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Effects of surroundings on upconversion luminescent properties of rare earth luminescence centers

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ABSTRACT A special core/shell/shell structured $NaYF_4$/ $NaYF_4$:Yb^{3+},Er^{3+}/ $NaYF_4$ (CSS) nanocrystal was designed to ensure each luminescence center on the emitting shell having the same surroundings, which includes a support core $NaYF_4$ nanoparticle in the center coated by a thin emitting shell $NaYF_4$:Yb^{3+},Er^{3+} and another $NaYF_4$ shell with adjustable thickness as the outer shielding shell. Green upconversion fluorescence intensity $I_g(d)$ of CSS nanoparticles shows exponential relationship with the thickness d of the shielding shell. When d decreased to 0, $I_g(0)$ decreased ~356 times as compared with $I_g(\infty)$ due to the drastic fluorescence quenching of rare earth luminescence centers by surroundings. Our experimental results indicate that ~ 90% of the severe effect of surroundings can be eliminated by coating ~4 nm- thick $NaYF_4$ shielding shell.

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1. Introduction

Upconvertion (UC) nanocrystals have attracted great interest for their applications in biomedicine,[1-3] owning to their unique optical properties, such as deep penetration in tissues, no autofluorescence, no toxicity and absence of photobleaching.[4-6] To facilitate applications in biomedicine, monodisperse nanocrystals are needed.[7] In general, long chain organic surfactants were essential to prevent aggregation and realize monodisperse nanocrystals in solvents. In general, surfactants and solvents in surroundings as high vibrational energy functional groups tend to act on some unsaturated dangling bonds of surface atoms, which result in undesirable nonradiative relaxation under multiphonon assisted processes.[8]

So far, the most efficient method to minimize the associated nonradiative relaxation is surface coating by low phonon energy materials,[9-11] which could remarkably decrease surface defects and diminish the interaction between the surface atoms of nanoparticles and the high vibrational energy functional groups or solvents in surroundings. In recent years, surface coating has been the dominant method to shield the effects of surroundings. The effect of surface coating to fluorescence properties of nanoparticles have been discussed in detail.[12,13] Luminescence dynamics of core/shell nanoparticles have been studied by Dorman et al..[14] Furthermore, critical shell thickness to shield high frequency vibrating modes from outside has been explored.[15,16] In general, a luminescent nanoparticle contains a lot of luminescence centers, which can be attributed to the fact that the particle has different distance from the surface, hence suffer different effects from surroundings. Therefore, it is not possible to isolate the surrounding effect to individual luminescence centers in a nanoparticle. To overcome this issue, a special core/shell/shell structured $NaYF_4$/ $NaYF_4$:Yb^{3+},Er^{3+}/ $NaYF_4$ (CSS) nanocrystal was designed and fabricated to investigate accurately the effect from surroundings.

The special CSS nanoparticle proposed here ensures all luminescence $NaYF_4$:Yb^{3+},Er^{3+} centers distributed on a thin spherical shell with the same interference from surroundings. Drastic quenching of luminescence centers by surroundings was observed without the outer shielding shell, and we proved that the effect can be eliminated by a homogeneous shell with a thickness of a few nanometers.

2. Experimental methods

2.1 Synthesis of $NaYF_4$ core nanoparticles

$NaYF_4$ core nanoparticles were synthesized according to a typical method:[17] 1 mmol YCl_3 mixed with 6 ml oleic acid and 15 ml 1-octadecene were added into a 50 ml round bottom flask. The reaction was purged with N_2 throughout the overall process. The resulting mixture was heated to 160 ^oC with stirring vigorously until the solution became clear. Thereafter, the solution was cooled down to 50 ^oC, followed by injection of 3 mL methanol solution containing NaOH (0.1g) and NH_4F (0.148g), and stirred for 30 min. Then, the methanol and water in reaction mixture were evaporated at 100 ^oC for 30 min. Subsequently, the reaction mixture was heated to 310 ^oC for 90 min with constant stirring. Finally, the reaction mixture was naturally cooled down to room temperature. The synthesized products were washed with ethanol and centrifugally separated to get the nanoparticles without impurities. After several times purification, the obtained nanoparticles were stored in nonpolar organic solvents (cyclohexane used in the experiment).

2.2 Synthesis of core/shell $NaYF_4/NaYF_4:Yb^{3+},Er^{3+}$ (CS) nanoparticles

The core/shell nanoparticles were synthesized according to the method reported by Guo et al..[18] The powders of YCl_3 (0.671 mmol), $YbCl_3$ (0.172 mmol) and $ErCl_3$ (0.017 mmol) were added into a 50 ml round bottom flask containing 5.17 ml oleic acid and 12.92 ml 1-octadecene, which were heated to 160 ^oC for 30 min to make the rare earth ions dissolved completely in the organic solvent. Then the resulting mixture was cooled down to 80 ^oC, followed by the cyclohexane dispersion of $NaYF_4$ core nanoparticles (1 mmol) injected with vigorous magnetic stirring for 30 min before the reaction mixture was cooled down to 50 ^oC. Subsequently, NaOH (0.086 g) and NH_4F (0.127 g) dissolved in 5 ml methanol were added into the resulting mixture. Water and methanol in the mixture needed to be evaporated before being heated to 310 °C for 90 min under N_2 atmosphere. Finally, the resulting mixture was naturally cooled down to room temperature. The purification process is similar to that of the core nanoparticles.

2.3 Synthesis of CSS nanoparticles

The synthesis process of the CSS nanoparticles is similar to the procedure of the core/shell nanoparticles. To synthesize CSS nanoparicles, CS nanoparticles presynthesized should be used as seeds. Note that the dose of $NaYF_4$ precursor needed for coating was adjusted according to the desired thicknesses of $NaYF_4$ shielding shells. The detail information about the preparation of CSS nanoparticles is given in Table S1.

2.4 Characterizations

X-ray diffraction (XRD) pattern was measured using Rigaku D/MAX-2600/PC with the Cu Kα radiation (λ= 1.5406 Å) at the scanning step of 0.02°. Transmission electron microscope (TEM) images were obtained using FEI Tecnai TF20. The fluorescence spectra were measured at room temperature using a 980 nm diode laser as an excitation source with the power of 100 mW. A monochromator (Zolix Instrument SBP 300) coupled with photomultiplier (Zolix Instrument PMTH-S1-CR131) was used to detect emissions. All fluorescence spectra were measured under the same conditions. The time-resolved spectra were measured by A monochromator (Zolix Instrument SBP 300) with photomultiplier (Zolix Instrument PMTH-S1-CR131) or IR detector (Zolix Instrument D InGaAs 2600-TE). Finally, the decay profiles were recorded by a Tektronix TDS 5052 digital oscilloscope.

3. Results and discussion

Schematic illustration for the synthesis process of CSS nanoparticles is shown in Fig. 1 and the TEM images of nanoparticles at every stage in the synthesis of CSS nanoparticles are shown in Fig. 2 and Fig. S1. As shown in Fig.1, $NaYF_4$ core nanoparticles with the average size of ~17.4 nm were synthesized, which were non-luminescent and served only as a support for thin layer rare earth luminescence centers, the corresponding TEM image is shown in Fig. 2(a). A thin emitting shell of $NaYF_4$:20% Yb^{3+},2% Er^{3+} with the thickness of ~2 nm was coated onto the $NaYF_4$ supporting core nanoparticle, which can make each luminescence center having almost the same distance from outside and suffering the same interference from surroundings. A corresponding TEM image of CS nanoparticles is shown in Fig. 2(b). Here, cation exchange or materials diffusion during the growth process of nanoparticles would not be considered so that the sizes of the supporting core nanoparticle and thickness of the emitting shell are assumed fixed.[19] Finally, a thickness-adjustable non-luminescence $NaYF_4$ shell as a shielding layer was coated onto the thin emitting shell to eliminate the effect from surface functional groups and solvents in surroundings. Based on the three steps above, the synthesis of CSS nanoparticles was completed and a typical TEM image is shown in Fig. 2(c). By adjusting the thickness of the shielding shell, the change of interference from surroundings to rare earth luminescence centers can be tested. When the thickness of the shielding shell is close to zero, the true effect from surroundings on rare earth luminescence centers was obtained.

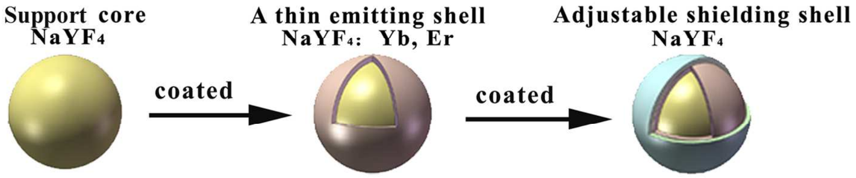

Fig. 1 Schematic illustration of the overall synthesis process of CSS nanoparticles.

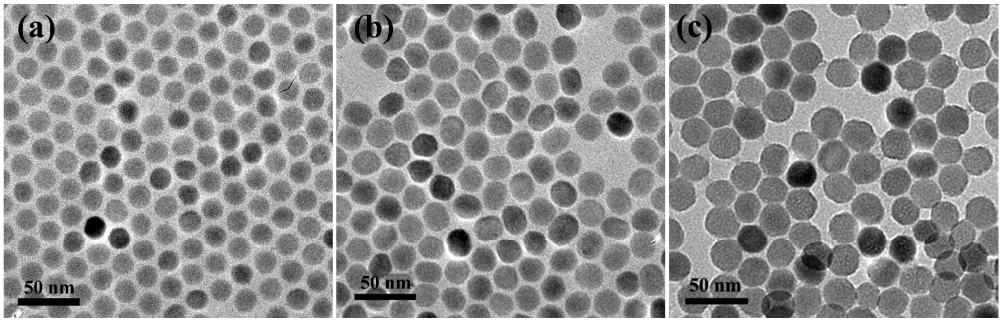

Fig. 2 TEM images of (a) $NaYF_4$ core nanoparticles, (b) CS nanoparticles, and (c) CSS nanoparticles.

An x-ray powder diffraction (XRD) analysis of CSS nanoparticles was performed, and the results are shown in Fig. 3, and the XRD patterns of core and CS nanoparticles are shown in Fig. S2. The XRD pattern of CSS nanoparticles shows that the as-prepared product is the hexagonal $NaYF_4$, which corresponds with the JCPDS card 16-0334 of β-$NaYF_4$. Several extra diffraction peaks in CSS nanoparticles can be observed and assigned to the peaks of $NaYF_4$ with slight shift which can be attributed to the lattice distortion in the emitting shell $NaYF_4$, Yb^{3+}, Er^{3+} with high concentration doping of Yb^{3+} and interfaces of core-shell-shell structure.[20] Besides, little impurity peaks of YF_3 and YbF_3 can be observed, which are induced by the complex coating process of shells.

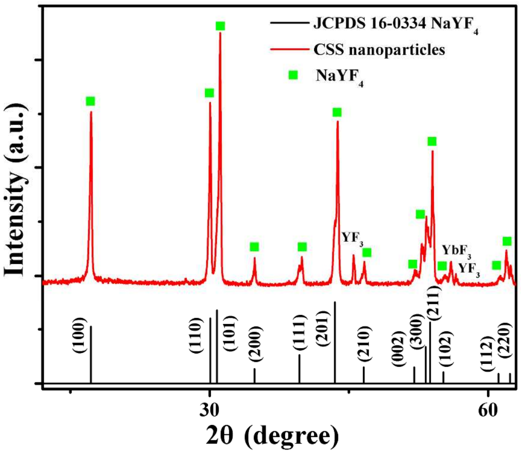

Fig. 3 Typical XRD pattern of as-prepared CSS nanoparticles and the standard pattern of β- $NaYF_4$ nanocrystals.

In the measurement of UC fluorescence spectra, the concentrations of CSS nanoparticles in cyclohexane were adjusted to be the same for all shielding shells of different thicknesses. The well known UC mechanism of green emission is illustrated in Fig. 4(a). First, Yb^{3+} ions absorb laser photons of 980 nm and are excited from the ground state $^2F_{7/2}$ to the excited state $^2F_{5/2}$. Then, excited Yb^{3+} ions transfer the excitation energy to Er^{3+} ions and the energy level $^4I_{11/2}$ of Er^{3+} is populated firstly. Subsequently, Er^{3+} ions at the $^4I_{11/2}$ level absorb the energy of excited Yb^{3+} ions and are excited to the $^4F_{7/2}$ level. But the Er^{3+} ions at the $^4F_{7/2}$ energy level would relax rapidly to $^2H_{11/2}$ and $^4S_{3/2}$ levels, leading to the emission of 530 nm ($^2H_{11/2} \rightarrow {}^4I_{15/2}$) and 543 nm ($^4S_{3/2} \rightarrow {}^4I_{15/2}$).[15] Fig. 4(b) shows the green UC fluorescence spectra of CSS nanoparticles under the excitation of 980 nm laser diode with the power of 100 mW. The inset at the lower-right corner in Fig. 4(b) presents the local amplification of emission spectrum of CSS nanoparticles without shielding shells. To facilitate the observation of surrounding effects on rare earth luminescence centers, the green UC fluorescence intensity $I_g(d)$ is normalized by $I_g(\infty)$. The relationship between the intensity of green UC fluorescence $I_g(d)$ of CSS nanoparticles and the thickness of shielding shell d is shown in Fig. 4(c). An exponential relationship was demonstrated between the intensity of green UC fluorescence of CSS nanoparticles and the thickness d of shielding shell. When the thickness of shielding shell decreases to 0, green UC fluorescence intensity of CSS nanoparticles was reduced by ~356 times compared with $I_g(\infty)$, which is attributed to the low $I_g(0)$ caused by the drastic fluorescence quenching of rare earth luminescence centers from surroundings. On the other hand, ~90% the effect of surroundings can be eliminated by coating a shielding shell with the thickness of ~4 nm. The increase in total particle size after the thin layer coating is not significant for biomedical applications.

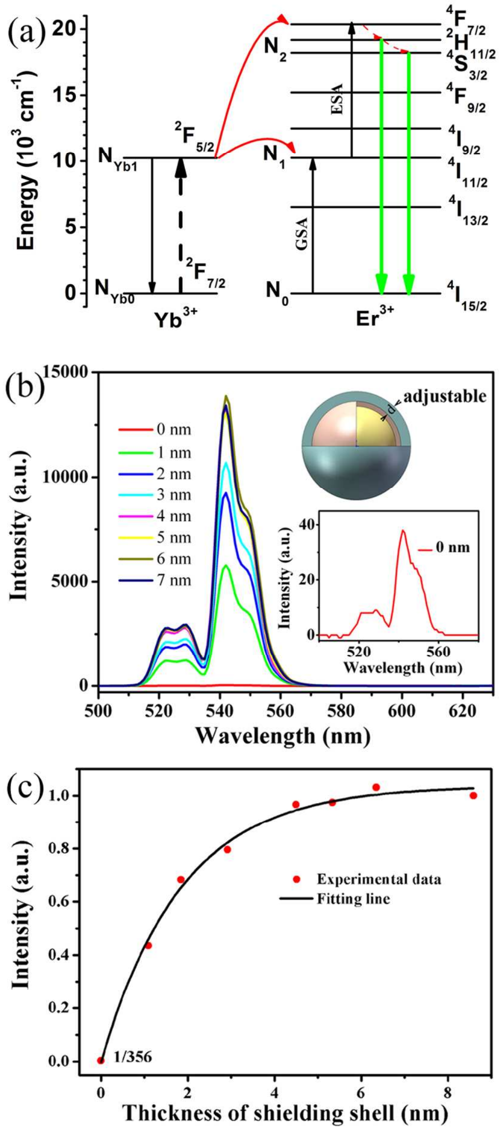

Fig. 4 (a) The schematic energy-level diagram of Yb^{3+} and Er^{3+} codoped system and mechanism for generating the green UC emission, (b) the UC emission spectra of CSS nanoparticles with the shielding shells at different thicknesses and the inset in the lower-right corner shows the corresponding magnified emission spectrum of CSS nanoparticles without shielding shell, (c) the relationship between intensity of green UC emissions and the thickness *d* of the shielding shell in CSS nanoparticles.

In order to theoretically investigate the effect of surface functional groups and solvents in surroundings on the luminescence properties of the emitting shell, rate equations in the steady states based on the processes of energy transitions may be used:

$$\frac{\mathrm{d}N_1}{\mathrm{d}t}=0=W_0N_{Yb1}N_0-W_1N_{Yb1}N_1-\frac{N_1}{\tau_1} \qquad (1.1)$$

$$\frac{\mathrm{d}N_2}{\mathrm{d}t}=0=W_1N_{Yb1}N_1-\frac{N_2}{\tau_2} \qquad (1.2)$$

$$\frac{\mathrm{d}N_{Yb1}}{\mathrm{d}t}=0=\sigma_{Yb}\rho N_{Yb0}-W_0N_{Yb1}N_0-W_1N_{Yb1}N_1-\frac{N_{Yb1}}{\tau_{Yb}} \qquad (1.3)$$

where N_i (i= 0, 1, 2) are populations of the $^4I_{15/2}$, $^4I_{11/2}$, and $^2H_{11/2}/^4S_{3/2}$ states of the Er^{3+}, respectively; N_{Yb0} and N_{Yb1} are the populations of ground and exited states of Yb^{3+}, respectively; τ_x are the decay times of relevant levels; W_0 and W_1 are the energy transfer rates from the excited state of Yb^{3+} to the N_0 and N_1 levels of Er^{3+}, respectively; ρ denotes the laser photon number density; σ_{Yb} is the absorption cross section of Yb^{3+} ions. Upconversion terms $W_1N_{Yb1}N_1$ in equations (1.1) and $W_0N_{Yb1}N_0$ and $W_1N_{Yb1}N_1$ in equation (1.3) will be neglected due to the fact that the rates of energy transfer in the UC processes are much less than the decay rates of relevant energy levels. Considering this fact, based on equations (1.1-1.3), the populations N_2 of $^2H_{11/2}/^4S_{3/2}$ state can be expressed as follows,

$$N_2=N_0W_0W_1(\sigma_{Yb}\rho N_{Yb0})^2\tau_{Yb}^2\tau_2\tau_1 \qquad (1.4)$$

$$I_{green}=AN_2\propto\tau_{Yb}^3\tau_2 \qquad (1.5)$$

where A is the radiation rate of green UC emission; A, W_0, W_1 are not affected by the thickness of shielding shell, hence they are considered constants here; σ_{Yb}, ρ and N_{Yb0} are also constants; the decay time of $^4I_{11/2}$ energy level of Er^{3+} (τ_1) is almost the same as that of $^2F_{5/2}$ energy level of Yb^{3+} (τ_{Yb}).[21]

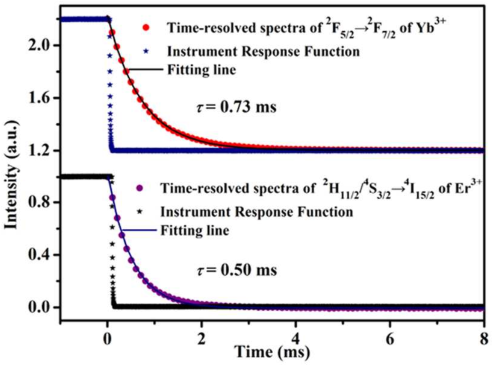

Fig. 5 Typical time-resolved spectra of $^2H_{11/2}/^4S_{3/2}\rightarrow{}^4I_{15/2}$ transition of Er^{3+} (τ_2) and $^2F_{5/2}\rightarrow{}^2F_{7/2}$ transition of Yb^{3+} (τ_{Yb}) in CSS nanoparticles with ~ 4 nm thick shielding shells.

Time resolved spectra of $^2H_{11/2}/^4S_{3/2}\rightarrow{}^4I_{15/2}$ transition of Er^{3+} (τ_2) and $^2F_{5/2}\rightarrow{}^2F_{7/2}$ transition of Yb^{3+} (τ_{Yb}) in CSS nanoparticles are measured and typical time resolved spectra were shown in Fig. 5. The theoretical and experimental intensity of green UC emissions and decay times of energy levels $^2F_{5/2}$ (τ_{Yb}) of Yb^{3+} and $^2H_{11/2}/^4S_{3/2}$ (τ_2) of Er^{3+} in CSS nanoparticles are listed in Table 1. The relationship between intensity of the green UC emission and the thickness of shielding shell agree well with experimental observations. The low $I_g(0)$ of CSS nanoparticles is attributed to the serious effect of surroundings to the rare earth luminescence centers.

Table 1. Decay times of $^2F_{5/2}\rightarrow{}^2F_{7/2}$ transition of Yb^{3+} (τ_{Yb}) and $^2H_{11/2}/^4S_{3/2}\rightarrow{}^4I_{15/2}$ transition of Er^{3+} (τ_2). The theoretical and experimental intensity of green UC emissions in CSS nanoparticles with shielding shells at different thicknesses.

Thickness (nm)	0	1.0	1.8	2.9	4.4	5.3	6.3	8.5
τ_{Yb} (ms)	0.17	0.56	0.66	0.71	0.73	0.75	0.76	0.77
τ_2 (ms)	0.12	0.42	0.45	0.46	0.50	0.51	0.52	0.52
$\tau_{Yb}^3\tau_2$	0.00058	0.073	0.12	0.16	0.19	0.21	0.22	0.23
$I_g(d)$theory[a]	1/396	125/396	206/396	275/396	327/396	362/396	379/396	1
$I_g(d)$experiment[a]	1/356	155/356	243/356	283/356	344/356	347/356	367/356	1

[a] $I_g(d)$theory is the theoretical green UC fluorescence intensity normalized by the theoretical value of $I_g(\infty)$; $I_g(d)$ experiment is the experimental green UC fluorescence intensity normalized by the experimental value of $I_g(\infty)$.

3. Conclusions

Special CSS nanoparticles were synthesized and the effect of surroundings on rare earth luminescence centers was investigated. Based on the spectral analysis, it is clear that the green UC fluorescence intensity $I_g(d)$ of CSS nanoparticles shows exponential dependence on the thickness of the shielding shell. $I_g(0)$ is reduced by ~356 times compared to $I_g(\infty)$, indicating rare earth luminescent centers quenched severely. Fortunately, we can use a thin shielding shell to isolate the luminescence centers from functional groups with high vibrational energy in surroundings. Our results indicate that a ~4 nm-thick $NaYF_4$ shielding shell is sufficient, which can eliminate the interference by 90%.

Acknowledgements

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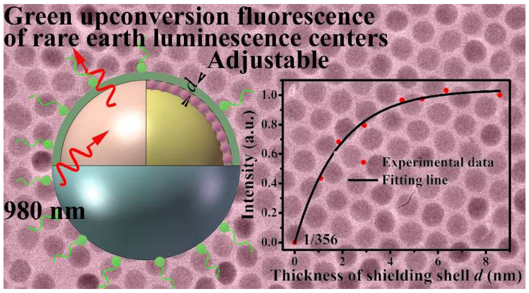

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