

Structure and luminescence investigations on the chromophore intercalated layered rare-earth hydroxides hybrids



Qingyang Gu*, Xia Liu, Yingxi Hu, Lifang Zhang, Yanyun Li

Department of Chemical Engineering, Beijing Institute of Petrochemical Technology, Beijing 102617, China

ARTICLE INFO

Article history:

Received 29 September 2016

Received in revised form 12 December 2016

Accepted 16 December 2016

Available online 16 December 2016

Keywords:

Layered rare-earth hydroxides

Intercalation

Composite

Niflumic acid

Luminescence

White emission

ABSTRACT

Niflumic acid (NFC) and surfactant 1-octane sulfonic acid sodium (OS) are intercalated into the gallery of NO₃ type layered europium hydroxide (NO₃-LEuH) by ion-exchange method. The prepared products display XRD patterns with series of diffractions attributing to layered materials. The composites correspond to a bilayered vertical arrangement. The thermal stability of the composites are enhanced after intercalation. Tunable luminescence of the composites is realized through the synergistic effect of layered europium hydroxide (LEuH) layer and NFC with different states and different excitation wavelength. Facile one-pot delamination of the composites achieves when dispersed in formamide (FM), which contributes to a white emission. This work may be beneficial to the fabrication of multifunctional chromophore intercalated layered rare-earth hydroxides (LRHs) hybrids, which may have wide applications in white emission materials.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Recently, multicolor luminescent materials, especially those with white emissions, have attracted increasing attention because of the potential applications in various important devices such as color-tunable phosphors [1], white-light-emitting devices [2], and multicolor light-emitting diodes (LEDs) [3]. However, considering the drawback of organic luminescent solid materials is liable to aggregate and has bad light & heat stability, one of the promising components in the design of multicolor materials are the combination of organic chromophores and the inorganic layered materials. Introducing the multifunctional organic chromophores into the inorganic layered materials, which may enhance the light&heat stability of the organics and the synergistic effect between the layers and interlayers may contribute to novel luminescence properties.

Inorganic layered structures are a large class of functional organizations, characterized by tunable interlayer volume and variable interlayer guests. Layered double hydroxides (LDHs) are one type of anionic inorganic layered materials exhibiting a large versatility *via* tunable composition and gallery space, showing various applications in catalysts [4], two-dimensional nano-reactors [5,6] and adsorbents [7–9]. Considerable attention has been focused on the fabrication of organic chromophore anions

intercalated LDHs. LDHs-chromophore hybrids present functionality such as enhanced photostabilization in comparison with individual components [10]. Much work involving fluorescence molecules intercalated LDHs have been reported [11–15].

Layered rare-earth hydroxides (LRHs), one new intriguing family of layered materials structurally similar to LDHs, with general formula of [RE(OH)_{2.5}·xH₂O]·[Aⁿ⁻]_{0.5/n} (RE = rare-earth ions, A = anions), have attracted increasing attention, due to the excellent property arising from lanthanide elements. The combination of the rare-earth elements and interlayer chemistry endows intercalated materials with wide applications [16–18]. However, there are few studies about the white emission materials based on chromophore intercalated LRHs hybrids.

Niflumic acid (NFC) is a well-known pharmaceutical compound, which has been used widely in the biological and medical chemistry field [19]. It is primarily used to treat different forms of rheumatism and relieve other inflammatory states. In addition, the luminescence property of NFC is worthy of attention in consideration of that the NFC shows strong luminescence in solid state but weak emission in solution. This phenomenon can be ascribed to the molecular stacking in the solid state restricting free rotation of NFC and thus increasing the conjugated degree and coplanarity of the NFC. Yan et al. [20] have intercalated the NFC into LDHs and investigated the mechano-responsive luminescence property. However, there has been a lack of studies focusing on the tunable luminescence for NFC in liquid state, which restricts its application as color display materials.

* Corresponding author.

E-mail address: guqingyang@bipt.edu.cn (Q. Gu).

Herein we prepare layered europium hydroxide (LEuH) composites co-intercalated with NFC and an anion surfactant 1-octane sulfonic acid sodium (OS). Tunable luminescence of the composites is realized through the synergistic effect of LEuH layer and NFC with different states (electrostatic interaction between LEuH layers and anionic NFC, hydrogen bonding between NFC and FM (formamide), as well as energy transfer of Eu^{3+} and NFC). Facile one-pot delamination of the composites achieves when dispersed in FM, which contributes to a white emission.

2. Experimental section

2.1. Preparation of NO_3^- -LEuH precursor

The NO_3^- type LEuH (NO_3^- -LEuH) was synthesized via hydrothermal method as previously reported [21,22]. An aqueous solution containing $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (1 mmol), hexamethylenetetramine (HMT, 1 mmol), NaNO_3 (13 mmol), in deionized water (80 mL) was heated at 90°C for 12 h in a Teflon-autoclave. After the reaction, the product was filtered, washed, and vacuum-dried (40°C for 24 h), obtaining the NO_3^- -LEuH precipitate.

2.2. Intercalation of NFC into LEuH by ion exchange method

The ion-exchange reactions between NO_3^- and the organic anions were processed at 70°C in a Teflon-autoclave. Firstly, the equimolar NFC and NaOH were added to 80 mL deionized water to obtain the mixed solutions. The NO_3^- -LEuH powder (~ 0.1 g) was dispersed into the above solutions, then reacted at 70°C for 24 h in a Teflon-autoclave. The resulting precipitates were collected by filtration, washed with deionized water, and dried at 40°C for 24 h.

For the OS co-intercalated composites, the molar ratio of OS and NFC were 1:1, 1:2, and 1:3, respectively. The as-prepared composites are noted as $1/x\text{OS-NFC-LEuH}$, in which $1/x$ is the molar ratio of OS to NFC, for example $1/2\text{OS-NFC-LEuH}$ represents the molar ratio of OS to NFC is 1:2.

2.3. Characterization techniques

The powder X-ray diffraction (XRD) patterns were collected by using a Phillips X'pert Pro MPD diffractometer with $\text{Cu-K}\alpha$ radiation at room temperature, with a step size of 0.0167° , scan time of 15 s per step, and 2θ ranging from 4.5 to 70° . The generator setting was 40 kV and 40 mA. For the small degrees, the XRD patterns were measured at room temperature with step size of 0.008° , scan time of 30 s per step. Fourier transformed infrared (FT-IR) spectra of the samples were recorded on a Nicolet-360 Fourier-Transform infrared spectrometer by the KBr method. Scanning electron microscope (SEM) observations were carried out by using a Hitachi S-4800 microscope at 5.0 kV. Thermo-gravimetric and differential thermal analysis (TG-DTA)

measurements were performed with a ZRY-2P thermal analyzer in air atmosphere. Luminescence spectra were obtained on Hitachi F-4500 spectrofluorimeter.

The metal ion contents were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Jarrel-ASH, ICAP-9000) after the solid products were dissolved in a 0.1 M HNO_3 . C, H and N contents were determined by using an Elementar vario EL elemental analyzer. The chemical formula of the products (Table 1) were determined based on the results of ICP and CHN analyses.

3. Results and discussion

3.1. Structure of LEuH precursor and composites

Based on ICP, CHN analyses and charge balance considerations, the estimated compositions of the LEuH precursor and the as-prepared composites are shown in Table 1. The presence of CO_3^{2-} may arise from HMT decomposition [23,24]. This results are in agreement with the XRD patterns.

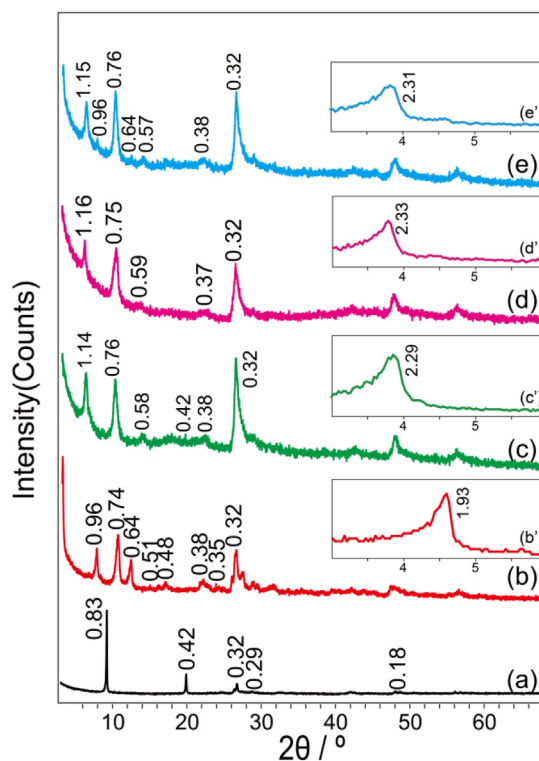


Fig. 1. XRD patterns of NO_3^- -LEuH precursor (a) and composites of NFC-LEuH (b,b'), OS-NFC-LEuH (c,c'), $1/2\text{OS-NFC-LEuH}$ (d,d'), $1/3\text{OS-NFC-LEuH}$ (e,e').

Table 1
Chemical compositions for LEuH precursor and the composites.

| Samples | Chemical formula | Wt%, Found | | | |
|-------------------------|---|------------|-------|------|------|
| | | Eu | C | H | N |
| NO_3^- -LEuH | $\text{Eu}(\text{OH})_{2.48}(\text{NO}_3)_{0.34}(\text{CO}_3)_{0.09} \cdot 0.69\text{H}_2\text{O}$ | 64.14 | 0.25 | 1.63 | 2.01 |
| NFC-LEuH | $\text{Eu}(\text{OH})_{2.48}(\text{C}_{13}\text{H}_8\text{F}_3\text{N}_2\text{O}_2)_{0.35}(\text{CO}_3)_{0.085} \cdot 1.48\text{H}_2\text{O}$ | 39.09 | 14.96 | 2.12 | 2.51 |
| OS-NFC-LEuH | $\text{Eu}(\text{OH})_{2.48}(\text{C}_{13}\text{H}_8\text{F}_3\text{N}_2\text{O}_2)_{0.23}(\text{C}_{13}\text{H}_9\text{F}_3\text{N}_2\text{O}_2)_{0.04}(\text{C}_8\text{H}_{17}\text{O}_3\text{S})_{0.29}(\text{CO}_3)_{0.012} \cdot 1.54\text{H}_2\text{O}$ | 37.05 | 17.28 | 3.11 | 1.58 |
| $1/2\text{OS-NFC-LEuH}$ | $\text{Eu}(\text{OH})_{2.48}(\text{C}_{13}\text{H}_8\text{F}_3\text{N}_2\text{O}_2)_{0.22}(\text{C}_8\text{H}_{17}\text{O}_3\text{S})_{0.27}(\text{CO}_3)_{0.012} \cdot 1.54\text{H}_2\text{O}$ | 38.84 | 16.87 | 2.93 | 1.94 |
| $1/3\text{OS-NFC-LEuH}$ | $\text{Eu}(\text{OH})_{2.48}(\text{C}_{13}\text{H}_8\text{F}_3\text{N}_2\text{O}_2)_{0.27}(\text{C}_8\text{H}_{17}\text{O}_3\text{S})_{0.25} \cdot 1.30\text{H}_2\text{O}$ | 37.74 | 15.13 | 2.74 | 1.54 |

Download English Version:

<https://daneshyari.com/en/article/4754140>

Download Persian Version:

<https://daneshyari.com/article/4754140>

[Daneshyari.com](https://daneshyari.com)