



# Fabrication of oriented oxide films from exfoliated yttrium hydroxide layers: Enhanced photoluminescence and unexplored behavior of energy transfer



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## ABSTRACT

Layered yttrium hydroxide (LYH) nanosheets doped with different activators ( $Tb^{3+}$  and/or  $Eu^{3+}$ ) were hydrothermally synthesized and then successfully delaminated into ultrathin nanosheets of down to 1–3 nm thickness via intercalation reactions and mechanical agitation. Using the LYH nanosheets, highly [001] oriented yttrium hydroxide films were constructed through spin-coating. Based on the quasi-topotactic transformation from yttrium hydroxide to cubic  $Y_2O_3$ , [111] oriented oxide films were achieved by proper annealing. For the highly oriented  $Y_2O_3:0.05Eu$  film, the enhanced photoluminescence was obtained compared with the powder form due to the higher exposure of (222) facets. Through adjusting the incorporated activation ions, films with different color were obtained, and energy transfer from  $Tb^{3+}$  to  $Eu^{3+}$  was observed for the alternatively multilayer film, although  $Eu^{3+}$  and  $Tb^{3+}$  were located in different layers.

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## 1. Introduction

Layered rare-earth hydroxide (LRH), as a relatively new type of anionic layered compounds, has attracted much attention during the recent years on account of their unique ability to combine the excellent properties of the rare-earth ions with the host-guest chemistry [1]. They may be delaminated into unilamellar or few-layer thick nanosheets with significantly 2D morphology, which are ideal building blocks for constructing films [2]. Another attractive aspect is that they can incorporate selected activator ions and generate abundant photoluminescent properties [3–9].

LRH compounds can basically be prepared by hydrothermal crystallization [10–12] and homogeneous precipitation via refluxing [13–15]. The above synthetic methodologies produce plate-like

LRH crystals of several microns in lateral dimension and tens to hundreds of nanometers in thickness, which are not suitable for preparing transparent luminescent films directly. On the other hand, according to the crystal habit of LRH, it has demonstrated that chemical precipitation at freezing temperature of 4 °C can directly produce ultrathin LRH nanosheets of 3–5 nm in thickness [16]. However, the nanosheets are assembled into aggregates like hydrangea-flower, which are also not suitable for preparing films directly. Therefore, hydroxide nanosheets derived from their layered host compound are indispensable. Delaminating layered compounds into nanosheets can be achieved by swelling the pristine crystals via exchange of the interlayer anions with significantly larger ones, followed by exfoliation in a proper medium under mechanical agitation. The exfoliation technology has been successful for several types of layered inorganic materials, such as layered double hydroxides (LDHs) [17], graphite [18], metal oxides [19], phosphates [20], and chalcogenides and *h*-BN [21], to name a few.

The crystal structure of the LRH compounds can be viewed as a repetitive stacking of the host layer and interlayer anions along *c*-

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axis (the [001] direction), and the host layer constructed via edge sharing of 8-fold  $[\text{Ln}(\text{OH})_7\text{H}_2\text{O}]$  and 9-fold  $[\text{Ln}(\text{OH})_7\text{H}_2\text{O}]$  coordination polyhedral. Due to the special structure features, the significant 2D morphologies of the exfoliated LRHs are well suited for the construction of highly [001] oriented film with improved luminescence than that of LRH powder form, ascribed to that the film maximizes the exposure more Ln activators located in the host layer to the excitation light and thus obtain higher emission intensity. Additionally, the flat surface of the highly oriented films may reduce the scattering of the excitation light, which also result in the higher emission intensity.

Generally speaking, the photoluminescence behavior of LRH is less than rare-earth oxides because the hydroxy in LRH structure provide the channels of nonradiative relaxation.  $\text{Y}_2\text{O}_3$  doped with  $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$  ions are the best-known red-emitting and green-emitting phosphors, respectively, owing to its excellent chemical durability and stability, excellent luminescence efficiency, and high color purity [22–24]. Due to that,  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  and  $\text{Y}_2\text{O}_3:\text{Tb}^{3+}$  are widely used in the field of cathode ray tubes (CRTs), field emissive displays (FEDs), flat panel displays (FPDs), and plasma display panels (PDPs) [25]. Among the low-dimension  $\text{Y}_2\text{O}_3:\text{RE}$  phosphors (RE = rare-earth element), the 0-dimensional (0D) nanoparticles and 1-dimensional (1D) nanotubes/nanowire have been extensively studied for their controllable synthesis and potentially new optical properties [26–29]. However, the 0D and 1D oxides are not suitable for forming ultrathin luminescent film with high density and smooth surface. 2D nanosheets are the potential ideal candidate for the preparation of the film with high quality. In the solution-based processing methodology, oxide are mostly produced via controlled precursor synthesis followed by proper annealing, and the LRH provides a 2D template for the formation of 2D oxide. Moreover, the projection in the [001] direction for LRHs crystal and [111] direction for the cubic oxide crystal present close similarities in terms of rare-earth stomic configuration, the phase transformation from LRH to cubic oxide is a quasitopotactic one [30–32]. Thus the [001] oriented LRH film would transform to a [111] oriented oxide film via quasi-topotactic atomic arrangements under proper annealing [3–7], which should result in an enhanced exposure of the close-packed (222) facets of the oxide crystal and thus stronger luminescence.

According to the literature [33,34], the  $\text{Y}_2\text{O}_3$  doped 5 at%  $\text{Eu}^{3+}$  and the  $\text{Y}_2\text{O}_3$  doped 5 at%  $\text{Tb}^{3+}$  have the optimal photoluminescence properties, thus in this context, efforts have been made to fabricate oriented oxide luminescence films by employing the exfoliated nanosheets of  $(\text{Y}_{0.95}\text{Eu}_{0.05})_2(\text{OH})_5\text{NO}_3 \cdot n\text{H}_2\text{O}$  (LYH:0.05Eu) and  $(\text{Y}_{0.95}\text{Tb}_{0.05})_2(\text{OH})_5\text{NO}_3 \cdot n\text{H}_2\text{O}$  (LYH:0.05Tb) as precursor building blocks, and followed by proper annealing. Three kinds of multilayer films ( $\text{Y}_2\text{O}_3:0.05\text{Eu}$  films,  $\text{Y}_2\text{O}_3:0.05\text{Tb}$  films and the mixed films formed by  $\text{Y}_2\text{O}_3:0.05\text{Eu}$ , and  $\text{Y}_2\text{O}_3:0.05\text{Tb}$ ) were prepared via “layer-by-layer” method, and the films were characterized by XRD, SEM, AFM, PL/PLE and TEM usually used in the structure characterization of the nonlinear luminescent materials [35–37].

## 2. Experimental

### 2.1. Materials

The starting rare-earth sources are  $\text{Y}_2\text{O}_3$  (4N),  $\text{Tb}_4\text{O}_7$  (4N) and  $\text{Eu}_2\text{O}_3$  (4N), which are purchased from Huizhou Ruier Rare-Chem. Hi-Tech. Co. Ltd (Huizhou, China). Sodium dodecyl sulfate (AR), ammonium hydroxide solution (25%) and nitric acid (63 wt%) were purchased from Sinopharm Chemical Reagent Co. Ltd. Rare-earth nitrate solution was prepared by dissolving the oxide with a proper amount of nitric acid, followed by evaporation to dryness at

90 °C to remove superfluous  $\text{HNO}_3$ .

### 2.2. Preparation of $(\text{Y}_{0.95}\text{Ln}_{0.05})_2(\text{OH})_5\text{NO}_3 \cdot n\text{H}_2\text{O}$ (Ln = Eu, Tb) and their exfoliated nanosheets

The first step is to synthesize  $(\text{Y}_{0.95}\text{Ln}_{0.05})_2(\text{OH})_5\text{NO}_3 \cdot n\text{H}_2\text{O}$  (Ln = Eu, Tb) powder. For each run of the synthesis, the total concentration of  $\text{Ln}^{3+}$  was kept constant at 0.02 mol/L and the Ln/(Y+Ln) (Ln = Eu, Tb) atomic ratio was fixed at 5 at%. In a typical synthetic procedure, a proper amount of ammonium hydroxide solution (25%) was added to the mixed nitrate solution until pH ~7. After stirring for 30 min, the resultant suspension was transferred into a Teflon lined stainless-steel autoclave and heat treated at 100 °C for 12 h. After natural cooling, the hydrothermal product was collected via centrifugation, washed with distilled water and ethanol, and finally dried in the air at 50 °C for 12 h to yield a white powder.

The above obtained powder is need to be exfoliated into ultrathin nanosheets, thus the anion exchange is the first step, the large  $\text{C}_{12}\text{H}_{25}\text{SO}_3^-$  ( $\text{DS}^-$ ) was employed to exchange the  $\text{NO}_3^-$ . 0.05 mmol LRH was added into an aqueous solution containing 0.25 mmol Sodium dodecyl sulfate (SDS), following by reacting at room temperature for 48 h under mechanical agitation. The exchanged product was then dispersed into 100 mL formamide in a capped conical beaker, and gently agitated until the solution becomes transparent. The exfoliated LRH nanosheets were collected via centrifugation at 25000 rpm for 1 h. The colloidal suspension (0.5 mg/mL) was obtained by dispersing LRH nanosheets into 5 mL ethanol, and then ultrasonic treatment for 5 min.

### 2.3. Preparation of oriented luminescent films

Multilayer films of the exfoliated LRH nanosheets were fabricated by applying the layer-by-layer assembly procedure, that is, colloidal suspension was dripped onto the rotating quartz glass substrate for a certain number of times. Notably, the glass substrate were (1) sequentially immersed in acetone, ethanol, deionized water for ultrasonic treatment for 5min, respectively, and then placed into  $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$  solution (volume ratio of 3/1) at 80 °C for 1 h; (2) immersed in  $\text{NH}_4\text{OH}/\text{H}_2\text{O}_2/\text{H}_2\text{O}$  solution for 10min, and dried at 80 °C; (3) immersed in  $\text{CH}_3\text{OH}/\text{HCl}$  (63 wt%) solution for 20 min, and then treated in  $\text{H}_2\text{SO}_4$  (98 wt%) for 20 min, finally rinsed by deionized water.

### 2.4. Characterization techniques

Phase identification was performed via X-ray diffractometry (XRD, X'Pert PRO, PANalytical B.V.) using nickel-filtered  $\text{Cu-K}\alpha$  radiation operated at 40 kV/40 Ma. Fourier transform infrared spectroscopy (FT-IR, Model Spectrum RXI, Perkin-Elmer, Shelton, Connecticut) was undertaken by the standard KBr method. Morphology and microstructure analysis were achieved via transmission electron microscopy (TEM, Model JEM-2000FX, JEOL, Tokyo) and field emission scanning electron microscopy (SEM, JSM6380-LV, JEOL). Topographical images of the individual nanosheets were obtained via atomic force microscope (AFM, Nanosurf easyScan 2, Switzerland). Photoluminescence properties were measured at room temperature with FP-6500 spectrofluorometer (JASCO, Tokyo) equipped with a 60-mm-diameter integrating sphere (Model ISF-513, JASCO) and a 150-W Xe-lamp as the excitation source.

## 3. Results and discussion

Fig. 1(a) compares XRD patterns of  $(\text{Y}_{0.95}\text{Eu}_{0.05})_2(\text{OH})_5\text{NO}_3 \cdot n\text{H}_2\text{O}$

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