Research Article

Efficient Color Tuning of Upconversion Luminescence from Core-Shell Oxysulfide Nanoparticles

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The \( \text{Y}_2\text{O}_2\text{S}:\text{Er}^{3+}\@\text{Y}_2\text{O}_2\text{S}:\text{Yb}^{3+},\text{Ho}^{3+} \) core-shell up-conversion (UC) nanoparticles were successfully synthesized by the homogeneous co-precipitation method. The \( \text{Y}_2\text{O}_2\text{S}:\text{Er}^{3+}\@\text{Y}_2\text{O}_2\text{S}:\text{Yb}^{3+},\text{Ho}^{3+} \) core-shell nanoparticles exhibit bright green emissions under 980 nm excitation, while the triple-ion doped \( \text{Y}_2\text{O}_2\text{S}:\text{Er}^{3+},\text{Yb}^{3+},\text{Ho}^{3+} \) sample presents mainly red emissions. The intensity ratio of green-to-red emission of the core-shell and conventional triple-ion doped samples are 2.8 and 0.3, respectively. Investigations on the UC mechanisms show that emissions from \( \text{Er}^{3+} \) and \( \text{Ho}^{3+} \) ions are achieved simultaneously in the core-shell nanoparticles. This is due to the efficient energy transfers of \( \text{Yb}^{3+}\rightarrow\text{Ho}^{3+} \) within the shell layer and \( \text{Yb}^{3+}\rightarrow\text{Er}^{3+} \) between the shell and the core. While the triple-ion doped \( \text{Y}_2\text{O}_2\text{S}:\text{Er}^{3+},\text{Yb}^{3+},\text{Ho}^{3+} \) sample exhibits mainly the emissions of \( \text{Er}^{3+} \) along with weak luminescence of \( \text{Ho}^{3+} \) ion. Since the cross relaxation between \( \text{Er}^{3+} \) and \( \text{Ho}^{3+} \) ions in the \( \text{Y}_2\text{O}_2\text{S}:\text{Er}^{3+},\text{Yb}^{3+},\text{Ho}^{3+} \) nanoparticles can effectively suppress the emissions of \( \text{Ho}^{3+} \) ions. Yet, in the core-shell structure, this cross relaxation can be successfully restrained in the core-shell structure where \( \text{Er}^{3+} \) is in the core and \( \text{Ho}^{3+} \) is in the shell. Therefore, the construction of core-shell structure can improve the luminescence efficiency and provide a route for adjustment of emission color.

1. Introduction

Upconversion luminescence (UCL) materials with unique luminescent properties have become the research focus due to their promising applications in anti-counterfeiting, solar cells, three-dimensional display and solid-state lasers [1–3]. Rare earth oxysulfide (\( \text{RE}_2\text{O}_2\text{S} \), \( \text{RE} = \) rare earth) is an ideal optical functional material [4–11] due to their excellent thermal and chemical stability. In addition, \( \text{RE}_2\text{O}_2\text{S} \) materials possess low phonon energy, which is important for efficient UCL [12–16]. It has been reported that the UCL efficiency of \( \text{RE}_2\text{O}_2\text{S} \) is comparable to that of \( \beta\)-\( \text{NaYF}_4 \) at excitation of 980 nm [12–14]. Meijerink et al. have shown that the UC internal quantum efficiency of \( \text{Gd}_2\text{O}_2\text{S}:\text{Er}^{3+} \) is higher than that of \( \beta\)-\( \text{NaYF}_4\@\text{Er}^{3+} \) under 1550 nm excitation [15]. Therefore, rare earth oxysulfide is an ideal UC host material holding various promising properties. Furthermore, it is known that the efficiency of UCL is lower than that of conventional luminescence due to its intrinsic luminescence processes, and the tuning of emission color is very limited [16]. Recently, it has been proven that the core-shell structure can effectively improve the properties of UCL and the intensive researches focus on the fluoride material [17, 18]. There are only a few reports about the core-shell structures constructed based on the host material of oxysulfide [19, 20].

In this work, we have successfully synthesized the core-shell nanoparticles (NPs) of \( \text{Y}_2\text{O}_2\text{S}:\text{Er}^{3+}\@\text{Y}_2\text{O}_2\text{S}:\text{Yb}^{3+},\text{Ho}^{3+} \) by using homogeneous co-precipitation method combined with the solid-gas sulfidation route. The UCL properties of \( \text{Y}_2\text{O}_2\text{S}:\text{Er}^{3+}\@\text{Y}_2\text{O}_2\text{S}:\text{Yb}^{3+},\text{Ho}^{3+} \) and triple-ion doped \( \text{Y}_2\text{O}_2\text{S}:\text{Er}^{3+},\text{Yb}^{3+},\text{Ho}^{3+} \) samples were investigated under excitation of 980 nm laser. We found that the core-shell \( \text{Y}_2\text{O}_2\text{S}:\text{Er}^{3+}\@\text{Y}_2\text{O}_2\text{S}:\text{Yb}^{3+},\text{Ho}^{3+} \) exhibits bright green emission, while \( \text{Y}_2\text{O}_2\text{S}:\text{Er}^{3+},\text{Yb}^{3+},\text{Ho}^{3+} \) presents red emission due to the new channels of energy transfers in the core-shell structure. Further, the cross relaxation between \( \text{Er}^{3+} \)
and Ho$^{3+}$ ions can be successfully restrained in the core-shell structure, which lead to the emissions from both of the Er$^{3+}$ and Ho$^{3+}$ ions. Therefore, the core-shell structure provides a new route for adjustment of luminescence color and improvement of luminescence efficiency.

2. Material and Methods

2.1. Synthesis of the Core-Shell NPs. The precipitates of the core material, Y(OH)CO$_3$:12% Er$^{3+}$, were obtained by mixing the solution of urea (99% purchased from Tianjin Bodi Chemical Co., Ltd) in 0.8 L solution (7.5 mol/L) and rare earth nitrates Re(NO$_3$)$_3$ (99.99%, Guangzhou Rare Earth Industry Group CO., Ltd) in 0.2 L solution. The mole ratio of Y, Er ions is 88 : 12. After the centrifuging and washing with water and isopropanol, the core material of Y$_2$O$_3$:Er$^{3+}$ powder was achieved by annealing the precipitates at 600°C for 1 h. To coat the shell layer on the core material, we first added the Y$_2$O$_3$:Er$^{3+}$ into the urea solution (6 mol, 0.8 L) at 60°C, and then mixed the solution (0.2 L) of Re(NO$_3$)$_3$ (Re = Y, Yb, Ho, with mole ratio of 91 : 8 : 1) by bath sonication at 80°C for 30 mins. After the similar processes of cooling down, centrifuging, washing and drying, we obtained the precursor of Y$_2$O$_3$:Er$^{3+}$@Y$_2$O$_3$:Yb$^{3+}$,Ho$^{3+}$. The precursor of the reference sample, Y(OH)CO$_3$:12% Er$^{3+}$,8%Yb$^{3+}$,1%Ho$^{3+}$, were obtained in the similar processes by mixing the solution of urea with Re(NO$_3$)$_3$ (Re = Y, Er, Yb, Ho with mole ratio of 79 : 12 : 8 : 1). Then, the core-shell NPs of Y$_2$O$_3$: 12%Er$^{3+}$@Y$_2$O$_3$:8%Yb$^{3+}$ and Y$_2$O$_3$:Er$^{3+}$,Yb$^{3+}$,Ho$^{3+}$ were finally achieved by annealing the precursor at 600°C. The last step is the sullfination process. The oxides and sulfur powders were put into a quartz tube which was heated up to 800°C for 30 mins. In this process, Argon was used as protection atmosphere. The above RE-ions doping concentrations were optimized on basis of a series of experimental results as shown in the supporting information.

2.2. Characterization. X-ray diffraction (XRD) patterns were recorded at 40 kV and 40 mA by using a Rigaku D/Max-Ultima X-ray diffractometer with Cu K$\alpha$ ($\lambda = 0.15406$ nm) radiation. The UC luminescence spectra were measured by using the Hitachi F-4500 spectrometer equipped with a 980 nm laser diode (with power density of 0.15w/mm$^2$). The slit width is 2.5 nm and the scanning speed is 2400 nm/min. The morphology and size of NPs was characterized by using a JEM-2000EX transmission electron microscope (TEM).

3. Results and Discussion

Figure 1 (a) and (b) show the XRD patterns of Y$_2$O$_2$S:Er$^{3+}$ and Y$_2$O$_2$S:Er$^{3+}$@Y$_2$O$_2$S:Yb$^{3+}$,Ho$^{3+}$ nanocrystals and (c) standard card of hexagonal Y$_2$O$_2$S (JCPDS: No.24-1424).

Figure 1: XRD spectra of (a) Y$_2$O$_2$S: Er$^{3+}$, (b) Y$_2$O$_2$S: Er$^{3+}$@Y$_2$O$_2$S: Yb$^{3+}$, Ho$^{3+}$ nanocrystals and (c) standard card of hexagonal Y$_2$O$_2$S (JCPDS: No.24-1424).
**Ho**$^{3+}$ were obtained as shown in Figure 2(b). It can be observed that the NPs remain the spherical shape with an enlarged mean particle size of 55 nm. This increase of the particle size after the shell coating indicates the formation of the core-shell structure [21, 22]. The final products of Y$_2$O$_2$S: Er$^{3+}$@Y(OH)CO$_3$:Yb$^{3+}$, Ho$^{3+}$ were obtained after the sulfidation process at a high temperature of 800°C, as shown in Figure 2(c). It can be seen that the particles aggregate together after calcination. These agglomerating particles make it challenging to obtain an accurate statics particle size distribution.

The core-shell Y$_2$O$_2$S:Er$^{3+}$@Y$_2$O$_2$S:Yb$^{3+}$, Ho$^{3+}$ UC NPs exhibit bright UCL of green color, while the Yb$^{3+}$, Er$^{3+}$, Ho$^{3+}$ triple-doped Y$_2$O$_2$S NPs show red emission color. As shown in Figure 3, both samples present the green UC emission in the range of 516-570 nm and red ones at 623-698 nm. Compared with the spectrum of Y$_2$O$_2$S:Yb$^{3+}$, Ho$^{3+}$ sample, the visible emissions of the core-shell sample centered at 545, 655 and 750 nm, correspond to the 5S$_2$, 5F$_4$ → 5I$_7$ transitions of Ho$^{3+}$ ions, respectively. And the red emissions from Ho$^{3+}$ ions, yet the conventional triple-ion doped sample present red UCL from Er$^{3+}$ ions.

**Figure 2:** TEM images of (a) the precursor of the core NPs (Y(OH)CO$_3$:12% Er$^{3+}$), (b) the precursor of the core-shell NPs (Y$_2$O$_2$S:Er$^{3+}$@Y(OH)CO$_3$:Yb$^{3+}$, Ho$^{3+}$), and (c) the final products of Y$_2$O$_2$S: Er$^{3+}$@Y$_2$O$_2$S:Yb$^{3+}$, Ho$^{3+}$ NPs.

While the red UCL from Er$^{3+}$ ions is dominant in the high level of 4F$_{7/2}$ through 4I$_{11/2}$ level. The Er$^{3+}$ ion at levels of 5I$_5$ then decays to the 4I$_{13/2}$ state, and enhances the red emission simultaneously. However, the cross relaxation between Er$^{3+}$ and Ho$^{3+}$ ions is effectively suppressed by constructing the core-shell structure where Er$^{3+}$ is in the core and Ho$^{3+}$ is in the shell. Therefore, the core-shell sample exhibits dominant green emissions from Ho$^{3+}$ ions, yet the conventional triple-ion doped sample present red UCL from Er$^{3+}$ ions.

THE POSSIBLE UCL PROCESSES OF Y$_2$O$_2$S:Er$^{3+}$@Y$_2$O$_2$S:Yb$^{3+}$, Ho$^{3+}$ samp le under 980 nm excitation are shown in Figure 4. The UCL of Ho$^{3+}$, Yb$^{3+}$ ions present green, red and weak NIR emissions. Firstly, the sensitizer of Yb$^{3+}$ ion is excited to the 2F$_{5/2}$ energy level after absorbing the 980 nm photon via ground state absorption (GSA) process. Then the Ho$^{3+}$ ion is excited to the high levels of 5S$_2$ and 5F$_4$ via continuous energy transfer (ET) processes of ET1 and ET2 from Yb$^{3+}$ ion (process (1) and process (2) in Figure 4). The excited Ho$^{3+}$ ion at levels of 5S$_2$ and 5F$_4$ generates green emission through the 5S$_2$ → 5I$_4$ → 5I$_6$ transition, and a small portion of them decays to the intermediate state of 5I$_7$ via 5S$_2$ → 5F$_2$ → 5I$_7$ to exhibit weak NIR emission [1]. This process of NIR emission will populate the 5I$_7$ level. In addition, the cross relaxation (CR) processes of 5S$_2$, 5F$_4$ (Ho$^{3+}$) + 5I$_6$ (Ho$^{3+}$) → 5I$_4$ (Ho$^{3+}$) + Ho$^{3+}$ (Cr1) and 5I$_6$ (Ho$^{3+}$) + 5I$_8$ (Ho$^{3+}$) → 5I$_6$ (Ho$^{3+}$) + 5I$_8$ (Ho$^{3+}$) (Cr2) may occur and further populate the energy level of 5I$_7$. Then Ho$^{3+}$ ions at the state of 5I$_7$ will be pumped to the high excited state of 5I$_4$ after absorbing the 980 nm photon, and then emit red UCL through the 5I$_4$ → 5I$_3$ transition.

In terms of the UCL processes of Yb$^{3+}$, Er$^{3+}$ ions, the Yb$^{3+}$ is firstly pumped to the excited level of 2F$_{5/2}$ by absorbing a 980 photon, and then return to the ground state by transferring the energy to an Er$^{3+}$ ion in the core via ET3 and ET5, as shown in Figure 4. These ET processes will excite the Er$^{3+}$ from ground state of 4I$_{15/2}$ to the high level of 2F$_{7/2}$ through 4I$_{11/2}$ level. The Er$^{3+}$ ion at 2F$_{7/2}$ then decays to the 2H$_{11/2}$ and 2S$_{3/2}$ levels via non-radiative relaxation, producing green emission through the 2H$_{11/2}$ → 4I$_{15/2}$, and 2S$_{3/2}$ → 4I$_{13/2}$ transitions [6, 7]. The excited Er$^{3+}$ ion at 4I$_{11/2}$ level can also decay to the 4I$_{13/2}$ state,
and then populate to the $^{4}F_{9/2}$ by absorbing a 980 photon. Then the red emission from Er$^{3+}$ ion occurs via transition of $^{4}F_{9/2}$ → $^{4}I_{15/2}$.

Notably, due to the small distance between the Er$^{3+}$ and Ho$^{3+}$ ions in the Y$_2$O$_2$S: Yb$^{3+}$, Er$^{3+}$, Ho$^{3+}$ sample, the cross relaxations of $^{5}S_{2}$, $^{5}F_{4}$ (Ho$^{3+}$) + $^{4}I_{11/2}$ (Er$^{3+}$) → $^{5}I_{4}$ (Ho$^{3+}$) + $^{4}F_{9/2}$ (Er$^{3+}$) (CR3) can easily occur in the conventional triple-ion doped sample. This CR3 process significantly increases the population of Er$^{3+}$ ion at the $^{4}F_{9/2}$ level, which results in the much stronger red emission (due to
4F9/2 → 4I13/2 in the Y2O2S: Yb3+, Er3+ sample than that of the core-shell Y2O2S: Er3+ @ Y2O2S: Yb3+, Ho3+ sample. Meanwhile, this CR3 process also decreases the population of Ho3+ ion at the 5S2, 5F4 states, thereby, suppressing the green emission in the Y2O2S: Yb3+, Er3+, Ho3+ sample. The different UCL and ET processes in the Y2O2S: Yb3+, Er3+, Ho3+ and core-shell Y2O2S: Er3+ @ Y2O2S: Yb3+, Ho3+ samples indicate the formation of the core-shell structure and provide a possible route for adjustment of emission color.

Further, the fluorescence decay curves of Y2O2S: Er3+ @ Y2O2S: Yb3+, Ho3+ (Core-Shell) and Y2O2S: Yb3+, Er3+ samples were measured as shown in Figure 5. All the decay curves present non-exponential profile due to the relaxation and energy transfer processes between the Yb3+ ions and Er3+, Ho3+ ions. According to the lifetime equation of \( \tau = \int_0^\infty \frac{I(t)\,dt}{\int_0^\infty I(t)\,dt} \), where \( \tau \) is the calculated luminescence lifetime and \( I(t) \) is the luminescence intensity at time after the cutoff of the excitation light, the calculated lifetimes of green and red emissions of Y2O2S: Yb3+, Er3+ and Y2O2S: Er3+ @ Y2O2S: Yb3+, Ho3+ samples are listed in Table 1. It shows that lifetimes of red and green emissions of the core-shell Y2O2S: Er3+ @ Y2O2S: Yb3+, Ho3+ sample are much longer than that of the Y2O2S: Yb3+, Er3+ sample. This is owing to the effective protection of the shell layer for the emissions of Er3+ ions in the core. In addition, due to the non-radiative relaxation of 4I13/2 → 4I13/2 in the red emission process, the rising time of the red emission at 670 nm is much longer than that of the green emission at 548 nm. Therefore, the fluorescence decay measurements support the luminescence mechanisms.

### 4. Conclusion

The Y2O2S:Er3+@Y2O2S:Yb3+, Ho3+ core-shell NPs are synthesized by the homogeneous co-precipitation method combining with the solid-gas sulfidation route. Investigations on the UCL show that the emissions from Er3+ and Ho3+ ions are achieved simultaneously in the core-shell NPs. This is due to the efficient energy transfers of Yb3+ → Ho3+ within the shell layer and Yb3+ → Er3+ between the shell and the core. However, the core-shell Y2O2S: Er3+ @ Y2O2S: Yb3+, Ho3+ and the triple-ion doped Y2O2S: Yb3+, Er3+, Ho3+ samples present mainly green emission from Ho3+ ions (IG/IR = 2.8) and red luminescence from Er3+ ions (IG/IR = 0.3), respectively. The reason is that the cross relaxation between Er3+ and Ho3+ ions can easily occur due to the small distance between them in the Y2O2S: Yb3+, Er3+, Ho3+ sample. While on the other hand, this cross relaxation can be successfully suppressed by the core-shell structure where Ho3+ is in the shell and Er3+ is in the core. Therefore, the unique core-shell Y2O2S nanostructure could offer new channels for energy transfers and presents novel UC luminescence properties.

### Data Availability

The data used to support the findings of this study are included within the article.
Conflicts of Interest

There is no conflict of interest regarding the publication of this paper.

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Supplementary Materials

The supplementary material provides the experiments on the optimum rare earth doping concentrations and the particle size distribution of the precursors of the core and core-shell nanoparticles. (Supplementary Materials)

References


