Green, Cubic $\text{Y}_2\text{O}_3$: $\text{Tb}^{3+}$ Nanospheres: Synthesis and Photoluminescence Property


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ABSTRACT

In this study, $\text{Tb}^{3+}$-doped $\text{Y}_2\text{O}_3$ green nanospheres were prepared via the simple, cost-effective urea homogeneous precipitation method without additives. The specimens annealed above 800°C are well matched with the cubic phase (JCPDS, 41-1105), and the crystallinity increases with raising the annealing temperature. All the as prepared samples consist of well separated spherical particles with diameter size varying from 200nm to 700nm. Obviously, the average size of the separated spherical particles decreases by the raising of the annealing temperature while the photoluminescence intensity excited by either 275nm or 300nm increases.

Keywords: $\text{Y}_2\text{O}_3$, synthesis, photoluminescence property

1 INTRODUCTION

Luminescent light-emitting nanoparticles have potential applications in high-definition displays[1], lasers[2], and bioimaging[3][4]. Among these particles, rare-earth phosphors doped with lanthanide ions have advantageous optical properties for their superior photostability[5]. $\text{Y}_2\text{O}_3$ is one of the most popular studied as a host matrix. In this study, $\text{Tb}^{3+}$-doped $\text{Y}_2\text{O}_3$ green nanospheres were prepared via the simple, cost-effective urea homogeneous precipitation method without additives. Nanospheres were characterized by X-ray diffraction, Scanning electron microscope, Photoluminescence spectroscopy, and UV spectrophotometer.

2 EXPERIMENTAL

2.1 Preparation

All reagents were of analytical grade and used as received without further purification. Monodispersed $\text{Y}_2\text{O}_3$ nanospheres were prepared via the simple, cost-effective urea homogeneous precipitation method. In a typical synthesis, 0.005mol $\text{Y(NO}_3)_3·6\text{H}_2\text{O}$, 0.1mol $\text{CO(NH}_2)_2$, and 0.00015mol $\text{Tb(NO}_3)_3·6\text{H}_2\text{O}$ were dissolved in 150ml deionized water. The mixture was vigorously stirred for 30min and ultrasonic dispersed for 20min to form a clear solution. Then the solution was sealed and heated up to 98°C for 2.5h. Subsequently, the precipitate was centrifuged, washed with deionized water and alcohol to remove remaining ions, which was then dried at 70°C for 24h under vacuum. Finally, the precipitate was calcined in a tube furnace at 800°C, 900°C, 1000°C, 1200°C for 2h under the protection of Ar gas to obtain the oxide particles.

2.2 Characterization

The X-ray diffraction (XRD) patterns were recorded by SHIMADZU LabX XRD-6000 with Cu Kα radiation (40kV, 30mA). The scanning electron microscopy (SEM) images were recorded by a JEOL JSM-6390A system. The PL measurements were performed with a Hitachi F-7000 spectrophotometry equipped with a 150W Xenon lamp as an excitation source. The UV-Vis-NIR absorption of the as prepared powders were performed on a SHIMADZU UV-3600.

3 RESULT AND DISCUSSION

3.1 Structural and Morphological Characterization

X-ray diffraction (XRD) patterns of $\text{Y}_2\text{O}_3$ specimens are reported in Fig 1.(a); All diffraction patterns are well matched with cubic phase $\text{Y}_2\text{O}_3$(JCPDS, 41-1105)[6], corresponding to (211), (222), (400), (411), (332), (431), (440), (611), (622), which indicates that the addition of the $\text{Tb}^{3+}$ ions have not altered the crystal lattice frame. No additional peaks appeared indicate there are no impurities in these samples and the $\text{Tb}^{3+}$ cations are effectively built into the host lattice. The peaks' intensity becomes higher and the size of nanoparticles part of
nanospheres increases. Fig 1.(b) The EDS of the as prepared specimens, consisting of elements Y, O, Tb, is in line with the XRD patterns. The SEM images showing in Fig 2. All the as prepared samples consist of well separated monodisperse spherical particles with diameter size varying from 200nm to 700nm. Obviously, the average size of the separated spherical particles decreases by the raising of the annealing temperature, due to the shrinkage of the lattice.

![SEM images of Tb$^{3+}$-doped Y$_2$O$_3$ nanospheres annealed at different temperature](image)

Fig 2. SEM images of Tb$^{3+}$-doped Y$_2$O$_3$ nanospheres annealed at different temperature: (a) 800$^\circ$C; (b) 900$^\circ$C; (c) 1000$^\circ$C; (d) 1200$^\circ$C.

Fig 3.(a) TEM image of Tb$^{3+}$-doped Y$_2$O$_3$ nanosphere annealed at 900$^\circ$C. The diameter of this single nanosphere is nearly 310nm, made up of a number of nanoparticles. Fig 3.(b) HRTEM image of an edge of the single nanosphere signed No. 1 in Fig 3.(a). The HRTEM image clearly demonstrates the lattice fringes for the cubic phase of Tb$^{3+}$-doped Y$_2$O$_3$ and from the micrograph we have determined the lattice spacing in the particle to be 0.42nm (for a particular set of planes), which corresponds to the (211) plane of cubic phase of the materials[6].

![TEM image of Tb$^{3+}$-doped Y$_2$O$_3$ nanospheres](image)

Fig 3. TEM image of Tb$^{3+}$-doped Y$_2$O$_3$ nanospheres annealed at 900$^\circ$C: (a) a single nanosphere; (b) HRTEM image of a single nanosphere’s edge.

3.2 Photoluminescence and Absorption Property

Photoluminescence (PL) and PL excitation (PLE) were measured at room temperature. The electronic transition spectra for the range of 400-700nm are shown in Fig 4. The fluorescence of Tb$^{3+}$ originated from the transition of $^5D_4 \rightarrow ^7F_J$ manifolds of Tb$^{3+}$. Tb$^{3+}$ dope-
Fig 4. Photoluminescence spectrum of Tb³⁺-doped Y₂O₃ nanospheres annealed at different temperature: (a) PLE spectra monitoring at $\lambda_{em} = 545$ nm; (b) PL spectra under $\lambda_{ex} = 275$ nm; (c) PL spectra under $\lambda_{ex} = 300$ nm; (d) PL decay curve corresponding to $^5D_4 \rightarrow ^7F_5$.

Fig 5. Absorption spectrum of Tb³⁺-doped Y₂O₃ nanospheres annealed at different temperature.

d phosphors can be excited by either 275 nm or 300 nm ultraviolet light Fig 4.(a), where Tb³⁺ $(4f^8)$ are excited to higher $4f^75d^1$ levels and then nonradiatively relax to $^5D_4$ excited states[6]. Obviously the PL intensity excited by 275 nm is higher than 300 nm from Fig 4.(a). Due to the relatively large energy gap between $^5D_4$ and $^7F_3$ ground states this relaxation process occurs radiatively and we get the spectra in the visible range. Among all the transitions of Tb³⁺, the predominance one is $^5D_4 \rightarrow ^7F_5$ at 545 nm by the larger value of the reduced matrix at $J=5$ and Judd-Ofelt theory. Fig 4.(b), Fig 4.(c) show the PL spectrum excited by 275 nm and 300 nm. The PL intensity largely improves with the raising of annealing temperature, especially the annealing temperature above 1000°C. With the annealing temperature raised, the crystallinity become higher, groups -OH, NO$_3^-$, CH$_2$- decrease sharply, and the shrinkage of the lattice occurs[7]. This decrease the concentration quenching caused by impurity ions. As a result the PL intensity increases greatly. Fig 4.(d) The lifetime value of the fast decay component is found to be higher with the annealing temperature raised, due to the reduction in the surface hydroxyl groups[7]. Fig 5. shows the absorption spectrum, it can clearly be seen the absorption property range from 200 nm to 600 nm decreases with the raising of annealing temperature. Two peaks near to 275 nm and 300 nm, the intensity the latter is higher than the former, contribute to PL spectrum excited by 275 nm and 300 nm. This is in line with the PLE spectrum and PL spectrum, the intensity the latter is lower.
than the former.

4 CONCLUSIONS

Tb$^{3+}$-doped Y$_2$O$_3$ green nanospheres were prepared via the simple, cost-effective urea homogeneous precipitation method without additives. The specimens annealed above 800°C are well matched with the cubic phase (JCPDS, 41-1105), and the average size of the separated nanospheres consisting of nanoparticles decreases by the raising of the annealing temperature while the photoluminescence (PL) intensity excited by either 275nm or 300nm increases. This is in line with the absorption spectrum. In addition, the lifetime value of the fast decay component become higher with the annealing temperature raised, due to the reduction in the surface hydroxyl groups.

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