

Synthesis of $\text{Gd}_2\text{O}_2\text{S} : \text{Eu}^{3+}$ hollow sphere by a hydrothermal method assisting with reduction route

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$\text{Gd}_2\text{O}_2\text{S} : \text{Eu}^{3+}$ hollow spheres were successfully synthesized through a hydrothermal method assisting with reduction route from commercially available Gd_2O_3 , Eu_2O_3 , HNO_3 , $(\text{NH}_4)_2\text{SO}_4$ and $\text{CO}(\text{NH}_2)_2$ (urea) as the starting materials. The as-synthesized products were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), field emission scanning electron microscopy (FE-SEM) and photoluminescence (PL) spectra. The XRD and FT-IR results demonstrate that the precursor has highly crystalline in nature and could be converted into pure $\text{Gd}_2\text{O}_2\text{S}$ phase at 800 °C for 2 hrs in the hybrid atmosphere of flowing argon and hydrogen (90%Ar + 10%H₂). SEM and FE-SEM observations show that the obtained $\text{Gd}_2\text{O}_2\text{S}$ particles possess hollow sphere structure, which has a typical size of about 10 μm in diameter and about 1 μm in shell thickness. PL spectroscopy reveals that the strongest red emission peak is located at 628 nm under 277 nm and 330 nm UV light excitation for the $\text{Gd}_2\text{O}_2\text{S} : \text{Eu}^{3+}$ (5%mol) hollow spheres, which corresponds to the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition of Eu^{3+} ions. Decay study demonstrates that the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition of Eu^{3+} ions has a single exponential decay behavior. The fitting result shows the lifetime for the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition under 277 nm and 330 nm UV light excitation is 0.5692 ms and 0.5435 ns, respectively.

Key words: Gadolinium oxysulfide, Hydrothermal synthesis, hollow sphere, Urea-ammonium sulfate (UAS) system, Photoluminescence.

Introduction

Recently, hollow micro/nanostructures have aroused extensive interest owing to their unique outstanding properties [1-3], including porous shell, good permeation, low density, high loading capacity, controlled-release viability, enhanced catalytic activity, and excellent luminescent properties, making them a wide range of potential applications in drug-delivery carriers [4-5], efficient catalysis [6], bio-imaging [7], and so on. A lot of effort has been devoted to the development of different methods for the design and fabrication of hollow structures. Most of the systems reported for the formation of hollow spherical materials were based on template-assisted processes, which is the most straightforward and feasible method [3-4, 8-10]. However, this template directing strategy suffers from many disadvantages including high cost, complicated procedures and environmental pollution problems, etc. Thus, it is desirable to develop template-free strategies for the synthesis of hollow structures. This strategy mainly relies on various well-known phenomena such as Ostwald ripening, Kirkendall effect and chemically induced self-transformation, which all have been widely employed for fabricating hollow spheres due to its simple and economical characteristic [11-15]. Especially, a

water-based template-free method provides a number of merits such as simplicity, convenience, environmental, and so on.

Gadolinium oxysulfide ($\text{Gd}_2\text{O}_2\text{S}$) is a wide bandgap (4.6-4.8 eV) semiconductor and, often exhibit favorable properties such as excellent chemical durability, high thermal stability, innocuity and high luminescent efficiency, which may have great potential and wide applications in efficient phosphorescent host materials, X-ray intensifying screens for medical diagnosis, laser materials, X-ray-computed tomography (X-CT), up-conversion bio-imaging, and so on [16-19]. In previous reports, efforts has been devoted to the synthesis of $\text{Gd}_2\text{O}_2\text{S}$ nano/micro materials, including solid-state reaction (SSR) method [20], combustion synthesis method [21], emulsion liquid membrane (ELM) method [22], gas sulfuration method [23], decomposition method [24], hydro/solvothermal method [25-26] and chemical precipitation method [27-29], etc. In particular, considerable researches have been focused on the synthesis of $\text{Gd}_2\text{O}_2\text{S}$ hollow sphere. For instance, as was reported [26], Jing Huang et al. reported a solvothermal preparation of $\text{Gd}_2\text{O}_2\text{S} : \text{Eu}^{3+}/\text{Gd}_2\text{O}_2\text{S}$ hollow microsphere and investigated its luminescence properties. To the best of our knowledge, preparation of the $\text{Gd}_2\text{O}_2\text{S}$ hollow spheres via a template-free method using a water-based system has rarely been reported. In this paper, we put forward a simple but effective hydrothermal method assisting with reduction route to synthesize $\text{Gd}_2\text{O}_2\text{S}$ hollow sphere without using any sacrificial templates based on a water-based

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urea-ammonium sulfate (UAS) system. Compared with the template synthesis, this method provides a number of merits such as environmental-friendly, simplicity, and convenience. Furthermore, structure, morphology and photoluminescence (PL) properties of the as-synthesized products have been also investigated.

Experimental Procedure

Materials and synthesis

Gd_2O_3 (99.9% purity), Eu_2O_3 (99.99% purity), HNO_3 (AR), $(\text{NH}_4)_2\text{SO}_4$ (AR) and $\text{CO}(\text{NH}_2)_2$ (urea, AR) were used as the starting materials without further purification. Gd_2O_3 and Eu_2O_3 powders were purchased from Shanghai New Materials Yuelong Co. Ltd, other reagents were purchased from Sinopharm Chemical Reagent Co. Ltd, China. Firstly, a $\text{Gd}(\text{NO}_3)_3$ solution with a Gd^{3+} ion concentration of 0.1 M, was prepared by dissolving Gd_2O_3 powder in diluted nitric acid, followed by adding $(\text{NH}_4)_2\text{SO}_4$ and $\text{CO}(\text{NH}_2)_2$ to form mixed solutions with molar ratio of 2 : 4 : 1 for $\text{Gd}^{3+} : \text{SO}_4^{2-} : \text{CO}(\text{NH}_2)_2$. The mixture solutions were then transferred into a 100 ml Teflon-linked stainless steel autoclave and some deionized water was added up to 75% of the total volume. The autoclaves were sealed and kept in an electric blast drying oven for 24 hrs under 120 °C for hydrothermal synthesis. When the autoclaves were cooled down to room temperature, the white precipitations were obtained. The resulted white precipitations were collected after filtration, washed with distilled water and ethanol several times and dried at 80 °C for 8 hrs to obtain the precursor. Finally, the precursor was reduced at 800 °C for 1 hr in the hybrid atmosphere of flowing argon and hydrogen (90%Ar + 10%H₂) to form the target products. Furthermore, trivalent europium ion (Eu^{3+}) doped target products were also obtained by a similar process. The concentration of Eu^{3+} ions was set 5 mol% and was compensated by an equivalent decrease of Gd^{3+} ions.

Characterization

Phase analysis was identified on a X-ray diffractometer (XRD, SHIMADZU-7000) operating at 40 kV and 30 mA, using Cu K α (1.5406 Å) radiation. 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 KBr method. The particle morphology were observed by a VEGA3 TESCAN scanning electron microscope (SEM) and a Hitachi UHR SU8010 FE-SEM. Photoluminescence (PL) spectra were obtained on a Hitachi F-4600 fluorescence spectrophotometer equipped with a 150 W xenon lamp as the excitation source. All measurements were performed at room temperature.

Results and Discussion

Formation and structure of the precursor

In the present hydrothermal system, the hydrolyzation process of $\text{Gd}(\text{NO}_3)_3$ and $(\text{NH}_4)_2\text{SO}_4$ can provide Gd^{3+} ions and SO_4^{2-} groups, respectively. Moreover, urea is a weak brønsted base and releases CO_3^{2-} and OH groups at temperatures up to 120 °C. It is noted that the anions (CO_3^{2-} , OH and SO_4^{2-} groups) are hard bases and Gd^{3+} ions are hard acids. Then it is easy to bond each other to form gadolinium hydroxyl, carbonate and sulfate according to hard-soft acid-base (HSAB) principle. The phase structure of the as-synthesized precursor was first examined by XRD. As shown in Fig. 1(a), the sharp diffraction peaks appear in the XRD pattern, indicating that the precursor has highly crystalline in nature. Unfortunately, there is no relevant crystal structure information in standard JCPD card database and the crystal structure of the precursor is yet to be unidentified. FT-IR analysis was then performed to further gain more insight into the structure and composition of the precursor. As shown in Fig. 1(b), the broad characteristic band appearing around 3430 cm^{-1} and the weak peak at 1640 cm^{-1} in the precursor are assigned to the characteristic –OH stretching vibration and bending vibration of water molecules, respectively. In addition, one peak at ~3540 cm^{-1} can be attributed to structural hydroxyl group (OH). The sharp peak at 1440 cm^{-1} and the two splitting peaks around 1500 cm^{-1} and 1540 cm^{-1} are attributed to ν_3 mode of carbonate. The three peaks at about 1000 cm^{-1} , 840 cm^{-1} and 740 cm^{-1} are assigned ν_1 , ν_2 and ν_4 modes of carbonate, respectively. Moreover, the characteristic peaks appeared in the range of 1170–

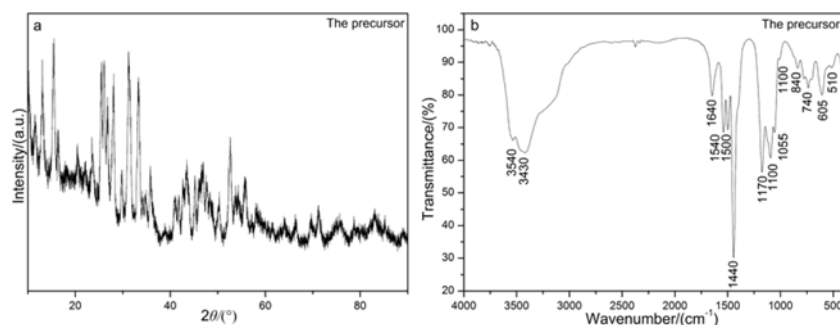


Fig. 1. XRD pattern and FT-IR spectrum of the precursor.

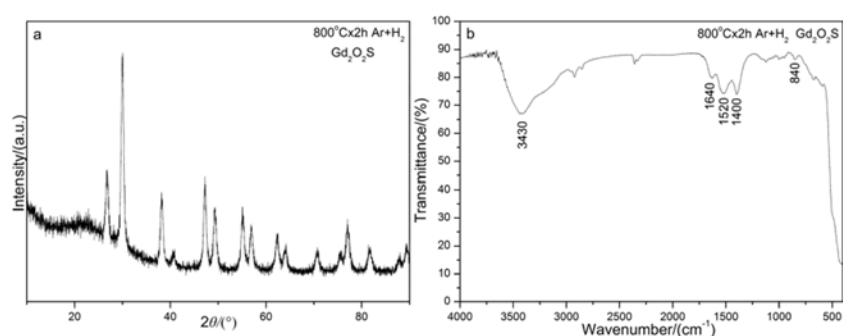
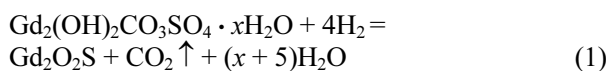


Fig. 2. XRD pattern and FT-IR spectrum of the final reduction product.

1055 cm^{-1} and 605 cm^{-1} belong to the vibrations of the sulfate groups. In sum, the FT-IR spectrum indicates that the precursor is mostly composed of gadolinium hydroxyl, carbonate and sulfate groups with some crystal water.

Structure of the reduction products

Fig. 2 shows the XRD pattern and FT-IR spectrum of the reduction products. Shown in Fig. 2(a), the obtained diffraction peaks are well consistent with the data reported in JCPDS card No.00-026-1422, indicating that the reduction product is composed of pure $\text{Gd}_2\text{O}_2\text{S}$ phase. Based on our previous reports [29-30], the chemical reactions in the formation of the $\text{Gd}_2\text{O}_2\text{S}$ phase can be formulated as follows [Eqs.(1)]:



Moreover, obvious change was observed in FT-IR spectrum of the $\text{Gd}_2\text{O}_2\text{S}$ compared with its precursor. As shown in Fig. 2(b), the absorption peak of 3540 cm^{-1} disappears, suggesting the dehydroxylation of hydroxyl groups. The broad absorption peaks centered at 3430 cm^{-1} and 1640 cm^{-1} still exist because the $\text{Gd}_2\text{O}_2\text{S}$ sample is also easy to adsorb water from the ambient atmosphere. The three characteristic peaks of ν as O-C-O (1520 and 1440 cm^{-1}) and $\pi\text{-CO}_3^{2-}$ (840 cm^{-1}) demonstrated the presence of the CO_3^{2-} groups, which was caused by absorbed water and CO_2 from ambient atmosphere on the surface of the $\text{Gd}_2\text{O}_2\text{S}$ sample. The SO_4^{2-} absorption peaks (1170 cm^{-1} , 1100 cm^{-1} and 605 cm^{-1}) become negligible, indicating the reduction of SO_4^{2-} groups to S^{2-} in reducing atmosphere. However, the chemisorbed water molecule and CO_3^{2-} groups do not influence the XRD results as described above.

Morphologies of the synthesized products

Fig. 3 shows SEM images of (a) the precursor, (b) the $\text{Gd}_2\text{O}_2\text{S}$ hollow spheres and (c) EDS pattern. It is clear from Fig. 3(a) that the precursor particles are spherical in shape, well dispersed and have an average diameter of about $15\text{ }\mu\text{m}$ in size. Interestingly, the cracked sphere as marked by an arrow in Fig. 3(a) clearly indicates that the precursor particles possess hollow sphere structure. The SEM image of the corresponding reduction

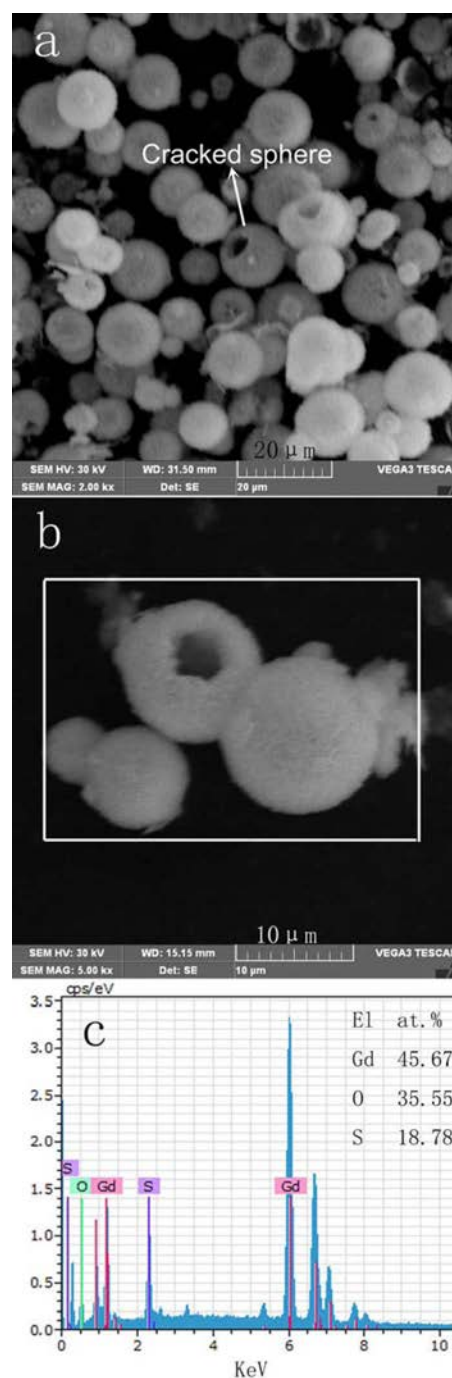


Fig. 3. SEM images of (a) the precursor, (b) the $\text{Gd}_2\text{O}_2\text{SO}_4$ hollow spheres and (c) EDS pattern.

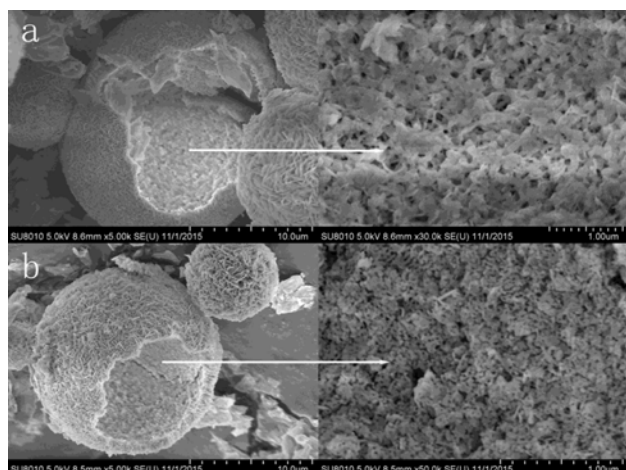


Fig. 4. FE-SEM image of the precursor and the $\text{Gd}_2\text{O}_2\text{SO}_4$ hollow spheres.

product ($\text{Gd}_2\text{O}_2\text{S}$) is also shown in Fig. 3(b). It can be seen from the SEM image that the $\text{Gd}_2\text{O}_2\text{S}$ inherits its parents' morphologies, which is still composed of spherical particles with hollow structure and an average diameter of about 10 μm in diameter. Moreover, the EDS analysis was conducted to gain the composition of the reduction product and the result is shown in Fig. 3(c), which demonstrates that the hollow spheres consist of gadolinium (Gd), oxygen (O), and sulphur (S) elements. The elemental ratios of Gd to O and S contained in the $\text{Gd}_2\text{O}_2\text{S}$ hollow spheres is quantified as 45.67 : 35.55 : 18.78 and is close to 2 : 2 : 1, which is the further evidence of the formation of $\text{Gd}_2\text{O}_2\text{S}$ phase. To clarify the possible formation mechanism, the morphologies of the precursor and the $\text{Gd}_2\text{O}_2\text{S}$ hollow spheres were further characterized by FE-SEM. The FE-SEM image of the precursor shown in Fig. 4(a) exhibits the detailed outer and interior structure information. Careful observation shows that the outer surface of the precursor is composed of numerous nanosheets and these nanosheets assemble randomly to form cage-like morphology. The right part in Fig. 4(a) reveals the interior microstructure of the precursor. It is clearly seen that the coarse interior is composed of a large quantity of small nanoparticle aggregation. The FE-SEM image of the $\text{Gd}_2\text{O}_2\text{S}$ hollow spheres is also shown in Fig. 4(b), which clearly reveals that the $\text{Gd}_2\text{O}_2\text{S}$ hollow sphere has a typical size of about 10 μm in diameter and about 1 μm in shell thickness, which is similar to that of the precursor except for size shrinkage in external diameter and interior particle due to the higher density of gadolinium oxysulfide than that of the precursors. Based on the above experimental results, a possible mechanism for the formation of the $\text{Gd}_2\text{O}_2\text{S}$ hollow spheres was proposed as follows. First, numerous tiny nuclei was formed in the present hydrothermal reaction system and the growth of the nucleus lead to the formation of nanoparticles. Second, for the minimization of surface energy, a great deal of

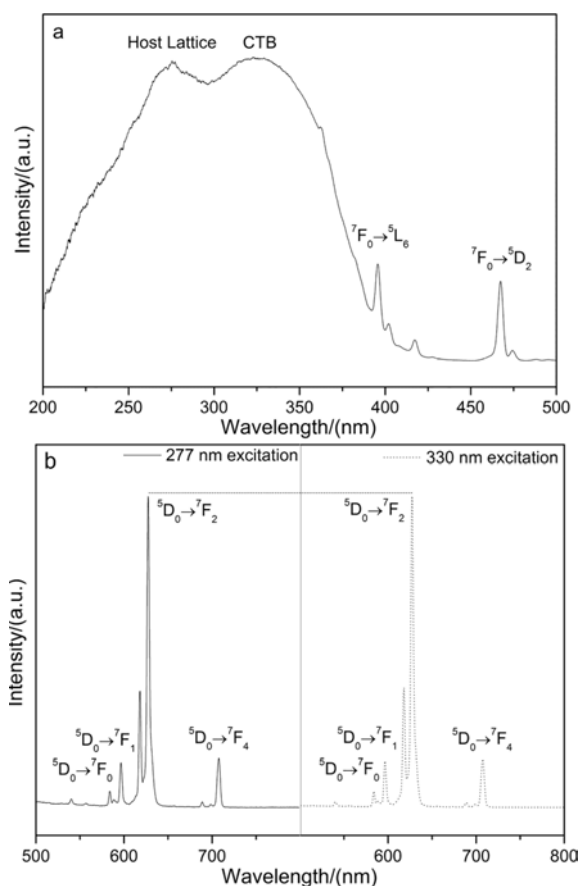


Fig. 5. Excitation (a) and emission (b) spectra of the $\text{Gd}_2\text{O}_2\text{S} : \text{Eu}^{3+}$ hollow spheres.

nanoparticles tends to aggregate and assemble into a spherical structure during the reaction process. Finally, the hollow spheres were formed by Ostwald ripening process. Such a process involves dissolution-recrystallization and further growth processes. The smaller nanoparticles in the interior dissolved gradually and the nanosheets in the outer layers grew larger and faceted at the expense of the inner ones, which was accompanied by the formation of the interior space. Also, further work is underway to investigate the details of the self-assembly growth mechanism.

PL spectra of the $\text{Gd}_2\text{O}_2\text{S} : \text{Eu}^{3+}$ hollow sphere

Fig. 5 shows the excitation and emission spectra of the $\text{Gd}_2\text{O}_2\text{S} : \text{Eu}^{3+}$ hollow sphere. As can be seen from Fig. 5(a), two broad excitation bands with almost the same intensity appear in the excitation spectrum. One excitation band located at 277 nm is attributed to the band gap self-absorption of $\text{Gd}_2\text{O}_2\text{S}$ host lattice, corresponding to its fundamental absorption edge of 4.6 eV in energy according to basic quantum mechanics formula (2)

$$E = 1240/\lambda(\text{nm}) \text{ (eV)} \quad (2)$$

Where E is photon energy, while λ is wavelength of

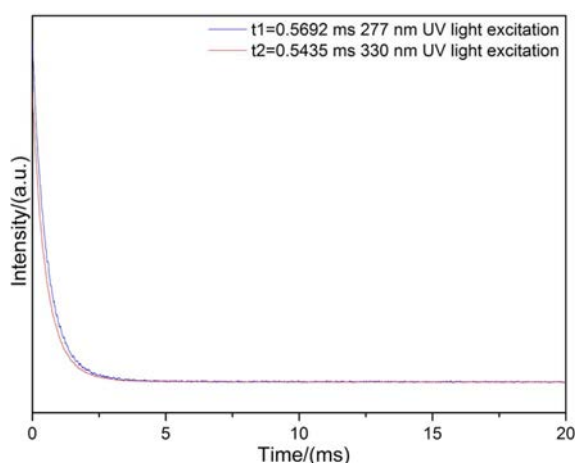


Fig. 6. The decay curve of the $^5D_0 \rightarrow ^7F_2$ transition for the $Gd_2O_2S : Eu^{3+}$ hollow spheres under 277 nm and 330 nm UV light excitation.

photon. The other broad absorption band with a maximum at 330 nm exists, which is resulted from the charge-transfer (CT) transitions between O^{2-} and Eu^{3+} ions. The weak narrow peaks in the near UV range of the excitation spectrum are assigned to intra-configurational $4f-4f$ transitions of Eu^{3+} ions in the oxysulfide host lattice, and the peaks at 395 nm and 465 nm are attributed to the $^7F_0 \rightarrow ^5L_6$ and $^7F_0 \rightarrow ^5D_2$ transitions of Eu^{3+} ions. In addition, the intra-configurational $4f^6$ excitation lines of the Eu^{3+} ions are very weak, indicating that the excitation of Eu^{3+} ions through the CT state for emission would be very efficient. The emission spectra of the $Gd_2O_2S : Eu^{3+}$ phosphor under 277 nm and 330 nm and UV light excitation (Fig. 5(b)) demonstrates the well-known $^5D_0 \rightarrow ^7F_j$ ($j = 0, 1, 2, 3, 4$) transitions of Eu^{3+} ions. The strongest emission peak located at 628 nm corresponds to the forced electric dipole $^5D_0 \rightarrow ^7F_2$ transition of Eu^{3+} ions. These are typical emission peaks of Eu^{3+} ions in an oxysulfide host.

Fig. 6 shows the decay curve of the $^5D_0 \rightarrow ^7F_2$ transition of Eu^{3+} ions under 277 nm and 330 nm UV light excitation for the $Gd_2O_2S : Eu^{3+}$ hollow sphere. Shown in Fig. 6, the two decay curves can be well fitted into single exponential function of $I = I_0 + A \exp(-t/\delta)$, in which τ is lifetime of Eu^{3+} ions. The fitting result shows the lifetime for the $^5D_0 \rightarrow ^7F_2$ transition under 277 nm and 330 nm UV light excitation is 0.5692 ms and 0.5435 ms, respectively.

Conclusions

Pure $Gd_2O_2S : Eu^{3+}$ hollow spheres have been successfully achieved by a hydrothermal method assisting with reduction route. The present study shows that the precursor could be transformed into pure Gd_2O_2S hollow spheres with a typical size of about 10 μm in diameter and about 1 μm in shell thickness at 800 $^{\circ}C$ for 2 hrs in the reduction atmosphere. The strongest red emission peak located at

628 nm under 277 nm and 330 nm UV light excitation was observed for the $Gd_2O_2S : Eu^{3+}$ (5%mol) hollow spheres. In summary, we have demonstrated a hydrothermal method assisting with reduction route is feasible for synthesizing the Gd_2O_2S hollow spheres. Although the mechanism of the formation of the hollow sphere structures is not very clear and is still under investigation, we expect that the Gd_2O_2S hollow spheres could be employed in drug delivery carriers and biotechnology fields due to their large specific area, loading capacity and good stability.

Acknowledgments

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