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Preparation and upconversion luminescence of Y_2O_3:Yb^{3+}, Ho^{3+} nanocrystalline powders coated with SiO_2

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ABSTRACT

Y_2O_3:Yb^{3+}, Ho^{3+} nanocrystalline powders were prepared via a reverse-strike co-precipitation method, which were agglomerated shown from FESEM image. After dispersing and then coating with SiO_2 by Stöber method, spherical and uniform particles were obtained. The upconversion luminescent properties of these samples were studied under the excitation of 980 nm. Enhanced upconversion luminescence was observed in the sample coated with SiO_2. Possible upconversion mechanism was proposed.

1. Introduction

The ultrasensitive fluorescent labeling materials have been widely studied for their analytical and biophysical applications [1–3]. Traditionally, the commonly used fluorescent labels are organic dyes, such as rhodamine, fluorescein isothiocyanates (FITC), and cyanine dyes (Cy3, Cy5 and Cy7). Recently, semiconductor nanocrystals have been applied in biological detections [2,4,5]. They preserve high quantum yield, tunable emission wavelength and high stability against photobleaching. However, the main problem of these materials is the autofluorescence (noise) from the analytes under UV and visible light. Due to the unique fluorescent properties, up-conversion fluorescent labels have attracted much attention for their potential application in bio-labeling. By absorbing two or more photons of low near-infrared (NIR), the upconversion materials can emit visible light or even UV light, which show very low background light and minimal photodamage to biological tissues. Moreover, the commercially high-power laser diodes used as the excitation sources are available now at a relatively low cost for the rapid development of semiconductor. Therefore, it will be extraordinarily convenient to employ upconversion materials for the purpose of bio-labeling.

Recently, Y_2O_3:RE^{3+} has been chosen as upconversion luminscent material for its favorable physical and chemical properties and ease of synthesis in nanometer region. Especially, the host material yttria preserves relatively low phonon energy ($\sim$430–550 cm^{-1}) [6], which would reduce the possibility of non-radiative process and then increase the upconversion efficiency. Several studies reported the upconversion properties of nanocrystalline and bulk Y_2O_3 synthesized by different procedures, such as sol–gel method, chemical vapor synthesis, combustion method, and co-precipitation method [7–12]. Meanwhile, nanocrystalline powders can be modified by surface treatment, for example, coating with the same material or some other material. This modification can reduce the surface unsatured bond density and defects and thus enhance luminescence of the powders [13]. Further, selective attachment to cell bonds of specific bacteria can be achieved after the powders are properly coated, which is in favor of application in fluorescent labeling. Therefore, it is necessary to modify the surface of Y_2O_3 nanocrystalline powders.

In this paper, we synthesized the Y_2O_3:Yb^{3+}, Ho^{3+} nanocrystalline powders via a reverse-strike co-precipitation method and the as-prepared powders were coated with SiO_2 by Stöber method. The upconversion luminescent properties of these samples were studied and possible upconversion mechanism was proposed.

2. Experimental

Y_2O_3:Yb^{3+}, Ho^{3+} nanocryatalline powders were prepared by a reverse-strike co-precipitation method. Details of the procedure were presented previously [12]. The as-prepared powders were carefully dispersed and then coated with SiO_2 by Stöber method. Analytical grade tetraethyl orthosilicate (TEOS), ethanol and ammonia water were used as the starting materials. TEOS, ethanol and ammonia water were mixed with a certain ratio and the mixture was kept stirring when Y_2O_3:Yb^{3+}, Ho^{3+} nanocrystalline powders were slowly added. The TEOS hydrolysis reaction can be expressed as following:

$$Si(OC_2H_5)_4 + 4H_2O \rightarrow Si(OH)_4 + 4C_2H_5OHSi(OH)_4 \rightarrow SiO_2 + 2H_2O$$

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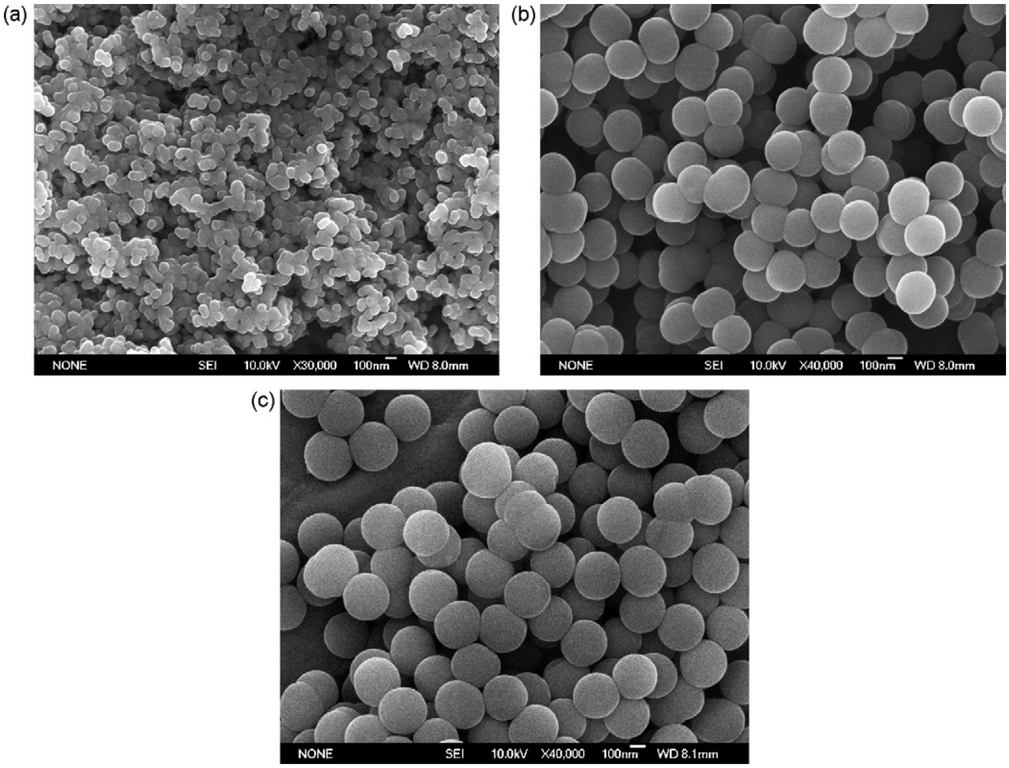

Fig. 1. FESEM images for (a) Y_2O_3:Yb^{3+}, Ho^{3+} calcined at 1000 °C for 2 h, (b) SiO_2–Y_2O_3:Yb^{3+}, Ho^{3+} dried at 120 °C for 5 h and (c) SiO_2–Y_2O_3:Yb^{3+}, Ho^{3+} calcined at 550 °C for 2 h.

After reaction, the slurry was dispersed ultrasonically, filtered, washed with ethanol for several times and dried at 120 °C to obtain the SiO_2 coated Y_2O_3:Yb^{3+}, Ho^{3+} powders. The particle size of the coated powders can be controlled by the amount of ethanol and ammonia water within a certain range. We employed a volume ratio of ethanol and ammonia water to be 2:1 and a solid load of 40 wt.% Y_2O_3:Yb^{3+}, Ho^{3+} nanocrystalline powders.

The morphology and particle size were detected by the field emission scanning electron microscope (FESEM, JSM-6700F, JEOL, Japan). Upconversion luminescence spectra of the samples were recorded at room temperature by a spectrofluorometer (Fluorolog-3, Jobin Yvon, France) equipped with Hamamatsu R928 photomultiplier tube. A 980 nm continuous wave diode laser was used as the excitation source.

3. Results and discussion

Fig. 1 shows the FESEM pictures of the prepared Y_2O_3:Yb^{3+}, Ho^{3+} powders and SiO_2-coated Y_2O_3:Yb^{3+}, Ho^{3+} powders. It can be seen from Fig. 1(a) that the powders synthesized by reverse-strike co-precipitation method were agglomerated with 60 nm in diameter when calcined at 1000 °C for 2 h. Fig. 1(b) and (c) are typical FESEM pictures of SiO_2-coated Y_2O_3:Yb^{3+}, Ho^{3+} powders dried at 120 °C for 5 h and then calcined at 550 °C for 2 h, respectively. The coated powders were spherical in shape and very uniform in size with an average size of about 200 nm (Fig. 1(b)). Even after calcined at 550 °C for 2 h, the coated powders were still uniform in size, with no apparent grain growth.

Fig. 2 shows the upconversion luminescent spectra of the prepared Y_2O_3:Yb^{3+}, Ho^{3+} powders and the coated powders excited by a 980 nm continuous wave laser diode. There were three dominant emission bands. The green emission centered at 549 nm dominates the whole spectrum corresponding to the multiplets $^5F_4$, $^5S_2 \rightarrow {}^5I_8$ transition of the Ho^{3+} ions. The red emission was detected around 666 nm associated with the $^5F_5 \rightarrow {}^5I_8$ transition. The very weak infrared emission centered around 755 nm was also observed, which was assigned to the $^5F_4$, $^5S_2 \rightarrow {}^5I_7$ transition. What is more, the upconversion intensity of the sample coated with SiO_2 was stronger than that of the uncoated sample. Surface modification may contribute to this phenomenon. SiO_2 coating in our case, to some extent, might eliminate the defect on the surface of the nanocrystalline powders and accordingly reduce the probability of multiphonon relaxation process. Therefore, the upconversion luminescent intensity of the powders was enhanced after coated with SiO_2.

To clarify the upconversion emission mechanism, we measured the dependence of the emission intensity (I_{up}) on the excitation power (I_{ex}). The number of exciting photons (n) required in the upconversion process was approximated by the formula $I_{up} \propto (I_{ex})^n$ [14]. As shown in Fig. 3, $n = 2.02$, 1.80 and 1.67 for the $^5F_4$, $^5S_2 \rightarrow {}^5I_8$, $^5F_5 \rightarrow {}^5I_8$ and $^5F_4$, $^5S_2 \rightarrow {}^5I_7$ transition, respectively. It implied that two photons were involved in the upconversion process.

The upconversion mechanism in Yb–Ho system has been widely studied in many host materials [15–17]. Because of the character-

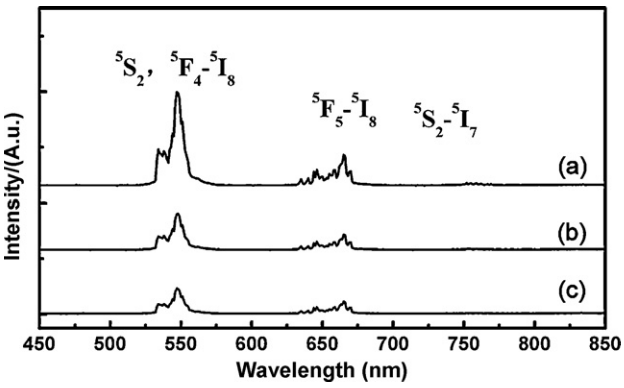

Fig. 2. Upconversion spectra of the prepared powders excited by 980 nm LD, (a) Y_2O_3:Yb^{3+}, Ho^{3+} calcined at 1000 °C for 2 h, (b) SiO_2–Y_2O_3:Yb^{3+}, Ho^{3+} dried at 120 °C for 5 h and (c) SiO_2–Y_2O_3:Yb^{3+}, Ho^{3+} calcined at 550 °C for 2 h.

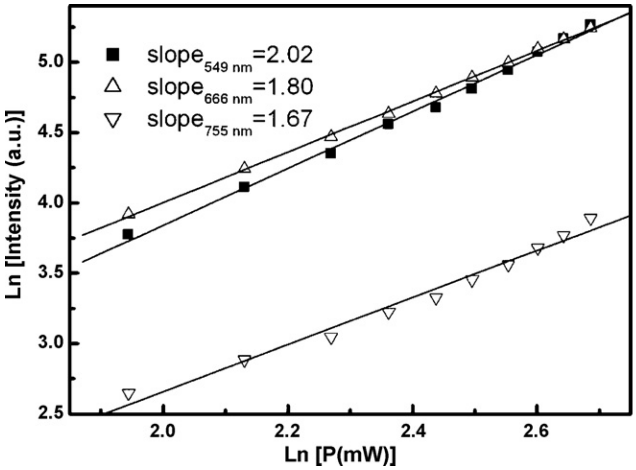

Fig. 3. Upconversion emissions intensity as a function of the excitation power.

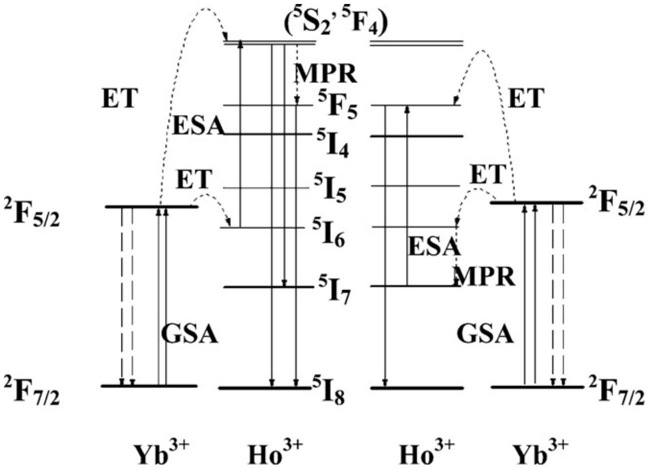

Fig. 4. Energy level diagrams of Yb^{3+} and Ho^{3+} co-doped materials under the excitation with 980 nm.

istic energy levels of Ho^{3+} ions and the excitation source, energy transfer for the sensitizing effect of Yb^{3+} ions plays an important role for the resulting upconversion emissions. Fig. 4 shows the partial energy level diagram, showing the energy transfer from Yb^{3+} to Ho^{3+}. Firstly, Yb^{3+} ions were excited to the $^2F_{5/2}$ level through ground state absorption (GSA) process and then transferred their energy to Ho^{3+} ions, which would populate the $^5I_6$ level. Subsequently, Ho^{3+} ions in the $^5I_6$ level was further excited to the upper $^5F_4$, $^5S_2$ levels by energy transfer (ET) and excited state absorption (ESA). Finally, radiation emission from $^5F_4$, $^5S_2$ levels to $^5I_8$ and $^5I_7$ levels of Ho^{3+} ions occurred and the green and infrared emission bands were observed, respectively. Two ways may be responsible for the population of the $^5F_5$ level. One is by multiphonon relaxation (MPR) process from $^5F_4$, $^5S_2$ levels. The other is that Ho^{3+} ions in the $^5I_6$ level transfered to the $^5I_7$ level by MPR and then was excited to the $^5F_5$ level by ET and ESA. Therefore we can observe the red emission band. The above upconversion processes were expressed as follows:

$$
\begin{array}{ll}
{}^2\mathrm{F}^{\mathit{:MROW>}}_{\mathit{<MML}}(\mathrm{Yb}^{3+}) + h\upsilon_{980} \rightarrow {}^2\mathrm{F}^{\mathit{:MROW>}}_{\mathit{<MML}}(\mathrm{Yb}^{3+}) & (\mathrm{GSA})\\
{}^2\mathrm{F}^{\mathit{:MROW>}}_{\mathit{<MML}}(\mathrm{Yb}^{3+}) + {}^5\mathrm{I}_8(\mathrm{Ho}^{3+}) \rightarrow {}^2\mathrm{F}^{\mathit{:MROW>}}_{\mathit{<MML}}(\mathrm{Yb}^{3+}) + {}^5\mathrm{I}_6(\mathrm{Ho}^{3+}) & (\mathrm{ET})\\
{}^2\mathrm{F}^{\mathit{:MROW>}}_{\mathit{<MML}}(\mathrm{Yb}^{3+}) + {}^5\mathrm{I}_6(\mathrm{Ho}^{3+}) \rightarrow {}^2\mathrm{F}^{\mathit{:MROW>}}_{\mathit{<MML}}(\mathrm{Yb}^{3+}) + ({}^5\mathrm{S}_2, {}^5\mathrm{F}_4)(\mathrm{Ho}^{3+}) & (\mathrm{ET})\\
({}^5\mathrm{S}_2, {}^5F_4)(\mathrm{Ho}^{3+}) \rightarrow {}^5\mathrm{F}_5(\mathrm{Ho}^{3+}) & (\mathrm{MPR})\\
{}^5\mathrm{I}_6(\mathrm{Ho}^{3+}) + h\upsilon_{980} \rightarrow ({}^5\mathrm{S}_2, {}^5\mathrm{F}_4)(\mathrm{Ho}^{3+}) & (\mathrm{ESA})\\
{}^5\mathrm{I}_6(\mathrm{Ho}^{3+}) \rightarrow {}^5\mathrm{I}_7(\mathrm{Ho}^{3+}) & (\mathrm{MPR})\\
{}^2\mathrm{F}^{\mathit{:MROW>}}_{\mathit{<MML}}(\mathrm{Yb}^{3+}) + {}^5\mathrm{I}_7(\mathrm{Ho}^{3+}) \rightarrow {}^2\mathrm{F}^{\mathit{:MROW>}}_{\mathit{<MML}}(\mathrm{Yb}^{3+}) + {}^5\mathrm{F}_5(\mathrm{Ho}^{3+}) & (\mathrm{ET})\\
{}^5\mathrm{I}_7(\mathrm{Ho}^{3+}) + h\upsilon_{980} \rightarrow {}^5\mathrm{F}_5(\mathrm{Ho}^{3+}) & (\mathrm{ESA})\\
({}^5\mathrm{S}_2, {}^5\mathrm{F}_4)(\mathrm{Ho}^{3+}) \rightarrow {}^5\mathrm{I}_8(\mathrm{Ho}^{3+}) + h\upsilon_{\mathrm{green}} & (\mathrm{RT})\\
{}^5\mathrm{F}_5(\mathrm{Ho}^{3+}) \rightarrow {}^5\mathrm{I}_8(\mathrm{Ho}^{3+}) + h\upsilon_{\mathrm{red}} & (\mathrm{RT})\\
({}^5\mathrm{S}_2, {}^5\mathrm{F}_4)(\mathrm{Ho}^{3+}) \rightarrow {}^5\mathrm{I}_7(\mathrm{Ho}^{3+}) + h\upsilon_{\mathrm{NIR}} & (\mathrm{RT})
\end{array}
$$

4. Conclusion

Y_2O_3:Yb^{3+}, Ho^{3+} nanocrystalline powders were prepared via a reverse-strike co-precipitation method. The spherical and uniform particles were obtained when coating the as-prepared powders with SiO_2 by Stöber method. The dominant green, weak red and infrared upconversion emissions were observed in these samples under excitation of 980 nm. The intensity of upconversion emissions became stronger after the powders were coated with SiO_2, which was ascribed to the elimination of the defect on the surface of nanocrystalline powders by SiO_2 coating. The dependence of the upconversion intensity upon the exciting power revealed that two photons were involved and the emitting levels were populated via energy transfer process.

Acknowledgments

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