

Preparation and luminescence of europium-doped lanthanum fluoride–benzoic acid hybrid nanostructures



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ABSTRACT

Europium-doped lanthanum fluoride (LaF₃:Eu³⁺) nanoparticles were synthesized using a solvothermal method, and they were then capped with benzoic acid (BA) ligands to form LaF₃:Eu³⁺-BA hybrid nanostructures. The LaF₃:Eu³⁺-BA hybrid nanostructures showed strong luminescence as a result of energy transfer from BA to the Eu³⁺ ions of the LaF₃:Eu³⁺ nanoparticles. The dominant excitation band for the LaF₃:Eu³⁺-BA hybrid nanostructures ranged from 200 nm to 300 nm. It has been shown that the luminescence of LaF₃:Eu³⁺-BA hybrid nanostructures strongly depends on the pH value and content of benzoic acid used in the preparation of the hybrid nanostructures. An X-ray diffraction technique, transmission electron microscopy, luminescence spectroscopy, Fourier transform infrared spectroscopy and a UV–vis spectrophotometer were used to characterize the products.

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1. Introduction

In recent years, lanthanide (Ln) doped inorganic nanoparticles have attracted considerable attention due to their high photo-stability and strong luminescence [1–3]. They have broad applications in lamps and display devices [4], components in optical telecommunication [5], light emitting diodes (LEDs) [6], novel optoelectronic devices [7], biological labels [8] and many others. One of the most interesting Ln-doped inorganic nanomaterials is the fluoride-based nanoparticles, such as the Ln-doped NaYF₄ and LaF₃ nanoparticles [8–10].

Much research has been devoted to luminescence enhancement of the Ln-doped fluoride nanoparticles. Enhanced luminescence has been realized by co-doping two different Ln ions in fluoride nanoparticles, such as Yb³⁺,Er³⁺ co-doped LaF₃ [11], Eu³⁺,Yb³⁺ co-doped LaOF [12], Eu³⁺/Tb³⁺ and Yb³⁺/Er³⁺ co-doped β-NaYF₄ [13–15], etc. A core-shell

nanostructure has also been employed to enhance luminescence intensity of the Ln-doped fluoride nanoparticles [16,17].

In recent years, much attention has been paid to the strong luminescence enhancement for inorganic–organic hybrid nanostructures. It has been shown that luminescence emission of Eu³⁺ ions can be effectively sensitized by some organic ligands [1,18–21], such as β-diketonate, aromatic acids, and others. Strong luminescence has been observed [18] in the Eu³⁺-doped LaF₃ (LaF₃:Eu³⁺) nanoparticles capped with thenoyltrifluoroacetone (TTA) ligands. LaF₃:Eu³⁺ and LaF₃:Tb³⁺ nanoparticles coated with benzoic acid and phthalic acid have also been reported to show strong luminescence [1]. In this luminescence sensitization process, the organic ligand with a strong optical absorption capability is first excited by the excitation wavelength, and then the absorbed energy is transferred to the associated Eu³⁺ ions which results in efficient emission via the Eu³⁺ ions.

Up till now, little research has been done to investigate how preparation conditions and content of organic ligands influence luminescence of LaF₃:Eu³⁺-based hybrid nanostructures. In this paper, we first synthesized LaF₃:Eu³⁺ nanoparticles using a solvothermal method [22].

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The advantage of the solvothermal method is that it is relatively easier to prepare dispersible, size-controlled and well-crystallized nanoparticles. The synthesized $\text{LaF}_3:\text{Eu}^{3+}$ nanoparticles were then capped with BA to form the $\text{LaF}_3:\text{Eu}^{3+}$ -BA inorganic-organic hybrid nanostructures. Effect of pH value and BA content on luminescence of the $\text{LaF}_3:\text{Eu}^{3+}$ -BA hybrid nanostructures was systematically investigated.

2. Experimental

2.1. Experimental reagents

Ammonium fluoride (NH_4F), lanthanum nitrate ($\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) and europium nitrate ($\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) with a purity of 99.99 % were used for the synthesis of $\text{LaF}_3:\text{Eu}^{3+}$ nanoparticles. Ammonia ($\text{NH}_3 \cdot \text{H}_2\text{O}$, 25–28 wt %) and nitrate (HNO_3) were used to adjust the pH value. Benzoic acid was used as a sensitizing agent. Absolute ethanol ($\text{C}_2\text{H}_5\text{OH}$) and ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$) were used as solvents. All reagents were of analytical grade, and used without further purification.

2.2. Synthesis procedure

2.2.1. Synthesis of $\text{LaF}_3:\text{Eu}^{3+}$ nanoparticles

$\text{LaF}_3:\text{Eu}^{3+}$ nanoparticles were synthesized following a modified literature procedure [23]. 1 mmol $\text{Ln}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Ln^{3+} : 95 mol% La^{3+} , 5 mol% Eu^{3+}) aqueous solution was dropped into the mixture of ethanol (20 ml) and ethylene glycol (10 ml) under stirring, then 3 mmol NH_4F aqueous solution was added into the solution and stirred for 10 min. Subsequently, the mixture was transferred to a 50 ml Teflon-lined autoclave and heated at 180 °C for 6 h to synthesize $\text{LaF}_3:\text{Eu}^{3+}$ nanoparticles. After completion of the reaction, the autoclave was allowed to cool down to room temperature. The $\text{LaF}_3:\text{Eu}^{3+}$ nanoparticles were separated by centrifugation (4000 rpm, 10 min) and washed subsequently with ethanol and water for three times. At last, they were dried in an oven at 80 °C for 8 h.

2.2.2. Adsorption of benzoic acid

1 mmol $\text{LaF}_3:\text{Eu}^{3+}$ nanoparticles were dissolved in 10 ml DI-water under ultrasound for 10 min, and then added into 10 ml ethanol with benzoic acid under stirring. After the mixture formed homogeneous suspension, the pH value was adjusted by a precision pH meter (S220-B, Mettler Toledo), and the mixture was stirred for 1 h. After the solution left for overnight, the $\text{LaF}_3:\text{Eu}^{3+}$ nanoparticles were decorated by benzoic acid ligands to form the $\text{LaF}_3:\text{Eu}^{3+}$ -BA hybrid nanostructures. After being separated by high speed centrifugation and washed with ethanol and water, the $\text{LaF}_3:\text{Eu}^{3+}$ -BA hybrid nanostructures were dried in the oven at 80 °C for 8 h.

2.3. Material characterization

The X-ray diffraction (XRD) pattern of the samples was measured by a Bruker D8 Focus diffractometer using nickel-filtered $\text{Cu K}\alpha$ radiation ($\lambda = 1.4518 \text{ \AA}$). Microstructural characteristics were investigated using a transmission electron

microscope (TEM, JEOL-2010). Luminescence excitation and emission spectra of all samples were recorded on a Hitachi F-4600 luminescence spectrophotometer, and the spectra were measured on pellets of pressed powder. Fourier transform infrared (FTIR) spectra were scanned by a Nicolet 380 Fourier transform infrared spectroscopy. The absorption spectra were measured on a UV-vis spectrophotometer. All measurements were conducted in air at room temperature.

3. Results and discussion

3.1. Crystal structures and microstructures

Fig. 1 shows the XRD patterns of the $\text{LaF}_3:\text{Eu}^{3+}$ nanoparticles, $\text{LaF}_3:\text{Eu}^{3+}$ -BA hybrid nanostructures, and the standard card of LaF_3 . The diffractive peak positions are in good accordance with the JCPDS 32-0483 of LaF_3 , which indicates that the as-prepared $\text{LaF}_3:\text{Eu}^{3+}$ nanoparticles were of a hexagonal crystal structure. It can be seen in Fig. 1 that BA ligand has little effect on the XRD pattern except for a slight broadening of the diffraction peaks, which should be due to the interaction between $\text{LaF}_3:\text{Eu}^{3+}$ and BA ligands. This confirms that the $\text{LaF}_3:\text{Eu}^{3+}$ nanoparticles are chemically stable in the BA-water/ethanol solution and that the soaking method does not diminish the quality of the $\text{LaF}_3:\text{Eu}^{3+}$ nanoparticles. TEM and HRTEM images of $\text{LaF}_3:\text{Eu}^{3+}$ are shown in Fig. 2. The $\text{LaF}_3:\text{Eu}^{3+}$ nanoparticles have excellent dispersibility and a uniform particle size of about 15 nm (Fig. 2b).

FTIR has been used to confirm that BA coordinates with $\text{LaF}_3:\text{Eu}^{3+}$ nanoparticles to form $\text{LaF}_3:\text{Eu}^{3+}$ -BA hybrid nanostructures. Fig. 3 shows the FTIR spectra of BA, $\text{LaF}_3:\text{Eu}^{3+}$ nanoparticles and $\text{LaF}_3:\text{Eu}^{3+}$ -BA hybrid nanostructures. The broad band at 3449 cm^{-1} characterizing mode is attributed to the surface O-H stretching vibration of nanoparticle, and it is relatively weakened by BA. The absorption peak at 1428 cm^{-1} can be assigned to symmetric stretching vibration of the carboxyl group [24]. The absorption peak at 706 cm^{-1} is from the out-of-plane

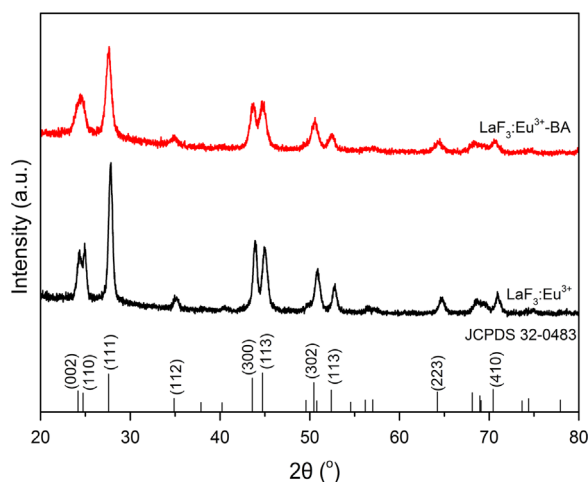


Fig. 1. XRD patterns of the $\text{LaF}_3:\text{Eu}^{3+}$ nanoparticles and the $\text{LaF}_3:\text{Eu}^{3+}$ -BA hybrid nanostructures.

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