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Synthesis of colloidal LaF_3: $0.04Yb^{3+}$, $0.01Er^{3+}$ nanocrystals with green upconversion luminescence

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Abstract: A synthesis of LaF_3:$0.04Yb^{3+}$,$0.01Er^{3+}$ nanocrystals with oleic acid as a capping ligand was presented. The X-Ray Diffraction (XRD) pattern indicated that the power was a single hexagonal phase. Transmission Electron Microscopy (TEM) demonstrated that the average size of the nanocrystals was less than 10 nm, with a narrow size distribution. The nanocrystals were dispersible in nonpolar solvents and form a fully transparent colloidal solution, and the solution was stable for several months without any aggregates. The Yb^{3+}-Er^{3+} codoped nanocrystal colloidal solution exhibited a bright green upconversion fluorescence under 980 nm excitation from a diode laser. The nanocrystals were potentially applicable in biolabeling and bioimaging.

Keywords: upconversion luminescence; colloidal; LaF_3:$0.04Yb^{3+}$,$0.01Er^{3+}$; nanocrystals; rare earths

In recent times, much attention has been paid to lanthanide-doped upconversion nanocrystals because of their potential applications in biological labeling[1-3]. Traditionally, organic dyes are usually used as biological fluorescence probes[4], however, the biological detection system has been recently developed based on semiconductor colloidal nanocrystals (quantum dots, QDs)[5,6] and dye-doped silica nanoparticles[7]. In addition, conjugated polymer nanoparticles as luminescence probes are also under investigation[8,9]. Compared to these fluorescence materials, upconversion nanocrystals have several advantages over those of the other fluorescent label materials. Above all, upconversion does not occur in the biological materials in nature, which avoids inherent autofluorescence[10]. Furthermore, upconversion usually occurs under infrared or near-infrared light excitation, which penetrates deep into the samples and reduces damage to cells and tissues[11].

As is known, the luminescence of lanthanide-doped upconversion phosphors is very easily quenched by high energy vibrations originating from the host materials and water molecules. Thus, fluoride materials with low phonon energy, such as, $NaYF_4$[1], LaF_3[12], and YF_3[13], are usually used as host matrices, to minimize the quenching of the excited state of rare-earth ions and increase the efficiency of upconversion luminescence. Control over particle size and dispersity is essential to recognize the upconversion nanocrystals as promising fluorescent probes. To date, great efforts have been focused on producing materials with monodispersity, small size, and high stability, for exploiting their biological applications. However, the synthesis of transparent colloidal solution based on RE doped materials has only been demonstrated in $NaYF_4$ samples[1,14,15]. On the other hand, the synthesis and control on the particle size distribution of other fluorides is also necessary to fully exploit the fluorides' peculiar properties and unique biological applications. In this article, the study is focused on the LaF_3 host. Although several articles have reported on the synthesis of water-soluble or oil-soluble LaF_3 nanoparticles[16,17], few literatures give the upconversion luminescence photographs of the transparent LaF_3:RE^{3+} colloidal solution. Here, the authors present the synthesis of LaF_3:$0.04Yb^{3+}$,$0.01Er^{3+}$ nanocrystals with oleic acid as a capping ligand. The nanocrystals are monodispersible and form a fully transparent colloidal solution, which is stable for a long time. Under 980 nm excitation from a diode laser, the solution presents a bright green upconversion fluorescence.

1 Experimental

In a typical preparation, 0.06 mmol oleic acid, 0.03 mmol

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NaOH, 10 ml ethanol, and 2 ml deionized water were mixed together under stirring. Then 1 ml 1.5 mol/L KF was added into this solution. After mixing, it was stirred for 0.5 h, after which 1 ml deionized water containing 0.475 mmol $La(NO_3)_3{\cdot}6H_2O$, 0.02 mmol $Yb(NO_3)_3{\cdot}6H_2O$ and 0.005 mmol $Er(NO_3)_3{\cdot}6H_2O$ was added under vigorous stirring. The mixture was agitated for another 30 min and then transferred into a 50 ml autoclave, sealed, and treated at 160 °C for 16 h. Subsequently, the mixture was allowed to cool to room temperature, and the nanocrystals were separated by centrifuge. The resultant was purified with ethanol and dried under vacuum.

The size and morphology of LaF_3:$0.04Yb^{3+}$,$0.01Er^{3+}$ were characterized by TEM (JEM, 2000EX 200 kV). Phase identification was performed via X-ray diffractometry (model Rigaku RU-200b), using nickel-filtered Cu Kα radiation (λ=0.15406 nm). The upconversion emission spectrum was measured with a Hitachi F-4500 fluorescence spectrometer. A 980 nm laser diode (2 W, Beijing Hi-Tech Optoelectronic Co. China) was used as the excitation source. The upconversion luminescence of the colloidal solution was acquired with a digital camera, under the same excitation source, with a 40 mg sample dispersed into 2 ml cyclohexane.

2 Results and discussion

2.1 XRD analysis

Fig.1 shows the XRD pattern of LaF_3:$0.04Yb^{3+}$,$0.01Er^{3+}$ nanocrystals, which is in good agreement with the standard values of bulk hexagonal LaF_3 (JCPDS No.82-0690). The broadening of the diffraction peaks is attributed to the small particle size. No impurity can be identified from the XRD pattern, which suggests that this synthesis is a promising method to prepare pure hexagonal phase LaF_3. In general, the nanocrystallite size can be estimated from the Scherrer equation, $D=0.941\lambda/\beta\cos\theta$, where D is the average grain size, λ is the X-ray wavelength (0.15406 nm), θ and β are the diffraction angle and full-width at half-maximum (FWHM) of an observed peak, respectively. The strongest (111) peak at 2θ=27.44° is used to calculate the crystallite size, and the result is 7.8 nm.

2.2 TEM observation

Fig.2 displays the transmission electron microscopy (TEM) image of the LaF_3:$0.04Yb^{3+}$,$0.01Er^{3+}$ nanoparticles. The TEM image shows that the mean particle size is less than 10 nm, as calculated from the XRD peaks, using the Scherrer equation. In addition, the TEM image also indicates that the particles have a sphere-like morphology. The electronic diffraction (inset in Fig.2) further indicates that the samples are well crystallized. The good dispersity of the samples in cyclohexane results from the coating of oleic acid molecules onto the surface of the nanocrystals. During the reaction process, the reaction of the rare-earth ions (Ln^{3+}) and the carboxyl of the oleic acids controls the release of Ln^{3+}. This results in the separation of nucleation and growth stages. According to the LaMer model, definite separation of nucleation and growth stages is the primary requisite for the formation of uniform particles. After the reaction, the oleic acid molecules appear on the surface with the hydrophobic alkyl chains left outside. Because of the presence of oleic acid, the nanocrystals can be dispersed in the nonpolar organic solvents and are colloidally stable for a long time, without any visible precipitation.

2.3 Upconversion emission spectrum

The room temperature upconversion spectrum of LaF_3:$0.04Yb^{3+}$,$0.01Er^{3+}$ nanocrystals is presented in Fig.3. Under 980 nm NIR excitation, four emission peaks in the visible range are assigned to $^2H_{9/2}\rightarrow{}^4I_{15/2}$ (408 nm), $^2H_{11/2}\rightarrow{}^4I_{15/2}$ (520 nm), $^4S_{3/2}\rightarrow{}^4I_{15/2}$ (541 nm), and $^4F_{9/2}\rightarrow{}^4I_{15/2}$ (651

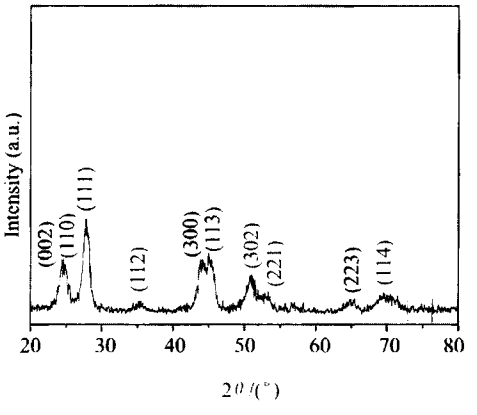

Fig.1 XRD pattern of hexagonal LaF_3:$0.04Yb^{3+}$,$0.01Er^{3+}$ nanocrystals

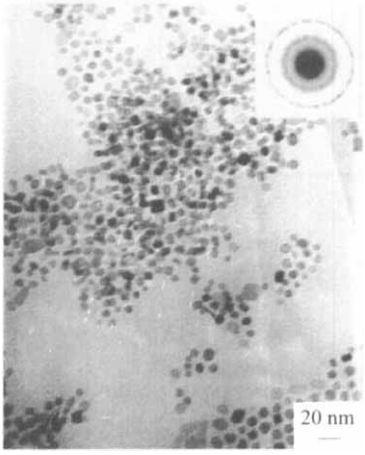

Fig.2 TEM image of LaF_3:$0.04Yb^{3+}$,$0.01Er^{3+}$ nanocrystals (Inset shows the electron diffraction pattern of LaF_3:$0.04Yb^{3+}$,$0.01Er^{3+}$)

nm) transitions of the Er^{3+} ions, respectively. Previously, the authors have conducted many researches on the mechanism of infrared-to-visible upconversion, based on Yb^{3+}-Er^{3+} codoped materials[18-20]. Fig.4 gives the schematic energy level diagrams of the green and red emissions for the Yb^{3+}/Er^{3+} upconversion pair. As indicated by the arrows, the Yb^{3+} ion is excited from the ground state $^2F_{7/2}$ to the excited state $^2F_{5/2}$ by a 980 nm photon. The Yb^{3+} ion may transfer the energy to the Er^{3+} ion, which promotes an electron from the $^4I_{15/2}$ state to the $^4I_{11/2}$ state, and if the latter is already populated, the electron may transit from the $^4I_{11/2}$ state to the $^4F_{7/2}$ state. Subsequently, nonradiative relaxations could populate the $^2H_{11/2}$ and $^4S_{3/2}$ states, which are the emitting levels for green fluorescence. On the other hand, the Er^{3+} ion populates the $^4I_{11/2}$ level mostly and nonradiatively relaxes to the long living $^4I_{13/2}$ level. The populated $^4I_{13/2}$ level may be excited to the $^4F_{9/2}$ level by the energy transfer process: $^2F_{5/2}\rightarrow{}^2F_{7/2}$ (Yb^{3+}):$^4I_{13/2}\rightarrow{}^4F_{9/2}$ (Er^{3+}). The emission from the $^4F_{9/2}$ level produces the red upconversion fluorescence.

2.4 Green upconversion fluorescence of LaF_3:0.04Yb^{3+}, 0.01Er^{3+} colloidal solution

Fig.5 shows photographs of the solution of LaF_3:0.04Yb^{3+}, 0.01Er^{3+} nanocrystals in cyclohexane with a concentration of 20 mg/ml. Fig.5(a) demonstrates that the colloidal solution is fully transparent. Fig.5(b) shows eye-visible upconversion luminescence under 980 nm excitation. It is observed that the height of the solution is reduced in Fig.5(b). This is because the 980 nm laser generates a lot of heat in the solution and results in volatilization. The green upconversion fluorescence of the transparent solution is attributed to the high crystal quality. RE ions on the crystal surface will probably not show the infrared-to-visible upconversion, because the luminescence of the RE ions will be efficiently quenched by the high energy C–H vibration from the oleic acid layer and the solvent. Therefore, the upconversion fluorescence originates from the emission of the RE^{3+} ions inside the nanocrystals.

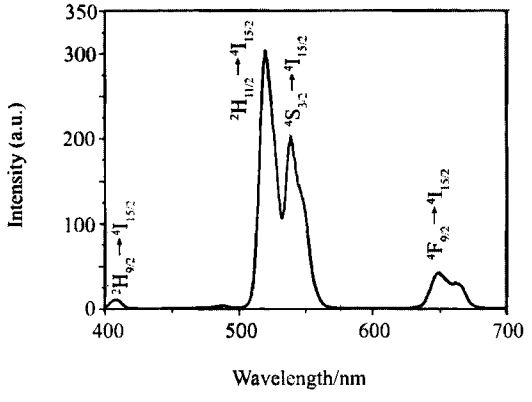

Fig.3 Room-temperature upconversion emission spectrum of the colloidal LaF_3:0.04Yb^{3+},0.01Er^{3+}

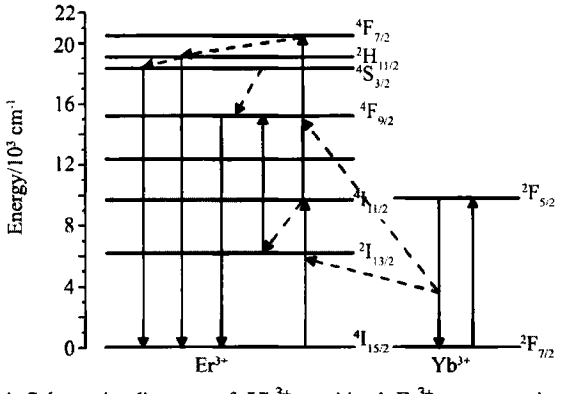

Fig.4 Schematic diagram of Yb^{3+}-sensitized Er^{3+} upconversion in LaF_3:0.04Yb^{3+}, 0.01Er^{3+} nanocrystals under 980 nm excitation

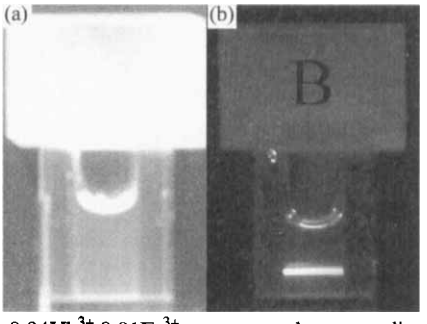

Fig.5 LaF_3:0.04Yb^{3+},0.01Er^{3+} nanocrystals were dispersed into cyclohexane (The volume of solution was 100 μl) (a); The green upconversion fluorescence photo of transparent colloidal LaF_3:0.04Yb^{3+},0.01Er^{3+} nanocrystals solution (b)

3 Conclusion

In conclusion, monodispersive upconversion LaF_3:0.04Yb^{3+},0.01Er^{3+} nanocrystals were synthesized. The Yb^{3+}-Er^{3+} codoped nanocrystals exhibited green upconversion fluorescence under 980 nm excitation. The organic ligand-modified particles were dispersible in nonpolar organic solvents, and form a fully transparent colloidal solution. These nanocrystals had potential applications in biolabeling and bioimaging.

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