Investigation on the preparation and luminescence emission of $\text{LaF}_3\text{:Eu}^{3+}@\text{LaF}_3/\text{SiO}_2$ core-shell nanostructure

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Abstract $\text{LaF}_3\text{:Eu}^{3+}$, $\text{LaF}_3\text{:Eu}^{3+}@\text{LaF}_3$, $\text{LaF}_3\text{:Eu}^{3+}@\text{CeF}_3$ and $\text{LaF}_3\text{:Eu}^{3+}@\text{SiO}_2$ nanoparticles were successfully synthesized via hydrothermal route and modified Stöber method. The surface property of $\text{LaF}_3\text{:Eu}^{3+}$ particle was successfully modified by coating LaF_3 and SiO_2 shell onto the particle, which resulted in the change of the surface property and luminescence emission of $\text{LaF}_3\text{:Eu}^{3+}$. It was found that the surface quenchers were decreased and thus the nonradiative pathways were reduced with core/shell structure, which not only enhanced the yellow emission of the sample, but also changed the intensity ratio of the yellow to orange emission. The dependence of the shell property and shell thickness on the luminescence emission spectra were investigated systematically. The current investigation can provide useful information for developing applications in biological imaging, detection, and sensing and other aspects.

Keywords core/shell nanostructure, photoluminescence, $\text{LaF}_3\text{:Eu}^{3+}@\text{LaF}_3$, $\text{LaF}_3\text{:Eu}^{3+}@\text{SiO}_2$.

1. Introduction

In comparison with luminescent organic dyes and quantum dots, lanthanide-doped luminescent nanoparticles (NPs) exhibit superior fluorescent and chemical properties, such as large (anti)Stokes shift, long excited state lifetime, and narrow luminescence bandwidth^[1,2,3], multicolor emission, high resistance to photobleaching and low long-term toxicity, which makes them highly suitable as alternatives to organic dyes and quantum dots in various biological fields^[4]. To improve the luminescence emission efficiency and spectral property, core shell structure has been regarded as an effective strategy by growing a suitable inorganic shell onto the luminescent particle. Many passivating inorganic shells, such as LaF_3 , LaPO_4 , and NaYF_4 have been used for improving the fluorescence of lanthanide-doped materials^[5].

Core/shell nanostructures are hybrid materials that are multifunctional and can simultaneously reveal the properties of the core and the shell^[6], the structure can help to improve the luminous efficiency, spectral property, and chemical and mechanical stability, etc. According to coating materials, the shell can be roughly divided into two categories, which are heterogeneous one (such as SiO_2 in current study) and homogeneous one (such as LaF_3 in current study). In general, heterogeneous shell is applied to rare earth doped fluorescent nanoparticle that is mainly to improve the water-solubility, chemical stability and dispersibility of the luminescence particle. Meanwhile, it can also help the surface of the particle get

necessary functional groups. It is well known that LaF_3 has a very low phonon energy and therefore can minimize the quenching of the excited-state lanthanide ions and thus has a high quantum yield^[7]. Since silica is highly biocompatible and its surface chemistry is well documented for biological interactions^[8], silica-coated luminescent $\text{LaF}_3:\text{Eu}^{3+}$ nanoparticles have a number of advantages over conventional biolabels as a probe in bioapplications. Comparing with heterogeneous shell, the cladding homogeneous shell is mainly applied to repair surface defects, reduce the energy transfer and possible quenching effect. Core/shell structures of $\text{LaF}_3:\text{Ln}^{3+}@\text{SiO}_2$ ^[8,9,10], $\text{CeF}_3:\text{Tb}^{3+}@\text{LaF}_3$ ^[4,11,12], $\text{CePO}_4:\text{Tb}^{3+}@\text{LaPO}_4$ ^[13], $\text{LaF}_3@\text{LaF}_3$ ^[5,7,14,15], $\text{NaYF}_4@\text{NaYF}_4$ ^[16,17] and their potential applications have been reported, but the investigation on the systematic comparison of heterogeneous and homogeneous shell is barely reported for rare earth doped luminescent nanomaterials.

Hydrothermal synthesis is considered as one of the useful and powerful pathways to prepare novel nanostructures, which can provide a very promising technique than conventional methods in terms of cost and potential development for large-scale production. In this paper, $\text{LaF}_3:\text{Eu}^{3+}$, $\text{LaF}_3:\text{Eu}^{3+}@\text{CeF}_3$ and $\text{LaF}_3:\text{Eu}^{3+}@\text{LaF}_3$ nanoparticles were prepared via hydrothermal method, and $\text{LaF}@\text{SiO}_2$ NPs were obtained by modified Stöber method. The thickness of the shell was controlled by adjusting the reaction time and precursor concentration. The luminescence property of the core/shell structures were investigated with laser spectroscopic technique.

2. Experimental

2.1. Materials

Chemicals for sample preparation were purchased from professional companies and used as received. Eu_2O_3 (99.9%) was purchased from Sigma-Aldrich Chemicals Co. NH_4F , $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and TEOS was supplied by Sinopharm Chemical Reagent Co., Ltd. (China). $\text{Eu}(\text{NO}_3)_3$ was obtained by dissolving the corresponding oxide in dilute nitric acid at elevated temperature and followed by evaporating the superfluous nitric acid. Deionized water ($>18 \text{ M}\Omega\text{cm}^{-1}$) was used throughout the experiments for all aqueous solution.

2.2. Synthesis of luminescent $\text{LaF}_3:\text{Eu}^{3+}$ core particles

Eu^{3+} doped LaF_3 NPs were synthesized through hydrothermal method by using trisodium citrate as a capping agent. Typically, 0.98 mmol of $\text{La}(\text{NO}_3)_3$ and 0.02 mmol of $\text{Eu}(\text{NO}_3)_3$ ($\text{La}^{3+}:\text{Eu}^{3+}=98:2$) were added into 30 ml of aqueous solution containing 1.0 mmol of trisodium citrate. After vigorous stirring for 30 min, 3 mmol of NH_4F was introduced into the above solution. The mixed solution then was transferred into a Teflon bottle that was held in a stainless steel autoclave and maintained at 200 °C for 24 hours. As the autoclave was cooled to room temperature naturally, the precipitates were purified by centrifugation, washed with deionized water and ethanol in sequence, and then dried in air at 75 °C for 12 hours.

2.3. Synthesis of heterogeneous core/shell $\text{LaF}_3:\text{Eu}^{3+}@\text{SiO}_2$ nanostructure

Dispersing 70 mg of as-obtained $\text{LaF}_3:\text{Eu}^{3+}$ NPs into 100 mL ethanol and sonicate the solution at room temperature for 30 min, we then added 2 mL of ammonia solution and 9 ml deionized

water to the mixture, and followed by dropwise adding TEOS under continuous stirring. 10 μL , 25 μL , and 200 μL of TEOS were used to obtain 5 nm, 10 nm, and 25 nm silica shell on the prepared $\text{LaF}_3\text{:Eu}^{3+}$ nanoparticles.

2.4. Synthesis of homogeneous core/shell $\text{LaF}_3\text{:Eu}^{3+}@\text{LaF}_3$ nanostructure

The prepared $\text{LaF}_3\text{:Eu}^{3+}$ precipitate was dispersed in 30 mL of distilled water by sonication treatment. Meanwhile, 1.0 mmol of $\text{La}(\text{NO}_3)_3$ was added into above aqueous solution containing 1.0 mmol of trisodium citrate under vigorous stirring for 60 min. After that, 3.0 mmol of NH_4F was introduced into the solutions. The following procedure was the same as that stated for $\text{LaF}_3\text{:Eu}^{3+}$ NPs in previous section.

2.5. Characterization

The property of the samples containing their configuration, crystal structure and content elements were characterized by using Rigaku D/Max2550 XRD with graphite at a scan rate of $4.0^\circ/\text{min}$ and graphite monochromatic Cu K α radiation ($\lambda=0.15406\text{ nm}$), transmission electron microscope (TEM, JEOL 2100) and scanning electron microscope (SEM, Nova NanoSEM450). The samples were dispersed on a Cu grid covered with 550-nm thick amorphous carbon film. Fourier transform infrared spectroscopy (FT-IR) was recorded on a Bruker EQUINX55 spectrometer using KBr pellets. XPS (X-ray photoelectron spectroscopy) was carried out on an Axis Ultra (Kratos Analytical Ltd) instrument with photoelectrons generated by a nonmonochromatic Al K α irradiation (1486.6 eV) source at a residual gas pressure of below 5×10^{-9} Torr. The binding energies were referenced to the C 1s line at 284.8 eV from adventitious carbon.

2.6. Spectroscopic measurements

During the fluorescence spectroscopic measurements, all of the samples were excited by 355 nm pulsed laser (Nd^{3+} :YAG, Quanta Ray Lab-170). The pulse width of the laser is 2 ns and the repetition rate is 10 Hz. An SP 2750i monochromator (ACTON) equipped with a PIXIS 100 charge coupled device (CCD, ACTON) and a PD471 photomultiplier tube (PMT, ACTON) were used for fluorescence collection and detection. All of the measurements were conducted at room temperature.

3. Results and Discussion

3.1 XRD analysis

The crystallinity, crystal phase and composition of the as-prepared samples were investigated by XRD measurement. Fig. 1 shows the XRD pattern of $\text{LaF}_3\text{:Eu}^{3+}$ NPs, $\text{LaF}_3\text{:Eu}^{3+}@\text{LaF}_3$ NPs, $\text{LaF}_3\text{:Eu}^{3+}@\text{CeF}_3$ NPs and $\text{LaF}_3\text{:Eu}^{3+}@\text{SiO}_2$ NPs powder samples. All of the strong and sharp diffraction peaks are indexed to pure hexagonal phase (ICDS No. 32-0483). After coating with the silica layer, the diffraction pattern of the resulting material shows a reflection characteristic of amorphous SiO_2 in addition to the diffraction peaks of $\text{LaF}_3\text{:Eu}^{3+}$. Due to the amorphous nature of SiO_2 shell, no defined peak from the silica shell is observed. Since the doped Eu^{3+} ions have a very low concentration, the XRD spectra for core/shell

$\text{LaF}_3:\text{Eu}^{3+}$, $\text{LaF}_3:\text{Eu}^{3+}@\text{LaF}_3$, $\text{LaF}_3:\text{Eu}^{3+}@\text{CeF}_3$ and $\text{LaF}_3:\text{Eu}^{3+}$ present no obvious change.

Fig. 1. XRD images of (a) $\text{LaF}_3:\text{Eu}^{3+}$ NPs, (b) $\text{LaF}_3:\text{Eu}^{3+}@\text{LaF}_3$ NPs, (c) $\text{LaF}_3:\text{Eu}^{3+}@\text{CeF}_3$ NPs and (d) $\text{LaF}_3:\text{Eu}^{3+}@\text{SiO}_2$ NPs powder samples.

3.2 SEM & TEM observation

The morphology and structure of samples were investigated by SEM and TEM observations. A typical SEM image of the $\text{LaF}_3:\text{Eu}^{3+}$ and $\text{LaF}_3:\text{Eu}^{3+}@10.0\text{ nm LaF}_3$ NCs nanostructures are shown in Fig.2(A,B). The average diameter of $\text{LaF}_3:\text{Eu}^{3+}$ nanoplates is about 81 nm according to the histogram (Fig. 2E), the average edge length is about 42 nm and the thickness is about 38 nm. Fig. 2F indicates that the diameter of $\text{LaF}_3:\text{Eu}^{3+}@10\text{ nm LaF}_3$ is about 101 nm, the average length of the side edge is about 52 nm and the thickness of the plate is about 39 nm. $\text{LaF}_3:\text{Eu}^{3+}$ nanoparticles were then coated with a silica shell of controllable thickness by changing the reaction time and silica precursor concentration. The result of Fig.3C shows that the improved Stöber method helped us obtaining a uniform silica coating shell at $\text{LaF}_3:\text{Eu}^{3+}$ nanoparticles. According to the EDS spectrum (Fig. 2D), Si and O elements were also detected in the $\text{LaF}_3:\text{Eu}^{3+}@\text{SiO}_2$ nanocomposites in addition to peaks of the host material (Na, F) and dopant element (Eu^{3+}).

Fig 2. SEM images of $\text{LaF}_3:\text{Eu}^{3+}$ (A) and $\text{LaF}_3:\text{Eu}^{3+}@\text{LaF}_3$ (B) hexagonal nanoplates. (C): TEM image of $\text{LaF}_3:\text{Eu}^{3+}@\text{SiO}_2$ hexagonal NPs. (D): EDX spectra of $\text{LaF}_3:\text{Eu}^{3+}$ and $\text{LaF}_3:\text{Eu}^{3+}@\text{SiO}_2$ NPs. The inserts are corresponding TEM images. (E) and (F): Histogram of the corresponding diameter distribution of $\text{LaF}_3:\text{Eu}^{3+}$ and $\text{LaF}_3:\text{Eu}^{3+}@\text{LaF}_3$ NPs.

3.3 FT-IR spectra

Fig.3 shows FT-IR spectra of $\text{LaF}_3:\text{Eu}^{3+}$, $\text{LaF}_3:\text{Eu}^{3+}@\text{LaF}_3$, $\text{LaF}_3:\text{Eu}^{3+}@\text{CeF}_3$ and $\text{LaF}_3:\text{Eu}^{3+}@\text{SiO}_2$ core/shell NPs. After coating with LaF_3 and CeF_3 , all the vibrations of surface ligand keep unchanged. And the bands appeared at 3447.32 cm^{-1} and 1654.42 cm^{-1} in the spectra should be attributed to the asymmetric stretch and bend vibrational modes of water^[18]. The spectra exhibit absorption at 3447.32 cm^{-1} , which is assigned to the stretching vibration of -OH groups, appears in all the spectra. All of the spectra are similar to what has been reported

previously^[19]. For $\text{LaF}_3:\text{Eu}^{3+}@\text{SiO}_2$ NPs, a strong characteristic absorption band is presented at 1089.63 cm^{-1} , which is attributed to symmetric stretching vibration of Si-O-Si^[20]. The result proves that the $\text{LaF}_3:\text{Eu}^{3+}$ NPs are successfully coated with silica layer.

Fig 3. FT-IR spectra of the samples. (a) $\text{LaF}_3:\text{Eu}^{3+}$, (b) $\text{LaF}_3:\text{Eu}^{3+}@\text{LaF}_3$, (c) $\text{LaF}_3:\text{Eu}^{3+}@\text{CeF}_3$, (d) $\text{LaF}_3:\text{Eu}^{3+}@\text{SiO}_2$ NPs.

3.4 XPS spectra

For $\text{LaF}_3:\text{Eu}^{3+}@\text{CeF}_3$ core/shell NPs, X-ray photoelectron spectra (XPS) can help us to confirm the growth of CeF_3 shell around the $\text{LaF}_3:\text{Eu}^{3+}$ core, and thus prove the formation of $\text{LaF}_3:\text{Eu}^{3+}@\text{CeF}_3$ core/shell structure. For $\text{LaF}_3:\text{Eu}^{3+}$ NPs, the scanned spectrum indicated that the energies at $834.4\text{ eV}(3d_{5/2})$ and $851.0\text{ eV}(3d_{3/2})$ are assigned to La as presented in Fig. 4(a), but it is difficult to observe the peaks of Eu because of its low doped amount. The O 1s binding energies was observed at 532.6 eV . For $\text{LaF}_3:\text{Eu}^{3+}@\text{CeF}_3$ core/shell NPs, the energies at 881.6 and 900.7 eV in Fig. 4(b) are attributed to Ce $3d_{5/2}$ and $3d_{3/2}$ peaks, respectively. When the shell of CeF_3 is grown onto the core of $\text{LaF}_3:\text{Eu}^{3+}$ nanoplates to form the core/shell structure, the Ce $3d_{5/2}$ and $3d_{3/2}$ peaks drop dramatically in the spectrum, as shown in Fig. 4(b). The result of Fig. 4 indicates that the CeF_3 shell has successfully formed over the surface of $\text{LaF}_3:\text{Eu}^{3+}$ core. Thus the XPS measurement provides us a direct experimental evidence for $\text{LaF}_3:\text{Eu}^{3+}@\text{CeF}_3$ core/shell NPs^[12,21].

Fig 4. XPS spectra of $\text{LaF}_3:\text{Eu}^{3+}$ (a) and $\text{LaF}_3:\text{Eu}^{3+}@\text{CeF}_3$ (b) NPs. The inserts are corresponding

SEM images.

3.5 luminescence properties

The luminescence spectra of $\text{LaF}_3:\text{Eu}^{3+}@\text{SiO}_2$ heterogeneous core-shell nanostructure with different shell thickness are investigated with laser spectroscopic method. Based on the experimental observation, all the samples present characteristic patterns of $^5\text{D}_0$ to $^7\text{F}_j$ emission transitions. Luminescence emissions corresponding to the transitions of $^5\text{D}_0$ to $^7\text{F}_1$ (589 nm) and $^7\text{F}_2$ (612 and 618 nm) are shown in Fig. 5A. When the thickness of silica shell changes from 3.6 nm to 16 nm, the spectral feature of the luminescence emission keeps similar for $\text{LaF}_3:\text{Eu}^{3+}$ and $\text{LaF}_3:\text{Eu}^{3+}@\text{SiO}_2$ NPs under the same excitation condition, but the intensity changes accordingly. In comparison with $\text{LaF}_3:\text{Eu}^{3+}$ NPs, the core/shell-structured $\text{LaF}_3:\text{Eu}^{3+}@\text{SiO}_2$ enhances the yellow emission ($^5\text{D}_0$ - $^7\text{F}_1$) up to 1.29 times and decreases the orange ($^5\text{D}_0$ - $^7\text{F}_2$) emission by 0.39 times when SiO_2 shell thickness is 5.5 nm (Fig. 6b, c). The intensity ratio ($R_{Y/O}$) of yellow to orange emission increases from 1.60 to 5.98 with the increase of the shell thickness from 3.6 to 5.5 nm (Fig. 6a). For the homogeneous core/shell-structured $\text{LaF}_3:\text{Eu}^{3+}@\text{LaF}_3$ (Fig. 5B), the intensity of yellow emission from $\text{LaF}_3:\text{Eu}^{3+}@\text{LaF}_3$ NPs is increased by a factor of 1.92 times comparing with that of $\text{LaF}_3:\text{Eu}^{3+}$ NPs, while the intensity of the orange emission is decreased by a factor of 0.65. The intensity ratio $R_{Y/O}$ increases from 1.60 to 13.20 with shell thickness from 3.3 to 10.0 nm. Fig. 6b shows that the homogeneous LaF_3 shell enhances the emission intensity more effectively than heterogeneous silica shell for $\text{LaF}_3:\text{Eu}^{3+}$ core NPs. This is because that homogeneous LaF_3 shell better repairs the surface defect of the core particle since the function of the cladding homogeneous shell is mainly to repair the surface defects. In this experiment, a very suitable shell thickness of SiO_2 and LaF_3 (5.5 nm and 10.0 nm respectively) ensures luminous intensity of the samples reached its maximum, which is the most suitable distance making the luminescence ion far away from the surface quenching centers but does not affecting the radiation decay rate very much.

Fig 5. (A) Photoluminescence emission spectra of $\text{LaF}_3:\text{Eu}^{3+}$ (a), $\text{LaF}_3:\text{Eu}^{3+}@ 3.6 \text{ nm SiO}_2$ (b), $\text{LaF}_3:\text{Eu}^{3+}@ 5.5 \text{ nm SiO}_2$ (c) and $\text{LaF}_3:\text{Eu}^{3+}@ 16 \text{ nm SiO}_2$ (d) sample powders. (B) Photoluminescence emission spectra of $\text{LaF}_3:\text{Eu}^{3+}$ (a), $\text{LaF}_3:\text{Eu}^{3+}@ 3.3 \text{ nm LaF}_3$ (b), $\text{LaF}_3:\text{Eu}^{3+}@ 10.0 \text{ nm LaF}_3$ (c) and $\text{LaF}_3:\text{Eu}^{3+}@ 15.8 \text{ nm LaF}_3$ (d) sample powders.

The luminescence emission property can be influenced by many factors such as crystal structure, local symmetry, oxygen impurity, surface ligands and defects. The intensity increase

of the yellow emission could be attributed to the elimination of nonradiative centers by silica or LaF₃ shell^[22], which organically exists on the surface of the core LaF₃:Eu³⁺ NPs. In this core/shell structure, the surface quenchers are decreased, thus reducing the nonradiative pathways and suppressing the energy quenching in the energy-transfer process^[11,12].

It is well known that Eu³⁺ is often used as a probe to detect local environment in a matrix material. Observation on the intensity ratio ($R_{Y/O}$) of ⁵D₀-⁷F₁ to ⁵D₀-⁷F₂ of Eu³⁺ can reflect the property of local symmetry. Thus the change of the intensity ratio can give us the information on the local environment change of luminescence Eu ion^[23-25]. In the emission spectra of samples LaF₃:Eu³⁺@LaF₃ and LaF:Eu³⁺@SiO₂, the dominate emission corresponds to the magnetic dipole transition of ⁵D₀-⁷F₁, which suggest that the Eu³⁺ ions are located in a site with inversion symmetry^[8,26-28].

Fig 6. The intensity ratio, enhancement and attenuation factors of the samples. (a) The intensity ratios ($R_{Y/O}$) of yellow to orange emission, (b) Enhancement factors for yellow (⁵D₀-⁷F₁) emission, (c) Attenuation factors for orange emission (⁵D₀-⁷F₂) of LaF₃:Eu³⁺@LaF and LaF₃:Eu³⁺@SiO₂ core/shell structures. The corresponding samples are LaF₃:Eu³⁺@ 3.3 nm LaF₃ (R@R1), LaF₃:Eu³⁺@ 10.0 nm LaF₃ (R@R2), LaF₃:Eu³⁺@ 15.8 nm LaF₃ (R@R3) and LaF:Eu³⁺@ 3.6 nm SiO₂ (R@S1), LaF:Eu³⁺@ 5.5 nm SiO₂ (R@S2), LaF:Eu³⁺@ 16.0 nm SiO₂ (R@S3), respectively.

4. Conclusions

In summary, LaF₃:Eu³⁺, LaF₃:Eu³⁺@LaF₃, LaF₃:Eu³⁺@CeF₃ and LaF:Eu³⁺@SiO₂ has been successfully synthesized via a simple hydrothermal route and modified Stöber method. It was found that the surface quenchers were decreased and thus the nonradiative pathway was reduced with core/shell structure, which not only enhanced the yellow emission of the sample, but also changed the intensity ratio of the yellow to orange. The dependence of the shell property and shell thickness on the luminescence emission spectra indicates that a most suitable shell thickness of SiO₂ and LaF₃ are 5.5 nm and 10.0 nm for ensuring maximum luminous emission intensity of LaF₃:Eu³⁺. The current investigation can provide useful information for developing applications in biological imaging, detection, and sensing and other aspects.

Acknowledgement

This work is supported by the National Science Foundation of China (Grant no. 11174190 and 11574190).

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