# Supplementary Information

# In Situ Growth of Ultrasmall Cesium Lead Bromine Quantum Dots into Mesoporous Silica Matrix and Its Application in Flexible Light-Emitting Diode

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## Experimental section

**Materials:**The range of chemical agents used include oleic acid (OA, 90%, Adamas), oleylamine (OAm, 90%, Adamas), octadecene (ODE, 90%, Greagent), cesium carbonate ($Cs_2CO_3$, 99.9%, Adamas), lead bromide ($PbBr_2$, 99%, Adamas), toluene ($C_7H_8$, 99.5%, Greagent), acetone ($CH_3COCH_3$, 99.5%, Greagent), tetraethyl orthosilicate (TEOS, 99%, Aladdin), cetyltrimethylammonium bromide (CTAB, 99%, Adamas), sodium carbonate ($Na_2CO_3$, 99.8%, Greagent), ethanol ($C_2H_5OH$, 99.7%, Greagent), Methacrylic Acid Methyl Ester Polymer (PMMA, Adamas). All chemicals were used as received without any further purification.

**Preparation of cesium oleate solution.** Cesium oleate solution was prepared according to Protesescu's method. In brief, 0.814 g (2.5 mmol) of $Cs_2CO_3$, 2.5 mL of OA and 30 mL of ODE were loaded in a 100 ml three-neck flask and degassed under nitrogen atmosphere at 120 °C for 1 h, followed by heating at 180 °C until all $Cs_2CO_3$ reacted with OA completely. Then the Cs-oleate solution was kept at 180 °C until injection.

**Synthesis of $CsPbBr_3$ QDs.** The QDs was synthesized with a modified hot-injection method.[42] In a representative reaction, 0.138 g $PbBr_2$ (0.376 mmol) were dissolved in a 25ml three-neck flask containing 10 ml ODE, 1ml OAm and 1ml OA under nitrogen atmosphere at 120 °C for 30 min. After that, the reaction temperature was raised up to 180 °C and kept for another 10 min. Then 1 ml Cs-oleate solution in another three-neck flask was injected into the mixture rapidly, reacting for 10 s. The reaction mixture was cooled by the ice-water bath and the $CsPbBr_3$ QDs were obtained. Then, 10 ml of acetone was added to the crude solution, the QDs were collected from the crude solution by centrifugation with the speed of 9000 rpm and redispersed in toluene finally.

**Synthesis of m-$SiO_2$ spheres.** m-$SiO_2$ spheres were synthesized according to previous reported method.[43] Briefly, 50 mg of the as-prepared $SiO_2$ spheres were homogeneously dispersed in 9 mL of deionized water via ultrasonication for 15 min. After that, 1 ml (12.5 mg/ml) CTAB aqueous solution and further 30min stirring were required to the mixture before the introduction of 212 mg $Na_2CO_3$. After, the reaction was stirred at 35 °C for 12 h, 24h and 36h (marked as MS-12, MS-24, MS-36) to obtain the mesoporous silica with 4.3 nm, 5.1nm and 9.8nm pore size, the corresponding specific surface area were 544.6, 607.4 and 844.5 $m^2$ $g^{-1}$. The final products were washed with deionized water and ethanol and collected by centrifugation 3000 rpm for 5 min.

**Synthesis of $CsPbBr_3$/m-$SiO_2$ nanocomposites.** In a typical reaction, under nitrogen atmosphere, 0.092 g m-$SiO_2$ (1.537 mmol) was dissolved in a 25ml three-neck flask containing 1 ml OAm, 1 ml OA and 10 ml ODE, followed 30 min continuous stirring at 120 °C. After that, 0.138 g $PbBr_2$ (0.376 mmol) was added into the three-neck flask and the solution was maintained at 180 °C for another 30 min. Then 1 ml Cs-oleate solution in another three-neck flask was injected into the mixture rapidly reacting for 10 s. The mixture was cooled by the ice-water bath and the $CsPbBr_3$/m-$SiO_2$ nanocomposites were obtained. The products were collected from the crude solution by centrifugation with the speed of 3000 rpm and redispersed in toluene finally. The calculated ratio of m-$SiO_2$ to $CsPbBr_3$ (CPB) QDs is 5×$10^{-3}$ mmol/mg.

**Experiment of ion-exchange reaction.** With continuous stirring, 20 mg $ZnCl_2$ powder was swiftly added into the $CsPbBr_3$ and $CsPbBr_3$/m-$SiO_2$ solutions (5 mg/ml). 4 ml solution obtained from mixing 0.2 ml reaction solution with toluene was used for PL measurement every five minutes. All operations were operated in January, Shanghai.

**Manufacturing of LED Devices.** 365 nm ultraviolet chips were used to provide excitation. A certain amount of $CsPbBr_3$/m-$SiO_2$nanocomposites or $CsPbBr_3$ QDs were mixed with a PMMA/toluene solution. The obtained mixture was ultrasounded for 10 min and then coated onto a piece of quartz glass. The glass naturally volatilized at room temperature to form films. Finally, the LED was obtained by placing the film above a UV LED chip.

## Characterizations

Photoluminescence (PL) and absorption spectra were recorded with Hitachi F7100 and Cary 5000, respectively, in the range from 380 to 750 nm. A Talos 200C transmission electron microscope (TEM) and a highresolution transmission electron microscope (HRTEM) with an acceleration voltage of 200 kV were used to analyze the morphology of the as-synthesized QDs. SEM images of the mesoporous silica spheres were measured with SU8010. X-ray diffraction (XRD) analysis was performed using D/max 2200PC to acquire the information regarding the composition and structure of the products. X-ray photoelectron spectroscopy (XPS) was carried out with ESCALAB 250Xi to analyze the elemental composition. Thermal gravimetric analysis (TGA) was performed on a Netzsch Sta449C TGA with a thermal analysis gas station under Argon atmosphere with a heating rate of 5 K/min up to a temperature of 1860 K. Fourier transform infrared spectra (FTIR) were recorded in a Nicolet iN10 FTIR spectrometer in the range of 4000–400 $cm^{-1}$ in pressed KBr pellets.

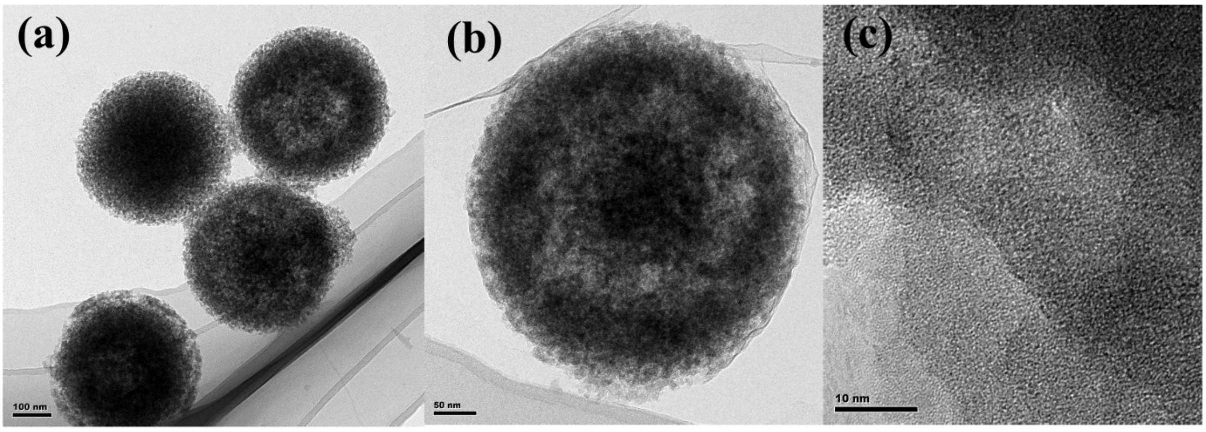

Figure S1. (a, b) TEM image of the mesoporous silica nanoparticles. (c) HRTEM image of the edge of the mesoporous silica.

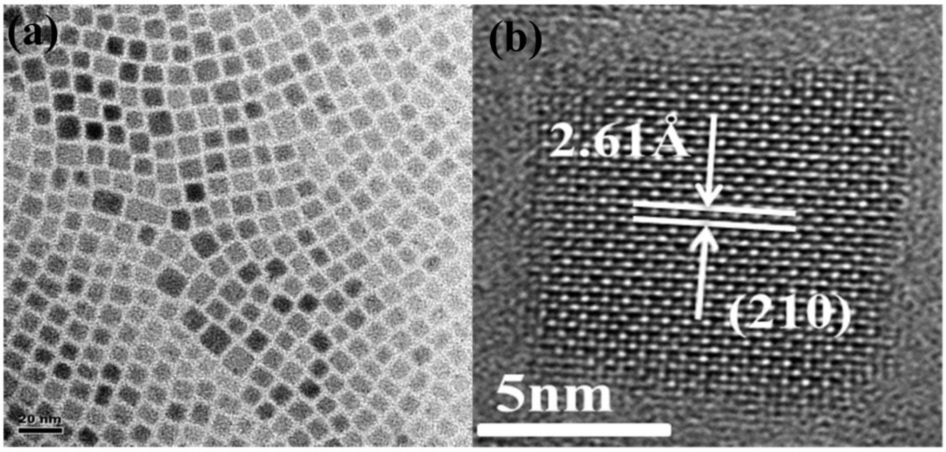

Figure S2. (a) Low-resolution TEM image of monodispersed $CsPbBr_3$ QDs. (b) HRTEM image of a $CsPbBr_3$ QDs.

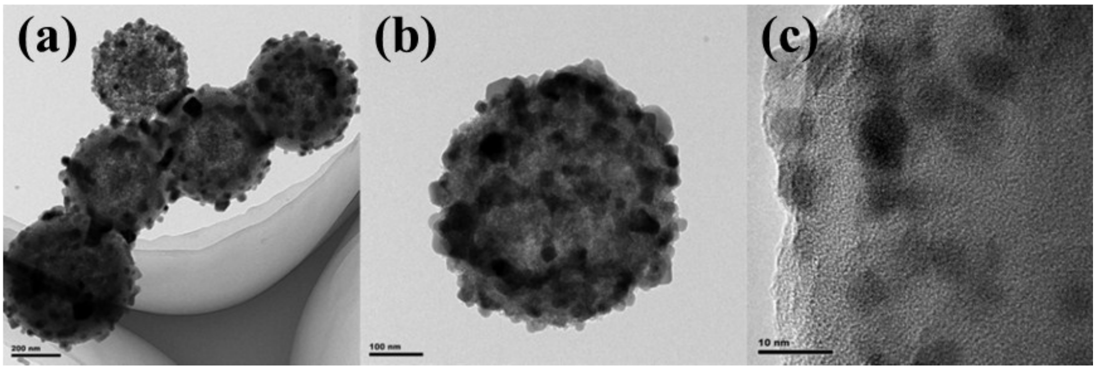

Figure S3. (a, b) TEM image of $CsPbBr_3$/m-$SiO_2$ nanocomposites. (c) HRTEM image of partial $CsPbBr_3$/m-$SiO_2$ nanocomposites.

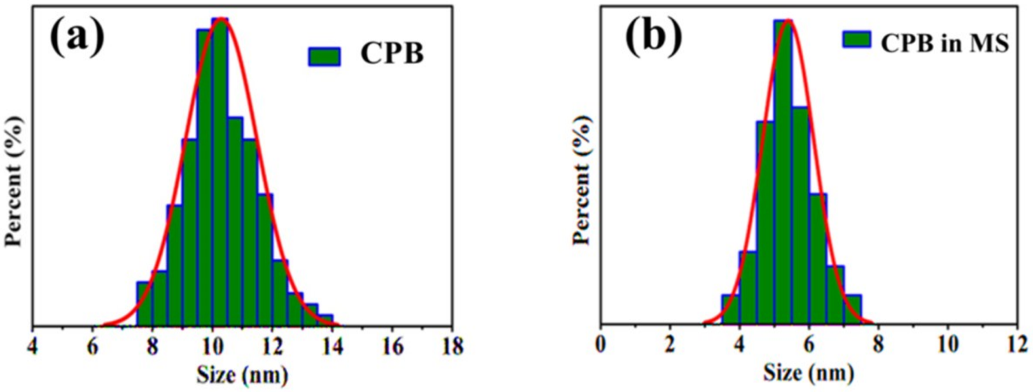

Figure S4.TEM size distribution histograms and the corresponding Gaussian fitting of $CsPbBr_3$ QDs and $CsPbBr_3$ QDs in m-$SiO_2$.

Table S1. Pore size and specific surface area of mesoporous silica with different reaction time.

| Samples | $S_{BET}$ ($m^2g^{-1}$) | Pore Size (nm) |
|---|---|---|
| 12-MS | 544.6 | 4.2 |
| 24-MS | 607.4 | 5.8 |
| 36-MS | 844.5 | 9.9 |

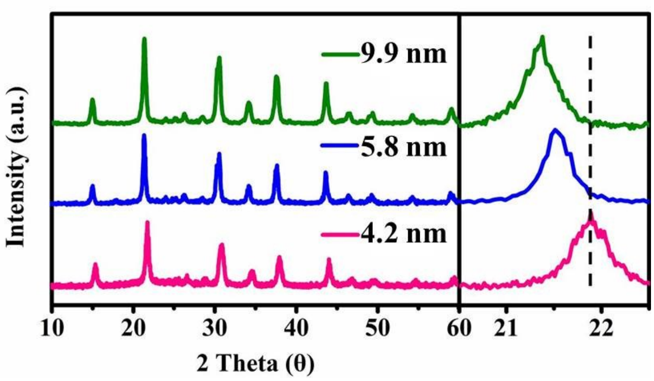

Figure S5. XRD patterns of $CsPbBr_3$/m-$SiO_2$ with different pore sizes and specific surface area.

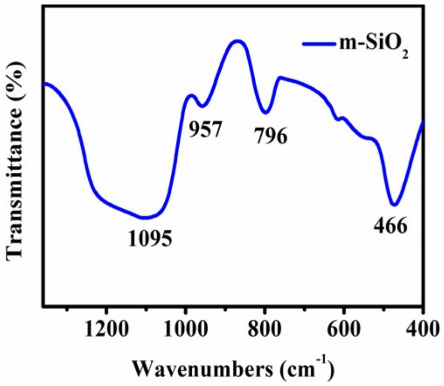

Figure S6. FTIR spectrum of m-$SiO_2$.

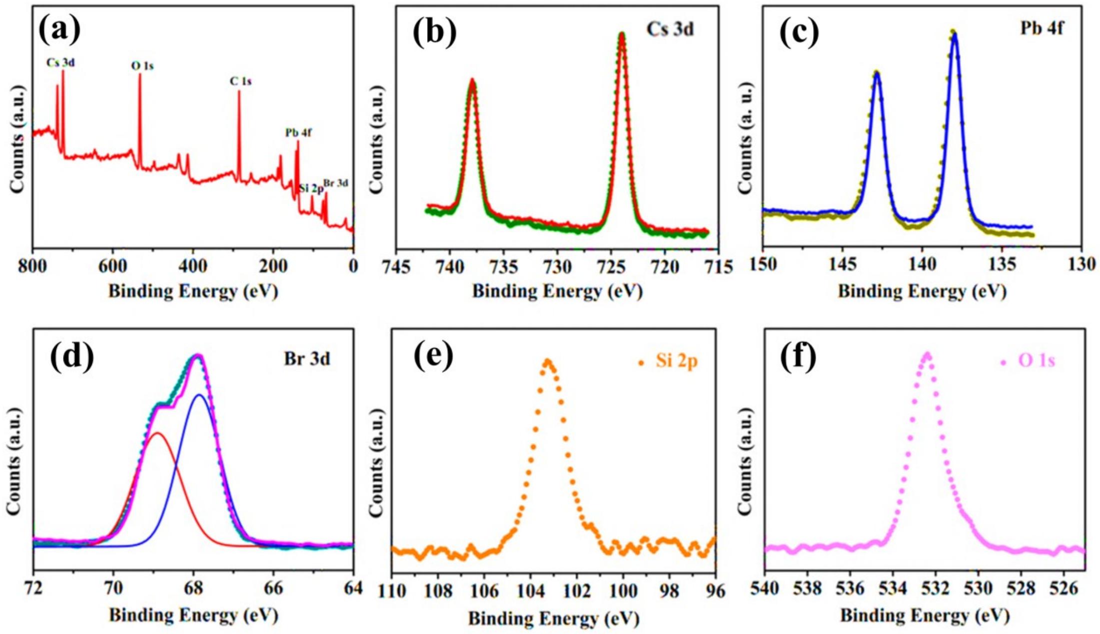

Figure S7. (a) XPS spectra of $CsPbBr_3$ QDs (solid line) and $CsPbBr_3/m\text{-}SiO_2$ nanocomposites (dotted line), high resolution spectra of (b) Cs 3d, (c) Pb 4f, (d) Br 3d, (e) Si 2p, (f) O 1s.

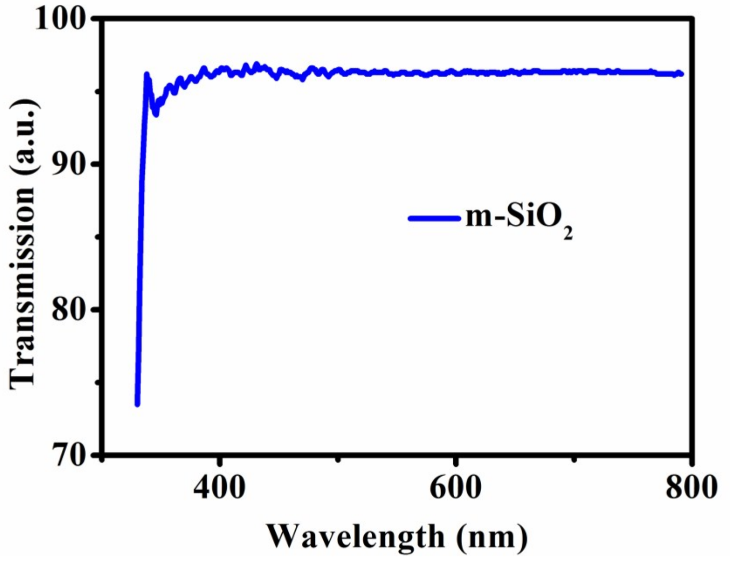

Figure S8. Transmittance test results of mesoporous silica.

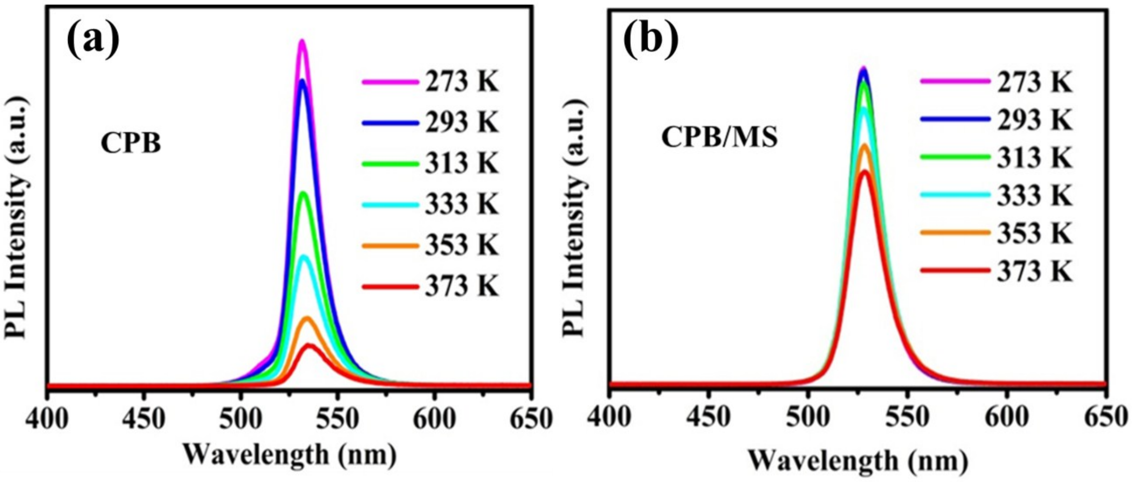

Figure S9. Temperature-dependent PL spectra of (a) $CsPbBr_3$ QDs and (b) $CsPbBr_3$/m-$SiO_2$ nanocomposites.

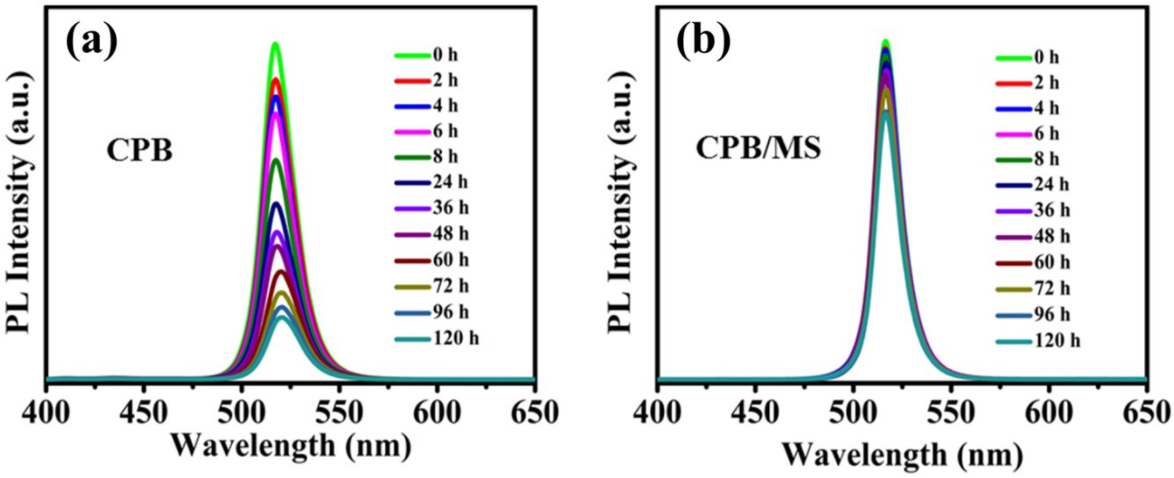

Figure S10. Attenuation of light intensity with the illumination time of (a) $CsPbBr_3$ QDs and (b) $CsPbBr_3$/m-$SiO_2$ nanocomposites.

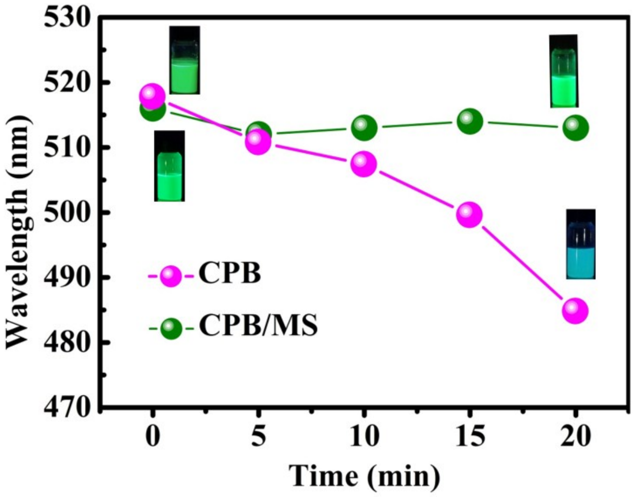

Figure S11. Change of emission peak of $CsPbBr_3$ QDs and $CsPbBr_3/m\text{-}SiO_2$ nanocomposites after ion exchange reaction.

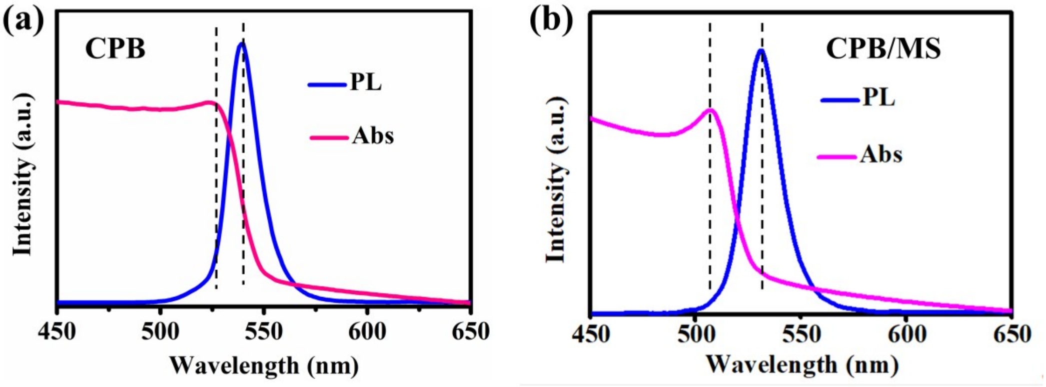

Figure S12. PL and absorbance spectra of $CsPbBr_3$ and $CsPbBr_3/m\text{-}SiO_2$ thin films.

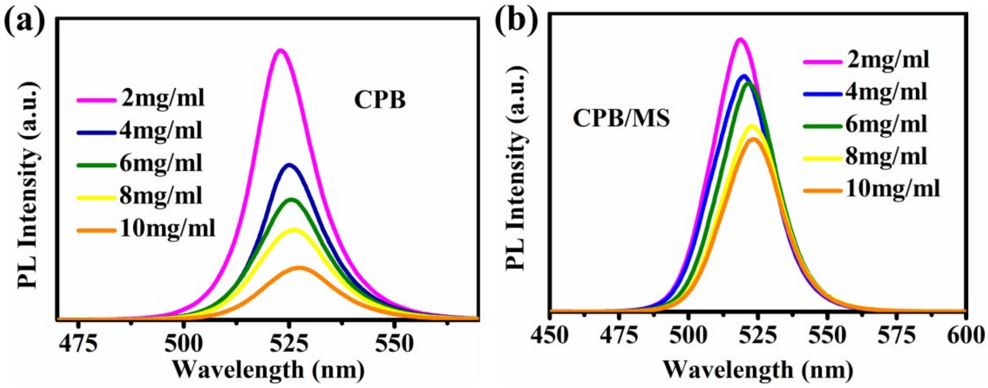

Figure S13. Changes of luminescence intensity with sample concentration.

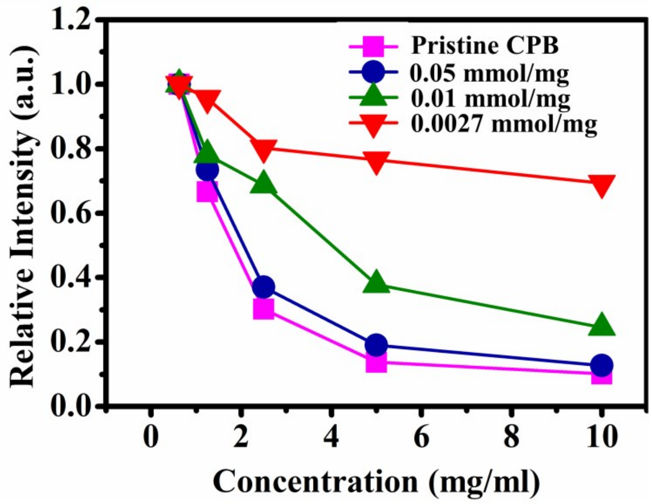

Figure S14. Changes of luminescence intensity off different contents $CsPbBr_3$ QDs in mesoporous silica with sample concentration

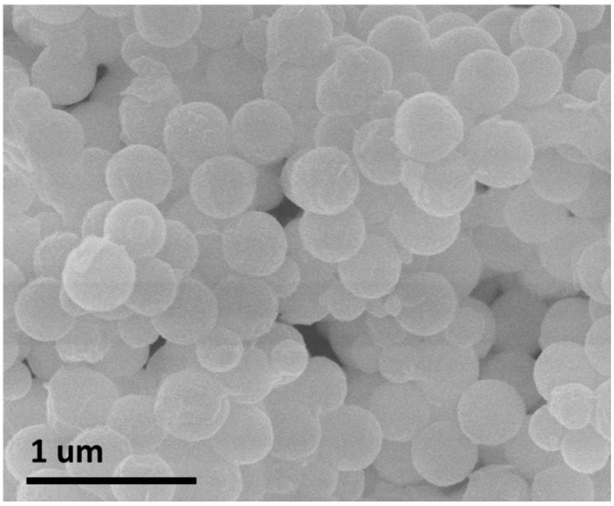

Figure S15. SEM image of mesoporous silica nanoparticles.

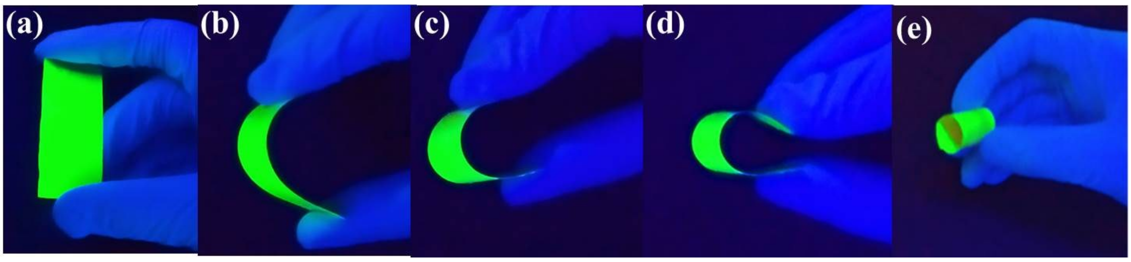

Figure S16. The luminescence pictures of flexible thin film with the bending angle from 0° (a), 45°, 90°, 135° to 180° under ultraviolet lamp.

## Reference

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