Electronic Supplementary Information

“Layered polymorph of rare earth hydroxides”

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Experimental details

RECl₃·6H₂O (RE = Sm, Eu, Gd, Tb, Dy, Er, and Y) (99.9%), potassium hydroxide (≥ 98%, flakes), and sodium hydroxide (≥ 98%, pellets) were purchased from Sigma-Aldrich Co.. Commercial Gd(OH)₃ (Alfa-Aesar Co.) was used as a reference material for comparison with the as-synthesized, layered gadolinium hydroxides. All reagents were used without further purification.

Preparation of RE₂(OH)₃Cl∙mH₂O.

RECl₃·6H₂O (10 mmol) and KOH (20 mmol) were dissolved in deionized water (40 mL). The KOH solution was then added drop-wise to the RECl₃·6H₂O solution with vigorous stirring at room temperature. The resulting mixtures (80 mL) were placed in a Teflon-lined stainless steel autoclave with a capacity of 100 mL at room temperature. The autoclave was then sealed and maintained at 130–150 ºC for 12 h. The solution was continuously stirred during the hydrothermal treatment. After the reaction was complete, the solid RE₂(OH)₃Cl∙mH₂O products were collected by filtration, washed with distilled water, and dried at 40 ºC for one day.

Preparation of layered RE(OH)₃∙nH₂O.

Solutions with pH = 8, 9, 10, 11, 12, 13, and 14 were prepared by dissolving NaOH (or KOH) in water. RE₂(OH)₃Cl∙mH₂O crude powders were dispersed in aqueous solutions of different pHs. After stirring these mixtures for 12 h at room temperature, the resulting precipitates were collected by filtration, washed with copious amounts of water to remove residual salts, and then dried at 40 ºC for one day. The remnant Cl⁻ ion in the recovered powders was measured using the ion chromatography (IC). The calcined products were obtained at various temperatures (100–800 ºC) for X-ray diffraction (XRD) analyses. After 1 h at the target temperatures, the furnace was programmed to power down for natural cooling.

Preparation of colloidal solutions containing layered RE(OH)₃∙nH₂O.

Typically, aqueous solutions were prepared by adding KOH solution (0.1 M) drop-wise to the RECl₃·6H₂O solution (0.05 M) with vigorous stirring at room temperature. After 12 h of stirring, precipitates were recovered by centrifugation (4000 rpm) and washed with water several times. The resulting slurries of RE₂(OH)₃Cl∙mH₂O (10 g/L) were ultra-sonicated in an
aqueous NaOH solution (1.0 M) and kept for 12 h with vigorous stirring at room temperature. Layered RE(OH)$_3$$\cdot$$n$H$_2$O slurries were recovered by repeated centrifugation (4000 rpm) and washed several times with water to completely remove Na$^+$ and Cl$^-$ ions. Vigorous shaking of these slurries in water produced translucent suspensions. A 1.0 g/L colloidal solution was stable for more than one month. In order to examine the stability of colloidal suspensions in an acidic solution, layered Gd(OH)$_3$$\cdot$$n$H$_2$O slurries (20 mg) were dispersed in phtalate buffer solutions (20 mL) at pH = 2, 3, 5, 6 and stirred at room temperature. After 1 hr, the small amount of the suspension was collected and centrifuged to remove the Gd(OH)$_3$$\cdot$$n$H$_2$O solids. The amount of Gd in the supernatant solutions was determined by inductively coupled plasma (ICP) analysis.

Characterizations.

XRD patterns of RE$_2$(OH)$_3$Cl$\cdot$mH$_2$O, layered RE(OH)$_3$$\cdot$$n$H$_2$O, and its calcined products were recorded with a Bruker D8 Advance diffractometer. Field emission scanning electron microscopy (FE-SEM) was performed with a Carl Zeiss LEO SUPRA 55 electron microscope operating at 30 kV. Specimens for the FE-SEM were coated with Pt-Rh for 180 s under vacuum. Electron diffraction (ED) observations were performed with a JEOL JEM-2100F electron microscope operating at 300 kV. Fourier transform infrared (FT-IR) spectra in a range of 3000 – 4000 cm$^{-1}$ were measured on a JASCO FT/IR-4200 infrared spectrophotometer using the KBr pellet technique. The nominal resolution was 4 cm$^{-1}$. To prepare pellets, powder samples (1.0 mg) were diluted with IR-grade KBr powder (200 mg) and subjected to a 10-ton pressure. Thermogravimetric (TG) curves were recorded in air at a heating rate of 5 °C/min using a Seiko Instruments TG/DTA320. Atomic force microscopy (AFM) was carried out by using Pucostation STD (Pucostation). Ultrasonicated Si substrate was dipped into the suspension in aqueous Gd(OH)$_3$$\cdot$H$_2$O solution (0.1 g/L) for 10 min and then washed with water. The size and size distribution of Gd(OH)$_3$$\cdot$H$_2$O sheets in the aqueous colloidal solution were measured by using a Particle size analyzer ELSZ-2 (Otsuka electronics Co. LTD). All measurements were repeated three times to verify the reproducibility of the results. Stable samples were prepared by dispersing Gd(OH)$_3$$\cdot$H$_2$O slurry in water (0.1 g/L).
Fig. S1 XRD patterns of $\text{RE}_2(\text{OH})_3\text{Cl}\cdot m\text{H}_2\text{O}$ and its products after reaction in aqueous solutions of different pHs, where RE = (a) Sm, (b) Eu, (c) Tb, (d) Dy, (e) Er, and (f) Y.
**Fig. S2** Thermogravimetry curves of (a) Gd$_2$(OH)$_3$Cl·$m$H$_2$O, (b) its product obtained after reaction in an aqueous solution at pH = 13, and (c) hexagonal Gd(OH)$_3$. Considering the possible water adsorbed to the particle surface and the variable amount of interlayer water, the 6.27 and 7.30 % observed weight loss below 200 °C in (a) and (b) are close to the 5.85 and 7.96 % calculated losses from the dehydration of Gd$_2$(OH)$_3$Cl·1.5H$_2$O and Gd(OH)$_3$·H$_2$O to Gd$_2$(OH)$_3$Cl and Gd(OH)$_3$, respectively. Because heating this product above 500 °C yields Gd$_2$O$_3$ oxide, the observed total ignition losses of 22.05 and 20.20 % are in close agreement with the calculated ones of 21.54 and 19.90 %, respectively, also in good agreement with those compositions.

**Fig. S3** SEM images of (a) the Gd$_2$(OH)$_3$Cl·1.5H$_2$O precursor and (b) layered Gd(OH)$_3$·H$_2$O.
**Fig. S4** ED patterns of layered RE(OH)$_3$·H$_2$O, where RE = (a) Sm, (b) Eu, (c) Tb, (d) Dy, (e) Er, and (f) Y.

**Table S1** Measured unit cell parameters of RE(OH)$_3$·nH$_2$O.

<table>
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<th>RE</th>
<th>Sm</th>
<th>Eu</th>
<th>Gd</th>
<th>Tb</th>
<th>Dy</th>
<th>Er</th>
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<td>7.26(1)</td>
<td>7.24(9)</td>
<td>7.16(1)</td>
<td>7.08(8)</td>
<td>7.03(9)</td>
<td>7.06(2)</td>
</tr>
<tr>
<td>$c$ (Å)</td>
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<td>7.75(6)</td>
<td>7.75(7)</td>
<td>7.70(3)</td>
<td>7.60(5)</td>
<td>7.59(4)</td>
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**Fig. S5** XRD patterns of (a) Gd$_2$(OH)$_3$Cl·1.5H$_2$O and (b) Gd(OH)$_3$·H$_2$O slurries. Compared to the bulk powder prepared under the hydrothermal condition (Fig. 1A), the XRD pattern of the Gd$_2$(OH)$_3$Cl·1.5H$_2$O slurry exhibits broad (00l) reflections and only (220) as a non-(00l) reflection because of the preferred orientation of nanosheets synthesized in the aqueous solution at room temperature. The systematic shifts of (00l) reflections toward higher diffraction angles after the reaction in aqueous NaOH solution (1.0 M) confirm the formation of a layered Gd(OH)$_3$·H$_2$O slurry.
Fig. S6 FE-SEM images of (a) Gd$_2$(OH)$_3$Cl·1.5H$_2$O and (b) Gd(OH)$_3$·H$_2$O slurries. The lateral dimension of irregular Gd(OH)$_3$·H$_2$O nanosheets is less than 100 nm. Compared to the 100 – 200 nm Gd$_2$(OH)$_3$Cl·1.5H$_2$O precursor slurry, the reduced lateral size results from a breakage or fracture of the sheets during the hydroxide ion exchange process.

Fig. S7 Atomic force microscopy (AFM) image of Gd(OH)$_3$·H$_2$O deposited on a Si substrate exhibits 40 – 100 nm lateral size of the sheets, which is consistent with that based on the SEM image. The height profiles along the white lines marked in the image show two distinct thicknesses of ~ 2.4 and ~ 4.2 nm for the nanosheets. Because the basal spacing of Gd(OH)$_3$·H$_2$O is around 0.775 nm (Table 1), these thicknesses indicate that the colloidal suspension contains predominantly nanosheets of 3 and 5 hydroxide layers. Sheets were randomly selected from the aqueous colloidal suspensions.
**Fig. S8** Hydrodynamic diameters of Gd(OH)$_3$·H$_2$O nanosheets dispersed in water, measured by dynamic light scattering (DLS) method. The diameters ranging from 120 nm to 300 nm, with a peak value at ~150 nm, are rather larger than the particle sizes observed in AFM images, suggesting that some (2 – 4) individual sheets may be agglomerated in the aqueous suspension, although the sedimentation does not occur.
Fig. S9 Photographs of aqueous colloidal suspensions containing Gd(OH)$_3$·H$_2$O (1.0 g/L) at pH = 3 phtalate buffer solution, which were acquired 1, 2, 4, and 12 h after the preparation of the colloidal suspensions. The light beam was irradiated from the side to demonstrate the Tyndall effect. A strong Tyndall effect was observed even after 4 h at pH = 3, which is indicative of the improved stability in a low pH physiological suspension. When measured 12 h after the preparation of colloidal suspensions, a weak Tyndall effect of the Gd(OH)$_3$·H$_2$O solution at pH = 3 indicates considerable dissolution at such long-term conditions.
Fig. S10 Photographs of aqueous colloidal suspensions containing RE(OH)$_3$\cdot$H$_2$O nanosheets (1.0 g/L) at pH ~ 7, where RE = (a) Sm, (b) Eu, (c) Tb, (d) Dy, (e) Er, and (f) Y. The light beam was irradiated from the side to demonstrate the Tyndall effect. All photographs were acquired one month after the preparation of the colloidal suspensions.