Water-assisted synthesis of stable and multicolored $CsPbX_3@SiO_2$ core-shell nanoparticles as fluorescent probes for biosensing

Cynthia Collantes,[a] William Teixeira,[a] † Victoria González Pedro,[a,b] María-José Bañuls,[a,b] †‡ Pedro Quintero-Campos,[a] Sergi Morais,[a,b,c] and Ángel Maquieira [a,b,c]*

[a] Instituto Interuniversitario de Investigación de Reconocimiento Molecular y Desarrollo Tecnológico (IDM), Universitat Politècnica de València-Universitat de València, Camino de Vera s/n, E46022 València, Spain.

E-mail: vigonpe@upvnet.upv.es

[b] Departamento de Química, Universitat Politècnica de València, Camino de Vera s/n, E46022 València, Spain.

[c] Unidad Mixta UPV-La Fe, Nanomedicine and Sensors, IIS La Fe, Valencia, Spain

SUPPORTING INFORMATION

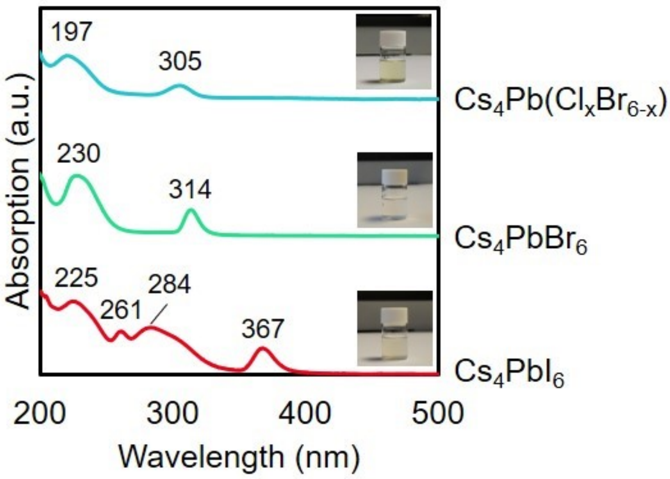


Figure S1. UV-Vis absorption spectra of Cs_4PbX_6 NCs (X = Cl/Br, Br and I).

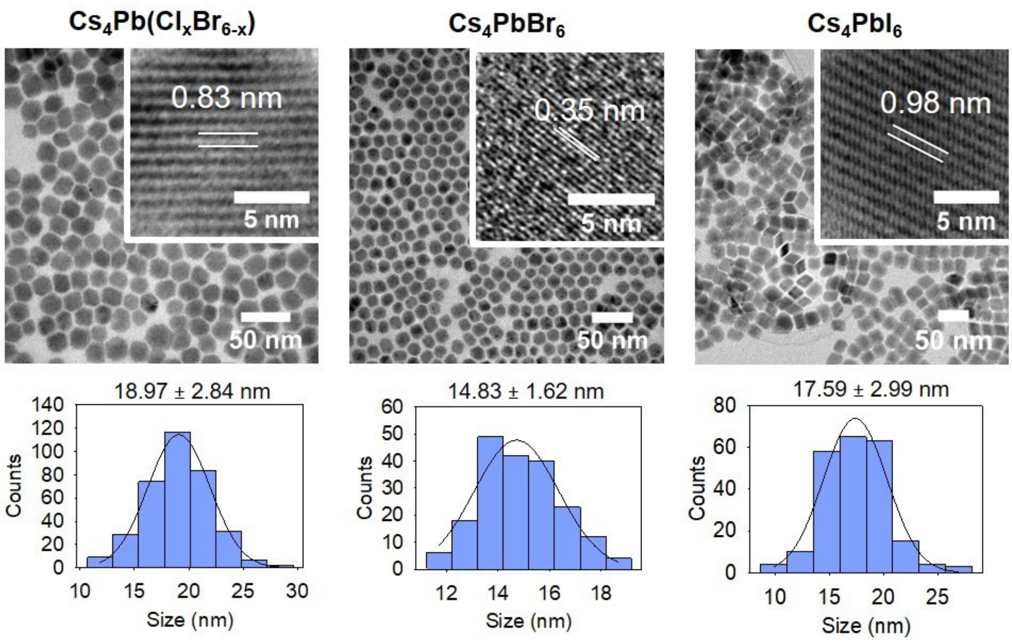


Figure S2. TEM images of Cs_4PbX_6 NC (X = Cl/Br, Br and I) and histograms of the particle size distribution.

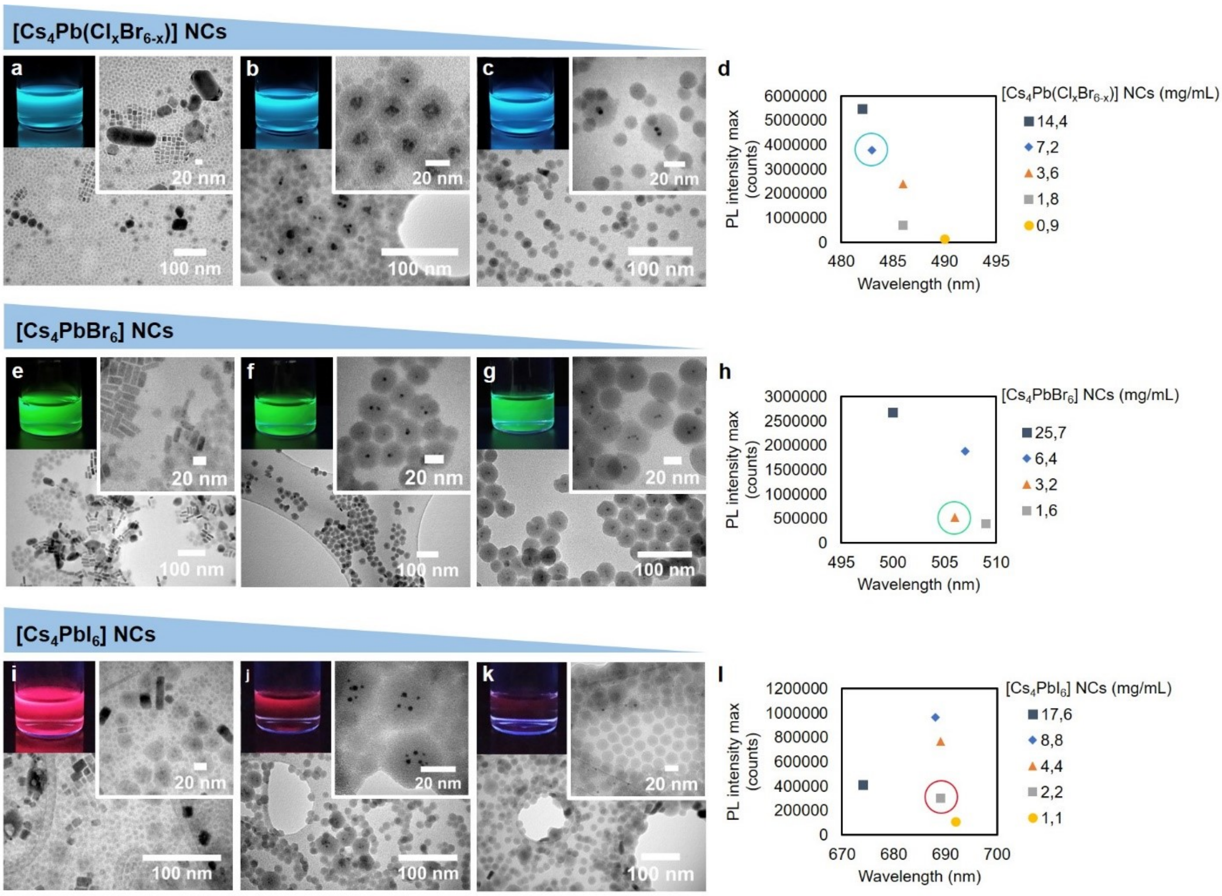


Figure S3. Characterization by TEM of the resulting $CsPbX_3@SiO_2$ NPs starting from a) 14.4, b) 7.2, c) 3.6 mg/mL $Cs_4Pb(Cl_xBr_{6-x})$ NCs e) 6.4, f) 3.2, g) 1.6 mg/mL Cs_4PbBr_6 NCs, i) 8.8, j) 2.2 k) 1.1 mg/mL Cs_4PbI_6 NCs. PL intensity at maximum emission for different concentrations of precursor NCs (d, h, and l).

Table S1. Description of the resulting $CsPbX_3@SiO_2$ samples prepared at different concentrations of Cs_4PbX_6 NCs

[$Cs_4Pb(Cl_xBr_{6-x})$] NCs (mg/mL)[1]	***Emission peak (nm)***	***Fwhm (nm)***	***Particle size (nm)***	***Core size (nm)***	***Cores/particle***
7.2	483	26	30	11	1
3.6	486	20	32	3	1
1.8	486	19	32	3	1
0.9	490	19	32	-	-
[Cs_4PbBr_6] NCs (mg/mL)[2]	**Emission peak (nm)**	**Fwhm (nm)**	**Particle size (nm)**	**Core size (nm)**	**Cores/particle**
3.2	506	22	22	4	1
1.6	509	22	25	2	2
[Cs_4PbI_6] NCs (mg/mL)[3]	**Emission peak (nm)**	**Fwhm (nm)**	**Particle size (nm)**	**Core size (nm)**	**Cores/particle**
2.2	689	33	33	2	5
1.1	692	38	15	-	-

[1] The most concentrated sample (14.4 mg/mL) is heterogeneous, containing: cubes 9 nm, hexagonal crystals of 60 nm, spheres of 8 nm with inappreciable core.
[2] The most concentrated sample (25.7 mg/mL) is heterogeneous, containing: cubes 9 nm, hexagonal crystals of 60 nm, spheres of 8 nm with inappreciable core. The next sample (6.4 mg/mL) is also heterogeneous: nanoplates of 23 nm long, spheres of 23 nm with inappreciable core.
[3] The most concentrated sample (17.6 mg/mL) is heterogeneous, containing: spheres of 5 and 26 nm with inappreciable core and irregular particles of 17 nm with dark contrast. The next sample (8.8 mg/mL) is also heterogeneous: cubes of 12 nm, spheres of 5 and 26 nm with inappreciable core. The sample 4.4 mg/mL is still heterogeneous with spheres of 29 nm with 2 cores and spheres of 5 nm with inappreciable core.

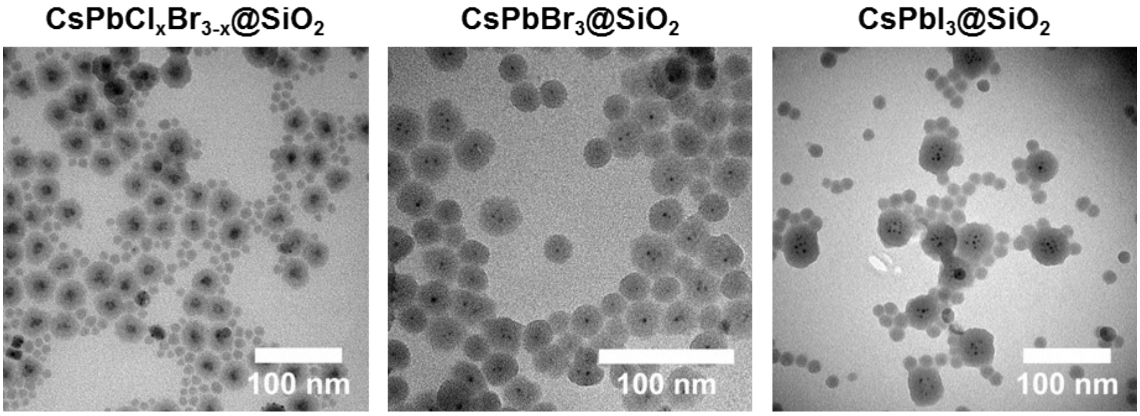
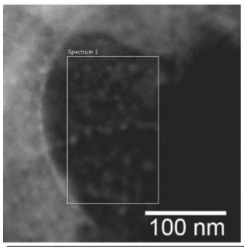


Figure S4. TEM images of CsPbX3@SiO2 NPs where it is appreciated the coexistence of core-shell and empty silica NPs.

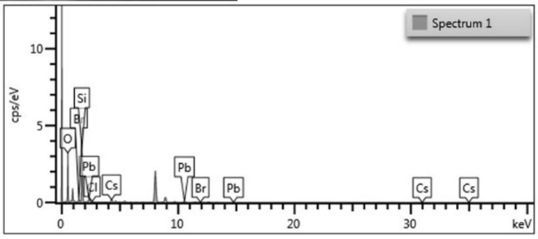
Table S2. Estimation of the ratio of core-shell to empty SiO_2 nanoparticles for each composition calculated from three TEM images.

	% core-shell	*% empty SiO2*	*Total particles (counts)*
$CsPb(Cl_xBr_{3-x})@SiO_2$	*29,1*	*70,9*	*693*
$CsPbBr_3@SiO_2$	*78,2*	*21,8*	*234*
$CsPbI_3@SiO_2$	*6,8*	*93,2*	*770*

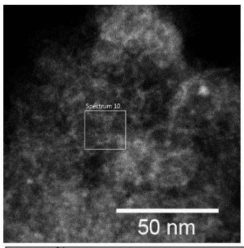
calcinated CsPb(Cl_xBr_{3-x})@SiO_2



Element	Wt%	Wt% Sigma	Atomic %
O	45,32	0,43	66,82
Si	35,52	0,36	29,83
Cl	0,36	0,08	0,24
Br	1,97	0,21	0,58
Cs	9,54	0,3	1,69
Pb	7,31	0,43	0,83
Total:	100		100



calcinated $CsPbBr_3$@SiO_2



Element	Wt%	Wt% Sigma	Atomic %
O	45,93	0,9	65,68
Si	39,6	0,8	32,26
Br	0,93	0,37	0,26
Cs	4,86	0,52	0,84
Pb	8,69	0,97	0,96
Total:	100		100

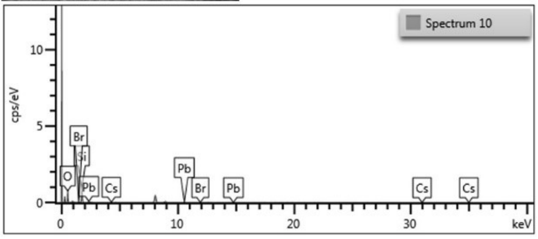


Figure S4. Elemental analysis of CsPb(Cl_xBr_{3-x}) @SiO_2 and $CsPbBr_3$@SiO_2 showing the atomic distribution of Si, O, Cl, Br, and Pb obtained by EDS TEM.

Table S2. Summary of polar solvent stability of different silica-coated metal halide perovskite core-shell NPs.

Polar solvent stability			
Water-triggered Cs_4PbBr_6 to $CsPbBr_3$ phase transition			
	Structural stability	***Water or polar solvent***	
$CsPb(Cl_xBr_{3-x})@SiO_2$	4 days (R.H~60%)	3 days in water solution*	This work
$CsPbBr_3@SiO_2$	4 days	4 days in water solution*	
$CsPbI_3@SiO_2$	Not stable		
$CsPbBr_3@SiO_2$	N.R.**	90 days water/ethanol solution	[1]
$CsPbBr_3@SiO_2$	N.R.	27 days ethanol	[2]
Ligand-assisted reprecipitation			
$CsPbBr_3@SiO_2$	4 weeks (R.H~75%)	40 min in water	[3]
Hot injection			
$CsPbBr_3@SiO_2$	30 days (R.H~40%)	8 days in hexane/water	[4]

*Thermal-treated NPs.

**Not reported

1 M. Li, X. Zhang and P. Yang, *Nanoscale*, 2021, **13**, 3860–3867.

2 C. Rossi, R. Scarfiello, R. Brescia, L. Goldoni, G. Caputo, L. Carbone, D. Colombara, L. De Trizio, L. Manna and D. Baranov, *Chem. Mater.*, 2022, **34**, 405–413.

3 Q. Zhong, M. Cao, H. Hu, D. Yang, M. Chen, P. Li, L. Wu and Q. Zhang, *ACS Nano*, 2018, **12**, 8579–8587.

4 F. Gao, W. Yang, X. Liu, Y. Li, W. Liu, H. Xu and Y. Liu, *Chem. Eng. J.*, 2021, **407**, 128001.