Flame synthesis and effects of host materials on Yb$^{3+}$/Er$^{3+}$ co-doped upconversion nanophosphors

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The upconversion nanophosphors (UCNPs) of Yb$^{3+}$/Er$^{3+}$ co-doped into Y$_2$O$_3$, La$_2$O$_3$, and Gd$_2$O$_3$ were synthesized via the combustion method and characterized by powder X-ray diffractometer (XRD), scanning electron microscopy (SEM) and upconversion fluorescence spectroscopy. The characterization results showed that at the same flame temperature (2705 K) and precursor concentration (0.1 M), pure monoclinic and cubic-phase phosphors were achieved on Gd$_2$O$_3$ and Y$_2$O$_3$ hosted UCNPs, respectively; while the mixed phases were observed on La$_2$O$_3$ hosted UCNPs. Further annealing process at 850 °C produced pure cubic-phase La$_2$O$_3$:Yb$^{3+}$, Er$^{3+}$ UCNPs; while there was no phase transition observed on Gd$_2$O$_3$:Yb$^{3+}$,Er$^{3+}$ UCNPs. The dependence of upconversion luminescence on precursor concentrations and host materials was then examined. The La$_2$O$_3$ and Gd$_2$O$_3$ hosts were shown to be the promising alternates for the commonly used Y$_2$O$_3$ hosts for rare-earth doped phosphors.

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1. Introduction

Rare-earth (RE) doped upconversion nanophosphors (UCNPs), which produce sharp visible luminescence with near-infrared (NIR) excitation, have broad applications spanning from ceramic solid-state lasers, luminescent displays, biolabeling and photodynamic therapy to authentication and security [1–10]. Compared to conventional down-conversion phosphors [11,12], UCNPs benefit from the availability of low cost and high power infrared lasers. In addition, the use of infrared excitation allows deeper tissue penetration and reduces background noise due to the absence of autofluorescence. Furthermore, the UC process has tunable optical properties and simultaneous detection of multiple targets. Therefore, UCNPs have received considerable interest not only from academic researchers, but also from commercial applications.

To prepare oxides hosted UCNPs, several different techniques, such as sol–gel [13], facile hydrothermal and coprecipitation [14], solution combustion synthesis [15], spray pyrolysis [16], and flame spray synthesis [17] have been reported. Among these methods, the flame based combustion synthesis methods have presented great commercialization potential with high production rates, broad temperature controllability, low cost, and synthetic flexibility on choosing host materials. Moreover, they can produce high purity nanoparticles with small primary size and narrow size distributions. For commercial application, besides choosing a suitable synthetic method, another task is to identify the most efficient UC phosphor system. So far, the hexagonal-phase NaYF$_4$ host is reported to be the most efficient for UCNPs, especially at nanoscale [9,10], however, the fluorides based UCNPs have the concerns of toxicity problem due to the fluorine-containing species. Furthermore, the fluoride hosts are impractical for the high temperature synthesis (>1000 °C) under the oxygen atmosphere. To date, the ceramic based oxides, such as Y$_2$O$_3$, La$_2$O$_3$, and Gd$_2$O$_3$ are found to be the most stable and low toxic host concerning the above factors [18]. Exploring deeper into the inside the crystalline structure, some photophysical properties of these oxides hosts are the same as those of fluorides based UCNPs, e.g., low phonon energy, transparent to visual light and in the absence of the low energy levels and interaction between the doped RE activator ions. Therefore, the oxide hosted phosphors have been actively investigated in parallel with those fluorides based phosphors.

Flame synthesis of the Y$_2$O$_3$:Yb$^{3+}$,Er$^{3+}$ UCNPs has been reported [17]. However, there is still no work on the flame synthesis of La$_2$O$_3$ and Gd$_2$O$_3$ hosted UCNPs. Therefore, both the fundamental and experimental investigations exploring their potential applications for UCNPs are still needed. In this paper, two new UCNPs of Yb$^{3+}$,Er$^{3+}$ co-doped into hosts of Re$_2$O$_5$ (Re = La and Gd) were prepared by the FSP synthesis and were characterized.

2. Experimental

Fig. 1 shows the process of FSP method and schematic of the FSP system. The flame nozzle consisted of three concentric stainless steel tubes. By varying the flow rates of all gases, the flame temperature and particle residence time can be controlled. For example, the oxygen nitrogen and methane flow rate was kept constant at 2, 1.23 and 0.6 L/min, respectively, the corresponding adiabatic flame temperature (Tad) was estimated at 2705 K by using CHEMKIN [19].
The particles were cooled and collected by using a filter paper. In this work, ethanol was selected as the solvent. The precursor solutions were prepared by dissolving a given amount of nitrates of metals in ethanol. Powder X-ray diffractometry (XRD) was used for the characterization of crystal phase and the estimation of the crystalline size. The morphology and size of particles were examined using a field-emission scanning electron microscope (FE-SEM, Philips XL30). PL spectra were measured with excitation at 980 nm using a NIR laser diode.

3. Results and discussions

In this work, to compare the effects of the hosts on the UC luminescence, the flame temperature was kept at 2705 K. Fig. 2 shows...
the XRD patterns of as-prepared three-differently hosted UCNPs at precursor concentration of 0.1 M. Fig. 2a and b shows a cubic-phase pattern of Y_2O_3:Yb^{3+}:Er^{3+} with Yb^{3+}:Er^{3+} doping ratios at 8:6 and 1:3, respectively, which are in a good agreement with JCPDS Card No. 41-1105 (Fig. 2c) corresponding to the cubic-phase of (211), (222), (400), (411), (420), (413), (440), (611), and (622) planes. For La_2O_3 and Gd_2O_3 hosts, it is seen from Fig. 2 (d–f), the Gd_2O_3:Yb^{3+}:Er^{3+} UCNPs exhibit a pure monoclinic structure (JCPDS card No. 42-1465, Fig. 2f). Fig. 2d shows that the La_2O_3:Yb^{3+}:Er^{3+} UCNPs are in mixed cubic and monoclinic structures. The above results indicated that the enthalpies to form monoclinic structures are lower for La_2O_3 and Gd_2O_3 than that for Y_2O_3. It has been shown that the Y_2O_3 hosted UCNPs in a monoclinic structure were more efficient than the UCNPs in cubic-structured hosts, therefore, in this work at the same synthetic conditions of using FSP synthesis method, our XRD results indicated that La_2O_3 and Gd_2O_3 are of great potential to be the hosts for UCNPs which could be obtained in relative low temperature.

Fig. 3 shows the XRD pattern of the La_2O_3 hosted UCNPs after annealing at 850 °C for 4 h. The annealed particles showed the La_2O_3 hosted UCNPs had crystalline transition from monoclinic to cubic-phase. This is similar to our previous observation on Y_2O_3:Eu phosphors [17], where the phase transition from monoclinic to cubic was achieved after annealing at 1200 °C for 2 h. It should be mentioned that we did not observe the phase transition from monoclinic to cubic on Gd_2O_3:Yb^{3+},Er^{3+} UCNPs under the same heating conditions (data not shown). The reasons should be correlated to the lattice structure and studies are currently underway.

The average crystallite size d of the three groups of UCNPs can be calculated by Scherrer equation: 
\[ d = \frac{0.94 \lambda}{B \cos \theta}, \]
where \( \lambda \) (=0.1540598 nm), \( \theta \) and \( B \) are the wavelength of the X-ray, the diffraction angle and the full width at half maximum of the XRD peaks, respectively; and 0.89 is a constant for spherical particles. The calculated crystallite sizes of the four UCNPs in Fig. 2 are 53.5 nm, 53.5 nm, 54.7 nm, and 51.2 nm, corresponding to the XRD patterns in Fig. 2a (Y_2O_3), 2b (Y_2O_3), 2d (La_2O_3), and 2f (Gd_2O_3), respectively. The close crystallite sizes suggest that when studying the host effects on the upconversion luminescence in this work, the size effect can be excluded.

Fig. 3 (a–c) shows the SEM images of the three UCNPs prepared from precursor concentrations of 0.01, 0.1 and 0.5 M. The corresponding histograms of size distribution are shown in Fig. 3 (d–f), respectively. The average particle sizes for the precursor concentrations of 0.01 M, 0.1 M and 0.5 M are 196 nm, 480 nm and 820 nm, respectively. For ultrasonic spray system, the atomized droplet size is related to the surface tension (T) and density (\( \rho \)) of the precursor solution, and the ultrasonic nebulizer frequency (f). The average droplet size (d) can be approximately determined by 
\[ d = \left( \frac{T}{\rho f^2} \right)^{1/3}, \]
where C is a constant. Therefore, it is seen that increasing the precursor concentration leads to the increase of the atomized droplet size and final particle size. These results indicate that besides controlling the flame temperature, the particle sizes can also be controlled by adjusting precursor concentration.

Accordingly, the UC emission spectra of all the above UCNPs are compared in Fig. 4. The results show that the UC luminescence intensities increase with increasing concentrations (Fig. 4 (a)). The enhancements are due to the decreasing surface to volume ratios, and therefore decreasing the surface functional groups of hydroxides and carbonates for quenching luminescence [6]. Fig. 4 (b) shows that both La_2O_3 and Gd_2O_3 hosted UCNPs have only one red emission peak, which confirming the monoclinic structure of the Gd_2O_3:Yb^{3+},Er^{3+}. For La_2O_3:Yb^{3+},Er^{3+} in mixed crystalline phase, only one red emission peak indicates that the emission from monoclinic particles is dominant. We observed that the annealed and cubic-structured La_2O_3:Yb^{3+},Er^{3+} UCNPs also exhibited higher UC luminescence than that of the Y_2O_3:Yb^{3+},Er^{3+} UCNPs in the same crystalline phase. One possible reason could be explained by the variation of the host cationic radius. For the oxides host, the ionic radii are: 0.92 Å (Y^{3+}), 0.97 Å (Gd^{3+}), and 1.14 Å (La^{3+}). An increase of cationic radius results in a reduced ion-lattice interaction. As a consequence, the radiative and non-radiative decay processes will decrease, leading to higher infrared-to-visible conversion efficiency in agreement with our experimental results.

![Fig. 3. SEM images and histograms of Y_2O_3:Yb:Er UCNPs prepared at: (a) 0.01 M; (b) 0.1 M; and (c) 0.5 M.](image-url)
4. Conclusions

Flame synthesis of UCNPs in two new oxide hosts, La$_2$O$_3$ and Gd$_2$O$_3$, were achieved. The effects of host materials and dopant concentration as well as precursor concentrations on the PL properties of these UCNPs were investigated and compared with those of Y$_2$O$_3$ hosted UCNPs. The results showed that at the same synthesis temperature, it was easier to obtain monoclinic-phase La$_2$O$_3$ and Gd$_2$O$_3$ hosted UCNPs. The synthetic achievements and spectroscopy studies should allow both fundamental research and potential applications of these oxides based nanophosphors.

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References


Fig. 4. PL spectra of the Y$_2$O$_3$:Yb:Er UCNPs prepared at different concentrations (a) and three UCNPs prepared in different hosts (b).