2.5 and (d) 1:5.

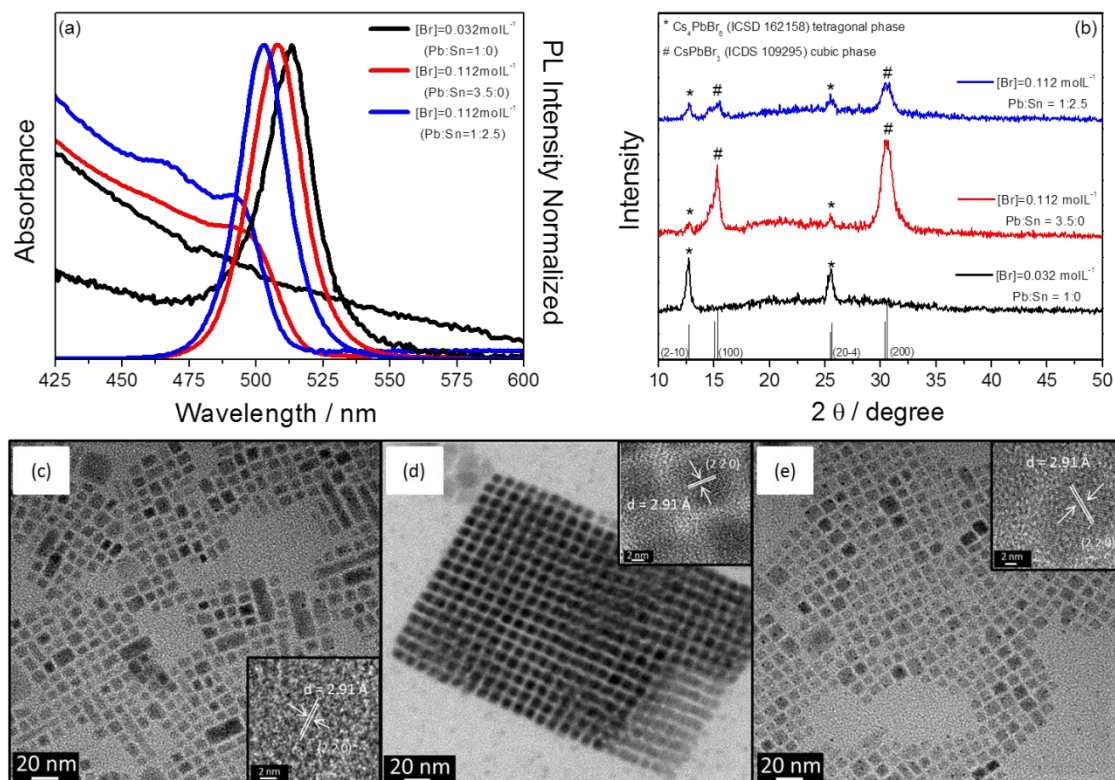


Figure S10: Comparative among different Br concentration synthesis. (a) Absorption and PL emission spectra, (b) X-ray diffractograms and (c-e) TEM images of Cs-Pb-Sn-Br perovskite NPs with different Br concentration synthesis: $[\text{Br}] = 0.032 \text{ molL}^{-1}$ – Pb:Sn = 1:0, $[\text{Br}] = 0.112 \text{ molL}^{-1}$ – Pb:Sn = 1:2.5 and $[\text{Br}] = 0.112 \text{ molL}^{-1}$ – Pb:Sn = 3.5:0, respectively. The insert are the HRTEM images.

Table S4: Experimental details and parameters of synthesis with different time reaction.

Time	5 sec	30 sec
Pb:Sn (molar ratio)	1:2.5	1:2.5
Temperature / °C	150	150
PL / nm	503	500
Bandgap / eV	2.43	2.44
PLQY / %	73.4	64.7
Stokes Shift	10 nm / 50.0 meV	15 nm / 76.7 meV
FWHM	21.2	24.2
Phase	* / #	#
Size / nm	6.18 ± 0.48	10.29 ± 1.61
Sn / % from EDX	7±2	0

= CsPbBr₃ (ICDS 109295) and * = Cs₄PbBr₆ (ICDS 162158)

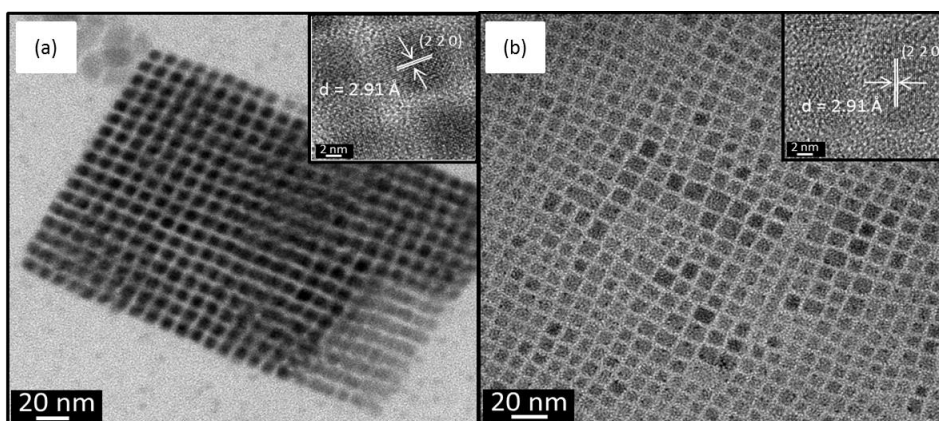


Figure S11: (a-b) TEM images of CsPb_{1-x}Sn_xBr₃ perovskite nanocrystals with time reaction: t = 5 sec and t = 30 sec, respectively. The insert are the HRTEM images.

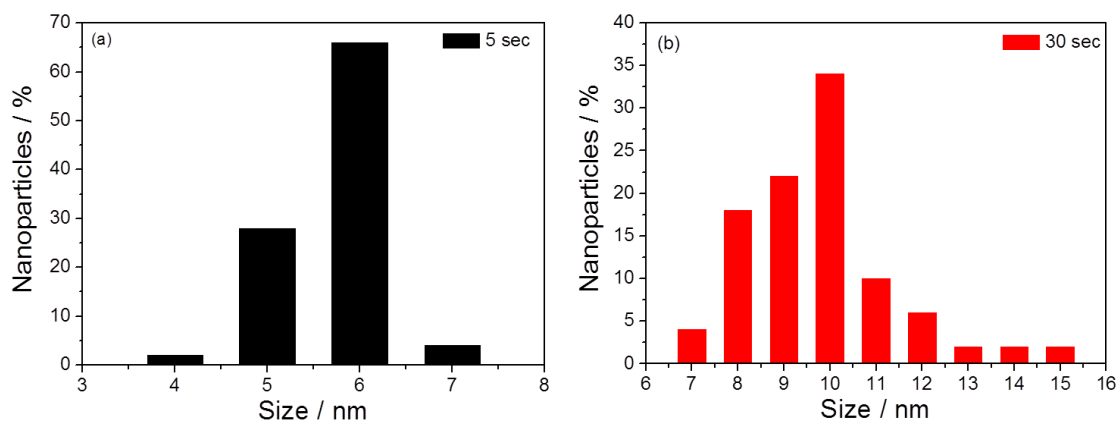


Figure S12: Size distribution of samples with different time reaction in (a) 5 sec and (b) 30 sec.

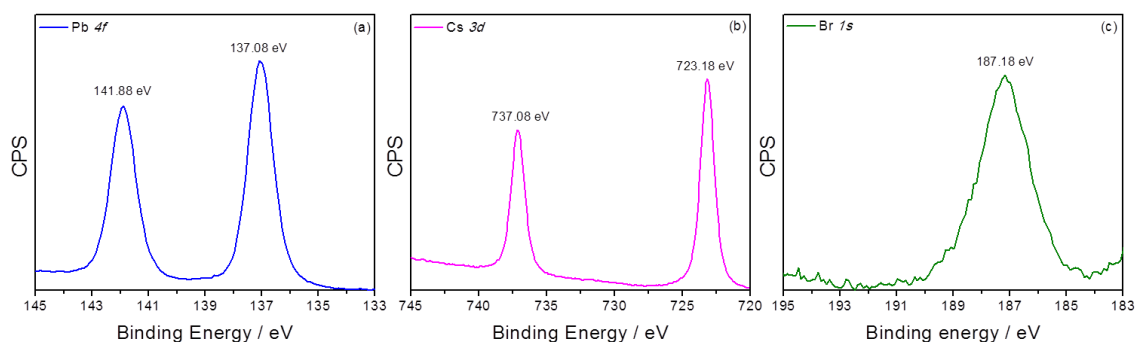


Figure S13: High resolution XPS spectra of (a) Pb, (b) Cs, and (c) Br.

Table S5: Fitted binding energies of the main XPS core levels

Element	3d _{5/2}	3d _{3/2}	4f _{7/2}	4f _{5/2}	1s
Cs		737.08 eV		723.18 eV	
Pb			137.08 eV	141.88 eV	
Sn	485.7 eV	495.8 eV			
Br					187.18 eV

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