Electronic Supplementary Information

Directional self-assembly of rare-earth hydroxocation nanosheets and paradodecatungstate anions

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Dalton Trans.
Experimental details

1. Synthesis of LEuH and LTbH slurries

Layered europium hydroxide (LEuH) and layered terbium hydroxide (LTbH), Eu$_2$(OH)$_5$Cl·nH$_2$O and Tb$_2$(OH)$_5$Cl·nH$_2$O, was prepared according to the previous procedures with slight modifications.$^1$ Deionized water was boiled and stored under nitrogen before use. An aqueous solution was prepared in first by adding KOH solution (0.1 M) dropwise to EuCl$_3$·6H$_2$O and TbCl$_3$·6H$_2$O solutions (0.05 M) with vigorous stirring at room temperature (molar ratio RE$^{3+}$:OH$^-$ = 1:2). After 12 h with stirring, the precipitate was recovered by centrifugation (4000 rpm) and washed with water several times. A slurry of the resulting LEuH and LTbH was ultra-sonicated in deionized water to prepare an aqueous colloidal suspension. LEuH and LTbH dispersed readily and produced a transparent suspension. Finally, the colloidal solution was filtered with PVDF-type syringe (0.45μm) to remove possible aggregates.

2. Synthesis of sodium paratungstate, Na$_{10}$H$_2$W$_{12}$O$_{42}$·nH$_2$O

Na$_{10}$H$_2$W$_{12}$O$_{42}$·nH$_2$O was prepared according to the literature method.$^2$ Typically, Na$_2$WO$_4$·2H$_2$O was dissolved in water to make the sodium tungstate solution (1.5 M). HCl solution (1 M) was then added until the ratio H$^+$/WO$_4^{2-}$ = 1.0 ~ 1.17. After aging the resulting solution at room temperature for a week, the white recrystallized product was recovered and dried at room temperature. The water content ($n$) was determined to be 13 by the TG analysis.
3. Self-assembly of LRH nanosheets and $[\text{H}_2\text{W}_{12}\text{O}_{42}]^{10-}$ polyanions

In a typical reaction, 10 mL aqueous solutions containing 2-fold molar excess of $[\text{H}_2\text{W}_{12}\text{O}_{42}]^{10-}$ polyanions were mixed with 200 mL of LEuH and LTbH colloidal solutions (1 g/L), respectively. The mixtures were kept at room temperature for 3 ~ 4 days without stirring. Resulting precipitates were recovered by filtration, washed with water, and dried at 40 °C for a day.

4. Characterization

The chemical compositions of products were determined by inductively coupled plasma (ICP; Thermo Elemental Thermo ICAP 6000) and thermogravimetry (TG; Seiko Instruments TG/DTA320 SSC/5200 S11). The powder X-ray diffraction patterns were recorded on a rotating anode installed diffractometer (MacScience Model M18XHF). Fourier transform infrared (FT-IR) spectra were measured by using the KBr pellet technique. The Cu K$_\alpha$ radiation used was monochromated by a curved-crystal graphite. Field emission scanning electron microscopy (FE-SEM) was carried out with a Carl Zeiss LEO SUPRA 55 electron microscope operating at 30 kV. The photoluminescence spectra were measured at room temperature using FP-6600 spectrophotometer (JASCO) with a Xenon flash lamp.
Figure S1. TGA curves of (a) LEuH and (b) LTbH before and after reactions in aqueous paradodecatungstate solutions.

Figure S2. XRD patterns of (a) LEuH and (b) LTbH before and after reactions in aqueous paradodecatungstate solutions.
Table S1. Thermogravimetric analysis data for LEuH and LTbH before and after reactions in aqueous paratungstate solutions

<table>
<thead>
<tr>
<th>compound</th>
<th>chemical composition</th>
<th>Total weight loss (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>observed</td>
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<tr>
<td>LEuH</td>
<td>Eu$_2$(OH)$_5$Cl $\cdot$ 2.0H$_2$O</td>
<td>23.8</td>
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<tr>
<td>LTbH</td>
<td>Tb$_2$(OH)$_5$Cl $\cdot$ 2.0H$_2$O</td>
<td>22.4</td>
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<tr>
<td>LEuH-W$_{12}$</td>
<td>Eu$<em>2$(OH)$<em>5$(H$<em>2$W$</em>{12}$O$</em>{42}$)$</em>{0.1}$ $\cdot$ 3.5H$_2$O</td>
<td>14.2</td>
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<tr>
<td>LTbH-W$_{12}$</td>
<td>Tb$<em>2$(OH)$<em>5$(H$<em>2$W$</em>{12}$O$</em>{42}$)$</em>{0.1}$ $\cdot$ 4.5H$_2$O</td>
<td>16.6</td>
</tr>
</tbody>
</table>

Figure S3. XRD patterns of (a) LEuH-W$_{12}$ and (b) LTbH-W$_{12}$ after TG analyses up to 1000 °C.
**Figure S4.** UV/Visible spectra of paradecatungstate solution (black), LEuH (dotted red), LEuH-W₁₂ (solid red), LTbH (dotted green), and LTbH-W₁₂ (solid green). Spectra of solid samples were taken after dispersing small amount of powder in water (1g/L).

**References for ESI**