

Preparation of size-controlled nanocrystalline infrared-to-visible upconverting phosphors $\text{Gd}_2\text{O}_3\text{:Yb,Er}$ by using a water-in-oil microemulsion system

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Abstract Nanocrystalline infrared-to-visible upconverting phosphors $\text{Gd}_2\text{O}_3\text{:Yb,Er}$ with narrow size distribution were prepared by using a microemulsion system (MES) of stability, which includes phases of Triton X-100 (surfactant phase (S)), *n*-hexanol (assistant surfactant phase (As)), cyclohexane (oil phase (O)) and solution (water phase (W)). From the microemulsion system we could get appearance-controllable nanocrystalline by adjusting the ratio of oil and surfactant. The X-ray diffraction results showed that the powders were cubic phase of Gd_2O_3 after being calcined in the air at 1273 K. The scanning electronic microscopy revealed that the particles were spherical. Red and green upconversion luminescences were obtained by 980 nm infrared excitation. We also investigated contributions of different ratio of surfactant to the appearance.

Keywords Upconversion · Infrared-to-visible · Microemulsion · Nanocrystalline

1 Introduction

Upconversion materials are such a kind of materials which can produce visible mission when they are excited by infrared. They are also called Reverse-Stokes-Law materials. Due to their characteristics, their emission of photon energy is higher when they are excited. Immunochromatographic assays have become popular diagnostic tools in a variety of settings because they are sensitive, fast, and easy

to use. Multiple assays can be performed simultaneously on the same membrane strip, since upconverting phosphors of different compositions with unique spectral emission spectra are available. As the need for rapid, sensitive, field-usable testing grows, new technologies will be needed to address current shortcomings and to keep up with demands for increased sensitivity, speed, and ease of use. upconverting phosphors promises to be a reporter system that can meet these demands, as upconverting phosphors assays are 10- to 100-fold more sensitive than assays using conventional colored beads. [5]

The water-in-oil (w/o) (micro)emulsion precipitation method has received special attention due to its ability to synthesize well-dispersed, uniform size nanoparticles. [1] In such a system, water, which is as a separate phase, just like spheres of large quantity and enwrapped by surfactant, well-disperse in the continuous oil.

2 Experimentations

Respective rare earth oxides (Gd, Yb, Er) were dissolved in nitric acid and then mixed together to be nitrate solution (0.01 mol/L; Gd:Yb:Er=90:8:2; A for short). A was water phase in the MES. So did oxalic acid solution (0.015 mol/L; B). Subsequently two similar W/O MES with different water phases were prepared by commixing three parts of A (or B; 50 ml), O (60 g), S (and As) with powerful stirring. When the W/O MES within A was magnetic stirred, the W/O MES within B was added to it slowly. Then, after stirring for 6~7 h to form rare earth oxalate precipitations, the precipitations were picked up by centrifugal separation from their reaction environment. The precursors had to be washed by acetone for 3 times. All processings above were finished in room temperature.

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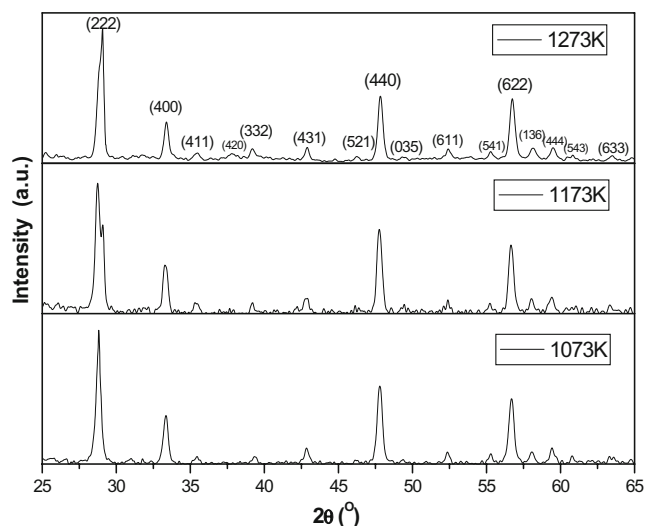


Fig. 1 X-ray diffraction patterns of the $Gd_2O_3:Yb,Er$ particles calcined at 1073K, 1173K and 1273K

After dried in air, The precursors of rare earth oxalate precipitations were calcined in the air under a series of temperatures for 1 or 2 h to obtain composite rare earth oxides ($Gd_2O_3:Yb,Er$).

The $Gd_2O_3:Yb,Er$ powders were characterized by X-ray diffraction (XRD), Scanning electron microscope (SEM) and the upconversion emissions were observed by the pump power of the diode laser.

3 Results and discussion

Refer to Fig. 1 The X-ray diffraction (XRD), the results showed that the powders were cubic phase of Gd_2O_3 after being calcined in the air under a series of temperatures.

It was found that the ratio of S and As had a significant effect on precipitation of rare earth precursors. MES as a means of preparing particles is easy operating. Its microcosmic reacting environment can realize special preparation of size-control and appearance-control by change ratio of S and As, replace S or As. In the experiment, three ratios of S

and As were prepared. When S/As=36(g):54(g) (sample 1), according to Fig. 2(a) and (b), they show the SEM images of $Gd_2O_3:Yb,Er$ particles prepared by using the W/O MES are claviform after being calcined at 1273K 1 or 2 h. These kinds of particles have a big length-diameter ratio, which proves that the ratio of S/As can control the morphology effectively. Contrasting with the particle prepared by using the W/O MES with a ratio of S/As=45(g)/45(g) (sample 2), as Fig. 3(a) and (b) shows, the $Gd_2O_3:Yb,Er$ particles were about 100 nm in size but high agglomerating. When the particle prepared by using the W/O MES with a ratio of S/As=54(g)/36(g) (sample 3), the SEM images (Fig. 4(a), (b) of the $Gd_2O_3:Yb,Er$ particles show the oxide particles which were calcined at 1273K for 1 or 2 h are less agglomerate and with a narrow granularity distribution of about 80 nm.

By changing the ratio of S and As, the result showed that W/O MES is effective in controlling both the size and morphology of the rare earth oxalate particles for the specifically environment of internal water droplet. Triton X-100, as a kind of nonionic surfactant which will not cause up reactivity between reagent and medium shows itself litmusless characteristic in the water. By the increase of *n*-hexanol in Triton X-100, S and As form a kind of mixed membrane which of more rigidity and compact, because the membrane is able to debase the interfacial tension of the microemulsion to enhance the interfacial intensity; But, when *n*-hexanol is beyond its proper quantity, it will cause an inverse effect can but dissociating in the organic phase.

For their ultrafine dimension, nano-particles behave extremely actively. They are apt to agglomerate together even after being calcined at high temperature. It is obviously that oxide particles with small dimension were calcined for short time. Nanoparticles of ultrafine dimension tend to grow up when being calcined at high temperature. The examination chose a process of slow temperature increase and short keep-on time.

Figure 5 shows the typical energy level diagram for the upconversion emission of $Gd_2O_3:Yb,Er$ under infrared

Fig. 2 SEM images of $Gd_2O_3:Yb,Er$ particles prepared by using the W/O MES within S/As=36(g):54(g). (a) Particles calcined for 1 h. (b) Particles calcined for 2 h

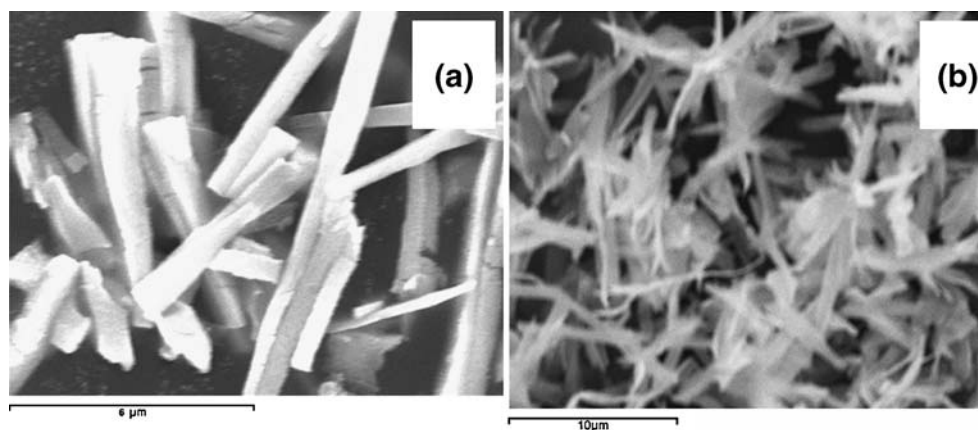
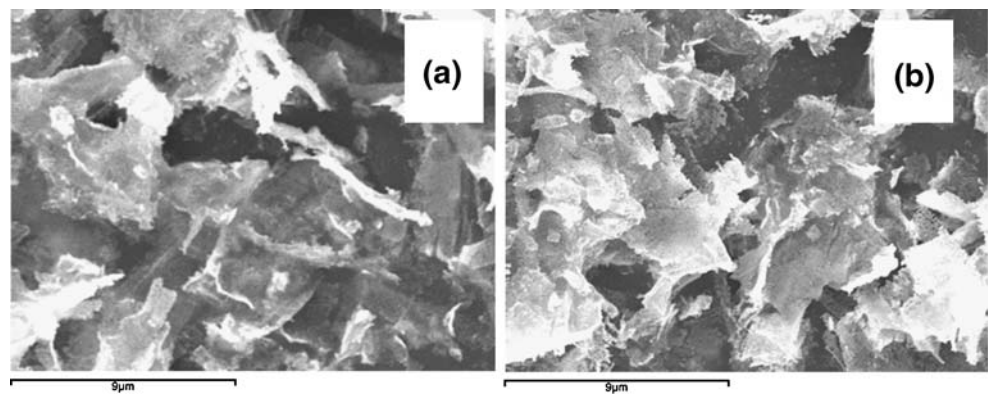


Fig. 3 SEM images of $Gd_2O_3:Yb,Er$ particles prepared by using the W/O MES within S/As=45(g):45(g). (a) Particles calcined for 1 h. (b) Particles calcined for 2 h



excitation ($\lambda_{ex}=980$ nm). The excitation process for upconversion emission of Er^{3+} ions has been well established in the literature [2–4]. When the Er^{3+} in excitation state absorb (ESA) and $Yb^{3+} \rightarrow Er^{3+}$ energy transfer (ET) occur, the Er^{3+} in $^4I_{15/2}$ state absorbs a photon of 980 nm, by a transition of ground state absorb (GSA) and more phonon relax (MPR) to produce the $^4I_{13/2}$. Before the Er^{3+} in $^4I_{11/2} \sim ^4I_{13/2}$ returning to the ground state, it will absorb a photon of 980 nm again by ESA to carry out another transition to state $^4F_{7/2} \sim ^4F_{9/2}$. By MPR $^4S_{3/2}$, $^2H_{11/2}$ and $^4F_{9/2}$, as a result, the ($^2H_{11/2}$, $^4S_{3/2}$) \rightarrow $^4I_{15/2}$ transitions and $^4F_{9/2} \rightarrow ^4I_{15/2}$ transition of Er^{3+} ions come into being.

Figures 6 and 7 show the upconversion emissions of $Gd_2O_3:Yb,Er$ particles prepared in the W/O MES under infrared excitation ($\lambda_{ex}=980$ nm). $Gd_2O_3:Yb,Er$ particles prepared by using the W/O MES within any ratio of S/As could produce upconversion emissions. We consider the reasons why the upconversion intensity of sample 1 is stronger than sample 2 and 3. For the same reason, those sample 2 is similar to sample 3, are the particle dimension. The upconversion emission intensity of particles calcined at 1273K for 1 h is weaker than those calcined at 1273K for 2 h. There is a inverse proportion between energy transfers probability and power of distance of Yb^{3+} (benefactor) and Er^{3+} (acceptor). Bigger particle dimension shortens the

distance of Yb^{3+} and Er^{3+} to increase the energy transfers probability. That is just the reason why upconversion intensity increases, which is propitious to biology assays.

Small and spherical particles are of fine fluidity, what is requested in biology assays. By controlling the reaction conditions we can change appearance and particle dimension to get fine characteristics for biology assays.

4 Conclusions

Nanocrystalline infrared-to-visible upconverting phosphors $Gd_2O_3:Yb,Er$ and with narrow size distribution were prepared by a using a stability of microemulsion system. The ratio of S/As operates on the appearance of the particles. For the mechanism of ESA and ET, red and green Upconversion luminescence were obtained by 980 nm infrared excitation (The green emission in the region at about 520 nm is corresponding to the ($^2H_{11/2}$, $^4S_{3/2}$) \rightarrow $^4I_{15/2}$ transitions; The red emission in the region at 650–700 nm is corresponding to the $^4F_{9/2} \rightarrow ^4I_{15/2}$ transition of Er^{3+} ions.). The dimension of particles also has some effect on the upconversion intensity. By controlling the reaction conditions we can change appearance and particle dimension to get fine characteristics.

Fig. 4 SEM images of $Gd_2O_3:Yb,Er$ particles prepared by using the W/O MES within S/As=54(g):36(g). (a) Particles calcined for 1 h. (b) Particles calcined for 2 h

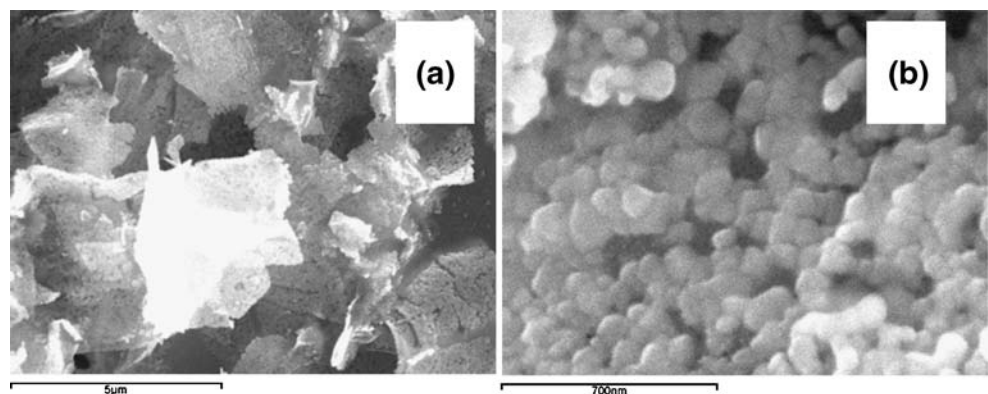


Fig. 5 The energy level diagrams of $\text{Gd}_2\text{O}_3\text{:Yb}^{3+}, \text{Er}^{3+}$ particles excited by 980 nm and possible upconversion processes

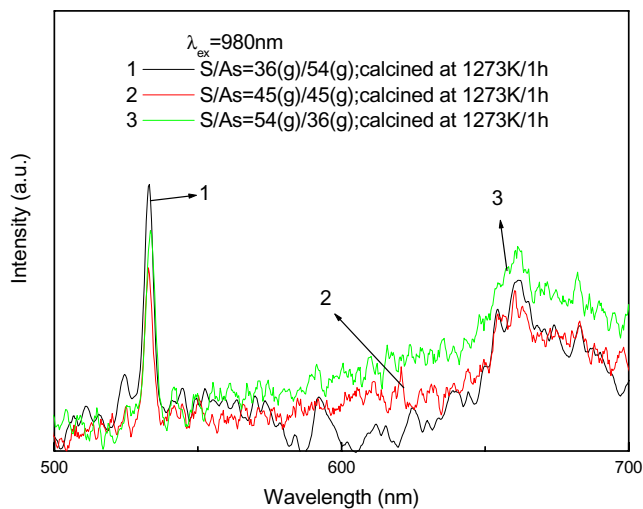
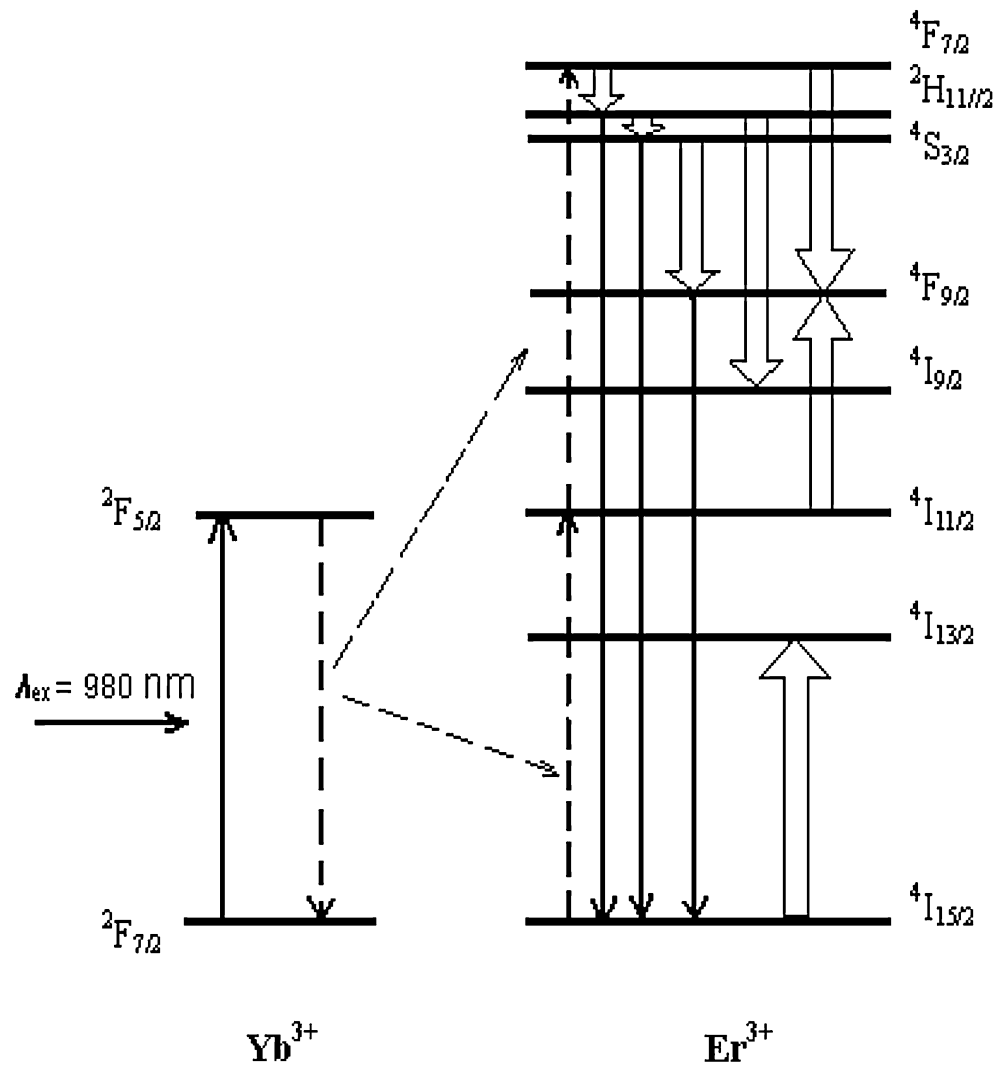


Fig. 6 Images for the upconversion emission spectrum of $\text{Gd}_{1.6}\text{Yb}_{0.3}\text{Er}_{0.1}\text{O}_3$ particles (calcined at 1273K/1 h) excited by 980 nm diode laser pump

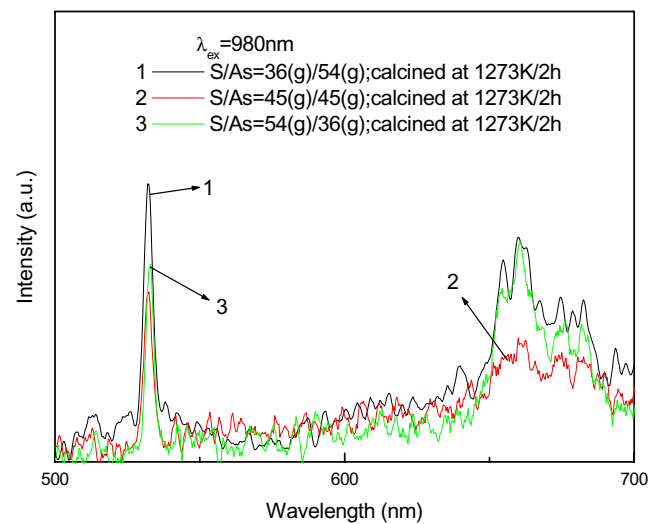


Fig. 7 Images for the upconversion emission spectrum of $\text{Gd}_{1.6}\text{Yb}_{0.3}\text{Er}_{0.1}\text{O}_3$ particles (calcined at 1273K/1 h) excited by 980 nm diode laser pump

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Further Reading

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