## **Supplementary Materials**

## Morphologically controlled synthesis of Cs<sub>2</sub>SnCl<sub>6</sub> perovskite crystals

## and their photoluminescence activity

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## Characteristics

Powder X-ray diffraction (XRD) patterns were determined using a Bruker AXS D8 Advance diffractometer (Voltage 50 kV, current 40 mA, Cu-Ka) with a step of 0.02°. High resolution transmission electron microscope (HR-TEM, JEM-2100) was employed to determine the size and morphology of nanoparticles. The XPS spectrum was measured using an ESCALAB 250Xi photoelectron spectrometer (Thermo Fisher, UK).



**Figure S1.** The XRD patterns of the Cs<sub>2</sub>SnCl<sub>6</sub> crystals prepared at different time with 5 mol/L HCl and 0.083 mol/L SnCl<sub>2</sub> solution.



**Figure S2.** The XRD patterns of the  $Cs_2SnCl_6$  crystals synthesized at different HCl concentrations (3, 5, 9, 10 mol/L) in the aqueous solution with 0.042 mol/L SnCl<sub>2</sub> solution.



Figure S3. The XRD patterns of the  $Cs_2SnCl_6$  crystals synthesized at different HCl concentrations in the aqueous solution with 0.083 mol/L  $SnCl_2$  solution.



Figure S4. The XRD patterns of the  $Cs_2SnCl_6$  crystals synthesized at different  $SnCl_2$  concentration in the aqueous solution with 5 mol/L HCl.



**Figure S5.** HR-TEM images of the  $Cs_2SnCl_6$  crystals prepared at normal temperature in the aqueous solution with 5 mol/L HCl and SnCl<sub>2</sub> concentration of (**a**, **b**) 0.208 mol/L, (**c**, **d**) 0.250 mol/L.



**Figure S6.** Summary of the crystal morphology and synthesis conditions (the crystal in the figure only represents its own morphology and does not represent a certain synthetic process).



Figure S7. UV-vis absorption spectroscopy of the  $Cs_2SnCl_6$  crystals prepared with 0.083 mol/mL  $SnCl_2$  and different concentration of HCl. The inset is the partial magnification between 300–400 nm.



**Figure S8.** (a) XPS survey spectrum of Cs<sub>2</sub>SnCl<sub>6</sub> crystals in Figure 8b. (b) High-resolution XPS spectra and peak fitting for Sn 3d