

## Immobilization of Gd(III)-DOTA Complexes in Layered Double Hydroxides Thin Film

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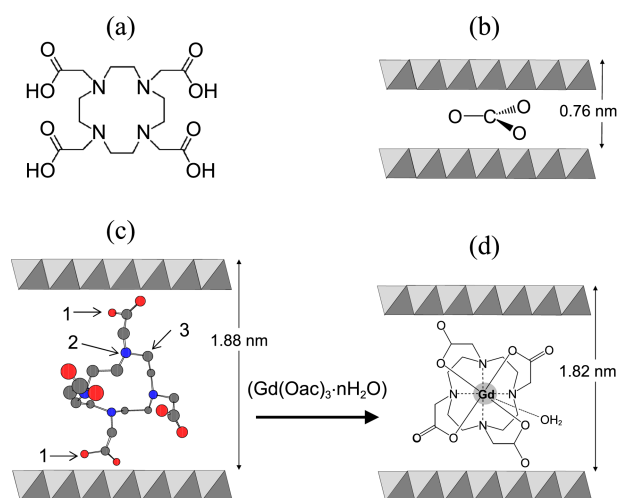
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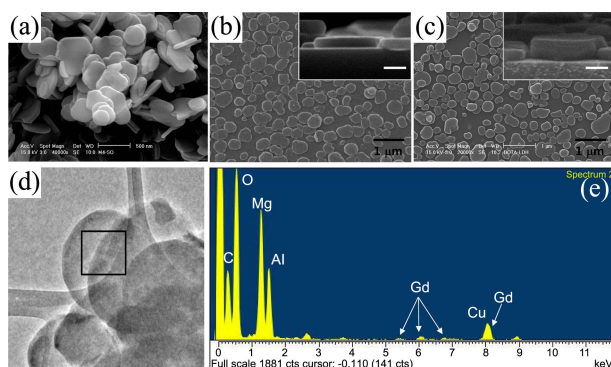
Lanthanide ion complexes of chelating ligands have been widely investigated in medicinal chemistry due to their exceptional stability and optical properties.<sup>1</sup> Recently, immobilization of the lanthanide ion (*e.g.*, Gd<sup>3+</sup>, Eu<sup>3+</sup>) complexes in two-dimensional layered solids such as layered double hydroxide (LDH) has provided them with enhanced thermal<sup>2</sup> and optical properties<sup>3</sup> compared to lanthanide complex salts. The LDH, a group of anion-exchangeable materials consisting of mixed metal hydroxide layers, can accommodate a wide range of anionic guests in their interlayer spaces for the potential uses as catalysts, separators and ion-immobilizers.<sup>4</sup> They consist of positively charged metal hydroxide layers, interlayer anions and water molecules represented by the general formula  $[M^{2+}_{(1-x)}M^{3+}_x(OH)_2]A^{n-}_{x/n} \cdot mH_2O$ , where M<sup>2+</sup> and M<sup>3+</sup> are divalent and trivalent metal ions, respectively, capable of occupying the octahedral holes of Brucite-like layers and A<sup>n-</sup> is a virtually hydrated anion positioned in the interlayer spaces between the layers.<sup>5</sup> Considering the interlayer structure of LDH, the hydrogen bonding network and electrostatic interaction within the host layers can provide the strong bonding and the homogeneous dispersion of the guest anions. Recently, we developed a simple way to produce the oriented thin film of the LDH particles on solid substrates, which has provided new hybrid thin films with tunable functionalities.<sup>6</sup> In this study, we employed the LDH thin film as a host material to immobilize Gd(III) complexes of 1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetic acid ligand, known as DOTA, as shown in Figure 1(a). It is well-known that the DOTA as a macrocyclic octacoordinating ligand forms very stable complexes in a solution with lanthanide(III) ions.<sup>7</sup> However, the specific size and the strong intermolecular interaction of macrocyclic ligands led to the incomplete incorporation of the lanthanide complexes in the interlayer spaces of LDH.<sup>3b</sup> Here, we report a direct intercalation of acidic DOTA ligand into the carbonate form of Mg<sub>2</sub>Al-LDH (LDH-carbonate) and a solid-state chelation of Gd(III) ions with the pre-intercalated DOTA ligand in LDH (LDH-DOTA).

We used a well-crystallized LDH-carbonate to prepare the oriented LDH thin film, and to immobilize the Gd(III)-DOTA complexes in the interlayer spaces of LDH (LDH-DOTA(Gd)). Figures 1(b), 1(c) and 1(d) show the possible interlayer configurations of carbonate, DOTA ligand, and DOTA(Gd) complex, respectively, in the LDH layers. The



**Figure 1.** Structure of DOTA ligand (a). Schematics for the possible configurations and interlayer separations of LDH-carbonate (b), LDH-DOTA (c) and LDH-DOTA(Gd) complex (d). In (c), atom labeling: oxygen (1), nitrogen (2), and carbon (3).

thin film of LDH-carbonate was prepared on Si(100) substrate by ultrasonically treating the clean Si substrate in the colloidal suspension of the LDH-carbonate, resulting in the oriented assembly of the LDH particles as a single particular layer on the substrate as shown in Figure 2(b). The incorporation of DOTA ligand into the LDH interlayers was carried out by a solvothermal treatment using organic media of the ethanol/toluene mixture (1%, v/v). In this reaction, the carbonates were directly exchanged with DOTA ligands, implying the DOTA<sup>2-</sup> anions in the gallery spaces of LDH, in which a small amount of ethanol increased the solubility of DOTA as well as provided the possible space for the fast diffusion of incoming guests into the interlayers spaces of LDH.<sup>6b,c</sup> This is ascribed to the partial de-protonation of the DOTA ligand by the ethanol during the intercalation reaction. The morphology and the lateral size of the LDH particles was found to be preserved after the intercalation reaction and the chelation of Gd(III) ions as shown in Figure 2(c). The insets in Figure 2(c) indicate the dominant layer expansion of the LDH particle through the incorporation of the DOTA ligand into the interlayers of LDH. The presence of element Gd in the LDH-DOTA(Gd) particles, which was scraped from the film sample, was confirmed by energy dispersive

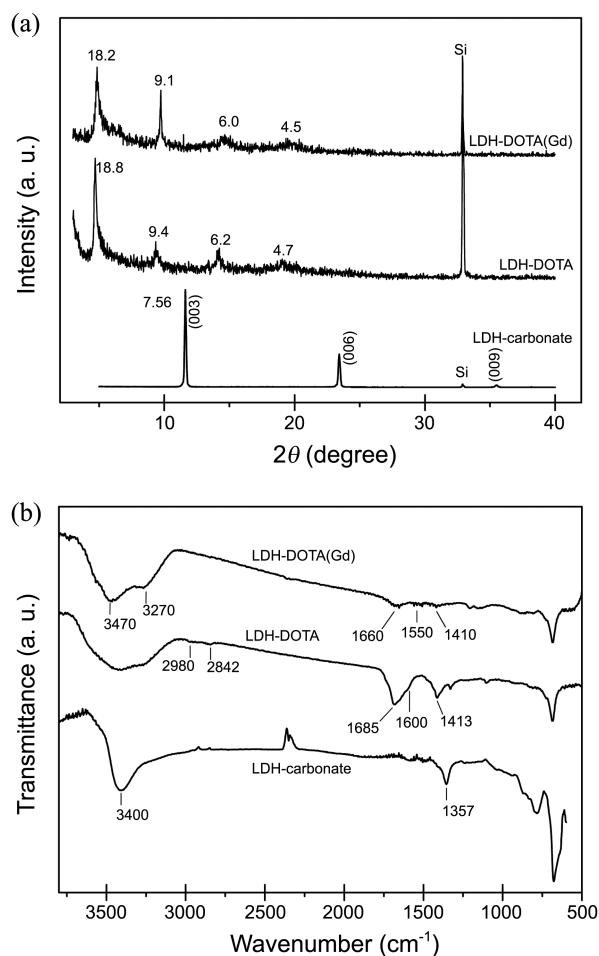


**Figure 2.** SEM images of LDH-carbonate powder (a), top-view of the thin film of LDH-carbonate (b) and the thin film of LDH-DOTA(Gd) complex (c). TEM image (d) and EDX (e) of LDH-DOTA(Gd) particles. Insets in (b) and (c) show the cross-sectional views of selected particles. The scale bar in inset figures is 200 nm.

X-ray spectroscopy (EDX) as shown in Figures 2(d) and 2(e).

The XRD patterns (Figure 3(a)) of the LDH-carbonate film showed only intense (00 $l$ ) reflections, indicating the highly oriented LDH particles along the crystallographic  $c$  axis perpendicular to the substrate plane. The low-angle reflection at  $11.6^\circ/2\theta$  ( $d = 7.56 \text{ \AA}$ ) corresponds to the interlayer separation by the carbonate ions. The peaks of the LDH-carbonate disappeared after the intercalation reaction with the DOTA ligand, though their (00 $l$ ) reflections were maintained with the preferred orientation, demonstrating the successful exchange of DOTA ligands with the carbonate ions in the LDH-carbonate. The result also suggested that the stacked LDH layers were filled with a highly oriented structure of the DOTA ligands between the LDH layers. Assuming the thickness of the LDH host layer,  $4.8 \text{ \AA}$ , the estimated gallery height of  $14 \text{ \AA}$  suggested the vertical accommodation of the DOTA ligand relative to the LDH layers as shown in Figure 1(c), which is in close agreement with the maximal dimension ( $13\text{--}15 \text{ \AA}$ ) of some related complexes  $[\text{Gd}(\text{DOTA})(\text{H}_2\text{O})]^{1-}$  and  $[\text{Gd}(\text{dtpa})(\text{H}_2\text{O})]^{2-}$  (dtpa = diethylene triamine pentaacetate) from the crystallographic data.<sup>7a,8</sup> The XRD pattern of LDH-DOTA(Gd) showed a decrease of  $0.6 \text{ \AA}$  in the interlayer separation compared to the case of the LDH-DOTA. This could be caused by a change in the conformation of the DOTA ligand within the interlayer space upon chelating the Gd(III) ions (Figure 1(d)). The high order of (00 $l$ ) reflections of the LDH-DOTA(Gd) was also observed with the well-oriented structure of the DOTA(Gd) complexes in the interlayers. Importantly, the second-order peak is intense and sharp for the LDH-DOTA(Gd), in contrast to that observed for the LDH-DOTA. This change can be attributed to the marked increase in electron density at the mid-plane of the interlayers<sup>9</sup> due to the presence of the Gd(III) ions. The result also demonstrated the chelation of Gd(III) with the vertically arranged DOTA ligand in the interlayers of LDH.

In the FT-IR spectra (Figure 3(b)), the LDH-carbonate film showed characteristic peaks for the carbonate ions at



**Figure 3.** XRD patterns (a) and FT-IR spectra (b) of LDH-carbonate, LDH-DOTA and LDH-DOTA(Gd) complex. Unit of the  $d$ -values in (a) is  $\text{\AA}$ .

$1357 \text{ cm}^{-1}$ , and the hydroxyl groups in the LDH host layers and interlayer water molecules at  $3400 \text{ cm}^{-1}$ . The spectra for the LDH-DOTA showed expected characteristic peaks for the intercalated DOTA<sup>2-</sup> ligand in the LDH galleries. The peaks at  $1600$  and  $1413 \text{ cm}^{-1}$  are assigned to the anti-symmetric and symmetric stretching modes, respectively, of COO<sup>-</sup>, and the weak peaks at  $2980$  and  $2842 \text{ cm}^{-1}$  are assigned to C-H stretching modes. The peak at  $1685 \text{ cm}^{-1}$  is assigned to the un-ionized COOH groups of the DOTA<sup>2-</sup>, and the very broad band centered at  $3500 \text{ cm}^{-1}$  is ascribed to the intermolecular hydrogen bonding of the COOH groups with the neighboring DOTA. These two bands are significantly lowered in the LDH-DOTA(Gd), implying the chelation of Gd(III) ions with the DOTA<sup>4-</sup> ligand. The two weak bands at  $1550$  and  $1410 \text{ cm}^{-1}$  in the LDH-DOTA(Gd) are also ascribed to the coordinated COO<sup>-</sup> groups<sup>10</sup> of the DOTA<sup>4-</sup> ligand with the Gd(III) ions. The broad band centered at  $3270 \text{ cm}^{-1}$  could be assigned to the coordinated water molecule, suggesting the presence of the  $[\text{Gd}(\text{DOTA})(\text{H}_2\text{O})]^{1-}$  complexes<sup>7a,11</sup> in the interlayer spaces of LDH as shown in Figure 1(d). The atomic ratio of Al:Gd was  $2.0:0.12$ , obtained by the EDX result, implying the partial chelation of Gd(III) ions with the DOTA ligands. Although the nature of the

strong metal-ligand interaction between the Gd(III) ions and the DOTA ligands increases the stability of the complexes in the solution, the low chelating capability of the pre-intercalated DOTA ligands might be ascribed to the large lateral dimension ( $\sim 8.0 \text{ \AA}$ )<sup>7a</sup> and the low charge density (estimated  $1.6 \text{ e/nm}^2$ ) of the  $[\text{Gd}(\text{DOTA})(\text{H}_2\text{O})]^{1-}$  complexes. Additionally, the FT-IR spectra revealed that un-coordinated DOTA ligands remained in the LDH-DOTA(Gd).

In summary, the Gd(III) ion complexes of DOTA as a macrocyclic ligand were immobilized in the interlayer spaces of the LDH films by an intercalation reaction using an ethanol/toluene mixture, in which the pre-intercalated DOTA ligand in the LDH was able to chelate the Gd(III) ions. The XRD and the FT-IR results confirmed the successful exchange of the DOTA ligand with the carbonate ions in the pristine LDH film and the solid-state chelation of Gd(III) ions with the ligands. The current study can be extended to fabricate new hybrid films for the development of optoelectric devices containing lanthanide ions.

### Experimental

#### Preparation and Characterization of LDH-DOTA(Gd)

**Thin Film.** LDH-carbonate,  $[\text{Mg}_4\text{Al}_2(\text{OH})_{12}]\text{CO}_3 \cdot n\text{H}_2\text{O}$ , was prepared using the coprecipitation method.<sup>5a,b</sup> The resulting precipitate was hydrothermally treated in deionized water at  $180 \text{ }^\circ\text{C}$  to obtain a larger crystal size and to improve crystallinity of LDH-carbonate, followed by drying at  $70 \text{ }^\circ\text{C}$ .<sup>12</sup> The thin film of LDH-carbonate was prepared on silicon (100) wafers.<sup>6</sup> To prepare the LDH-DOTA, the thin film of LDH-carbonate was transferred into a Teflon-coated autoclave vessel containing 20 mg of DOTA and a binary mixture of ethanol and toluene, and heated at  $120 \text{ }^\circ\text{C}$  for 72 h. The LDH-DOTA(Gd) was prepared by immersing the sample in 5 mM of ethanolic  $\text{Gd}(\text{acetate})_3 \cdot n\text{H}_2\text{O}$  solution for 1 h. The XRD patterns were measured using a Rigaku D/MAX-2000 Ultima using  $\text{Cu-K}\alpha$  radiation ( $\lambda = 1.5405 \text{ \AA}$ ). The SEM and TEM images were taken on a JEOL 7401F and a 300 kV, respectively. FT-IR was undertaken on a Biorad FTS 6000 equipped with a DuraSampl IR II diamond accessory with an ATR mode.

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