Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information

Improved The Stability of γ-$CsPbI_3$ Nanowires Enabled by Lattice Immobilization Through Pb-O Anchor in SBA-15

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Experimental methods

Materials and Chemicals.

Lead iodide (PbI_2, ≥ 99.0%), lead bromide ($PbBr_2$, ≥ 98.0%), cesium iodide (CsI, ≥ 99.9%) and cesium bromide (CsBr, ≥ 99.5%) were purchased from Aladdin, and Dimethylsulfoxide (DMSO, ≥ 99.7%) were acquired from Beijing Chemical Works. SBA-15 was synthesized as reported before.[1]

Precursors Preparation.

The $CsPbI_3$ precursor solution was prepared by mixing equimolar ratios of lead iodide (PbI_2) and cesium iodide (CsI) in DMSO under atmosphere at room temperature, with sonication for 0.5 h to dissolve them completely. The concentration was 0.13 M. Precursors of other compositions are prepared by mixing particular volume of $CsPbBr_3$ and $CsPbI_3$ precursor solution.

$CsPbX_3$@SBA-15 Synthesis.

Before use, the SBA-15 powder was added into a three-neck flask and vacuumized in Schlenk line for 2 h. Then the $CsPbI_3$ precursor solution was injected into the flask under a vacuum followed by stirring for 30 min. The liquid was kept standing for 12 hours and then the precipitation was separated as wet solids. After that, the wet solid was put into a vacuum oven at 60°C for 24 h to get it dried, and calcined at 623 K for 3h under Ar flow before further characterization. Bulk $CsPbI_3$ used as a control sample was prepared by drying the $CsPbI_3$ precursor solution with no SBA-15 template addition in a vacuum oven at 60°C for 24 h. Powders of other mixed halide compositions were synthesized using the same method with some modification, with an exact ratio of halide in the precursor.

Structural Analysis.

Ambient X-Ray Diffraction (XRD) patterns were recorded on a PANalytical X'Pert3 powder diffractometer, using Cu Kα radiation (λ =1.5406 Å). Temperature-dependent XRD was performed on Bruker D8 Discover and the dwelling time was 1 hour to ensure the thermal equilibrium before measurements. Low-resolution transmission electron microscopy (TEM) and selected area electron diffraction (SAED) images were obtained on a JEOL JEM-2100 operated at 200 kV. High-resolution TEM (HRTEM) and scanning transmission electron microscopy (STEM) images were obtained on a JEOL JEM-2100F field emission TEM operated at 200 kV. Small Angle X-ray Scattering (SAXS) patterns were conducted on a Bruker Nanostar SAXS instrument using Cu Kα radiation (λ = 0.154 nm at 40 kV and 40 mA). The nitrogen adsorption−desorption isotherms were obtained with a high precision Belsorp-mini apparatus (Bel Japan, Inc.). X-ray Photoelectron Spectroscopy (XPS) was performed on Axis Ultra X-ray imaging photoelectron spectrometer (Al Kα radiator). The C_{1s} peak energy was calibrated to 284.8 eV for all measured samples. The X-ray Absorption Fine Structure (XAFS) spectra at Pb L_{III} edge (E_0 = 13030 eV) were obtained under fluorescence mode with a standard Lytle ion chamber (samples with SBA-15) and transmission mode (samples without SBA-15) on the BL14W1 beamline of the Shanghai Synchrotron Radiation Facility (SSRF, 3.5 GeV, "top-up" mode with constant currents of 220 mA). The energy was calibrated with reference to the pure Pb foil absorption edge. Athena and Artemis software packages were employed for data processing and analysis. The normalization procedures for the X-ray absorption near-edge structure (XANES) results were processed by background subtraction of the experimental absorption coefficients. PbI_2 bulk materials were chosen as references. For the extended XAFS (EXAFS) spectra, the Fourier transformed (FT) data in the *R* space (the Pb-I shell) were analyzed using the first-shell approximation model. The passive electron factors (S_0^2) were confirmed by fixing the coordination number (CN) of Pb-I to be 6, fitting the obtained experimental data on PbI_2, respectively, and then fixed for further analysis. The other parameters were allowed to vary during the fit process, consisting of that describing local structure environment of CN, bond distance (*R*), and Debye–Waller factor(σ^2) around the absorbing atoms as well as the electronic properties.

Optical Measurements.

The UV−vis−NIR absorption spectra of the solid powders were obtained from the reflectance spectra obtained on SHIMADZU UV-3600 Plus. Photoluminescence spectra was carried out with a Jobin-Yvon HR800 laser Raman microscope with an excitation wavelength of 488 nm. The Linkam stage was used to run the stated temperature procedure, and the dwelling time was 10 minutes to ensure the thermal equilibrium before measurements. Confocal laser scanning microscopy images were obtained on a Nikon A1R-si confocal laser scanning microscope with an excitation wavelength of 488 nm. The photographs of the powder sample were obtained under the UV lamp at 365 nm.

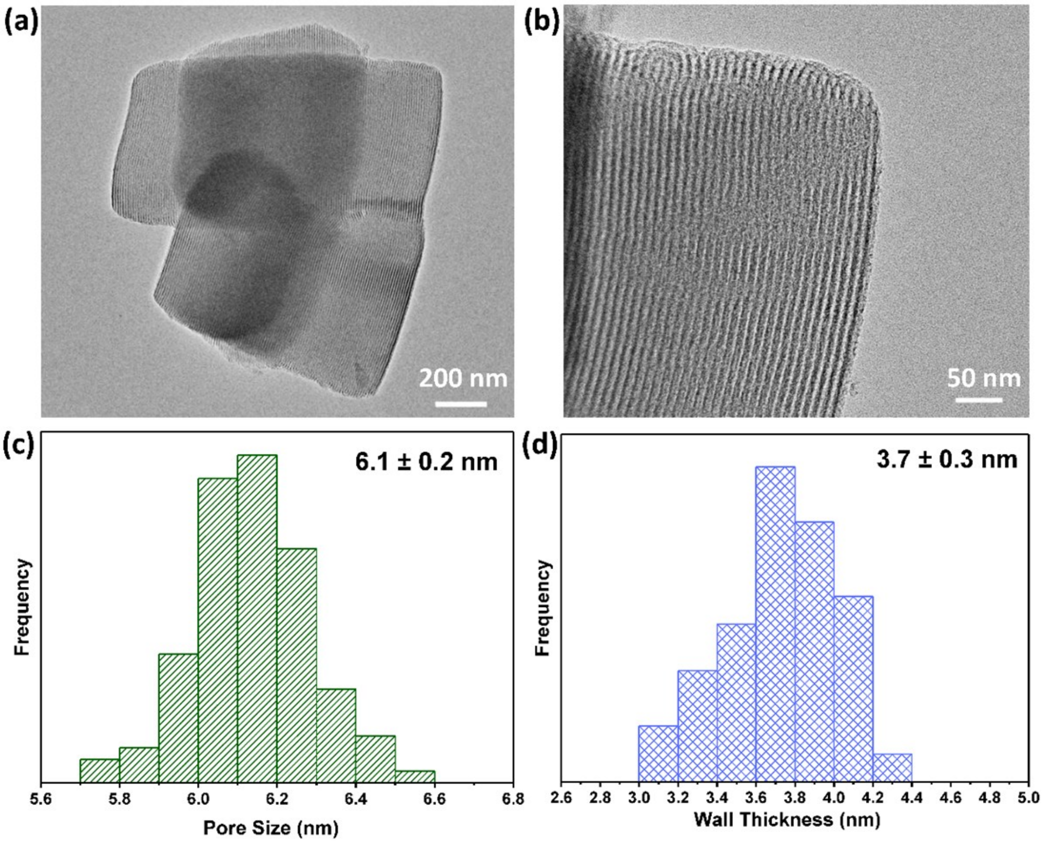

Fig. S1 (a) TEM image, (b) magnified TEM image, (c) the pore size distribution and (d) the wall thickness distribution of SBA-15 template.

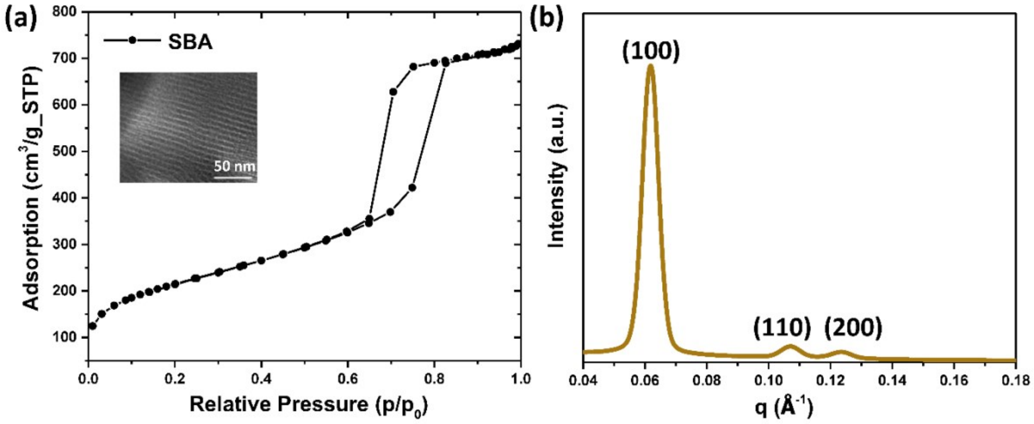

Fig. S2 (a) N_2 adsorption-desorption isotherms (inserted: the TEM image) of SBA-15. (b) Small-angle X-ray scattering (SAXS) pattern of SBA-15.

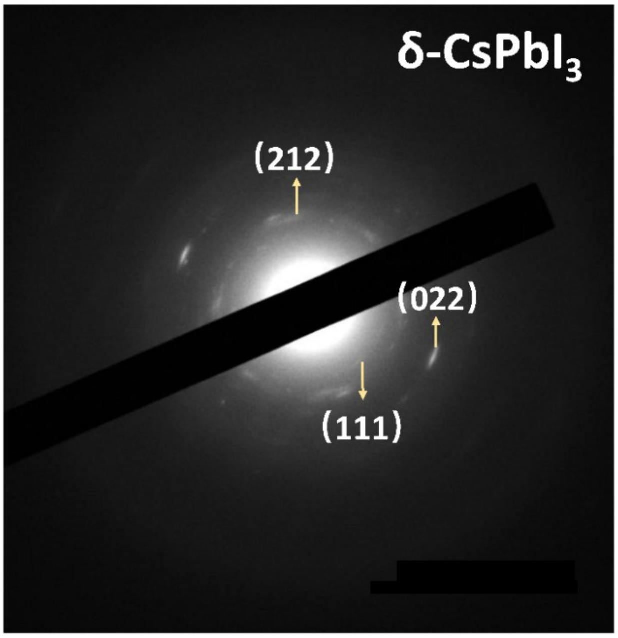

Fig. S3 SAED pattern of CsPbI$_3$@SBA-15 (fresh).

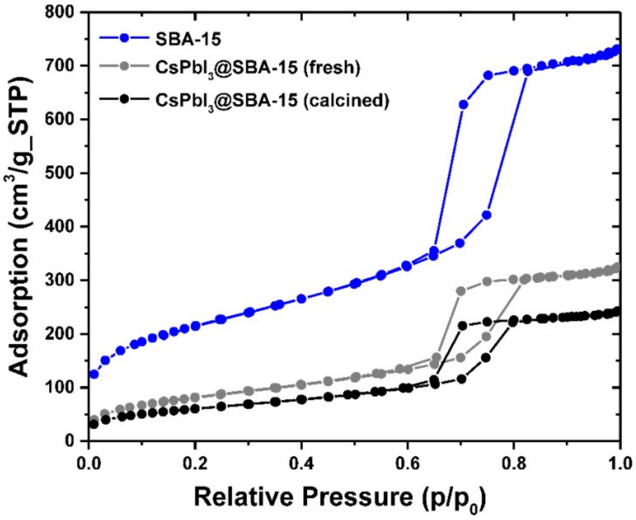

Fig. S4 N$_2$ adsorption-desorption isotherms of the samples as-listed.

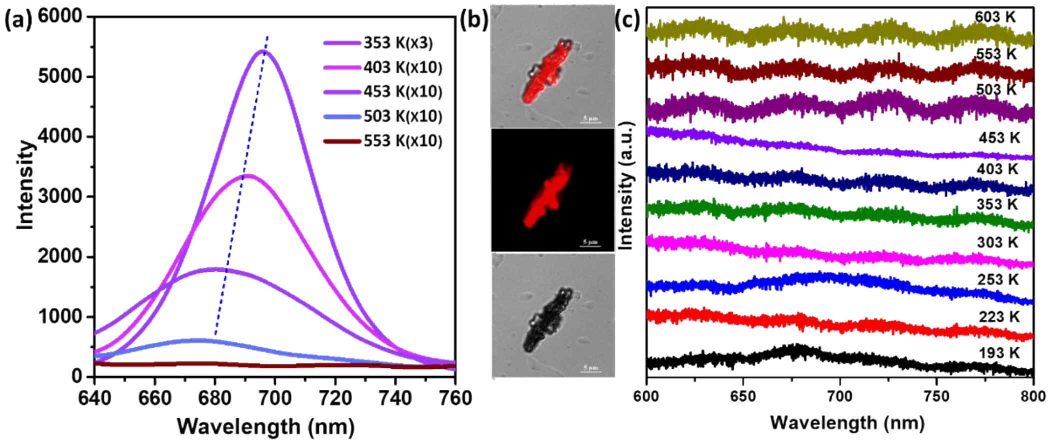

Fig. S5 (a) Temperature-dependent PL spectra of γ-$CsPbI_3$@SBA-15. (b) Confocal images of γ-$CsPbI_3$@SBA-15. (c) Temperature-dependent PL spectra of $CsPbI_3$ (calcined).

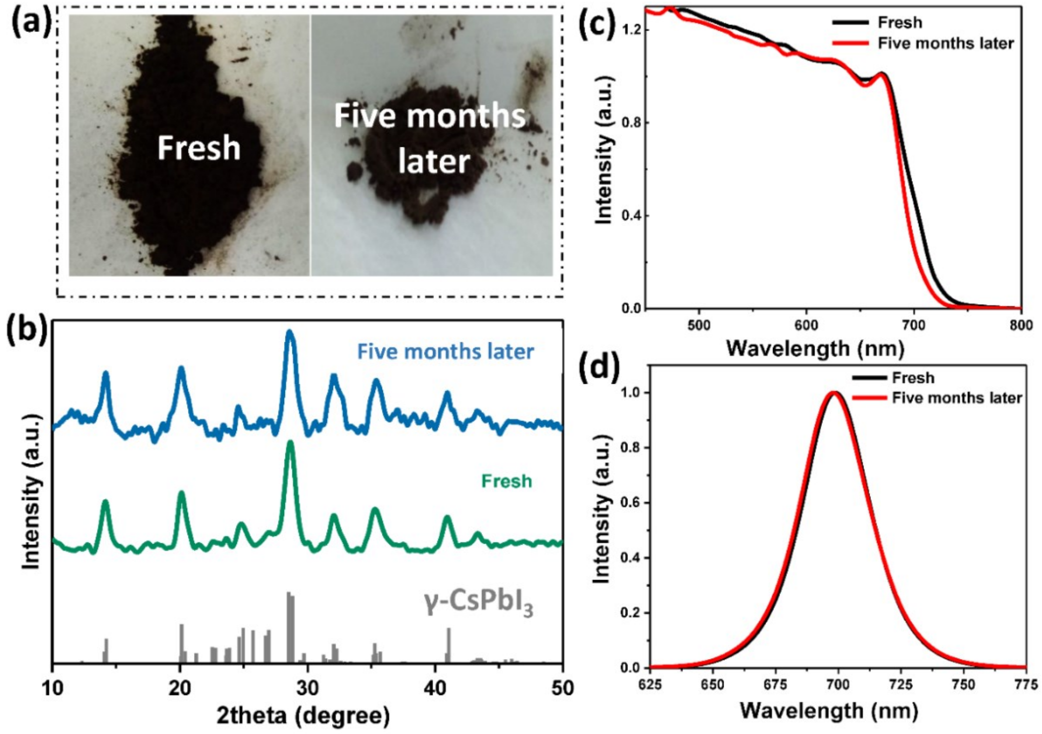

Fig. S6 Comparison of γ-$CsPbI_3$@SBA-15 exposed in the air for five months. (a) Photographs. (b) XRD patterns. (c, d) Absorption and PL spectra.

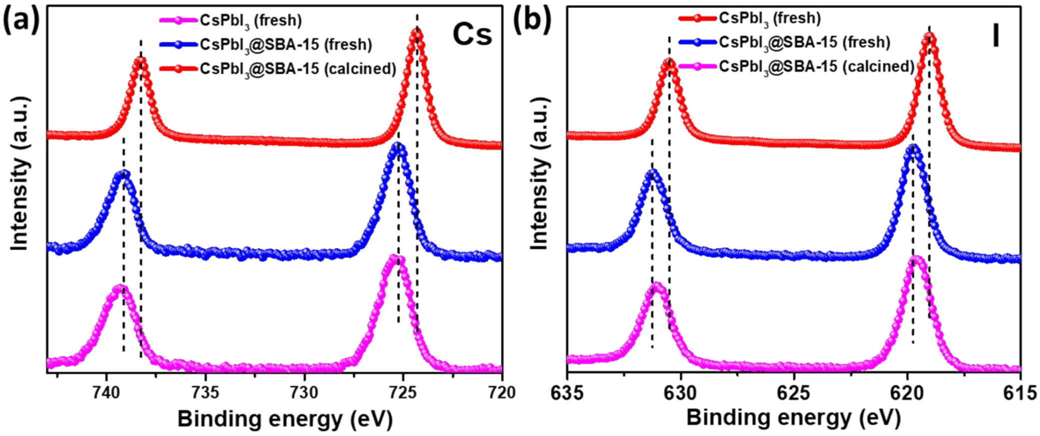

Fig. S7 XPS results of Cs (a) and I (b) for the $CsPbI_3$ samples.

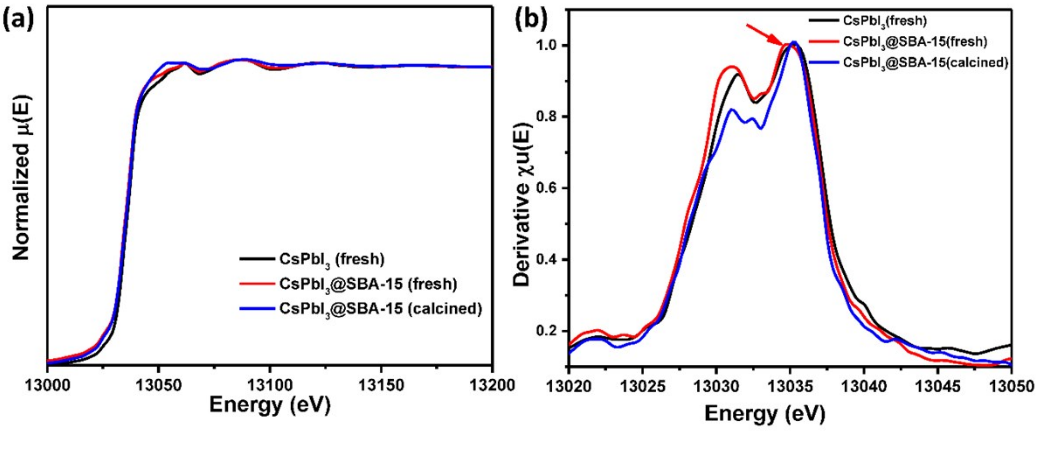

Fig. S8 (a) Normalized Pb L_{III}-edge XANES data and (b) their derivative spectra for the $CsPbI_3$ samples.

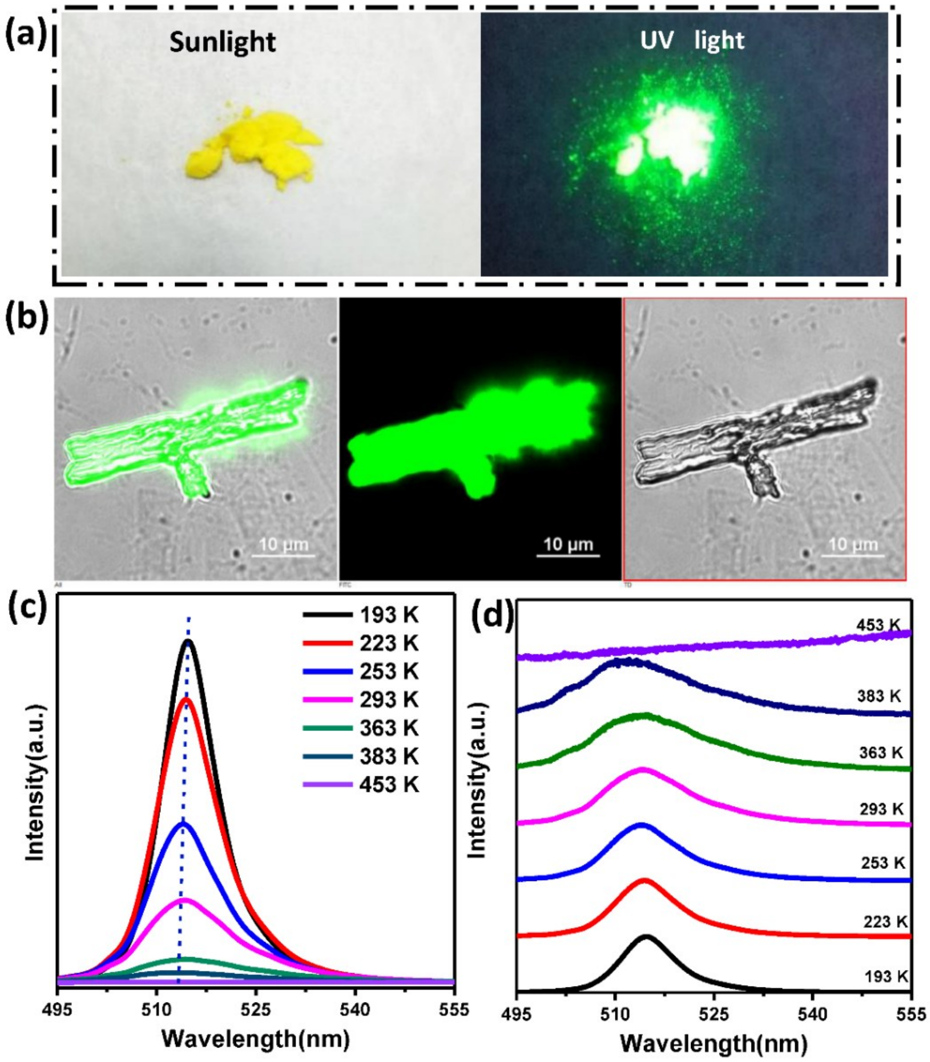

Fig. S9 CsPbBr$_3$@SBA-15. (a) Photographs under natural and UV light. (b) Confocal images. (c, d) Temperature-dependent PL spectra.

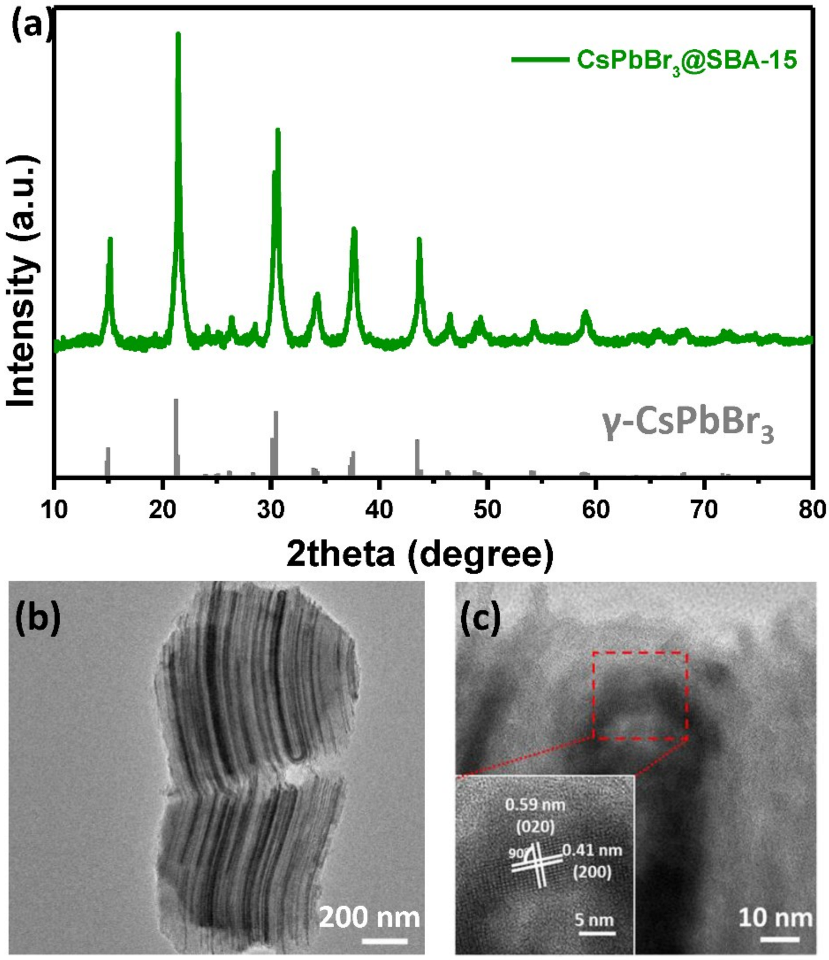

Fig. S10 CsPbBr$_3$@SBA-15. (a)XRD pattern. (b, c) TEM and HRTEM images.

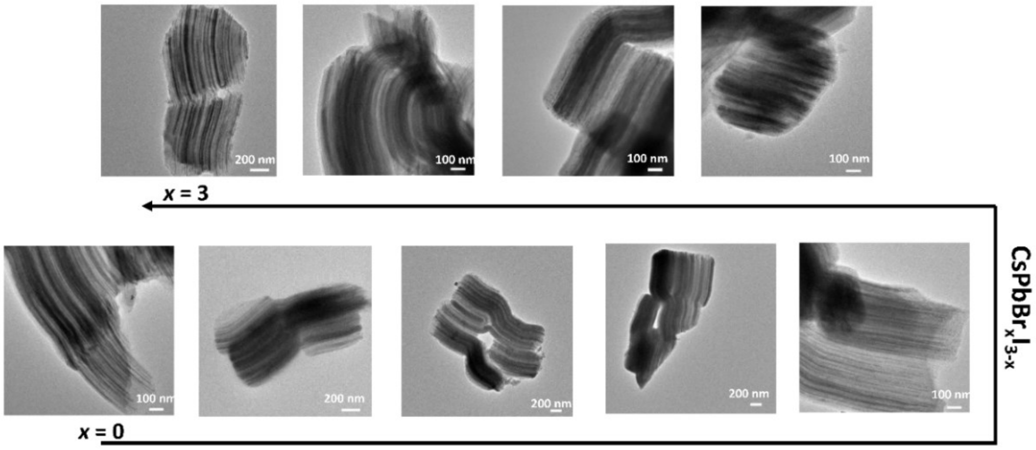

Fig. S11 TEM images of CsPbBr$_x$I$_{3-x}$@SBA-15 (x = 0~3).

Table S1. Parameters of SBA-15 from the N_2 adsorption-desorption isotherms.

	SBA - 15
BET Surface Area(m^2/g)	745.95
Average Pore Volume(cm^3/g)	1.16
Average Pore Size(nm)	6.1

Table S2. Parameters of $CsPbBr_3$@SBA-15 from the N_2 adsorption-desorption isotherms and the obtained filling ratio.

	BET Surface Area (m^2/g)	Average Pore Volume (cm^3/g)	Filling Ratio (%)
SBA-15	745.95	1.16	\
$CsPbBr_3$@SBA-15	261.84	0.44	65

Table S3. The fitting results of the Pb L_{III}-Edge k_2-weighted EXAFS spectra.

Samples	$CsPbI_3$ (fresh)	$CsPbI_3$ @SBA-15 (fresh)	$CsPbI_3$ @SBA-15 (calcined)	$CsPbI_3$ @SBA-15 (calcined)
Shell	Pb-I	Pb-I	Pb-I	Pb-O
R(Å)[c1]	3.00±0.03	2.88±0.01	3.09±0.01	\
σ(Å)[d1]	0.002±0.002	0.003±0.009	0.020±0.002	\
R_1(Å)[c2]	3.18±0.02	3.10±0.01	\	1.93±0.02
σ_1(Å)[d2]	0.002±0.002	0.014±0.003	\	0.030±0.009
R_2(Å)[c3]	3.14±0.02	3.14±0.01	\	2.28±0.01
σ_2(Å)[d3]	0.002±0.002	0.030±0.009	\	0.010±0.008
R_3(Å)[c4]	3.43±0.03	3.28±0.01	\	\
σ_3(Å)[d4]	0.002±0.002	0.010±0.006	\	\
ΔE_0(eV)	-2.8±0.9	-6.6±0.8	-6.4±0.7	-6.4±0.7
R-factor	0.018	0.015	0.016	0.016

[c1, c2, c3, c4] Distance between absorber and backscatter atoms. Each R comes from different scattering paths arising from different Pb-I and Pb-O distances. In the sample $CsPbI_3$@SBA-15(calcined), three different scattering paths (one path from Pb-I and two from Pb-O are selected) are used to analyze the data. Other two samples were fit with four paths from Pb-I shell. [d1, d2, d3, d4] The mean-square relative displacement of absorber and backscatter atoms.

References

[1] Zhao, D.; Feng, J.; Huo, Q.; Melosh, N.; Fredrickson, G. H.; Chmelka, B. F.; Stucky, G. D., Triblock Copolymer Syntheses of Mesoporous Silica with Periodic 50 to 300 Angstrom Pores. *Science* **1998**, *279*, 548.