Synthesis of $Y_2O_2S: Eu^{3+}, Mg^{2+}, Ti^{4+}$ hollow microspheres via homogeneous precipitation route

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Abstract
A phosphorescent material in the form of $Y_2O_2S: Eu^{3+}, Mg^{2+}, Ti^{4+}$ hollow microspheres was prepared by homogeneous precipitation using monodispersed carbon spheres as hard templates. $Y_2O_3: Eu^{3+}$ hollow microspheres were first synthesized to serve as the precursor. $Y_2O_2S: Eu^{3+}, Mg^{2+}, Ti^{4+}$ powders were obtained by calcinating the precursor in a CS$_2$ atmosphere. The crystal structure, morphology and optical properties of the composites were characterized. X-ray diffraction measurements confirmed the purity of the $Y_2O_2S$ phase. Electron microscopy observations revealed that the $Y_2O_2S: Eu^{3+}, Mg^{2+}, Ti^{4+}$ particles inherited the hollow spherical shape from the precursor after being calcined in a CS$_2$ atmosphere and that they had a diameter of 350–450 nm and a wall thickness of about 50–80 nm. After ultraviolet radiation at 265 or 325 nm for 5 min, the particles emitted strong red long-lifetime phosphorescence originating from Eu$^{3+}$ ions. This phosphorescence is associated with the trapping of charge carriers by Ti$^{4+}$ and Mg$^{2+}$ ions.

Keywords: homogeneous precipitation method, yttrium oxysulfide, hollow microsphere, luminescence

1. Introduction
During the last half-century, there has been rapid development in the field of long-lifetime phosphors because of their potential applications such as safety indicators, fluorescent lamps, emergency illumination systems and cathode ray tubes [1–5]. However, further improvement is still required to obtain full-color luminescence. The progress in red long-lifetime phosphors is still very limited compared with those of other colors [5]. Therefore, long-lifetime red phosphors with strong luminescence and high chemical stability are urgently required. It is known that oxysulfide phosphors generally have high luminescence efficiencies, and yttrium oxysulfide has long been known as an excellent host material for red phosphors. In 1999, $Y_2O_2S: Eu^{3+}, Mg^{2+}, Ti^{4+}$ was first synthesized via a solid-state reaction and exhibited a red afterglow which lasted longer than 3 h [6]. Since then, this type of phosphor has generally been synthesized by a solid-state reaction at a high temperature [7–9] followed by calcining at a temperature above 1000 °C. As a result, agglomerations of particles are often formed. Progress in the systemic research on $Y_2O_2S: Eu^{3+}, Mg^{2+}, Ti^{4+}$ has been very slow and its luminescence mechanism is not well understood. Therefore, the preparation of high-quality long-lifetime red oxysulfide phosphors remains a challenge.

The development of the long-lifetime phosphors has focused on materials that have a one-dimensional nanoscale structure. Various nanocrystalline phosphors with a controlled morphology have been synthesized such as rare earth hydroxides [10–13]. Regarding the rare-earth oxysulfides, La$_2$O$_2$S, Gd$_2$O$_2$S and Eu$_2$O$_2$S have been produced in the form of nanorods [14–16], La$_2$O$_2$S and Nd$_2$O$_2$S as nanowires [17] and Y$_2$O$_2$S as nanotubes [11]. However, there is still a need for an effective route for synthesizing high-quality,
well-shaped, hollow spheres with a single-crystal structure and high phase purity. SiO$_2$/Y$_2$O$_3$: Eu and YOF/YOCI hollow spheres were synthesized by Liu and Hong [18] and Wang et al., respectively [19], and Eu$^{3+}$-doped hollow spheres of Y$_2$O$_3$, YOF, La$_2$O$_3$, LaOF were synthesized by Wang and Li [20]. However, hollow spheres of lanthanide oxysulfide have not been prepared yet. Such hollow spheres of rare-earth-doped phosphors can reduce the consumption of expensive rare-earth metals in the synthesis. Additionally, owing to the low density of hollow spherical materials, such phosphors can be well dispersed, thereby enhancing the uniformity and packing density of a phosphor coating [21].

In this work, Y$_2$O$_3$: Eu$^{3+}$, Mg$^{2+}$, Ti$^{4+}$ hollow microspheres have been prepared through homogeneous precipitation, using monodisperse carbon spheres as hard templates, followed by treatment in a CS$_2$ atmosphere [15]. The homogeneous precipitation technique has the advantages of a low processing temperature, high homogeneity and high purity of the products; it therefore is a promising method for synthesizing hollow spherical materials. The Y$_2$O$_3$: Eu$^{3+}$, Mg$^{2+}$, Ti$^{4+}$ hollow microspheres exhibit long-lifetime red emission after UV illumination at room temperature, revealing their potential for photoluminescence applications.

2. Experimental details

The following chemicals were used in the synthesis: Y$_2$O$_3$ (99.999%, Hunan Institute of Rare Earth), Eu$_2$O$_3$ (99.999%, Hunan Institute of Rare Earth), HNO$_3$ (reagent grade, Guangzhou Chemical Reagent Factory), sulfur (reagent grade, Chemical Reagent Factory, Tianjin Fu Chen), C$_6$H$_5$O$_6$ (analytical grade, Guangzhou Chemical Reagent Factory), H$_2$NCONH$_2$ (analytical grade, Guangzhou Chemical Reagent Factory), Mg(OH)$_2$: 4MgCO$_3$: 6H$_2$O (analytical grade, Beijing Chemical Plant), TiO$_2$ (analytical grade, Shanghai Titanium Dioxide Plant) and Na$_2$CO$_3$ (analytical grade, Guangzhou Chemical Reagent Factory). All reagents were used as received without further purification.

The synthesis consisted of two steps. First, the precursor of Y$_2$O$_3$: Eu$^{3+}$ hollow microspheres was synthesized using monodisperse carbon spheres as templates [21]. In the second step, Y$_2$O$_3$: Eu$^{3+}$, Mg$^{2+}$, Ti$^{4+}$ phosphors were prepared by a gas-assisted sulfur treatment in which the Y$_2$O$_3$: Eu$^{3+}$ precursor was calcined using CS$_2$ as a sulfurization agent. Sulfur powder was placed in a sealed graphite crucible and preheated at 800 °C for 4 h. During the heat treatment, the sulfur reacted with graphite to form CS$_2$, which was absorbed in the pores of the graphite layer. Then, the dried precursors and a mixture of Mg(OH)$_2$: 4MgCO$_3$: 6H$_2$O and TiO$_2$ (5% Eu$^{3+}$, 1% Mg$^{2+}$ and 1% Ti$^{4+}$) were placed in the graphite crucible and calcined at 1100 °C for 4 h.

Bulk powder samples were prepared by a solid-state reaction. The starting materials were Y$_2$O$_3$, Eu$_2$O$_3$, Mg(OH)$_2$: 4MgCO$_3$: 6H$_2$O and TiO$_2$ in a molar ratio of 5%: 1%: 1%. Na$_2$CO$_3$ (containing about 30 wt% Y$_2$O$_3$) and excess sulfur were mixed. The required amounts of raw materials were weighed, ball milled, ground, pressed into disc-shaped pellets and sintered at 1100 °C for 4 h in a sealed graphite crucible. Finally, the as-sintered products were washed with 5% acetic acid and then with hot deionized water to remove flux residue to obtain the bulk sample of Y$_2$O$_3$: Eu$^{3+}$, Mg$^{2+}$, Ti$^{4+}$ powder for further characterization.

Both the as-prepared Y$_2$O$_3$: Eu$^{3+}$ precursor and the final Y$_2$O$_3$: Eu$^{3+}$, Mg$^{2+}$, Ti$^{4+}$ phosphorescent products were characterized. The structures of the products were determined using a Rigaku D/max-II B x-ray diffractometer with Cu K$_{α 1}$ $\lambda = 0.15405$ nm radiation) with a 0.02° (20) min$^{-1}$ scanning step. The powder morphologies were observed using a scanning electron microscopy (SEM, Philips XL-30) and a transmission electron microscopy (TEM, Philips TECNAI 10). Photoluminescence spectra and intensity were measured using a spectra fluorophotometer (Hitachi F-4500). Thermoluminescence (TL) curves were recorded using a FI-427A1 instrument (Beijing Nuclear Instrument Factory) in the temperature range 30–300 °C at a heating rate of 2 °C s$^{-1}$. All measurements were carried out at room temperature except for the TL measurements.

3. Results and discussion

3.1. Crystal structure of the products

Figure 1 shows x-ray diffraction (XRD) patterns of the Y$_2$O$_3$ precursor produced by the homogeneous precipitation technique and of Y$_2$O$_3$: S after power after calcination in a CS$_2$ atmosphere with the standard Y$_2$O$_3$: S stick pattern (PDF #24–1424) added as a reference. No diffraction peaks appear in curve (a), indicating that the carbon template coated with the yttrium compound was amorphous before calcination. In contrast, sharp peaks are observed for Y$_2$O$_3$ (curve (b)) and Y$_2$O$_3$: S (curve (c)) with no peaks indicating impurities. Y$_2$O$_3$ has a cubic structure after calcination at 800 °C for 2 h and Y$_2$O$_3$: S has a hexagonal structure after sulfur treatment at 1100 °C for 4 h. The lattice parameters of Y$_2$O$_3$: S, $a = 0.3785$ nm and $c = 0.6589$ nm, are very close to the standard values provided in the powder diffraction file PDF #24–1424.
shows the photoluminescence excitation and emission spectra of the Y$_2$O$_2$S : Eu$^{3+}$, Mg$^{2+}$, Ti$^{4+}$ hollow microsphere phosphor calcined in a CS$_2$ atmosphere at 1100 °C for 4h. Both the excitation and emission spectra are similar to those of the bulk Y$_2$O$_2$S : Eu$^{3+}$, Mg$^{2+}$, Ti$^{4+}$ phosphor. The excitation spectrum has two peaks at about 260 and 325 nm, assigned to the Eu$^{3+}$–O$^{2-}$ charge transfer band (CTB) and the Eu$^{3+}$–S$^{2-}$ CTB, respectively. When the phosphors are excited at 336 nm, they produce visible emission typical for transitions between different energy levels of the Eu$^{3+}$ ion. The strongest red lines at 615 and 625 nm correspond to the transitions from the $5D_0$ level to the $^7F_{2}$ level of Eu$^{3+}$. From the emission spectra, we can confirm the formation of the oxysulfide host from the strongest emission at 625 nm. Neither the Mg$^{2+}$ ion nor the Ti$^{4+}$ ion significantly affects the shape of the excitation and emission spectra.

3.5. Luminescence property of the synthesized red phosphor

Figure 5 shows the photoluminescence excitation and emission spectra of the Y$_2$O$_2$S : Eu$^{3+}$, Mg$^{2+}$, Ti$^{4+}$ hollow microsphere phosphor. The afterglow decay curves are steeper for the hollow microsphere phosphor than for the bulk sample prepared by a solid-state reaction. This can be expressed by the following exponential equation:

$$I(t) = I_0 e^{-nt}.$$  

Here $n$ is the decay factor, which was equal to 1.03 in our case. This finding suggests that long-lifetime phosphorescence occurs at room temperature through the tunneling recombination between distant electron and hole pairs in the crystal [24, 25].

The afterglow decay curves are steeper for the hollow microspherical Y$_2$O$_2$S : Eu$^{3+}$, Mg$^{2+}$, Ti$^{4+}$ phosphor than for the bulk sample prepared by a solid-state reaction. This can be

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**Figure 2.** SEM image of the well-dispersed carbon microsphere templates.

It is clear that the substitution of Y$^{3+}$ with trace amounts of Eu$^{3+}$, Mg$^{2+}$ and Ti$^{4+}$ does not markedly change the crystal structure and lattice parameters of Y$_2$O$_2$S.

3.2. Morphology of the carbon microspheres templates

Figure 2 shows an SEM image of the well-dispersed carbon microsphere templates. They reveal that carbon microspheres with a uniform shape and size were obtained by the hydrothermal carbonization of glucose, showing the advantage of this method in preparing particles with a uniform size. All the particles are bulb-shaped with a diameter of about 300–400 nm.

3.3. Morphology of the Y$_2$O$_3$ precursor

Figure 3(a) shows an SEM image of the Y$_2$O$_3$ precursor after calcination at 800 °C revealing uniform hollow microspheres. Although the carbon microsphere templates were removed during the calcinations, the particles retained their spherical structure. Thus, the carbon microsphere templates played an important part in obtaining the hollow Y$_2$O$_3$ microspheres.

3.4. Morphology of the Y$_2$O$_2$S : Eu$^{3+}$, Mg$^{2+}$, Ti$^{4+}$ hollow microspheres

Figure 3(b) shows an SEM image of the sulfur-treated Y$_2$O$_2$S. The calcination of Y$_2$O$_3$ in the CS$_2$ atmosphere resulted in the formation of Y$_2$O$_2$S. The produced hollow oxysulfide microspheres have a similar size to the initial Y$_2$O$_3$ precursor particles, implying that the shape of the hollow microspheres can be preserved in the high-temperature sulfur treatment.

TEM images of the final Y$_2$O$_2$S product (figure 4) reveal hollow microspheres with a diameter of 350–450 nm and a wall thickness ranging from 50 to 80 nm, as estimated from figure 4(b). Several hollow microspheres are broken (figures 3(b) and 4(a)), presumably due to the high temperature of the sulfur treatment, but most of them retain the shape of the precursor particles.

In our previous experiments [22, 23], when the precursor was calcined in a different gas flow, the final products did not remain the shape of the precursor particles. Therefore, we conclude that the atmosphere in which the calcination occurs plays an important role in retaining the shape of the hollow microspheres. Additionally, this atmosphere may be a key factor resulting in the similar morphologies of the Y$_2$O$_3$ precursor and the final Y$_2$O$_2$S product. However, the associated mechanisms require further elaboration.
3.7. Thermoluminescence

The peaks between 50 and 110 °C in the thermoluminescence curve have been previously associated with the afterglow [26].

Our thermoluminescence data for the Y$_2$O$_3$: Eu$^{3+}$, Mg$^{2+}$, Ti$^{4+}$ phosphor (figure 7) exhibit a peak at approximately 80 °C, which is in the above temperature range. The thermoluminescence curves are similar for the hollow microsphere phosphor and the sample synthesized by a solid-state reaction at a high temperature. According to [27], defects introduced by doped ions play a key role in...
In this study, a long-lifetime phosphorescent material in the form of Y$_2$O$_2$S:Eu$^{3+}$, Mg$^{2+}$, Ti$^{4+}$ hollow microspheres has been prepared through homogeneous precipitation followed by sulfur treatment. Electron microscopy indicates that the spheres have a uniform size and a smooth surface and that they inherited the shape of the Y$_2$O$_3$ precursor, despite calcination in a CS$_2$ atmosphere at 1100°C for 4 h. This phosphor emits bright red phosphorescence originating from the Eu$^{3+}$. The introduction of Mg$^{2+}$ and Ti$^{4+}$ ions was beneficial for the formation of electron and hole traps, which resulted in long-lifetime light emission.

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