

Hydrothermal synthesis combined with calcination of $\text{Gd}_2\text{O}_2\text{SO}_4:\text{Yb}^{3+},\text{Er}^{3+}$ nanoparticles and their up-conversion luminescence

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The $\text{Gd}_2\text{O}_2\text{SO}_4:\text{Yb}^{3+},\text{Er}^{3+}$ nanoparticles were synthesized by a general and facile hydrothermal synthesis followed by calcination utilizing commercially available Gd_2O_3 , Yb_2O_3 , Er_2O_3 , HNO_3 , urea and $\text{C}_{12}\text{H}_{25}\text{SO}_4\text{Na}$ as the starting materials. The precursor and the synthetic products were characterized by a variety of characterization tools. The results reveal that the precursor is composed of gadolinium hydroxyl, carbonate and sulfate groups and could be converted into pure $\text{Gd}_2\text{O}_2\text{SO}_4$ phase by calcining at 800°C for 2 hrs in air. The good crystallinity and dispersion of near-spherical $\text{Gd}_2\text{O}_2\text{SO}_4$ nanoparticles were obtained with an average diameter of about 50 nm. Under 980 nm infrared light excitation, the $\text{Gd}_2\text{O}_2\text{SO}_4:\text{Yb}^{3+},\text{Er}^{3+}$ nanoparticles present the strongest red emission (664 nm), which corresponds to the $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$ transition of Er^{3+} ions. Moreover, two green emission peaks are located at 546 nm and 526 nm, resulting from the $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ and $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$ transitions of Er^{3+} ions, respectively. When the concentration of Er^{3+} ions reaches 2%, the $\text{Gd}_2\text{O}_2\text{SO}_4:\text{Yb}^{3+},\text{Er}^{3+}$ nanoparticles shows the highest luminescence. The $\text{Ln}(\text{I}_{\text{up}})\text{-Ln}(\text{P})$ plots confirm that the up-conversion (UC) excitation belongs to two-photon ($^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$ and $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$) and three-photon ($^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$) absorption mechanisms.

Key words: Rare earth oxysulfate, Nanoparticles, Hydrothermal synthesis, Up-conversion luminescence (UCL).

Introduction

In recent years, rare-earth ions (RE^{3+}) doped materials have attracted considerable attention due to their distinct low phonon energy, high specific surface area, low symmetry and low cost technology [1]. Among these RE^{3+} ions, Er^{3+} ion is suitable candidate in up-conversion (UC) materials because of its narrow emission spectral lines and abundant energy levels [2]. Furthermore, Yb^{3+} ions, the efficient sensitizers with a large absorption cross section at around 980 nm, can efficiently transfer the excitation energy to Er^{3+} ions and increase the efficiency of the UC process [3, 4]. Thus, the Yb^{3+} and Er^{3+} co-doped nanoparticles have been developed as a new class of promising UC materials and widely applied in biological fields for immunoassay detection, gene delivery, drug carriers and selective catalysis [5], which can exhibit the ability to absorb infrared light and emit visible light via a two-or-more-photon system [6]. It is well known that the UC efficiency and the spectral range of materials mainly depend on the host matrix [7]. For example, Yb^{3+} and Er^{3+} ions used as sensitizers/activators in oxides [8, 9], oxysulfides [10, 11], fluorides [12], etc, have been extensively investigated for the predominant mechanisms of excited state absorption and energy transfer UC.

Recently, Gen Chen and co-workers reported a facile

biomolecule-assisted hydrothermal route for fabrication of the Yb/Er co-doped $\text{Y}_2\text{O}_2\text{SO}_4$ hollow sphere and examined its UPL properties [13]. Compared with $\text{Y}_2\text{O}_2\text{SO}_4$, gadolinium oxysulfate ($\text{Gd}_2\text{O}_2\text{SO}_4$) has been a promising UC host matrix due to its unique magnetic property, giving it a potential application in the biotechnology field. However, to the best of our knowledge, there are no reports on the UC mechanism of $\text{Gd}_2\text{O}_2\text{SO}_4:\text{Yb}^{3+},\text{Er}^{3+}$ nanoparticles. So far, various synthetic approaches have been explored to prepare RE^{3+} doped $\text{Gd}_2\text{O}_2\text{SO}_4$ nano/micro particles including, thermal decomposition method [14], co-precipitation method [15], homogeneous precipitation method [16], hydrothermal method [17], electrospinning method [18], complexation-thermal decomposition (CTD) method [19], biomolecular template method [20] and so on. In the present work, the $\text{Gd}_2\text{O}_2\text{SO}_4:\text{Yb}^{3+},\text{Er}^{3+}$ nanoparticles were synthesized via a facile hydrothermal method followed by calcination in air from commercially available Gd_2O_3 , Yb_2O_3 , Er_2O_3 , HNO_3 , urea and $\text{C}_{12}\text{H}_{25}\text{SO}_4\text{Na}$ as the starting materials. Moreover, their UCL properties were also investigated in detail.

Experimental Procedure

Gd_2O_3 (99.99% purity), Yb_2O_3 (99.99% purity), Er_2O_3 (99.99% purity), HNO_3 (AR), urea (AR) and $\text{C}_{12}\text{H}_{25}\text{SO}_4\text{Na}$ (CP) were used as the starting materials without further purification. Gd_2O_3 , Yb_2O_3 and Er_2O_3 powders were purchased from Jining TianYi New Materials Co. Ltd, China and other reagents were purchased from Sinopharm

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Chemical Reagent Co. Ltd, China. Firstly, a clear solution of $\text{Gd}(\text{NO}_3)_3$ with a Gd^{3+} ion concentration of 0.1 M was obtained by dissolving Gd_2O_3 powers in diluted nitric acid, and the $\text{Er}(\text{NO}_3)_3$ (0.1 M) and the $\text{Yb}(\text{NO}_3)_3$ (0.1 M) solutions were also prepared using the same procedure. Accompanied with vigorous stirring, a uniform mixture solution was formed by slowly adding a certain amount of $\text{Gd}(\text{NO}_3)_3$, $\text{C}_{12}\text{H}_{25}\text{SO}_4\text{Na}$ and urea with a molar ratio of 2 : 1 : 1 for Gd^{3+} : SO_4^{2-} : $\text{CO}(\text{NH}_2)_2$. After that, the mixture solution was transferred to 100 mL Teflon-lined stainless steel autoclave with some deionized water added up to 75% of the total volume. Then the autoclave was sealed and heated in an electric blast drying oven for hydrothermal synthesis at 120 °C for 24 hrs. After the mixture cooled to room temperature naturally, the resulting white precipitations were collected by filtration and washed with distilled water and absolute ethanol for several times and dried at 80 °C for 8 hrs successively to obtain the precursor. Finally, the as-prepared precursor was calcined to produce $\text{Gd}_2\text{O}_2\text{SO}_4$ nanoparticles in air at 800 °C for 2 hrs. The corresponding $\text{Gd}_2\text{O}_2\text{SO}_4$: 10% Yb^{3+} , $x\text{Er}^{3+}$ ($x = 1\%$, 2%, 5%, 8% and 10%) nanoparticles were also synthesized in the same way. Here, x represents the molar ratio.

DSC-TG-DTG was performed using a Netzsch STA449F3C integrated thermal analyzer in a temperature range of 25–1400 °C at a heating rate of 10 °C·min⁻¹ under an air flow. Fourier transform infrared spectra (FT-IR) were recorded in the region of 4000–400 cm⁻¹ using a Bruker Vertex 70 FT-IR spectrophotometer by the KBr method. Phase analysis was identified by X-ray diffractometer (XRD, SHIMADZU-7000) operating at 40 kV and 30 mA, using Cu K α (1.5406 Å) radiation. The particle morphologies, selected area electron diffraction (SAED) patterns and high resolution transmission electron microscopy (HRTEM) images were taken by a JEOL-2010 transmission electron microscope operated at an acceleration voltage of 200 kV with Gatan Digital Micrograph software packages for measuring crystal plane spacing. Up-conversion luminescence (UCL) spectra were obtained on a Hitachi F-4600 fluorescence spectrophotometer equipped with an external power-controllable 980 nm semiconductor laser as the excitation source. All measurements were performed at room temperature.

Results and Discussion

Thermal decomposition behavior of the precursor

In order to explore the chemical stability as well as the calcination temperature of the precursor for the continuous steps investigation [26], the DSC-TG-DTG graphs were conducted from room temperature to 1400 °C in flowing air atmosphere and the results are shown in Fig. 1. The TG curve shows two main stages of the weight loss and particularly the overall weight

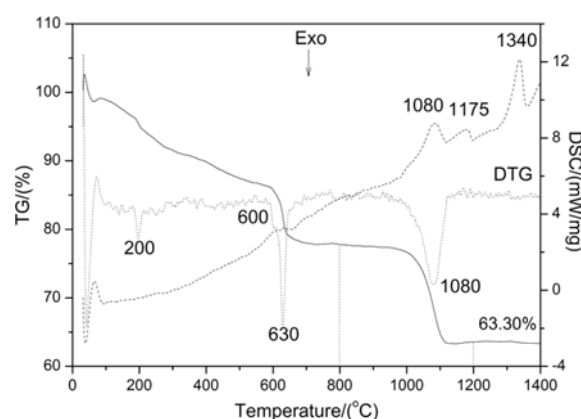


Fig. 1. DSC-TG-DTG curves of the precursor in flowing air atmosphere.

loss is observed approximately 36.70 wt%. The first weight loss between room temperature to ~800 °C is about 21.30 wt% in the TG curve, and the strong peak of DTG is at about 630 °C in the DTG curve, which seem to be caused by the removal of physically absorbed water, the complete dihydroxylation and the decomposition of CO_3^{2-} groups of the precursor. There is a relatively steady upward trend with a weak endothermic peak at around 600 °C in the DSC curve. The second weight loss of 15.4 wt% starting at ~800 °C is attributed to the gradual decomposition of the target $\text{Gd}_2\text{O}_2\text{SO}_4$ phase (DTG maxima: 1080 °C). The exothermic peaks centered at 1080 °C, 1175 °C and 1340 °C on the DSC curve indicate that the above process is an exothermic reaction caused by the crystallization of the Gd_2O_3 phase. These results will be consistent with those obtained by FT-IR and XRD in the following section. From what has been discussed above, 800 °C was used to as the reasonable calcination temperature for the synthesis of pure $\text{Gd}_2\text{O}_2\text{SO}_4$ nanoparticles in the present study.

Structural and phase analysis

FT-IR analysis of the materials is both significant to gain further understanding of structure and decomposition mechanism, which depicts the changes of the precursor and its calcination products at 800 °C and 1200 °C for 2 hrs in air. Evidence of the presence of water molecules, the CO_3^{2-} groups and the SO_4^{2-} groups in the precursor can be obtained from FT-IR spectroscopy (Fig. 2(a)), as shown by the broad absorption peaks of the physically absorbed water, hydroxyl groups (near 3470 cm⁻¹ and 1640 cm⁻¹), the CO_3^{2-} groups (near 1540 cm⁻¹, 1430 cm⁻¹, 840 cm⁻¹ and 770 cm⁻¹) and the SO_4^{2-} groups (near 1110 cm⁻¹ and 600 cm⁻¹), which confirms the precursor is mostly composed of gadolinium hydroxyl, carbonate and sulfate groups. With increasing calcination temperature to 800 °C (Fig. 2(b)), the broad absorption band centered at 3470 cm⁻¹ become negligible, indicating the removal of hydroxyl groups from the precursor. The absorption bands of the CO_3^{2-} groups (near 1540 cm⁻¹, 1430 cm⁻¹, 840 cm⁻¹ and 770 cm⁻¹) fade away, suggesting the

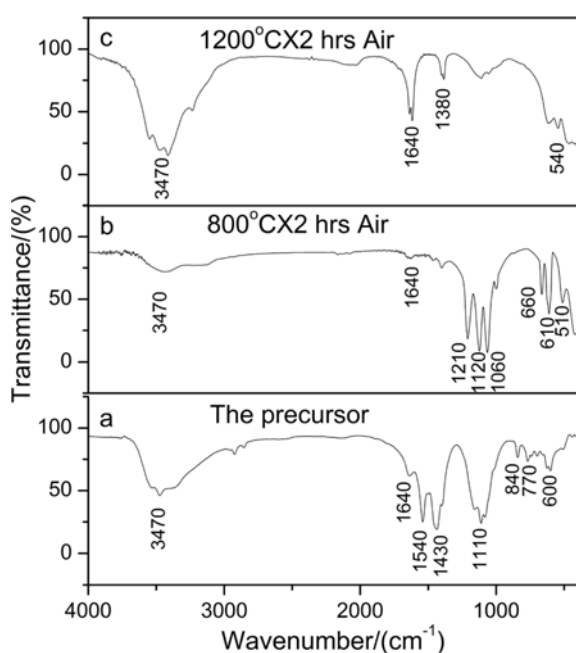


Fig. 2. FT-IR spectra of the precursor and its calcination products at 800 °C and 1200 °C for 2 hrs in air.

decomposition of the CO_3^{2-} groups in the precursor. The broad SO_4^{2-} absorption bands (1110 cm^{-1} and 600 cm^{-1}) split into some narrow peaks (1210 cm^{-1} , 1120 cm^{-1} , 1060 cm^{-1} , 660 cm^{-1} and 610 cm^{-1}) and a new absorption peak centered about 510 cm^{-1} appears, which corresponds to the characteristic vibration peak of Gd-O bond in the calcined product, indicating that the precursor has been transformed into $\text{Gd}_2\text{O}_2\text{SO}_4$ phase. Further increasing the calcination temperature to 1200 °C, as seen from Fig. 2(c), the peak centered at 1110 cm^{-1} become much weaker, resulting from the decomposition of SO_4^{2-} groups in the calcined product. Moreover, the absorption peaks of Gd-O bond still exist. These results will be consistent with those obtained by the XRD in the following section. It is noted that the broad absorption band (near 3470 cm^{-1}) and the weak absorption peak (near 1640 cm^{-1}) in the calcined product can be assigned to the characteristic peaks of absorbed water. Besides, the absorption peak near 1380 cm^{-1} demonstrates the presence of the CO_3^{2-} groups, which was caused by absorbed H_2O and CO_2 from ambient atmosphere on the surface of the calcined product.

To investigate the phase transformation process, Fig. 3 shows XRD patterns of the precursor and its calcination products at 800 °C and 1200 °C for 2 hrs in air, respectively. XRD analysis shows that the precursor is crystalline state in structure with essentially diffraction peaks and kept an unknown phase, as shown in Fig. 3(a). After the precursor calcined at 800 °C (Fig. 3(b)), well defined diffraction peaks appeared, which were well indexed as the pure $\text{Gd}_2\text{O}_2\text{SO}_4$ phase matched with the standard value according to standard JCPDS

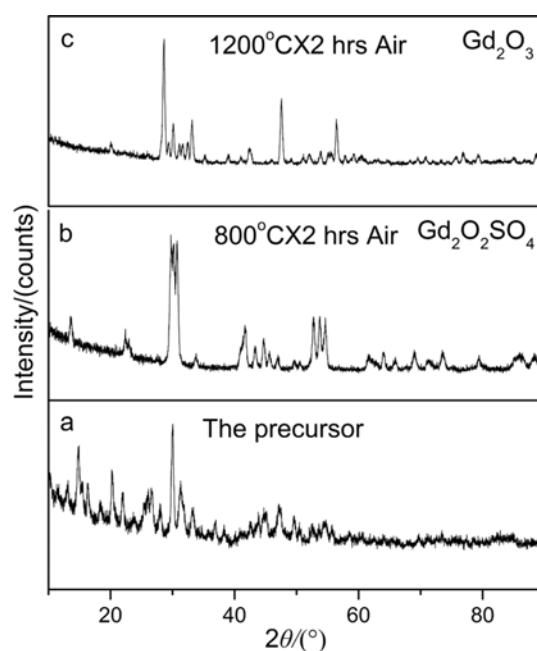


Fig. 3. XRD patterns of the precursor and its calcination products at 800 °C and 1200 °C for 2 hrs in air.

No.00-041-683. With the increasing calcination temperature to 1200 °C (Fig. 3(c)), the obtained diffraction patterns are well consistent with the data reported in standard JCPDS card No.00-070-903, indicating that the precursor could be converted into pure Gd_2O_3 phase, and no other impurity phases can be observed. Phase evolution upon calcination corresponding well with the thermal behavior analyzed before (Fig. 1). The analysis of the results given above is also consistent with the DSC-TG-DTG and the FT-IR spectra investigations.

Morphological analysis

The morphology and structure details of the precursor and the target $\text{Gd}_2\text{O}_2\text{SO}_4$ nanoparticles were characterized by TEM technique. Figure 4 reveals TEM, SAED and HRTEM images of the precursor and its corresponding calcined product. As shown in Fig. 4(a), the precursor, existing in a form of scattered distribution, consists of crashed ice-like aggregates with angular pieces on a large scale. After the precursor calcined at 800 °C for 2 hrs in air, shown in Fig. 4(b), the obtained target $\text{Gd}_2\text{O}_2\text{SO}_4$ is near-spherical in shape, well dispersed and have an average diameter of about 50 nm in size. The shrinkage in size and variable morphology from ice-like pieces to near-spherical samples might be due to the thermal decomposition of thin and angular pieces resulting in more ultrafine $\text{Gd}_2\text{O}_2\text{SO}_4$ nanoparticles. Besides, the SAED pattern shown in Fig. 4(c) contains concentric rings and dot patterns, indicating the polycrystalline nature of the $\text{Gd}_2\text{O}_2\text{SO}_4$ nanoparticles. The diffraction rings are indexed as (013) and (114) reflections of the $\text{Gd}_2\text{O}_2\text{SO}_4$ phase and coincident with the result of XRD. The HRTEM image (Fig. 4(d)) shows

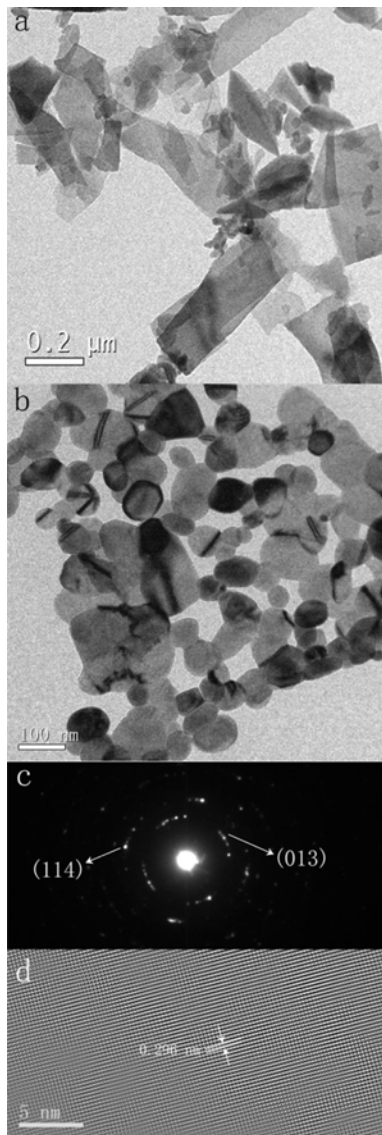


Fig. 4. TEM, SAED and HRTEM images of the precursor and its corresponding calcined product. (a) the precursor, (b) $\text{Gd}_2\text{O}_2\text{SO}_4$ nanoparticles, (c) SAED pattern of $\text{Gd}_2\text{O}_2\text{SO}_4$ nanoparticles, (d) HRTEM of $\text{Gd}_2\text{O}_2\text{SO}_4$ nanoparticles.

clear lattice fringes. The HRTEM measuring distinct lattice spacing of 0.296 nm corresponded to the (013) crystallographic planes of the $\text{Gd}_2\text{O}_2\text{SO}_4$, according to the standard JCPDS card (No.00-041-683).

UCL properties

Figure 5 shows the UCL emission spectra of the $\text{Gd}_2\text{O}_2\text{SO}_4:10\%\text{Yb}^{3+},x\text{Er}^{3+}$ nanoparticles ($x = 1\%, 2\%, 5\%, 8\%$ and 10%) under 980 nm infrared light excitation at room temperature. A significant feature of these spectra can be clearly observed that the relative intensity of UCL emission vary with the concentration of Er^{3+} ions. The three distinct emission bands centered at 526 nm, 546 nm and 664 nm are attributed to the $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$ (green), the $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ (green) and the $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$ (red) transitions of Er^{3+} ions, respectively. Typically,

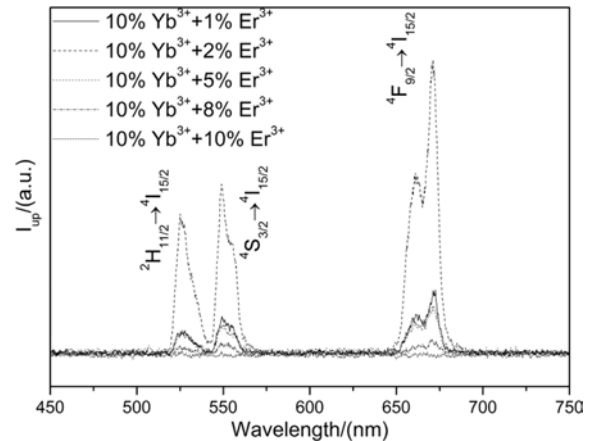


Fig. 5. The UCL emission spectra of the $\text{Gd}_2\text{O}_2\text{SO}_4:10\%\text{Yb}^{3+},x\text{Er}^{3+}$ nanoparticles ($x = 1\%, 2\%, 5\%, 8\%$ and 10%) under 980 nm infrared light excitation.

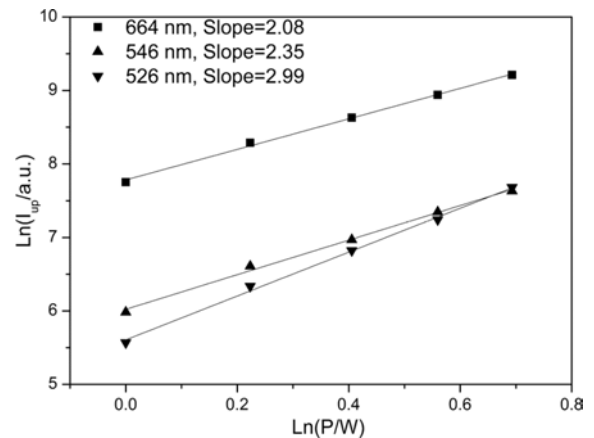


Fig. 6. The $\text{Ln}(I_{\text{up}})\text{-Ln}(P)$ plots of the UCL emission for the $\text{Gd}_2\text{O}_2\text{SO}_4:10\%\text{Yb}^{3+},2\%\text{Er}^{3+}$ nanoparticles.

it is found that $\text{Gd}_2\text{O}_2\text{SO}_4:10\%\text{Yb}^{3+},2\%\text{Er}^{3+}$ nanoparticle exhibits the strongest intensity of red and green emission, which indicates the successful cooperative luminescence with the suitable concentration between Yb^{3+} and Er^{3+} ions.

It is well known that the unsaturated UCL is related with the number of photons according to the relational expression $I_{\text{up}} \propto P_{\text{pump}}^n$, where I_{up} is the UCL emission intensity, P_{pump} is the pump laser power, and n represents the number of pump photons required to populate the emitting states [11]. Figure 6 shows the dependence of three UCL emissions for the $\text{Gd}_2\text{O}_2\text{SO}_4:10\%\text{Yb}^{3+},2\%\text{Er}^{3+}$ nanoparticles under 980 nm infrared light excitation in the $\text{Ln}(I_{\text{up}})\text{-Ln}(P)$ plots. A gradual rising trend in the straight line for both green and red emissions can be observed while the exciting power changes from 1 W to 2 W. The n values of the $\text{Gd}_2\text{O}_2\text{SO}_4:10\%\text{Yb}^{3+},2\%\text{Er}^{3+}$ are calculated to be 2.35 and 2.05 for the 546 nm green emission and 664 nm red emission, respectively, which are all around 2, indicating that UCL excitation belong to two-photon process. Particularly, it is found that the 526 nm green

emission produces a slope value of 2.99, which means a three-photon process probably participated in the green UCL excitation process.

Conclusions

A general and facile hydrothermal synthesis followed by calcination has been developed for the synthesis of well dispersed near-spherical $\text{Gd}_2\text{O}_2\text{SO}_4$ nanoparticles with an average diameter of about 50 nm. Meanwhile, Yb^{3+} and Er^{3+} ions co-doped $\text{Gd}_2\text{O}_2\text{SO}_4:\text{Yb}^{3+},\text{Er}^{3+}$ nanoparticles were also successfully synthesized and showed abundant UCL properties under 980 nm infrared light excitation. Besides, the green and red emission bands consist of $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ (546 nm) and $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$ (664 nm) identified two-photon UCL processes, and three-photon UCL process is observed in the $\text{Ln}(\text{I}_{\text{up}})\text{-Ln}(\text{P})$ plots for green emission centered at 526 nm ($^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$). In sum, the as-synthesized $\text{Gd}_2\text{O}_2\text{SO}_4:\text{Yb}^{3+},\text{Er}^{3+}$ nanoparticles are expected to bring new potential applications in biological fields with further fundamental and detail research, such as immunoassay detection, bio-probes and other biotechnology fields.

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