Research Article

Hydrothermal Synthesis and Tunable Multicolor Upconversion Emission of Cubic Phase Y$_2$O$_3$ Nanoparticles

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Highly crystalline body-centered cubic structure Y$_2$O$_3$ with lanthanide (Ln) codopants (Ln = Yb$^{3+}$/Er$^{3+}$ and Yb$^{3+}$/Ho$^{3+}$) has been synthesized via a moderate hydrothermal method in combination with a subsequent calcination. The structure and morphology of Y(OH)$_3$ precursors and Y$_2$O$_3$ nanoparticles were characterized by X-ray diffraction and transmission electron microscopy. The results reveal that the Y$_2$O$_3$ nanoparticles possess cubic phase and form the quasispherical structure. The upconversion luminescence properties of Y$_2$O$_3$ nanoparticles doped with different Ln$^{3+}$ (Yb$^{3+}$/Er$^{3+}$ and Yb$^{3+}$/Ho$^{3+}$) ions were well investigated under the 980 nm excitation. The results show that the Yb$^{3+}$/Er$^{3+}$ and Yb$^{3+}$/Ho$^{3+}$ codoped Y$_2$O$_3$ nanoparticles exhibit strong red and light yellow upconversion emissions, respectively. It is expected that these Y$_2$O$_3$ nanoparticles with tunable multicolor output and intense red upconversion emission may have potential application in color displays and bioimaging.

1. Introduction

In the last few years, upconversion (UC) nanoparticles have attracted great attention in many research areas owing to their unique antistokes emission processes of converting a longer wavelength radiation to short wavelength emission [1–3]. Lanthanide-doped rare-earth oxides and related materials are common phosphors in optical display devices and fluorescent bioimaging applications [4–12].

Y$_2$O$_3$, as one of the most important rare-earth materials, was considered as an ideal candidate for biological applications, because of their higher mechanical, thermal, and chemical stability [13–15]. Rare-earth oxides were usually synthesized by thermal decomposition of their oxysalt precipitates such as hydroxide and oxalate at a certain temperature [16–19]. However, the thermal decomposition method requires high temperature and inert gases protection, resulting in complex experimental operations. Therefore, it is of significant importance to develop a simple method for the preparation of rare-earth oxide nanoparticles. Recently, Ln-doped Y$_2$O$_3$ shows great potential application in optical display and lighting [20]. So, further investigations of tunable multicolor UC emission Y$_2$O$_3$ nanoparticles via codoping Ln ions (Yb$^{3+}$/Er$^{3+}$ and Yb$^{3+}$/Ho$^{3+}$) are still of great interest. Up to now, there are many researches to regulate the multi-color output of UC nanomaterials via doping rare-earth ions [21–25]. For example, Garry’s group have reported that Yb$^{3+}$, Er$^{3+}$, Ho$^{3+}$, and Tm$^{3+}$ codoped Y$_2$O$_3$ nanocrystals can generate red, green, blue, and white light [25]. However, to the best of our knowledge, few studies have focused on the synthesis of spherical-like Y$_2$O$_3$ nanoparticles with tunable multicolor UC emissions by using facile hydrothermal method.

In this paper, different Ln$^{3+}$ (Yb$^{3+}$/Er$^{3+}$ and Yb$^{3+}$/Ho$^{3+}$) ions codoped Y(OH)$_3$ nanosheets have been successfully synthesized based on a facile and mild hydrothermal method. And the cubic phase Y$_2$O$_3$ nanoparticles were calcinated from these Y(OH)$_3$ precursors. In addition, the UC luminescence properties of the Y$_2$O$_3$ doped with different Ln ions (Yb$^{3+}$/Er$^{3+}$ and Yb$^{3+}$/Ho$^{3+}$) were investigated under 980 nm
excitation. The UC mechanism and CIE (Commission Internationale de l’Eclairage 1931 chromaticity) chromaticity coordinates were studied in detail.

2. Experimental

Y(NO$_3$)$_3$·6H$_2$O (99.99%), Er(NO$_3$)$_3$·6H$_2$O (99.99%), Yb(NO$_3$)$_3$·5H$_2$O (99.99%), and Ho(NO$_3$)$_3$·5H$_2$O (99.99%) were purchased from Sinopharm Chemical Reagent Co., Ltd (China). All other chemical reagents are of analytical grade and used directly without further purification.

2.1. Synthesis of Different Ln$^{3+}$ Codoped Y$_2$O$_3$ Nanoparticles.

Y(OH)$_3$ nanosheets were synthesized by a facile hydrothermal method [26, 27]. For a typical protocol, 1 mmol (total amounts) of Ln (NO$_3$)$_3$ (Ln = Y, Yb, Er, and Ho) with designed molar ratio (Y : Yb : Er = 78 : 20 : 2 and Y : Yb : Ho = 78 : 20 : 2) was added into 20 mL deionized water. And then the obtained solution was rapidly adjusted to pH = 14 by adding 10 wt% NaOH solution. The obtained mixture was then transferred into a 50 mL stainless Teflon lined autoclave and reacted at 120°C for 12 h. After reaction, the system was naturally cooled to room temperature. The resulting products were collected, washed several times with de-ionized water to remove residual NaOH, and then dried at 80°C for 3 h. Y$_2$O$_3$ nanoparticles were synthesized by sintered Y(OH)$_3$ precursor at 500°C for 6 h.

2.2. Characterizations. X-ray powder diffraction (XRD) patterns were recorded by using a D/max 2500/PC system X-ray diffractometer at 40 kV and 250 mA using Cu Kα radiation ($λ = 1.5406$ Å). The morphology and size of the samples were characterized by transmission electron microscopy (TEM, JEOL-2100F) equipped with an Oxford’s energy dispersive X-ray spectroscopy (EDS). The UC emission spectra were recorded by a spectrophotometer (R 500) equipped with 980 nm laser diode as the excitation source. The digital photographs of the as-prepared samples were taken by a commercial digital camera (Canon 650D).

3. Results and Discussion

3.1. Crystal Phase and Morphology Analysis. The phase composition of the as-prepared Y$_2$O$_3$:Yb/Er was investigated by XRD analysis. As shown in Figure 1, the samples present characteristic diffraction peaks centered at 20.60° (211), 29.32° (222), 33.90° (400), 36.08° (411), 39.96° (332), 43.62° (134), 48.72° (440), 53.44° (611), 56.38° (541), 57.88° (622), 59.30° (136), 60.72° (444), 64.76° (127), 71.28° (800), and 72.52° (811), which is matched well with the standard body-centered cubic Y$_2$O$_3$ (JCPDS card no. 88-1040). In addition, no other impurity diffraction peaks are observed, indicating that pure cubic phase nanoparticles were synthesized with good crystallinity and a homogenous Y-Yb solid solution structure was formed.

To reveal the morphology and structure, the as-prepared samples were characterized by TEM (Figure 2). The as-prepared Y(OH)$_3$:Yb/Er by hydrothermal method at 120°C for 12 h consists of nanosheet and frizzy nanosheet (Figure 2(a)). Y$_2$O$_3$:Yb/Er calcinated from the precursor of Y(OH)$_3$:Yb/Er at 500°C for 6 h present agglutinate structure of sphere-like nanoparticles (Figures 2(b) and 2(c)). As shown in Figure 2(d), the obvious lattice fringes in the high resolution transmission electron microscopy (HRTEM) images confirm the high crystallinity of the as-prepared Y$_2$O$_3$:Yb/Er nanoparticles. The interplanar distances between the adjacent lattices were measured to 2.64 Å, matching well with the d$_{400}$ spacing of the cubic phase Y$_2$O$_3$ (JCPDS 88-1040). From the above results, we can see that rare-earth hydroxides are unstable compounds. When the temperature reached a certain value, the nanosheet and frizzy nanosheet hydroxides were burnt to stable sphere-like nanoparticles. During the TEM measurement, the elemental components of the Y$_2$O$_3$:Yb/Er nanoparticles were detected by EDS. The sphere-like nanoparticles are mainly composed of Y, Er, Yb, and O, indicating that the doped Yb$^{3+}$ and Er$^{3+}$ were successfully incorporated into the Y$_2$O$_3$ host (Figure 2(e)). It is noted that the signals of Cu are attributed to the TEM copper grid.

3.2. Upconversion Luminescence Properties. It is well known that multicolor UC luminescence can be achieved by doping various sensitizers and active Ln ions. Here, we discuss the UC luminescence properties of Y$_2$O$_3$ nanoparticles through codoping Yb$^{3+}$/Er$^{3+}$ and Yb$^{3+}$/Ho$^{3+}$ ions. Under 980 nm excitation, the corresponding UC luminescence spectra and the proposed energy transfer mechanism are shown in Figure 3. As demonstrated in Figure 3(a), the UC spectra of Y$_2$O$_3$:Yb/Er nanoparticles show the characteristic Er$^{3+}$ UC emissions including the green emission peaks (522 nm and 541 nm) and the red emission peak centered at 660 nm. More importantly, it can be seen that the Y$_2$O$_3$:Yb/Er nanoparticles possess significant stronger red luminescence at 660 nm, which is different from previously reported NaYF$_4$ host that is usually presenting green UC emission [28]. Figure 3(c) shows the energy level diagram of the possible energy transfer processes between Yb$^{3+}$ and Er$^{3+}$. With absorbing 980 nm photon, the Yb$^{3+}$ is excited to the $^2F_{5/2}$ energy level and then transfers its energy to the nearby Er$^{3+}$ ion. Immediately
following excited state absorption, transfer of energy from excited state \( \text{Yb}^{3+} \) resulted in populating the \( ^4\text{F}_{7/2} \) state of \( \text{Er}^{3+} \). The excited state \( ^4\text{F}_{7/2} \) electrons of \( \text{Er}^{3+} \) nonradiatively relax to the \( ^2\text{H}_{11/2} \), \( ^4\text{S}_{3/2} \), and \( ^4\text{F}_{9/2} \) levels (\( \text{Er}^{3+} \)). With high \( \text{Yb}^{3+} \)-doped concentration, the green emissions are almost quenched and the intensity ratio of the red to the green emission is large, which results in strong red emission [29]. The dominant red UC emission is mainly attributed to the two energy-transfer processes

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^4\text{S}_{3/2} (\text{Er}^{3+}) + ^2\text{F}_{7/2} (\text{Yb}^{3+}) \rightarrow ^4\text{I}_{15/2} (\text{Er}^{3+}) + ^2\text{F}_{5/2} (\text{Yb}^{3+}) \quad \text{and} \quad ^4\text{I}_{13/2} (\text{Er}^{3+}) + ^2\text{F}_{5/2} (\text{Yb}^{3+}) \rightarrow ^4\text{I}_{15/2} (\text{Er}^{3+}) + ^2\text{F}_{7/2} (\text{Yb}^{3+})
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[25, 29, 30]. The three emission peaks around at 522 nm, 541 nm, and 660 nm can be assigned to the \( ^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2} \) (green), \( ^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2} \) (green), and \( ^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2} \) (red) transitions of \( \text{Er}^{3+} \), respectively. As demonstrated in Figure 3(b), the relative intensity of green \( (^5\text{S}_2/F_4 \rightarrow ^1\text{I}_8) \) to red \( (^5\text{F}_3 \rightarrow ^5\text{I}_8) \)
emission of the Ho$^{3+}$ ion is stronger than the ratio of green to red emission of Er$^{3+}$. The insets of Figures 3(a) and 3(b) show the corresponding digital photographs of the water solution of the Y$_2$O$_3$:Yb/Er and Y$_2$O$_3$:Yb/Ho, respectively. As demonstrated, the eye-visible red and yellow light can be readily observed.

To further reveal the UC multicolor output, we have calculated the CIE chromaticity coordinates of Y$_2$O$_3$:Yb$^{3+}$/Er$^{3+}$ and Y$_2$O$_3$:Yb$^{3+}$/Ho$^{3+}$. As shown in Figure 4, the chromaticity coordinates for Y$_2$O$_3$:Yb$^{3+}$/Er$^{3+}$ ($X = 0.6611$, $Y = 0.3357$) (Figure 4, point a) and Y$_2$O$_3$:Yb$^{3+}$/Ho$^{3+}$ ($X = 0.3884$, $Y = 0.6026$) (Figure 4, point b) are fallen into the red and yellow region, respectively, which is consistent with the results of the UC spectra and the digital photographs. The CIE diagram indicates that the UC colors including strong red and yellow can be obtained via co-doping Yb$^{3+}$/Er$^{3+}$ and Yb$^{3+}$/Ho$^{3+}$ in Y$_2$O$_3$ host material, respectively.

4. Conclusions

In summary, we have successfully synthesized spherical-like cubic phase Y$_2$O$_3$ nanoparticles with tunable multicolor UC emissions by using facile hydrothermal method. On the basis of the analysis of the XRD and TEM, the as-prepared Y(OH)$_3$:Yb/Er nanocrystals are composed of nanosheet and frizzy nanosheet and then the Y$_2$O$_3$:Yb/Er nanoparticles with a quasispherical cubic phase structure were obtained by calcining precursor. Under the excitation of the 980 nm laser, multicolor visible emissions including strong red and yellow can be obtained via co-doping Yb$^{3+}$/Er$^{3+}$ and Yb$^{3+}$/Ho$^{3+}$
in Y\textsubscript{2}O\textsubscript{3} host material, respectively. These UC nanoparticles with multicolors suggest that they have potential application in color displays and biolabels.

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