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Reduced photon quenching in Ce-doped NaYF\(_4\):Yb/Ho upconversion nanoparticles with core/shell structure

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The use of red light or near-infrared radiation as a luminescent probe for in vivo bio imaging is crucial in order to restrict the strong absorption of short-wavelength light below 600 nm in tissue. It is demonstrated that the emission color of Yb/Ho codoped NaYF\(_4\) nanoparticles can be tuned from green to red by incorporating Ce\(^{3+}\) ions. However, compared with that of the NaYF\(_4\):Yb/Ho nanoparticles, the photoluminescence intensity of the Ce\(^{3+}\)-tridoped NaYF\(_4\):Yb/Ho nanoparticles is drastically reduced. In this work, Ce\(^{3+}\)-incorporated core/shell NaYF\(_4\):Yb\(^{3+}\) 50\%@NaYF\(_4\):Ho\(^{3+}\) 0.5\% nanoparticles are prepared. A strong red emission and a high-intensity ratio between the red emission and green emission are obtained in these upconversion nanoparticles. The emission intensity increases by a factor higher than 120 when compared with that of the NaYF\(_4\):Yb/Ho/Ce nanoparticles. This result indicates that the Ce\(^{3+}\) incorporation into the NaYF\(_4\):Yb/Ho nanoparticles promotes a strong quenching effect and reduces the emission intensity; however, the quenching effect can be significantly reduced by incorporating the Ce\(^{3+}\) ions into the core/shell NaYF\(_4\):Yb\(^{3+}\) 50\%@NaYF\(_4\):Ho\(^{3+}\) 0.5\% nanoparticles. A theoretical model is proposed to explain the presence of the quenching effect in the NaYF\(_4\):Yb/Ho/Ce nanoparticles, demonstrating that the quenching is mainly related to the interaction between the Yb\(^{3+}\) and Ce\(^{3+}\) ions.

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Due to their interesting properties, including absence of autofluorescence, low photobleaching, strong penetration abilities, low toxicity, etc., rare-earth-doped upconversion nanoparticles (UCNPs) have attracted increasing interest\(^{[1,2]}\). These special features provide UCNPs with a great potential for applications in several fields, such as solar cells, solid-state lasers, boilables, and imaging\(^{[3,4]}\). In particular, among the various applications, in vivo imaging based on UCNPs is expected to be a promising photoluminescence imaging technique, as it provides high sensitivity and spatial resolution, leading to predictive models for potential clinical applications\(^{[5,6]}\). For in vivo imaging, long-wavelength light (above 600 nm) is necessary as the luminescent probe, as the tissue strongly absorbs light with a short wavelength (below 600 nm)\(^{[7]}\). However, three of the most important types of UCNPs, i.e., Yb/Er-, Yb/Tm-, and Yb/Ho-codoped NaYF\(_4\) nanoparticles, radiate green, blue, and green light, respectively\(^{[8,9]}\).

Presently, most of the research on red-emission UCNPs mainly focuses on the Yb/Er-codoped NaYF\(_4\) nanoparticles, as they show a strong green emission (~550 nm) along with a weak dark-red emission (~660 nm). The color can be tuned from green to red using different methods: controlling the particle’s size or the Yb concentration\(^{[10,11]}\), changing the surface ligands\(^{[12,13]}\), partially replacing the Y site of the lattice by Mn\(^{2+}\) or Zr\(^{3+}\) ions\(^{[14,15]}\), etc. Similar to the Yb/Er-codoped NaYF\(_4\) nanoparticles, the Yb/Ho-codoped NaYF\(_4\) nanoparticles also show a strong green emission and a weak red emission, and it is possible to tune the emission color from green to red using different methods. Unfortunately, the tuning seems very hard to achieve. Until now, only one method has been reported to successfully tune the emission color from green to red in Yb/Ho-codoped NaYF\(_4\) nanoparticles by incorporating Ce\(^{3+}\) ions and inducing a cross-relaxation process between the Ho\(^{3+}\) and Ce\(^{3+}\) ions\(^{[16,17]}\). However, a significant quenching effect due to the Ce incorporation was simultaneously produced, and the upconversion (UC) photoluminescence intensity of the NaYF\(_4\):Yb\(^{3+}\), Ho\(^{3+}\) 1%, Ce\(^{3+}\) 15% nanoparticles was several orders of magnitude lower than that of the NaYF\(_4\):Yb\(^{3+}\), Ho\(^{3+}\) 1% nanoparticles.

In our previous research, core/shell structured NaYF\(_4\):Yb\(^{3+}\) at NaYF\(_4\):Ho\(^{3+}\) 1% nanoparticles were proven to enhance the red emission by increasing the Yb\(^{3+}\) concentration in the core\(^{[18]}\). Here, the Ce\(^{3+}\) ions were incorporated into the core/shell structured NaYF\(_4\):Yb\(^{3+}\)@NaYF\(_4\):Ho\(^{3+}\) nanoparticles to further enhance the red emission; in addition, a method to eliminate the quenching effect is proposed.

Two types of NaYF\(_4\):Yb\(^{3+}\) 50%@NaYF\(_4\):Ho\(^{3+}\) 0.5% nanoparticles with incorporated Ce\(^{3+}\) ions were prepared to investigate the influence of the Ce\(^{3+}\) ions. In addition, NaYF\(_4\):Yb\(^{3+}\) 20%, Ho\(^{3+}\) 0.5% and NaYF\(_4\):Yb\(^{3+}\) 20%, Ho\(^{3+}\) 0.5%, Ce\(^{3+}\) 20% nanoparticles were also prepared as the contrastive samples. All samples were prepared by the procedure described in our previous work\(^{[19]}\). Figure 1 shows the typical transmission electron microscopy morphologies of such nanoparticles. The monodispersed NaYF\(_4\):Yb\(^{3+}\) 20%, Ho\(^{3+}\) 0.5%, Ce\(^{3+}\) 20% nanoparticles exhibited an average size of ~24 nm, similar
particles did not affect the microstructure, morphology, Ce$^{3+}$ nanospheres, revealing that the Ce$^{3+}$ incorporation did not reduce the photoluminescence intensity of NaYF$_4$:Yb$^{3+}$:Ho$^{3+}$ 50% nanoparticles, as shown in Fig. 1(a). Compared with the NaYF$_4$:Yb$^{3+}$:50%@NaYF$_4$:Ho$^{3+}$ 0.5% nanoparticles without incorporated Ce$^{3+}$, the photoluminescence intensity of the NaYF$_4$:Yb$^{3+}$:50%@NaYF$_4$:Ho$^{3+}$ 0.5% nanoparticles shelled by NaYF$_4$:Ce$^{3+}$ 20% was reduced by ~8%, and the $I_{\text{red}}/I_{\text{green}}$ ratio was approximately equal to 7, slightly higher than that of the NaYF$_4$:Yb$^{3+}$:50%@NaYF$_4$:Ho$^{3+}$ 0.5% nanoparticles. This result indicated that an enhancement of the red emission of the NaYF$_4$:Yb$^{3+}$:50%@NaYF$_4$:Ho$^{3+}$ 0.5% nanoparticles was not achievable by only coating them with a Ce$^{3+}$-containing shell layer. When the Ce$^{3+}$ ions were incorporated into the shell of the NaYF$_4$:Yb$^{3+}$:50%@NaYF$_4$:Ho$^{3+}$ 0.5%, Ce$^{3+}$20% nanoparticles, the $I_{\text{red}}/I_{\text{green}}$ ratio was enhanced to 11, nearly twice that of the NaYF$_4$:Yb$^{3+}$:50%@NaYF$_4$:Ho$^{3+}$ 0.5% nanoparticles, although the photoluminescence intensity was also reduced by ~22%. However, the emission intensity of the NaYF$_4$:Yb$^{3+}$:50%@NaYF$_4$:Ho$^{3+}$ 50%, Ce$^{3+}$20% nanoparticles was enhanced by a factor of more than 120 compared with that of the NaYF$_4$:Yb$^{3+}$ 50%, Ho$^{3+}$ 1%, Ce$^{3+}$ 20% nanoparticles. These results demonstrated the weak quenching effect that exists in the NaYF$_4$:Yb$^{3+}$:50%@NaYF$_4$:Ho$^{3+}$ 0.5%, Ce$^{3+}$20% nanoparticles.

The dependence of the intensities of the green and the red UC emission band on the pump power for the NaYF$_4$:Yb$^{3+}$:50%@NaYF$_4$:Ho$^{3+}$ 0.5%, Ce$^{3+}$20% UCNPs was measured, as shown in Fig. 3. In general, the photoluminescence intensity increased on the pump laser power and obeyed the rule of $I_{\text{UCL}} \propto p^n$, where $I_{\text{UCL}}$ is the photoluminescence intensity, $p$ is the pump laser power, and $n$ is the number of laser photons required. The slope values for the green and the red emission bands of the NaYF$_4$:Yb$^{3+}$:50%@NaYF$_4$:Ho$^{3+}$ 0.5%, Ce$^{3+}$20% UCNPs approached 2, indicating that both the green and the red emissions involve a two-photon process for their generations. The slope values were in good agreement with previous results on Yb$^{3+}$/Ho$^{3+}$-codoped UCNPs.

High emission intensity was observed in the core/shell nanoparticles consisting of a core containing Yb$^{3+}$ ions and a shell containing Ho$^{3+}$ and Ce$^{3+}$ ions. This result

![Fig. 1. Transmission electron microscopy morphologies of (a) NaYF$_4$:Yb$^{3+}$ 20%, Ho$^{3+}$ 1%, (b) NaYF$_4$:Yb$^{3+}$ 20%, Ho$^{3+}$ 0.5%, Ce$^{3+}$ 20%, (c) NaYF$_4$:Yb$^{3+}$:50%@NaYF$_4$:Ho$^{3+}$ 0.5%, (d) NaYF$_4$:Yb$^{3+}$:50%@NaYF$_4$:Ho$^{3+}$ 0.5%@NaYF$_4$:Ce$^{3+}$ 20%, (e) NaYF$_4$:Yb$^{3+}$:50%@NaYF$_4$:Ho$^{3+}$ 0.5%, Ce$^{3+}$ 20% nanoparticles (the insets show the size distribution of the corresponding nanoparticles), and (f) SAED pattern of NaYF$_4$:Yb$^{3+}$:50%@NaYF$_4$:Ho$^{3+}$ 1%:Ce$^{3+}$ 20% nanoparticles.](image1)

![Fig. 2. Photoluminescence spectra of different types of Ce$^{3+}$ ion incorporations: (a) NaYF$_4$:Yb$^{3+}$ 20%, Ho$^{3+}$ 1% and (b) NaYF$_4$:Yb$^{3+}$:50%@NaYF$_4$:Ho$^{3+}$ 0.5% nanoparticles. (c) Photoluminescence intensity of the green and red emission bands. (d) The intensity ratios from the nanoparticles in (a) and (b).](image2)
implied that the strong quenching effect in the Yb/Ho/ Ce-tridoped NaYF<sub>4</sub> nanoparticles may be related to the interaction between the Yb<sup>3+</sup> and Ce<sup>3+</sup> ions. To verify and provide a theoretical background to this hypothesis, the steady-state rate equations were used. In this physical model, \( N_{Yb0} \) and \( N_{Yb1} \) are the population densities of the Yb<sup>3+</sup> ions in the ground and the excited states, respectively; \( N_0, N_1, N_2, N_3, \) and \( N_4 \) are the population densities of the \( ^5I_8, ^5I_7, ^5I_6, ^5F_5, \) and \( ^5S_2 F_4 \) states, respectively, of the Ho<sup>3+</sup> ions; and \( N_{Ce0} \) and \( N_{Ce1} \) are the population densities of the Ce<sup>3+</sup> ions in the ground and the excited states, respectively. In addition, \( W_0, W_1, \) and \( W_2 \) are the energy transfer rates from the excited Yb<sup>3+</sup> ions to the Ho<sup>3+</sup> ions, and \( R_1, R_2, R_3, \) and \( R_4 \) are the radiation rates of the energy states of the Ho<sup>3+</sup> ions. \( \beta_1 \) and \( \beta_2 \) are the phonon-assisted nonradiative relaxation rates from the \( ^5I_6 \) to \( ^5I_7 \) and from the \( ^5S_2 F_4 \) to \( ^5F_5 \) states, respectively, of the Ho<sup>3+</sup> ions; \( C_2 \) and \( C_4 \) are the coefficients of the cross relaxations between Ho<sup>3+</sup> and Ce<sup>3+</sup> ions in the \( ^5I_6 \) and \( ^5S_2 F_4 \) states, respectively; and \( M \) is the coefficient of the cross relaxation between the Yb<sup>3+</sup> and Ce<sup>3+</sup> ions. \( I \) is the laser intensity at 980 nm, \( \nu \) is the laser frequency, \( \sigma_{Yb} \) is the absorption cross section of the Yb<sup>3+</sup> ion, \( R \) is the radiation rate of the excited state of Yb<sup>3+</sup>, and \( R_{Ce} \) is the radiation rate of the excited state of Ce<sup>3+</sup>. The steady-state rate equations for the discussed system can be described as follows:

\[
0 = \frac{dN_1}{dt} = \beta_1 N_2 + C_2 N_2 N_{Ce0} - R_1 N_1 - W_1 N_{Yb1} N_1, \tag{1-1}
\]

\[
0 = \frac{dN_2}{dt} = W_0 N_{Yb1} N_0 - \beta_2 N_2 - C_4 N_4 N_{Ce0} - R_3 N_2 - W_2 N_{Yb1} N_2, \tag{1-2}
\]

\[
0 = \frac{dN_3}{dt} = W_1 N_{Yb1} N_1 + C_4 N_4 N_{Ce0} - R_3 N_3 + \beta_2 N_4, \tag{1-3}
\]

\[
0 = \frac{dN_4}{dt} = W_2 N_{Yb1} N_2 - R_4 N_4 - C_4 N_4 N_{Ce0} - \beta_2 N_4, \tag{1-4}
\]

After solving Eqs. (1) and (2), we obtained the following expressions:

\[
N_1 = \left[ \frac{(\beta_1 + C_2 N_{Ce0}) W_0 N_0}{R_1 (\beta_1 + C_2 N_{Ce0} + R_2)} - \frac{W_1}{R_1} \right] N_{Yb1}, \tag{3}
\]

\[
N_2 = \frac{W_0 N_0}{\beta_1 + C_2 N_{Ce0} + R_2 + W_2 N_{Yb1}} N_{Yb1}, \tag{4}
\]

\[
N_3 = \left[ \frac{(\beta_1 + C_2 N_{Ce0}) W_1}{R_1 + W_1 N_{Yb1}} + \frac{(\beta_1 + C_4 N_{Ce0}) W_2}{R_1 + C_4 N_{Ce0} + \beta_2} \right] \frac{W_0 N_0 (N_{Yb1})}{(R_2 + \beta_1 + C_2 N_{Ce0} + W_2 N_{Yb1}) R_3}, \tag{5}
\]

\[
N_4 = \frac{W_0 W_2 N_0 (N_{Yb1})^2}{(R_4 + C_4 N_{Ce0} + \beta_2)(R_2 + C_2 N_{Ce0} + \beta_1 + W_2 N_{Yb1})}, \tag{6}
\]

\[
N_{Yb1} = \frac{I \sigma_{Yb} N_{Yb0}}{h \nu (R_{Yb} + W_0 N_0 + W_1 N_1 + W_2 N_2 + M N_{Ce0})}, \tag{7}
\]

\[
N_{Ce0} = \frac{R_{Ce} N_{Ce1}}{C_2 N_2 + C_4 N_4 + M N_{Yb1}}. \tag{8}
\]

Then, we can obtain the intensities of the red and green lights by applying the following equations:

\[
I_r = N_3 h \nu_r R_3, \tag{9}
\]

\[
I_g = N_4 h \nu_g R_4, \tag{10}
\]

where \( \nu_r \) and \( \nu_g \) are the frequencies of the red light and green light, respectively. Furthermore, by combining Eqs. (5), (6), (9), and (10), we can derive the following expressions:

\[
I_r = \left[ \frac{(\beta_1 + C_2 N_{Ce0}) W_1}{R_1 + W_1 N_{Yb1}} + \frac{(\beta_1 + C_4 N_{Ce0}) W_2}{R_1 + C_4 N_{Ce0} + \beta_2} \right] \frac{W_0 N_0 (N_{Yb1})}{(R_2 + \beta_1 + C_2 N_{Ce0} + W_2 N_{Yb1}) h \nu_r}, \tag{11}
\]

\[
I_g = \frac{R_1 W_0 W_2 N_0 (N_{Yb1})^2}{(R_4 + C_4 N_{Ce0} + \beta_2)(R_2 + C_2 N_{Ce0} + \beta_1 + W_2 N_{Yb1})} h \nu_g. \tag{12}
\]
According to Eqs. (7) and (8), we know that

\[ N_{\text{Yb}^3\text{+}}N_{\text{Ce}^3\text{+}} \propto \frac{1}{1 + M}. \]  

(13)

Moreover, considering Eqs. (11) and (12), we can also obtain the following expressions:

\[ I_r \propto \frac{1}{(1 + M)^2\beta_1 + C_2(1 + M) + W_2(1 + M)}, \]  

\[ I_g \propto \frac{1}{[(R_1 + \beta_2)(1 + M) + C_4][(R_2 + \beta_1)(1 + M) + C_2 + W_2]}. \]  

(14)

(15)

Hence, from Eqs. (14) and (15), it was demonstrated that both the intensities of the red and green light decreases by the coefficient M of the cross relaxation between Yb\(^{3\+}\) and Ce\(^{3\+}\) ions, although the two cross relaxations between Ho\(^{3\+}\) and Ce\(^{3\+}\) ions can lead to an enhancement of the red light radiation by reducing the green light radiation, as shown in Fig. 4(b). This model is able to explain the low emission intensity of the Yb/Ho/Ce tridoped NaYF\(_4\) nanoparticles. When the Ho\(^{3\+}\) and Ce\(^{3\+}\) ions were moved to the shell layer, as shown in Fig. 4(c), the cross relaxation between the Yb\(^{3\+}\) and Ce\(^{3\+}\) ions could be reduced drastically as a result of the extended distance between the Yb\(^{3\+}\) and Ce\(^{3\+}\) ions, while the cross relaxation between the Ho\(^{3\+}\) and Ce\(^{3\+}\) ions was kept constant. Thus, high-intensity red light radiation was obtained for the NaYF\(_4\)Yb\(^{3\+}\)50\%@NaYF\(_4\)Ho\(^{3\+}\)0.5\%, Ce\(^{3\+}\)20\% nanoparticles. The ~22\% reduction of the NaYF\(_4\)Yb\(^{3\+}\)50\%@NaYF\(_4\)Ho\(^{3\+}\)0.5\%, Ce\(^{3\+}\)20\% nanoparticles, compared with that of the NaYF\(_4\)Yb\(^{3\+}\)50\%@NaYF\(_4\)Ho\(^{3\+}\)0.5\% nanoparticles (Fig. 2), mainly resulted from the cross relaxation between the Yb\(^{3\+}\) and Ce\(^{3\+}\) ions at the core/shell interface. The ~8\% reduction of the NaYF\(_4\)Yb\(^{3\+}\)50\%@NaYF\(_4\)Ho\(^{3\+}\)0.5\%@NaYF\(_4\)Ce\(^{3\+}\)20\% nanoparticles indicated that the quenching effect was further reduced by extending the distance between the Yb\(^{3\+}\) and Ce\(^{3\+}\) ions.

In conclusion, the Ce\(^{3\+}\) ions are incorporated into the Yb/Ho-codoped NaYF\(_4\) nanoparticles to enhance the red emission. The Ce\(^{3\+}\) incorporation enhances the intensity ratio between the red emission and the green emission of the NaYF\(_4\)Yb/Ho nanoparticles, but largely reduces the total photoluminescence intensity. However, when the Ce\(^{3\+}\) ions are incorporated into the shell of the core/shell NaYF\(_4\)Yb\(^{3\+}\)50\%@NaYF\(_4\)Ho\(^{3\+}\)0.5\% nanoparticles, the emission intensity is also enhanced by a factor of more than 120 compared with that of the NaYF\(_4\)Yb/Ho/Ce nanoparticles. This result indicates that the Ce\(^{3\+}\) incorporation into the NaYF\(_4\)Yb/Ho nanoparticles promotes a strong quenching effect that reduces the emission intensity; the quenching effect is significantly reduced by incorporating the Ce\(^{3\+}\) ions into the core/shell structured Yb/Ho codoped NaYF\(_4\) nanoparticles. A theoretical model is proposed to explain the quenching effect existing in the NaYF\(_4\)Yb/Ho/Ce nanoparticles, revealing that the quenching is mainly related to the interaction between the Yb\(^{3\+}\) ions and the Ce\(^{3\+}\) ions.

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References


![Fig. 4. (a) Energy level diagrams of Ho\(^{3\+}\), Yb\(^{3\+}\), and Ce\(^{3\+}\) ions and proposed UC mechanisms. (b) Schematic illustration of the proposed energy-transfer mechanisms in NaYF\(_4\)Yb/Ho nanoparticles. (c) Schematic illustration of the proposed energy-transfer mechanisms in core/shell NaYF\(_4\)Yb@NaYF\(_4\) Ho/Ce nanoparticles.](Image 45x137 to 285x273)
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