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Simple method for simultaneously achieving red and green up-conversion luminescence†

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The simultaneous emission of red and green light with high brightness and color purity was obtained from ${\rm Er^{3+}}$ -doped NaYbF₄-based up-conversion nanoparticles excited by 980 and 1550 nm excitation. The ${}^2{\rm F}_{5/2}$ level of Yb³⁺ showed high absorption efficiency at 980 nm. The ${}^4{\rm I}_{13/2}$ level of ${\rm Er^{3+}}$, an excellent UC intermediate with high energy and a long lifetime (milliseconds), absorbed more energy in the cross section $(6.0 \times 10^{-20} \ {\rm cm^2})$ than did the Yb³⁺ ${}^2{\rm F}_{5/2}$ level $(1.2 \times 10^{-20} \ {\rm cm^2})$ and was efficiently and directly pumped by light with a wavelength of ~1500 nm. In contrast to particles resulting from other methods using complex coating for achieving multi-color emission in a single sample, the as-prepared luminescent NaYbF₄:25% ${\rm Er^{3+}}$ up-conversion nanoparticles were designed to be single-layered and spherical and showed excellent dispersibility and uniform sizes. Nanoparticles prepared by this method exhibit a great advantage based on the simple preparation process and small particle size. On this basis, we expect to easily achieve the emission of three primary colors by these reasonably designed core–shell particles.

1. Introduction

Multi-color up-conversion luminescence (UCL) materials have major application prospects in biological imaging, multiple detection and treatment of disease, anti-counterfeiting and multicolor coding, and display areas.1-4 The tunable range of the upconversion (UC) emission color, however, is seriously limited due to the finite excitation wavelength, type of activator, and inappropriate emission levels, which also hinder the wide application of UCL materials.^{5,6} Current methods for achieving multicolor emission can be divided into three types. (1) The first type of method involves achieving emissions from multiple samples by exciting them with a single wavelength.7,8 Here, the emission color can be finely adjusted by changing the host,9 doping concentrations of rare earth ions, 10,11 particle size12,13 and crystal structure, 14,15 or co-doping with other ions. 16,17 Furthermore, the UCL color can be tuned using different activator combinations and core-shell structures excited with the single wavelength. 18,19 (2) The second type of method involves achieving emissions from multiple samples by exciting them with multiple wavelengths.20 These two methods usually face chromatic aberration problems resulting from different types of particles having inconsistent sedimentation rates and being unevenly mixed. (3) The third type of method involves achieving multi-color emission from a single sample under multi-wavelength excitation, and this method presents excellent application characteristics. Wen et al. prepared

Physics Department, Dalian Maritime University, Dalian, Liaoning 116026, PR China. E-mail: luoxixiandl@126.com NaYF₄ up-conversion nanoparticles (UCNPs) with a five-layer core–shell structure to obtain blue-green two-color emission under excitation with light of wavelengths of 980 and 808 nm.²¹ Deng *et al.*²² designed an unsteady UC full-color luminescence in NaYF₄ UCNPs with a five-layer core–shell structure by adjusting the pulse width. These UCNPs realize multi-color emission but require a relatively complex preparation process and large particle size. Consequently, there is an urgent need to obtain a simple method for realizing multi-color emission.

Green and red double color UCL has been realized in micronsized single Y₂O₂S:Yb³⁺, Er³⁺ UC materials under 980 and 1550 nm dual wavelength excitation.²³ Yb³⁺ and Er³⁺ ions form two sensitization systems excited at 980 and 1550 nm, respectively, and exhibit different UCL characteristics. In the current work, NaYbF₄:25% Er³⁺ UCNPs were shown to simultaneously emit red and green light when excited with light of wavelengths of 980 and 1550 nm.

2. Experimental

2.1 Materials

All materials purchased were used as described below without further purification. 1-Octadecene (OM; 90%), oleic acid (OA; 90%), Y(CH₃COO)₃·4H₂O, Yb(CH₃COO)₃, and Er(CH₃COO)₃ were purchased from Alfa Aesar. Ammonium fluoride (NH₄F), sodium hydroxide (NaOH), methanol, cyclohexane, and ethanol were purchased from Tianjinzhiyuan Chemical Reagent Co and used as received. For each experiment, Re(CH₃COO)₃ was dissolved in deionized water, and NaOH and NH₄F were dissolved in methanol solution in advance to reduce the experimental error.

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2.2 Synthesis of NaYbF₄:xEr³⁺ (x = 10, 25, 50, 90 mol%)

A volume of 3 mL of oleic acid and a volume of 7 mL of octadecene were added, respectively, to two vials by using a two-way valve, and a volume of 2 mL (0.4 mmol) of Re(CH₃COO)₃ (0.2 M) was added in proportion (Yb = 0.36, 0.3, 0.2, 0.04 mmol, as Er = 0.04, 0.1, 0.2, 0.36 mmol, respectively). A thermometer able to measure temperatures between 0 and 360 °C was inserted into each solution to precisely measure the temperature. The samples became pale yellow after being heating to 150 °C and kept at this temperature for 45 min, and a rare earth oleate precursor solution was obtained as the sample was cooled to room temperature. Methanol solutions of NaOH (1 mL, 1 M) and NH₄F (4 mL, 0.4 M) were added to the respective flasks, and kept at 50 °C for 40 min. The temperature was then increased to 100 °C in a vacuum environment in order to remove the methanol from the mixtures. Each solution was quickly heated (15 min) to 290 °C under an argon environment and then, when bubbles were no longer produced, kept warm at 290 °C for 1.5 h, and desired product was obtained as the solution was cooled to room temperature. A volume of 8 mL of an ethanol solution was added to each solution, and the resulting mixture was centrifuged at 9000 rad per min for 6 min. The resulting product in each case was dissolved in 4 mL of cyclohexane and 8 mL of ethanol, and the resulting solution was centrifuged at 9000 rad per min for 6 min. The previous step was then repeated with 4 mL of ethanol and 4 mL of methanol instead of 8 mL of ethanol. The resulting sample in each case was dissolved in 5 mL of cyclohexane and sealed and stored in a glass vial at 4 °C.

2.3 Characterizations

The size and morphology of each sample were determined by performing JEM-2100F high-resolution transmission electron microscopy (HRTEM). The UCL spectra were acquired by using an Edinburgh FS5 fluorescence spectrometer, and powertunable 980 nm-wavelength (maximum power: 800 mW) and 1550 nm-wavelength (maximum power: 800 mW) laser diodes (LDs) were used as excitation sources.

3. Results and discussion

⁴I_{11/2} of Er³⁺ was pumped directly by light with a wavelength of \sim 980 nm due to the relatively large energy absorption section $(1.7 \times 10^{-21} \text{ cm}^2)$ and millisecond-range lifetime of the ${}^4\text{I}_{11/2}$ level.23 In addition, the 4I13/2 level of Er3+ was found in the current work to be an excellent UC intermediate energy level with a long lifetime, and with an energy absorption cross section (6.0 \times 10⁻²⁰ cm²) much larger than that of the Yb³⁺²F_{5/2} level $(1.2 \times 10^{-20} \text{ cm}^2)$ and that was efficiently pumped by light with a wavelength of \sim 1500 nm. Therefore, a high UCL efficiency was achieved using Er3+ ions as the activator with 980 and 1550 nm dual-wavelength excitation.24 An efficient single red UCL was easily obtained at 1500 nm-wavelength excitation relying on the non-radiative ${}^4I_{9/2} \rightarrow {}^4I_{11/2}$ relaxation, which is based on the relatively short lifetime (10 microseconds) of Er³⁺ ions and small energy gap between ${}^4I_{9/2}$ and ${}^4I_{11/2}$ levels ($\Delta E \approx$ 1900 cm⁻¹).^{25,26} Fig. 3a and b are the main green and red double-

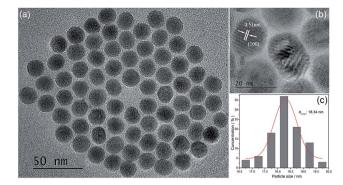
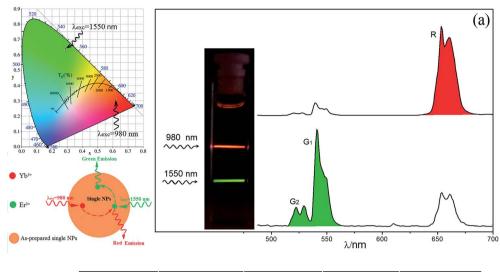


Fig. 1 (a), (b) HRTEM images and (c) corresponding particle size histograms of NaYbF₄:25% Er³⁺

color UCL mechanism of Y2O2S:Yb3+, Er3+ UC materials under 980 and 1550 nm dual-wavelength excitation. However, the opposite is the case for the β -NaYF₄ host, as β -NaYF₄:Er³⁺ (ref. 27 and 28) and LiYF₄:Er³⁺ (ref. 29) show yellow-green UCL when excited at a wavelength of 1500 nm. This condition remains unchanged even upon adding Yb3+ ions (Fig. S1f†), and highcolor-purity emission of red light is difficult to obtain from the β-NaYF₄ host. Therefore, in this work, spherical NaYbF₄:x% Er³⁺ UCNPs (Fig. 1), with an average particle size of 18.34 nm, were prepared through co-precipitation. The distance between adjacent lattice planes of this product was measured using the HRTEM images to be about 0.51 nm, which confirmed the product to be β-phase NaYbF₄ (Fig. 1b).

NaYbF₄:x% Er³⁺ showed different luminescence properties with different Er³⁺ doping concentrations and presented distinct emission colors under excitation with wavelengths of 980 nm and 1550 nm (Fig. S1†). Under excitation at 980 nm, NaYbF4:10% ${\rm Er}^{3+}$ showed green UCL with a red-to-green emission ratio (I_r/I_o) of 0.59 (Fig. S1a†) and NaYbF₄:25% Er³⁺ showed red UCL, specifically at 654 nm ($I_r/I_g = 3.29$, Fig. 2), whereas NaYbF₄:50% ${\rm Er}^{3+}$ exhibited decreased red UCL color purity $(I_{\rm r}/I_{\rm g}=2.19,$ Fig. S1†) and exhibited luminescence quenching. However, Wei et al.30 reported that NaYbF4:50 mol% Er3+ exhibits the optimal red UCL performance when excited with light at a wavelength of 980 nm, this condition is mainly resulted from the large particle size (~100 nm) and crystallinity (Fig. S2†). NaYbF₄:xEr³⁺ excited at 1550 nm showed a constant green UCL (Fig. S1b†) and exhibited the optimal emission characteristics when the doping concentration of Er^{3+} was 25 mol% ($I_{\mathrm{r}}/I_{\mathrm{g}}=0.45$, Fig. 2). Therefore, emission of both red and green light with high brightness and color purity was achieved using NaYbF₄:25% Er³⁺ subjected to dual-wavelength excitation, at 980 and 1500 nm; the corresponding CIE chromaticity coordinates were determined to be (0.62, 0.31) and (0.29, 0.64), respectively. The double-color UCL samples prepared by this method were each shown to have a simple structure and small particle size, and the preparation process was simple and easily controlled. Multi-color emission was achieved by adjusting the relative intensities of the two lasers (Fig. 2b).

The red and green UCL displayed by NaYbF₄:25% Er³⁺ under 980 and 1550 nm-wavelength excitation was attributed to different interaction mechanisms between Yb3+ and Er3+ excited



980 nm	0	28.41	32.13	37.06	44.25
1550 nm	38.03	38.03	38.03	38.03	38.03
					(b)
		×	×	X	×

Fig. 2 (a) CIE chromaticity coordinates, UCL spectra, and digital camera images of NaYbF₄:25% $\rm Er^{3+}$ under 980 and 1500 nm wavelength excitation. (b) Multi-color emission images of NaYbF₄:25% $\rm Er^{3+}$ under excitation with wavelengths of 980 nm (excitation power density = 0, 28.41, 32.13, 37.06, 44.52 mW mm⁻²) and 1550 nm (excitation power density = 38.03 mW mm⁻²) (Canon EOS 5D Mark III, Tv = 1 : 1250, Len: EF24-70 mm f/2.8 L II USM, Av = 2.8, ISO = 12800).

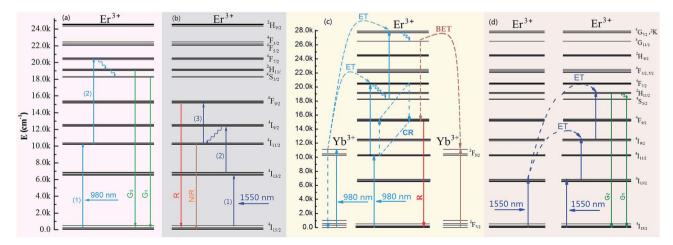


Fig. 3 (a, b) Double-color UCL mechanism of Er^{3+} under (a) 980 nm-wavelength and (b) 1500 nm-wavelength excitation. (c, d) UCL mechanism of NaYbF₄:25% Er^{3+} under (c) 980 nm-wavelength and (d) 1500 nm-wavelength excitation.

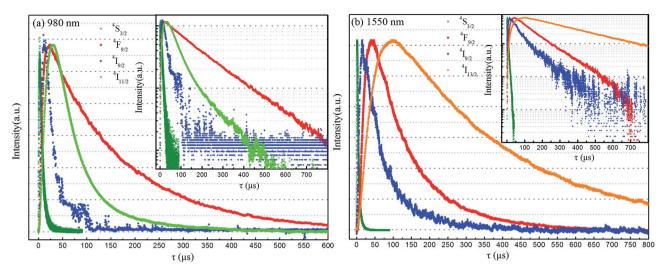


Fig. 4 Decay curves of the $Er^{3+4}S_{3/2}$ (550 nm), ${}^4F_{9/2}$ (654 nm), ${}^4I_{9/2}$ (800 nm), ${}^4I_{11/2}$ (1000 nm), ${}^4I_{13/2}$ (1535 nm) levels in an NaYbF₄: Er^{3+} sample under (a) 980 nm-wavelength and (b) 1550 nm-wavelength pulse LD excitation.

at these two excitation wavelengths. Wei et al.30 attributed the enhancement of red UCL in highly doped Er3+ samples to the cross relaxation (CR, ${}^{4}F_{7/2} + {}^{4}I_{11/2} \rightarrow {}^{4}F_{9/2}$, $+{}^{4}F_{9/2}$) process between Er3+ ions. The CR process was enhanced as the Er3+ concentration was increased, and with increasing I_r/I_g (Fig. S3†). However, the I_r/I_g of Er^{3+} -doped NaYbF₄: xEr^{3+} samples failed to increase as the Er³⁺ concentration was increased, indicating that the enhancement of red UCL was also related to Yb3+ codoping.31 Therefore, the enhancement of red UCL in NaYbF₄:25% Er³⁺ excited at 980 nm was due to the combined effect of the CR process and reverse energy transfer from the $\mathrm{Er}^{3+4}\mathrm{G}_{11/2}$ level to Yb^{3+} (Fig. 3c). The green emission displayed by NaYbF4:25% Er3+ excited with light of a wavelength of 1550 nm was mainly due to the radiation relaxation ${}^{4}I_{9/2} \rightarrow$ ⁴I_{11/2} occurring in other host being less likely to take place in NaYbF4 because of the low phonon energy, thus making the energy transfer process $Er^{3+} \rightarrow Yb^{3+} \rightarrow Er^{3+}$ difficult to transpire.32 Moreover, the lack of occurrence of the above CR process and the occurrence of weak red emission (Fig. 3d) were due to the difficulty in the ${}^4F_{7/2}$ level being pumped by light with a wavelength of 1550 nm (Fig. 4).

4. Conclusions

Single-layer spherical NaYbF₄:25% Er³⁺ UCNPs, with an average particle size of 18 nm, showed double-color emission, of red and green light, under dual-wavelength excitation, of 980 nm and 1550 nm wavelengths. In contrast to other methods for achieving multi-color emission from a single sample with complex coating processes, the as-prepared Er³⁺-doped NaYbF₄-based system is a single-layer structure. And compared with the existing research on multi-color luminescence, the method we have now described involves a simple preparation process, suggesting the potential of achieving mass production. And on this basis, the three primary colors may be expected to be easily achieved by a reasonable designed core–shell.

Conflicts of interest

There are no conflicts to declare.

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