**Electronic Supplementary Information** 

## Doping-Induced Evolutions of PbWO<sub>4</sub> Mesocrystals in Morphology and Optical Properties

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## **EXPERIMENTAL SECTION**

**Materials:** All chemicals were of analytical grade and were used as received without further purification. Deionized water was used throughout. Sodium tungstate dehydrate (Na<sub>2</sub>WO<sub>4</sub>·H<sub>2</sub>O), lead acetate trihydrate (Pb(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O), yttrium nitrate hexahydrate (Y(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O) and ethylene glycol were all supplied by Sinopharm Chemical Reagent Company.

**Preparation of Y-doped PbWO**<sup>4</sup> **Mesocrystals:** In a typical procedure, *x* mmol of yttrium nitrate hexahydrate and 5-*x* mmol of lead acetate trihydrate were dissolved in a mixed solvent with 70 ml ethylene glycol (EG) and 30 ml distilled water to form solution *A*. Meanwhile, solution *B* was obtained by dissolving 5 mmol of sodium tungstate dehydrate in the same EG-water mixture with a total volume of 100 mL. Afterwards, solution *B* was slowly added into the solution *A* to obtain milky precipitation at room temperature. After continuous stirring for 1 hour, the asobtained milky precipitation was kept at a constant temperature ( $25 \pm 2^{\circ}$ C) in order to naturally settle on the bottom of beaker. Then, as-prepared samples were washed twice using the same EG-water mixed solvent, and further cleaned three times with water and absolute alcohol respectively, and finally dried in a vacuum at 60°C for 4 hours.

**Characterization**: X-ray powder diffraction (XRD) patterns of as-synthesized samples were performed using a Rigaku D/max-RB diffractometer with Cu K $\alpha$  radiation ( $\lambda = 1.5406$ Å). Morphology of the products was acquired on a JEOL-6300F and Zeiss-Ultra 55 field-emission scanning electron microscopy (FE-SEM). High-resolution transmission electron microscopy (HRTEM) images and selective area electron diffraction (SAED) were recorded with a JEOL-2010 and Zeiss Liber 200 transmission electron microscopy. The atomic ratios of Pb<sup>2+</sup> and Y<sup>3+</sup> ions of asprepared samples were recorded by X-ray fluorescence (XRF, Axios) and the ratio of each sample was the average value after three measurements. Raman spectra were carried out on a LABRAM-HR Confocal Laser Micro-Raman spectrometer using an Ar<sup>+</sup> laser with 514.5 nm at room temperature. UV-Vis diffuse reflection spectra of samples were obtained from Shimadzu UV-3150. Photoluminescence of as-obtained

samples were recorded on a Fluorolog-3 Jobin Yvon spectrophotometer using a Xe lamp as the excitation source at room temperature.



Fig. S1 Overview FESEM images of  $Y^{3+}$ -doped PbWO<sub>4</sub> mesocrystals with different  $Y^{3+}$  doping concentrations. (a) 0 mol%, (b) 5 mol%, (c) 10 mol%, (d) 15 mol%. The scale bar in all images



corresponds to  $2 \mu m$ .

Fig. S2 Power X-ray diffraction (XRD) patterns of Y-doped PbWO<sub>4</sub> mesocrystals with different  $Y^{3+}$  doping amounts. The atomic ratios of  $Y^{3+}$  to  $Pb^{2+}$  were average values after three XRF

measurements.

Table S1. Various parameters such as peak position and calculated coherent length of  $D_{hkl}$  of XRD

peaks of Y-doped PbWO<sub>4</sub> mesocrystals shown in Figure 1.

(004) (200) (112) Samples 2 Theta **D**<sub>112</sub> (nm) 2 Theta 2 Theta  $D_{\theta\theta4}$  (nm)  $D_{2\theta\theta}$  (nm) Y-0 27.31 29.54 32.68 31.5 36.1 36.3 Y-5 27.39 21.4 29.57 20.2 32.72 24.4 Y-10 27.41 15.3 29.62 12.7 32.81 17.9 Y-15 27.55 12.6 29.83 11.5 32.95 16.4



Fig. S3. Low-magnification TEM images of PbWO<sub>4</sub> mesocrystals doped with trivalent rare-earth ions and divalent alkaline-earth ions.



Fig. S4 Three fitted Guassian emission curves (a-d) of Y-doped PbWO<sub>4</sub> mesocrystals with different Y<sup>3+</sup> concentrations: (a) 0 mol%, (b) 5 mol%, (c) 10 mol%, (d) 15 mol%. (e) the position of three fitted emission peaks as a function of Y<sup>3+</sup> concentrations.