Electronic Supplementary Information

Doping-Induced Evolutions of PbWO$_4$ 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 (Na₂WO₄·H₂O), lead acetate trihydrate (Pb(NO₃)₂·3H₂O), yttrium nitrate hexahydrate (Y(NO₃)₃·6H₂O) and ethylene glycol were all supplied by Sinopharm Chemical Reagent Company.

Preparation of Y-doped PbWO₄ 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 as-obtained milky precipitation was kept at a constant temperature (25 ± 2ºC) 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 60ºC 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 Kα radiation (λ = 1.5406Å). 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 Pb²⁺ and Y³⁺ ions of as-prepared 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⁺ 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 $\text{Y}^{3+}$-doped $\text{PbWO}_4$ mesocrystals with different $\text{Y}^{3+}$ 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$_4$ 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$_4$ mesocrystals shown in Figure 1.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$(112)$</th>
<th>$(004)$</th>
<th>$(200)$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2 Theta</td>
<td>$D_{112}$ (nm)</td>
<td>2 Theta</td>
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<tr>
<td>Y-0</td>
<td>27.31</td>
<td>36.1</td>
<td>29.54</td>
</tr>
<tr>
<td>Y-5</td>
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<tr>
<td>Y-15</td>
<td>27.55</td>
<td>12.6</td>
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</tbody>
</table>

Fig. S3. Low-magnification TEM images of PbWO$_4$ mesocrystals doped with trivalent rare-earth ions and divalent alkaline-earth ions.
Fig. S4 Three fitted Gaussian emission curves (a-d) of Y-doped PbWO$_4$ mesocrystals with different Y$^{3+}$ 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$^{3+}$ concentrations.