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Electronic Supplementary Information

Ultrasmall Water-stable CsPbBr3 Quantum Dots with High Intensity Blue Emission Enabled by Zeolite Confinement Engineering

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Materials and Methods

Materials

All reagents were used without further purification. CsBr and $PbBr_2$ were purchased from Aladdin Industrial Corporation. Silicon tetraacetate and tetrapropylammonium hydroxide were purchased from Innochem Corporation. Sodium tungstate dihydrate ($Na_2WO_4{\bullet}2H_2O$) and tetramethoxysilane were purchased from Aladdin Industrial Corporation. The ultrapure water was obtained from Milli-Q purification equipment.

Instruments

The transmission electron microscopy (TEM) and scanning TEM (STEM) images were taken on a Tecnai F20 electron microscope. Scanning electron microscopy (SEM) images were performed on a JSM-6510 (JEOL) electron microscope. The steady-state spectra and delayed photoluminescence spectra were measured using a HORIBA Scientific FluoroMax-4 spectrofluorometer. The quantum yields (QYs) were collected on an Edinburgh FLS920 with an integrating sphere. The FTIR absorption spectra were measured on a PerkinElmer spectrum 430 FT-IR spectrometer in the range of 400 to 4000 cm^{-1} with KBr pellets and corrected baseline after measurement. UV-vis adsorption spectra were measured by a Shimadzu UV-2550 spectrophotometer. The ^{29}Si MAX NMR spectra were measured on a Bruker AVANCE III 400 MHz NMR spectrometer.

Synthesis of W-S-1 zeolite

W-S-1 zeolite was synthesized on the basis of reported literature with a few modifications. The synthesis process was as follows: First, 20 g tetraethyl orthosilicate and 23.4 g tetrapropyl ammonium hydroxide were added into A beaker, and stirred for about 2 h until tetraethyl orthosilicate hydrolyzed into transparent solution. In a beaker B, 1.8 g sodium tungstate and 15.8 g ultrapure water were added and stirred until the sodium tungstate dissolved. Then, the solution in beaker B was slowly added into beaker A, and stirred for 4 h. Finally, the solution was loaded into 100 mL Teflon-lined stainless-steel autoclave and crystallized in the oven at 150 °C for 15 h under static conditions. After the reaction, the as-synthesized solid product was centrifuged, washed for several times, and then dried at 80 °C in the oven. Finally, the sample was calcined at 550 °C for 5 h to remove the organic temples.

Synthesis of $CsPbBr_3$@W-S-1 composite

First, CsBr and $PbBr_2$ with the same molar ratio were ground to mix evenly. Then, a small amount of CsBr/$PbBr_2$ mixture was spread on the bottom of the quartz boat, covered with graphite paper, and W-S-1 zeolite powder was placed on the graphite paper to ensure that the CsBr/$PbBr_2$ powder was not contact with the zeolite directly. After that, the quartz boat was put into the tube furnace, and blew with N_2. The tube furnace was programmatically heated to 700°C in a speed of 5°C/min, and kept for 30 min at 700°C and then cooled naturally to obtain a kind of white powder. Finally, the as-obtained with white powder was washed with water and ultrasound for 30 min to remove the bulk perovskite attached on the surface of zeolite.

Amino acid modification and silanization of $CsPbBr_3$@W-S-1 composite

The $CsPbBr_3$@W-S-1 composite was added to glycine aqueous solution, and drained by a vacuum oven, so that the glycine entered into zeolite channels and coordinated with perovskite, thus stabilizing the perovskite QDs in zeolite. Then amino acid modified $CsPbBr_3$@W-S-1 composite was silanized to avoid the loss of glycine in water via the reaction of tetramethyl orthosilicate with zeolite composite in toluene solvent at room temperature for 12-24 h.

Supplementary Figures and tables

$$2PbBr_2 + CsBr \rightarrow CsPb_2Br_5 \tag{1}$$

$$CsPb_2Br_5 + CsBr \rightarrow 2CsPbBr_3 \tag{2}$$

$$CsPb_2Br_5 \rightarrow CsPbBr_3 + PbBr_2 \tag{3}$$

$$PbBr_2 + CsBr \rightarrow CsPbBr_3 \tag{4}$$

Fig. S1. Reactions during the grinding and high temperature evaporation process.

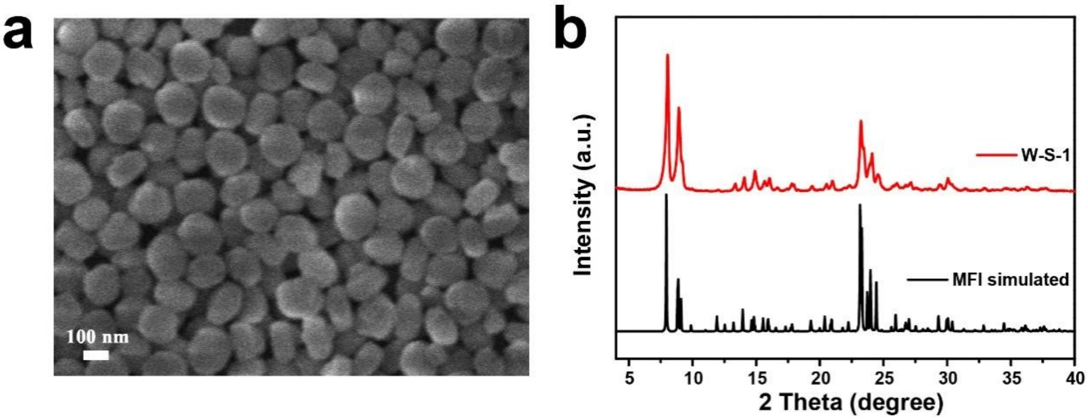

Fig. S2. (a) SEM image and (b) PXRD pattern of W-S-1 zeolite.

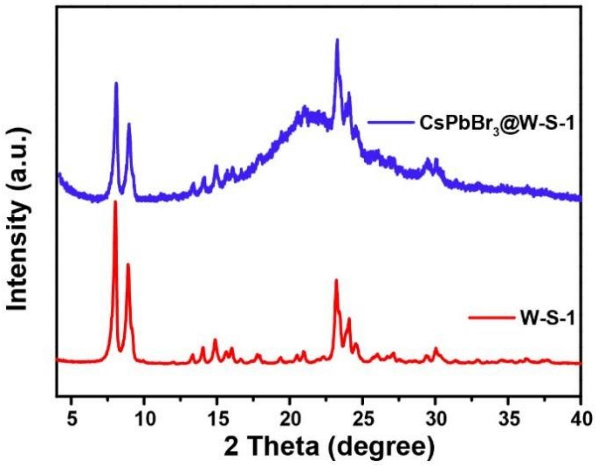

Fig. S3. PXRD patterns of W-S-1 and $CsPbBr_3$@W-S-1 composite.

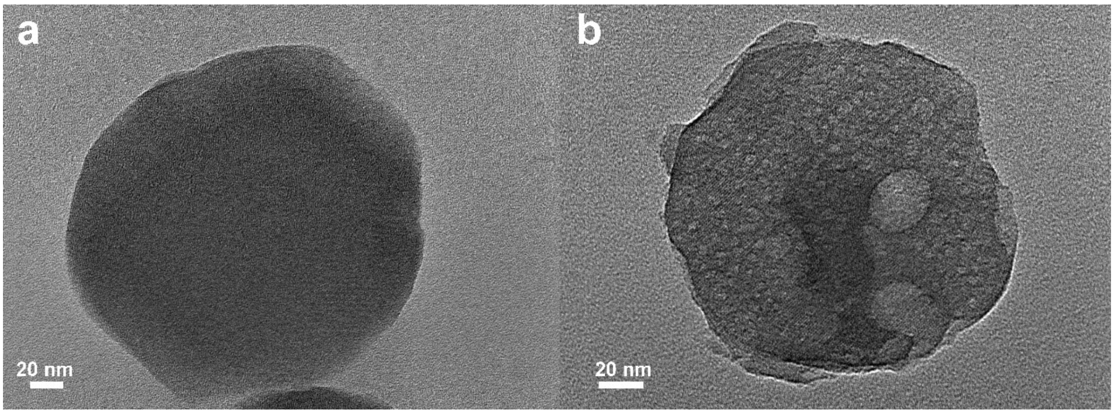

Fig. S4. TEM images of (a) W-S-1 and (b) $CsPbBr_3$@W-S-1 composite.

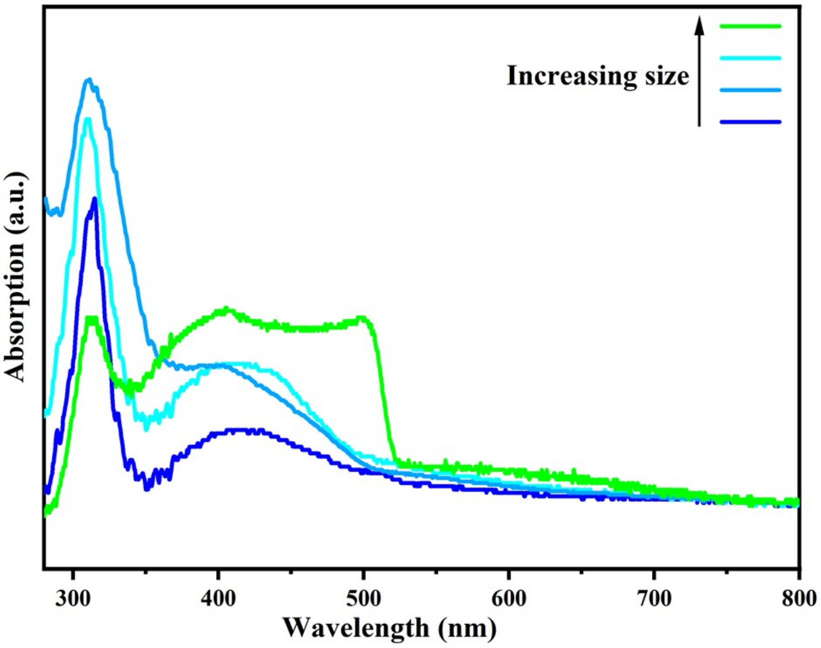

Fig. S5. UV-vis absorption spectra of $CsPbBr_3$@W-S-1 composites obtained in different conditions.

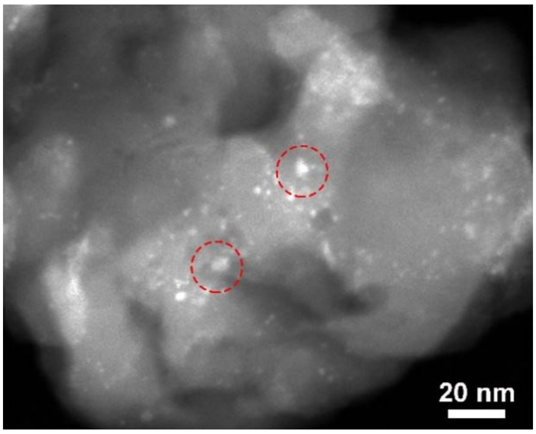

Fig. S6. STEM image of $CsPbBr_3$@W-S-1 composite.

Table S1. Synthetic condition of different sized $CsPbBr_3$ in zeolite matrix.

Average Size (nm)	Wavelength (nm)	Lifetime (ns)	$CsBr+PbBr_2$ （g）	Temperature（℃）	Time（min）
2	468	5.16	0.005	700	40
2.5	476	6.31	0.01	700	30
3.6	487	8.66	0.1	700	20
6	508	10.87	0.2	700	20

Table S2. The PL emission center and QYs of $CsPbBr_3$@W-S-1 composite (before modification and after modification).

Before modification		**After modification**	
Wavelength (nm)	QYs (%)	Wavelength (nm)	QYs (%)
460	11.24	468	39.32
474	12.36	476	48.21
486	10.95	487	76.93
509	28.40	508	57.71