Tens of micron-sized unilamellar nanosheets of Y/Eu layered rare-earth hydroxide: efficient exfoliation via fast anion exchange and their self-assembly into oriented oxide film with enhanced photoluminescence

To cite this article: Qi Zhu et al 2014 Sci. Technol. Adv. Mater. 15 014203

View the article online for updates and enhancements.
Tens of micron-sized unilamellar nanosheets of Y/Eu layered rare-earth hydroxide: efficient exfoliation via fast anion exchange and their self-assembly into oriented oxide film with enhanced photoluminescence

Qi Zhu\textsuperscript{1}, Ji-Guang Li\textsuperscript{1,2}, Xiaodong Li\textsuperscript{1}, Xudong Sun\textsuperscript{1}, Yang Qi\textsuperscript{3}, Miaoyong Zhu\textsuperscript{1} and Yoshio Sakka\textsuperscript{2}

\textsuperscript{1} Key Laboratory for Anisotropy and Texture of Materials (Ministry of Education), School of Materials and Metallurgy, Northeastern University, Shenyang, Liaoning 110819, People’s Republic of China
\textsuperscript{2} Advanced Materials Processing Unit, National Institute for Materials Science, Sengen 1-2-1, Tsukuba, Ibaraki 305-0047, Japan
\textsuperscript{3} Institute of Materials Physics and Chemistry, School of Sciences, Northeastern University, Shenyang, Liaoning 110819, People’s Republic of China
\textsuperscript{4} School of Materials and Metallurgy, Northeastern University, Shenyang, Liaoning 110819, People’s Republic of China
E-mail: LI.Jiguang@nims.go.jp

Received 20 July 2013
Accepted for publication 18 November 2013
Published 20 December 2013

Abstract
Layered rare-earth hydroxide (LRH) crystals of (Y\textsubscript{0.95}Eu\textsubscript{0.05})\textsubscript{2}(OH)\textsubscript{5}NO\textsubscript{3} \cdot \textit{n}H\textsubscript{2}O with a lateral size of \(\sim 300 \mu\text{m}\) and a thickness of \(\sim 9 \mu\text{m}\) have been synthesized via a hydrothermal reaction of mixed nitrate solutions in the presence of mineralizer NH\textsubscript{4}NO\textsubscript{3} at 200 \(^\circ\text{C}\) for 24 h. LRH exhibits the ability to undergo intercalation and anion exchange with DS\textsuperscript{−} (C\textsubscript{12}H\textsubscript{25}OSO\textsubscript{3}\textsuperscript{−}) via hydrothermal treatment. Compared with traditional anion exchange at room temperature, hydrothermal processing not only shortens the anion exchange time from 720 to 24 h but also increases the basal spacing. The arrangements of DS\textsuperscript{−} in the interlayer of LRH are significantly affected by the DS\textsuperscript{−} concentration and reaction temperature, and the basal spacing of the LRH-DS sample in the crystal edge is assumed to be larger than that in the crystal center. A higher DS\textsuperscript{−} concentration and reaction temperature both induce more intercalation of DS\textsuperscript{−} anions into the interlayer gallery, thus yielding a larger basal spacing. Unilamellar nanosheets with a lateral size of \(\geq 60 \mu\text{m}\) and a thickness of \(\sim 1.6 \text{ nm}\) can be obtained by delaminating LRH-DS in formamide. The resultant unilamellar nanosheets are single crystalline. Transparent (Y\textsubscript{0.95}Eu\textsubscript{0.05})\textsubscript{2}O\textsubscript{3} phosphor films with a uniform [111] orientation and a layer thickness of \(\sim 90 \text{ nm}\) were constructed with the nanosheets as building blocks via spin-coating, followed by proper annealing. The oriented oxide film exhibits a strong red emission at 614 nm (the \(5D_0\rightarrow 7F_2\) transition of Eu\textsuperscript{3+}), whose intensity is \(\sim 2\) times that of the powder form owing to the significant exposure of the (222) facets.

Keywords: layered rare earth hydroxide, exfoliation, anion exchange, unilamellar nanosheet, oriented fluorescent film
1. Introduction

Layered inorganic compounds, possessing a unique and fascinating ability to undergo intercalation and ion exchange, may be potentially exfoliated into unilamellar nanosheets or nanosheets a few layers thick [1, 2], which can be viewed as a class of inorganic macromolecules and thus bring about novel physicochemical properties associated with their thickness of nanometer order. Owing to the significant two-dimensional morphologies (lateral size up to microns, thickness down to nanometer level), the exfoliated nanosheets may serve as ideal building blocks for the construction of inorganic or hybrid organic–inorganic multifunctional films [3–7]. It is also due to this significant morphological anisotropy that the nanosheets tend to orient themselves with a certain crystallographic direction perpendicular to the substrate surface, which may introduce additional and sometimes greatly enhanced functionalities.

The most widely employed technique to produce two-dimensional nanosheets is exfoliation via intercalation of bulky organic molecules or ions into the interlayer spacing. Individual nanosheets have been successfully exfoliated from the layered inorganic materials, such as layered double hydroxides (LDHs) [8], graphite [9], metal oxides [10], phosphates [11] and chalcogenides [12]. Mainly due to this, the lateral size of the resulting exfoliated nanosheets is smaller than that of the starting layered inorganic solids. Despite the successes mentioned above, exfoliation proves to be an arduous and lengthy process because of the strong interlayer electrostatic interactions arising from the high charge density of the host layer, the high content of charge compensating ionic species sandwiched between the layers, or strong hydrogen bonding.

Layered rare-earth hydroxides (LRHs), with a general formula of \( \text{RE}(_2\text{OH})_3(\text{A}^{m-})_{1/m} \cdot n\text{H}_2\text{O} \) (RE: rare-earth ions; \( \text{A} \): intercalated anions), were first prepared by Gándara et al [13] via hydrothermal treatment of rare-earth nitrates in the presence of triethylamine (Et\(_3\)N). LRHs and the common LDHs \((\text{M}^{2+}\text{M}^{3+}(\text{OH})_2)_x[A^{m-}\text{M}^{3+}]^{x-} \cdot n\text{H}_2\text{O}\) both belong to the anion type of inorganic layered compounds, but LRHs have only one type of cation (\( \text{RE}^{3+} \)) in the host layer. Due to the unique electronic, optical, magnetic and catalytic properties of the rare-earth elements, LRHs have attracted continued attention since their emergence, and extensive efforts have been paid to their synthesis, structural characterization, anion exchanges, exfoliation and functionalities [14–36]. The thick LRH crystals have been exfoliated into nanosheets by other research groups via anion exchange with dodecylsulfate (DS') at room temperature, followed by lengthy mechanical agitation in formamide [18, 19]. The high charge density of LRHs, however, makes a complete exfoliation and particularly morphological (shape and thickness) control of the resultant nanosheets more challenging. Previous studies reported that the exfoliation of LRH crystals into nanosheets usually takes several days, and has proven to be an arduous and lengthy process [18]. Although in a recent paper [30], we obtained ultra-thin (down to \( \sim 4 \) nm) LRH nanosheets without exfoliation by employing tetrabutylammonium hydroxide (TBAOH, \((\text{C}_4\text{H}_{9})_4\text{N}^{+} \cdot \text{OH}^-\)) as a reactant for hydrothermal synthesis, the lateral size of the resultant nanosheets is smaller than 120 nm. Furthermore, the starting LRH crystals for delamination synthesized through current techniques are usually composed of platy micro-crystals of \(< 5 \mu\text{m} \) in lateral dimension, so the resulting exfoliated nanosheets consequently have an average lateral size of \( \lesssim 500 \) nm [18]. The small lateral size of nanosheets hindered a detailed investigation of their physicochemical properties and construction of new materials with a well-organized nanostructure. More recently, we found that larger LRH crystals can be obtained either by adding more mineralizer \( \text{NH}_4\text{NO}_3 \) or by raising the hydrothermal temperature, owing to the increased solubility of the compound and the enhanced mass transfer, both of which induce Ostwald ripening [36]. Submillimeter-sized crystals of \((\text{Y}_{0.05}\text{Eu}_{0.95})_2(\text{OH})_3\text{NO}_3 \cdot n\text{H}_2\text{O} \) LRH solid solutions in a phase pure form have been successfully synthesized [36]. The obtained crystals are ideal starting materials for obtaining larger nanosheets via delamination. The exfoliated nanosheets have a more significant two-dimensional morphology, which is beneficial to the construction of highly oriented fluorescent films via self-assembly. However, the exfoliation of large LRH crystals is rather challenging, and has not been well addressed prior to this work. In view of this, this work focuses on efficient exfoliation of submillimeter-sized LRH crystals into tens of micron-sized unilamellar nanosheets, and the functionalization of the nanosheets via the construction of oriented fluorescent films. The \( \text{Y}/\text{Eu} \) system was chosen here because its oxide is one of the most important red phosphors, finding wide applications in lighting and display areas such as fluorescent lamps, white light emitting diodes, plasma display panels, flat panel displays, field emission displays and cathode ray tubes [37].

2. Experimental details

2.1. Synthesis

The yttrium and europium sources are \( \text{Y(NO}_3)_3 \cdot 6\text{H}_2\text{O} \) (99.99% pure; Kanto Chemical Co., Inc., Tokyo, Japan) and \( \text{Eu(NO}_3)_3 \cdot 6\text{H}_2\text{O} \) (99.95% pure; Kanto Chemical Co., Inc.), respectively. The luminescence quenching concentration of \( \text{Eu}^{3+} \) in \( \text{Y}_2\text{O}_3 \) is widely observed to be \( \sim 5 \) at.%, and thus in this work the \( \text{Y}/\text{Eu} \) molar ratio is kept constant at 19:1. In a typical synthesis, 2 mmol of \( \text{RE(NO}_3)_3 \cdot 6\text{H}_2\text{O} \) (\( \text{RE} = \text{Y} \) and \( \text{Eu} \)) together with 300 mmol of ammonium nitrate \( \text{NH}_4\text{NO}_3 \) (99.0% pure; Kanto Chemical Co., Inc.), was dissolved in distilled water to make a total volume of 70 ml. After homogenizing under magnetic stirring at room temperature for 1 h, an amount of ammonium hydroxide solution (25%; Wako Chemical Co., Inc., Tokyo) was added until a \( \text{pH} \) of \( \sim 7 \) was reached. The resultant suspension was then transferred into a Teflon-lined stainless-steel autoclave of 100 ml capacity after being constantly stirred for 15 min. The autoclave was tightly sealed and put into an electric oven preheated to 200 °C. After 24 h of reaction, the autoclave was left to cool naturally to room temperature, and the
hydrothermal product was collected via centrifugation. The wet precipitate was washed with distilled water three times to remove the by-products, rinsed with absolute ethanol, and finally dried in air at 50°C for 24 h.

2.2. Anion exchange reaction, exfoliation and film construction

In a typical anion exchange reaction, 0.4 mmol of (Y0.90Er0.05)2(OH)3NO3·nH2O was dispersed into an aqueous solution (50 ml) of a proper amount of sodium dodecylsulfate (C12H25OSO3Na). The resultant suspension was then transferred into a Teflon-lined stainless-steel autoclave of 100 ml capacity after being constantly stirred for 5 min. The autoclave was tightly sealed and put into an electric oven preheated to selected temperatures. After 24 h of reaction, the autoclave was left to cool naturally to room temperature, and the hydrothermally anion-exchanged product was collected via centrifugation. The wet precipitate was then transferred into a Teflon-lined stainless-steel autoclave of 100 ml capacity after being constantly stirred for 24 h. Nanosheet film was self-assembled on a quartz substrate (10 mm in diameter) by a spin-coating process. Briefly, 0.5 ml of the transparent colloidal suspension was dropped on the substrates fixed on a spin coater. The rotating speed was held at 2000 rpm for 1 min, and a film was formed on the substrate by a self-assembly process, followed by slow air drying. Prior to the spin-coating process, the quartz substrates were ultrasonically washed in acetone, ethanol and distilled water, and then immersed in the solution of H2SO4:30% H2O2(3:1) at 80°C for 1 h. Subsequently, the substrates were kept in the solution of H2O:NH3OH·H2O(5:1:1) to render the surface hydrophilic. Finally, they were washed with distilled water three times. The oxide film was obtained by calcining the precursor film in air at 600°C for 4 h, with a heating rate of 10°C min⁻¹ at the ramp stage.

2.3. Characterization techniques

Phase identification was performed by x-ray diffractometry (XRD, Model PW3040/60, Philips, Eindhoven, the Netherlands) operating at 40 kV per 40 mA using nickel-filtered Cu Kα radiation and a scanning speed of 4.0° 2θ min⁻¹. The lattice constants of the samples were calculated from the XRD patterns using the software package X’Pert HighScore Plus version 2.0 (PAAnalysitcal B V, Almelo, The Netherlands). The morphologies of the products were observed via field emission scanning electron microscopy (FE-SEM; Model JSM-7001F, JEOL, Tokyo) and transmission electron microscopy (TEM; Model JEM-2000FX, JEOL, Tokyo). Fourier transform infrared spectroscopy (FTIR; Model Spectrum RXI, Perkin-Elmer, Shelton, Connecticut, USA) of the precursors and anion-exchanged products was performed by the standard KBr method. A Nanosurf easyScan 2 atomic force microscope (AFM) system (Switzerland) was employed to obtain topographical images of the nanosheets. The photoluminescence (PL) and PL excitation (PLE) spectra of the resultant phosphor films were measured using an LS-55 fluorescence spectrophotometer (Perkin-Elmer) at room temperature.

3. Results and discussion

3.1. Tens of micron-sized unilamellar nanosheets of Y/Eu LRH: efficient exfoliation via fast anion exchange

Sasaki and co-workers [18] first exfoliated LRH intercalated with DS⁻ (C12H25OSO3⁻) in formamide to produce unilamellar nanosheets. However, the resultant nanosheets were smaller than 500 nm due to the small size of the starting crystals (~5 µm), and the DS⁻ anion exchange and the exfoliation took several days. The present LRH with a lateral size of ~300 µm and a thickness of ~9 nm are attractive starting crystals for delamination, and an efficient exfoliation process is demonstrated herein.

Figure 1 shows the XRD patterns of LRH and DS⁻-intercalated LRH (denoted as LRH-DS hereafter) obtained by various treatments. Although the nitrate ions (NO₃⁻) are shown to freely exist in the interlayer gallery of LRH, the submillimeter-sized large crystals make it rather difficult for NO₃⁻ exchange with DS⁻ to occur at room temperature. Thus, anion exchange (ten-fold DS⁻) at 25°C for 30 days was performed to obtain LRH-DS, and the result is shown in figure 1(b). Figure 1(c) shows the XRD pattern of the LRH-DS sample obtained by hydrothermal anion exchange at 120°C for 24 h with the same DS⁻ concentration. Similar to figure 1(b), the (00l) reflections (monitored as the (002) and (004) reflections) shift to the lower-angle side, while the (h0l) reflections are at the same position, as compared with the XRD pattern in figure 1(a). At the same time, there are two sets of (00l) reflections in figures 1(b) and (c). For figure 1(b), the sharp and symmetric basal (00l) reflections at 1.55 and 1.06 nm indicate a basal spacing of ~3.10 nm, while the reflections at 1.25 and 0.84 nm indicate a basal spacing...
Figure 2. FE-SEM micrographs showing morphologies of (a) the submillimeter-sized \( \text{Y}_{0.95}\text{Eu}_{0.05}\text{NO}_3 \cdot n\text{H}_2\text{O} \) LRH crystals and (b) the nanosheets exfoliated from (a). Panel (c) is a TEM image of an exfoliated unilamellar nanosheet, and (d), (e) are the AFM images. Panel (f) is the height profile along the red line marked in (d). The inset in (b) shows the appearance of a colloidal suspension of the nanosheets in formamide with a clearly observable Tyndall effect under laser beam irradiation. The inset in (c) is the SAED pattern of an individual unilamellar nanosheet. The adsorption of by-products on the surface of the nanosheets and the wrinkle induce the vertical ripples in (d) and (e).

of \( \sim 2.50 \) nm. Similarly, in figure 1(c), the reflections at 1.70, 1.16 and 0.85 nm indicate a basal spacing of \( \sim 3.40 \) nm, and the reflections at 1.27, 0.82 and 0.64 nm indicate a basal spacing of \( \sim 2.54 \) nm. Because it may be easier for \( \text{NO}_3^- \) to exchange with the DS\(^-\) anion at the edge of the LRH crystal than in the crystal center, various basal spacings are postulated to exist in the anion exchange process. Besides, larger crystals would take a longer time to be intercalated with DS\(^-\) than the smaller ones, which would also induce different basal spacings. Although it cannot be excluded, this may not be the major reason for what is observed in figure 2(a), since most of the LRH crystals are submillimeter-sized. The above issues are systematically discussed below. The basal spacing, \( \sim 0.91 \) nm for the pristine \( \text{NO}_3^- \) form, has been expanded to \( \sim 2.50-3.40 \) nm via either room temperature exchange or hydrothermal anion exchange with DS\(^-\). However, the
hydrothermal process is easier and quicker to perform than the traditional anion exchange at room temperature; the processing time is shortened from 30 days (720 h) for room anion exchange to 24 h for the hydrothermal exchange, and the basal spacing is efficiently increased from ~3.10 nm (~2.50 nm) for the room anion exchange to ~3.40 nm (~2.54 nm) for hydrothermal exchange. This is mainly due to the faster anion exchange and the enhanced pressure arising from hydrothermal processing. When the LRH-DS (figure 1(c)) derived from starting LRH crystals (figure 2(a)) was dispersed in 70 ml of formamide, a transparent colloidal suspension was obtained after being constantly stirred for 24 h (inset in figure 2(b)), and a clear Tyndall effect was observed under laser beam irradiation, indicating the delamination of LRH-DS. Figures 2(b) and (c) show the morphologies of the exfoliated nanosheets, which suggests that most nanosheets have a lateral size of ≥ 60 μm. The uniform contrast observed from an isolated nanosheet under TEM (figure 2(c)) implies that the nanosheet is rather thin. Selected area electron diffraction (SAED) yielded well-arranged spot-like patterns, suggesting that the observed nanosheet is well crystallized and is of a single crystalline character (inset in figure 2(c)). The cell parameters calculated from the inset in figure 2(c) are $a = 1.27$ nm and $b = 0.72$ nm, in close agreement with those of bulk LRH [29]. The nanosheet thickness was estimated to be ~1.16 nm from the AFM height profile (figures 2(f)) along the red line marked in figure 2(d), indicating that the nanosheet is unilamellar. At the same time, the AFM morphologies of the nanosheets indicated that the nanosheets are very flat and smooth (figures 2(d) and (e)). Mainly due to the possible adsorption of DS$^-$ as well as formamide molecules on the surface of the nanosheets, the thickness of unilamellar nanosheets is larger than 0.93 nm (crystallographic thickness based on the crystal structure data) [18]. Comparing with the exfoliated LRH nanosheets reported in [18, 19], the unilamellar nanosheets obtained in this work showed a significantly larger lateral size and a more unabridged sheet shape, which is advantageous for further investigation on their physicochemical properties and fabrication of new materials.

3.2. The effects of DS concentration and reaction temperature on anion exchange

The arrangements of DS$^-$ in the interlayer of LRH are significantly affected by DS$^-$ concentration and reaction temperature. Figure 3 shows the XRD patterns of the LRH-DS obtained by the anion exchange procedure at various temperatures. Similar to figure 2, there are also two sets of (00l) reflections in figure 3, and the (00l) reflections shift to the lower-angle side while the (hk0) reflections are immobile, as compared with the XRD pattern in figure 3(a). At 100°C (figure 3(b)), the sharp and symmetric basal (00l) reflections at 1.75 and 1.18 nm indicate a basal spacing of ~3.50 nm, while the reflections at 1.20 nm indicate a basal spacing of ~2.40 nm. Calculating from figures 3(c)–(f), the basal spacing of LRH-DS obtained at 120, 140, 160 and 180°C is ~3.40 (~2.54), ~3.15 (~2.58), ~3.51 (~2.48) and ~3.72 nm (~2.56 nm).

![Figure 3. XRD patterns of the (Y,0.05Eu,0.05)$_2$OH$_3$NO$_3$·$n$H$_2$O LRH crystals (a) and the LRH-DS samples obtained by anion exchange at (b) 100°C, (c) 120°C, (d) 140°C, (e) 160°C and (f) 180°C for 24 h. The DS$^-$ concentration is ten-fold excess in mole. Panel (B) is the part of (A) at the 2θ range of 4.5–13.5°.](image)

![Figure 4. FTIR spectra for the (Y,0.05Eu,0.05)$_2$OH$_3$NO$_3$·$n$H$_2$O LRH crystals (a) and the LRH-DS samples obtained by anion exchange at (b) 100°C, (c) 120°C, (d) 140°C, (e) 160°C and (f) 180°C for 24 h. The DS$^-$ concentration is ten-fold excess in mole.](image)
Figure 5. Schematic illustrations showing the arrangements of $\text{DS}^-$ in the interlayer, as a function of reaction temperature and $\text{DS}^-$ concentration. Panels (a)–(c) are postulated structural models.

Figure 6. XRD patterns of the $(\text{Y}_{0.95}\text{Eu}_{0.05})_2(\text{OH})_5\text{NO}_3 \cdot n\text{H}_2\text{O}$ LRH crystals (a) and the LRH-DS samples obtained by the hydrothermal anion exchange procedure at 180°C for 24 h with (b) three-fold, (c) five-fold and (d) ten-fold excess of $\text{DS}^-$ anion (in mole). Panel (B) is the part of (A) at the $2\theta$ range of 4.5–12.0°.

Figure 7. FTIR spectra for (a) submillimeter-sized $(\text{Y}_{0.95}\text{Eu}_{0.05})_2(\text{OH})_5\text{NO}_3 \cdot n\text{H}_2\text{O}$ LRH crystals, and the LRH-DS samples obtained by the hydrothermal anion exchange procedure at 180°C for 24 h with (b) three-fold, (c) five-fold and (d) ten-fold excess of $\text{DS}^-$ anion (in mole).

Figure 8. XRD patterns of (a) the LRH nanosheet film on a quartz substrate and (b) the $(\text{Y}_{0.95}\text{Eu}_{0.05})_2\text{O}_3$ film annealed from (a) at 600°C for 4 h.

bands at around $\sim$1180 and $\sim$1062 cm$^{-1}$ are assigned to the stretching mode of the sulfate ($\text{OSO}_3^-$) [38, 39]. The strong absorption peaks at $\sim$2928 and $\sim$2848 cm$^{-1}$ are due to the asymmetric and symmetric CH$_2$ stretching vibrations, respectively, in the alkyl chain of DS, whereas the weak band at $\sim$2958 cm$^{-1}$ is assigned to the stretching mode of the terminal CH$_3$ group of the hydrocarbon tail [38, 39]. The above results confirm a complete replacement of nitrate anion by the DS$^-$ units in the gallery of LRH at the reaction temperature range of 100–180°C.

Since the starting LRH crystals have a large lateral size of $\sim$300 μm, it may be easier for NO$_3^-$ to exchange with the DS$^-$ anion at the edge of the LRH crystal than in the crystal center, thus the basal spacing of LRH-DS sample in the crystal edge is postulated to be bigger than that in the crystal center, which further induces various basal spacings existing in LRH-DS (figure 5). At the temperature range of 100–140°C, a smaller basal spacing ($\sim$3.50 nm (100°C), $\sim$3.40 nm (120°C), $\sim$3.15 nm (140°C)) and a larger basal spacing ($\sim$2.40 nm (100°C), $\sim$2.54 nm (120°C), $\sim$2.58 nm (140°C)) were found at a higher reaction temperature (figures 3(b)–(d)), suggesting that an elevated temperature may bring more DS$^-$ anions from the crystal edge to the center (figure 5). However, the large basal spacing increases to $\sim$3.51 nm with a further temperature increase up to 160°C, due to more external DS$^-$ anions intercalating into the interlayer gallery, especially at the edge (figure 3(e)). Another 20°C increase (up to 180°C) induces a larger basal spacing both for the crystal
center (~2.56 nm) and the crystal edge (~3.72 nm) (figures 3(f) and 5). Although the crystal edge is assumed to exhibit a larger basal spacing than the crystal center, there is a transition zone between the edge and the center, thus showing varied basal spacings in the intervent part (figure 5). This is the main reason for the broadened (00l) reflections, as shown in figures 3 and 6.

The arrangements of DS$^-$ in the interlayer of LRH are also significantly affected by the DS$^-$ concentration. Figure 6 shows XRD patterns of LRH and LRH-DS obtained by the hydrothermal anion exchange procedure at 180 °C for 24 h with various DS$^-$ concentrations. A larger basal spacing both for the crystal edge (~3.57 nm (three-fold), ~3.69 nm (five-fold), and ~3.72 nm (ten-fold)) and for the crystal center (~2.46 nm (three-fold), ~2.52 nm (five-fold), and ~2.56 nm (ten-fold)) were found at a higher DS$^-$ concentration (figures 6(b)–(d)), indicating that an enhanced DS$^-$ concentration induces more DS$^-$ anions intercalating into the interlayer gallery (figure 5). However, it may be easier for NO$_3^-$ to exchange with the DS$^-$ anion at the edge of the LRH crystal than in the crystal center, thus various basal spacings are postulated to exist in LRH-DS (figures 3 and 6).

Figure 7 shows FTIR spectra for LRH (figure 7(a)) and LRH-DS (figures 7(b)–(f)) obtained by the anion exchange procedure at various DS$^-$ concentrations. Similar to figure 4, a complete replacement of nitrate anion by the DS$^-$ units in the gallery of LRH have taken place at three- to ten-fold molar excess of DS$^-$ anion. A highly oriented oxide film with enhanced PL properties derived from ultra-large unilamellar nanosheets

Depositing 0.5 ml of colloidal nanosheet suspension (sample in figure 2) on a quartz substrate followed by spin-coating processing resulted in highly c-axis oriented films via self-assembly of the nanosheets (figure 8(a)). As there are DS$^-$ anions, formamide molecules and positively charged nanosheets in the colloidal suspension, the units would be self-assembled into new layered materials similar to LRH during the process of depositing and spin coating, thus exhibiting obvious (00l) reflections in figure 8(a). FE-SEM observations (figure 9(a)) confirm that the film has a flat surface and a microstructure significantly denser than the LRH films as constructed in the literature previously [19, 20]. Calcining the LRH films at 600 °C for 4 h yielded cubic-structured (Y$_{0.95}$Eu$_{0.05}$)$_2$O$_3$ films (figure 8(b)). Because the projection in the [001] direction for the LRH crystal and in the [111] direction for the cubic oxide crystal present close similarities in terms of rare-earth atomic configuration, the phase transformation is a quasitopotactic one [20]. Thus, the oxide film shows strong (222) and very weak non-(222) reflections, indicating that it is highly oriented, with [111] direction of the (Y$_{0.95}$Eu$_{0.05}$)$_2$O$_3$ structure perpendicular to the substrate surface. The oxide film annealed at 600 °C retained the original features of the LRH films well, though the surface turned a little rougher due to the disappearance of the gel structure and the shrinkage of the nanosheets by heating (figure 9(b)). The oxide film is semi-transparent (inset in figure 9(b)), and the thickness was estimated to be up to ~90 nm from the FE-SEM cross-sectional view (figure 9(b), right inset).
Unilamellar nanosheets with a lateral size of $\geq 60 \mu m$ and a thickness of $\sim 1.6 \text{ nm}$ can be obtained by efficient delamination of LRH intercalated with DS$^-$ ($\text{C}_{12}\text{H}_{25}\text{SO}_4^{-}$) in formamide. The exfoliated nanosheets are unilamellar and are of a single crystalline character.

A transparent ($Y_{0.95}\text{Eu}_{0.05})_2\text{O}_3$ phosphor film with a uniform [111] orientation and a layer thickness of $\sim 90 \text{ nm}$ was constructed with ultra-large nanosheets as building blocks by spin-coating followed by proper annealing. Owing to the [111] crystallographic orientation, the oriented oxide film exhibits a stronger red emission at 614 nm (the $^5\text{D}_0-^7\text{F}_2$ transition of Eu$^{3+}$), with an intensity $\sim 2$ times that of the powder form.

Acknowledgments

This work was supported in part by the National Natural Science Foundation of China (grants 51172038 and 50990303), the Special Fund for Basic Research in Central Universities (grants N110802001 and N120302001), the China Postdoctoral Science Foundation (grants 2012M520027 and 2013T60291), the Specialized Research Fund for the Doctoral Program of Higher Education (grant 20120421200056), the Liaoning Province Doctor Startup Fund (grant 20131035), and the Northeastern University Postdoctoral Science Foundation.

References


Figure 10. A comparison of the PLE/PL spectra of the powder and film forms. All the samples are annealed at 600 °C for 4 h, and the measurements are performed under identical conditions.

A concentration difference exists among different crystal planes. The (222) facet is a close-packed one and thus the occupancy of $Y^{3+}$ on (222) would be higher than that on other facets. As the Eu$^{3+}$ activators randomly replace $Y^{3+}$, it can be said that more Eu$^{3+}$ activators reside on (222) [30], thus resulting in a significantly enhanced red emission. Unlike the random distribution of nanoplates in our previous work [30], the two-dimensional large plates induce an exposure of the (222) facets to some extent even in the powder form, and thus the luminescence enhancement observed in this work is smaller than that reported previously [30].

4. Conclusions

In the present work, ($Y_{0.95}\text{Eu}_{0.05})_2\text{O}_3$-$n\text{H}_2\text{O}$ LRH crystals with a lateral size of $\sim 300 \mu m$ and a thickness of $\sim 9 \mu m$ have been synthesized by autoclaving (200 °C, 24 h) mixed solutions of the component nitrates in the presence of mineralizer $\text{NH}_4\text{NO}_3$, then efficiently delaminated into unilamellar nanosheets by hydrothermal anion exchange. Delaminated characterizations of the products by combined techniques of XRD, FTIR, FE-SEM, TEM, SAED, AFM and PLE/PL have yielded the following main conclusions:

1. LRH can undergo intercalation and anion exchange with DS$^-$ ($\text{C}_{12}\text{H}_{25}\text{SO}_4^{-}$), and hydrothermal processing not only significantly shortens the anion exchange time from 720 to 24 h, but also increases the basal spacing, compared with the traditional anion exchange at room temperature. The arrangements of DS$^-$ in the interlayer of LRH are significantly affected by DS$^-$ concentration and reaction temperature, and various basal spacings are postulated to exist in the crystal edges and center in the LRH-DS samples. An enhanced DS$^-$ concentration and an elevated reaction temperature can both induce the intercalation of more DS$^-$ anions into the interlayer gallery, thus yielding a greater basal spacing.

2. Unilamellar nanosheets with a lateral size of $\geq 60 \mu m$ and a thickness of $\sim 1.6 \text{ nm}$ can be obtained by efficient delamination of LRH intercalated with DS$^-$ ($\text{C}_{12}\text{H}_{25}\text{SO}_4^{-}$) in formamide. The exfoliated nanosheets are unilamellar and are of a single crystalline character.

3. A transparent ($Y_{0.95}\text{Eu}_{0.05})_2\text{O}_3$ phosphor film with a uniform [111] orientation and a layer thickness of $\sim 90 \text{ nm}$ was constructed with ultra-large nanosheets as building blocks by spin-coating followed by proper annealing. Owing to the [111] crystallographic orientation, the oriented oxide film exhibits a stronger red emission at 614 nm (the $^5\text{D}_0-^7\text{F}_2$ transition of Eu$^{3+}$), with an intensity $\sim 2$ times that of the powder form.
[34] Chu N K, Sun Y H, Zhao Y S, Li X, Sun G B, Ma S L and Yang X J 2012 Dalton Trans. 41 7409