

Green, Cubic Y₂O₃: Tb³⁺ Nanospheres: Synthesis and Photoluminescence Property

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ABSTRACT

In this study, Tb³⁺-doped Y₂O₃ 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: Y₂O₃, 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]. Y₂O₃ is one of the most popular studied as a host matrix. In this study, Tb³⁺-doped Y₂O₃ 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 Y₂O₃ nanospheres were prepared via the simple, cost-effective urea homogeneous precipitation method. In a typical synthesis, 0.005mol Y(NO₃)₃·6H₂O, 0.1mol

CO(NH₂)₂, and 0.00015mol Tb(NO₃)₃·6H₂O 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 precursor 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 K α 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 Y₂O₃ specimens are reported in Fig 1.(a); All diffraction patterns are well matched with cubic phase Y₂O₃(JCPDS, 41-1105)[6], corresponding to (211), (222), (400), (411), (332), (431), (440), (611), (622), which indicates that the addition of the Tb³⁺ ions have not altered the crystal lattice frame. No additional peaks appeared indicate there are no impurities in these samples and the Tb³⁺ cations are effectively built into the host lattice. The peaks' intensity increases and become more sharp with the raising of the annealing temperature from 800°C to 1200°C, while the peaks' width decreases. This indicates the crystallinity become higher and the size of nanoparticles part of

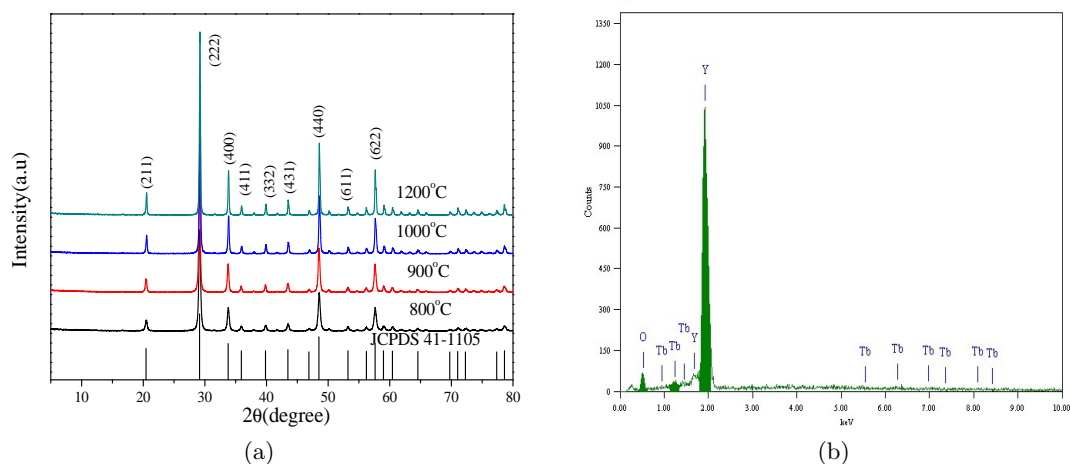


Fig 1. (a) XRD patterns of Tb^{3+} -doped Y_2O_3 nanospheres annealed at different temperature; (b) EDS of the as prepared specimens.

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.

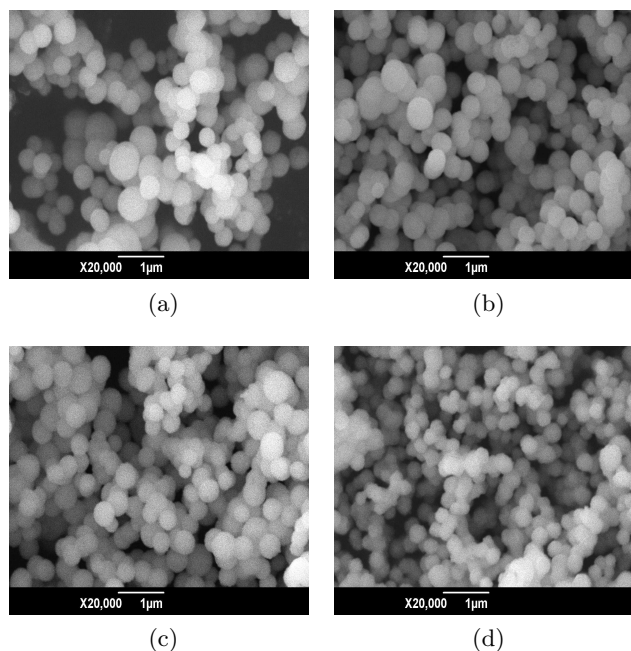


Fig 2. SEM images of Tb^{3+} -doped Y_2O_3 nanospheres annealed at different temperature: (a) 800°C; (b) 900°C; (c) 1000°C; (d) 1200°C.

Fig 3.(a) TEM image of Tb^{3+} -doped Y_2O_3 nanosphere annealed at 900°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_2O_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].

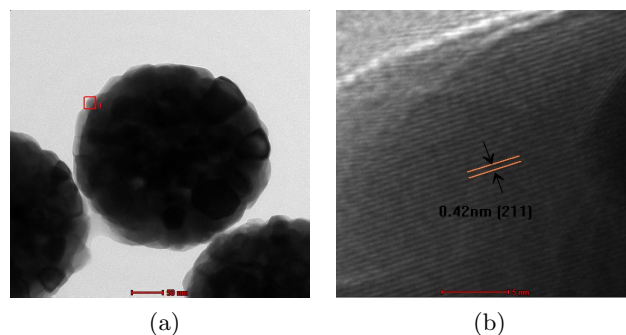


Fig 3. TEM image of Tb^{3+} -doped Y_2O_3 nanospheres annealed at 900°C: (a) a single nanosphere; (b) HRTEM image of a single nanosphere's edge.

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 $^5\text{D}_4 \rightarrow ^7\text{F}_j$ manifolds of Tb^{3+} . Tb^{3+} dope-

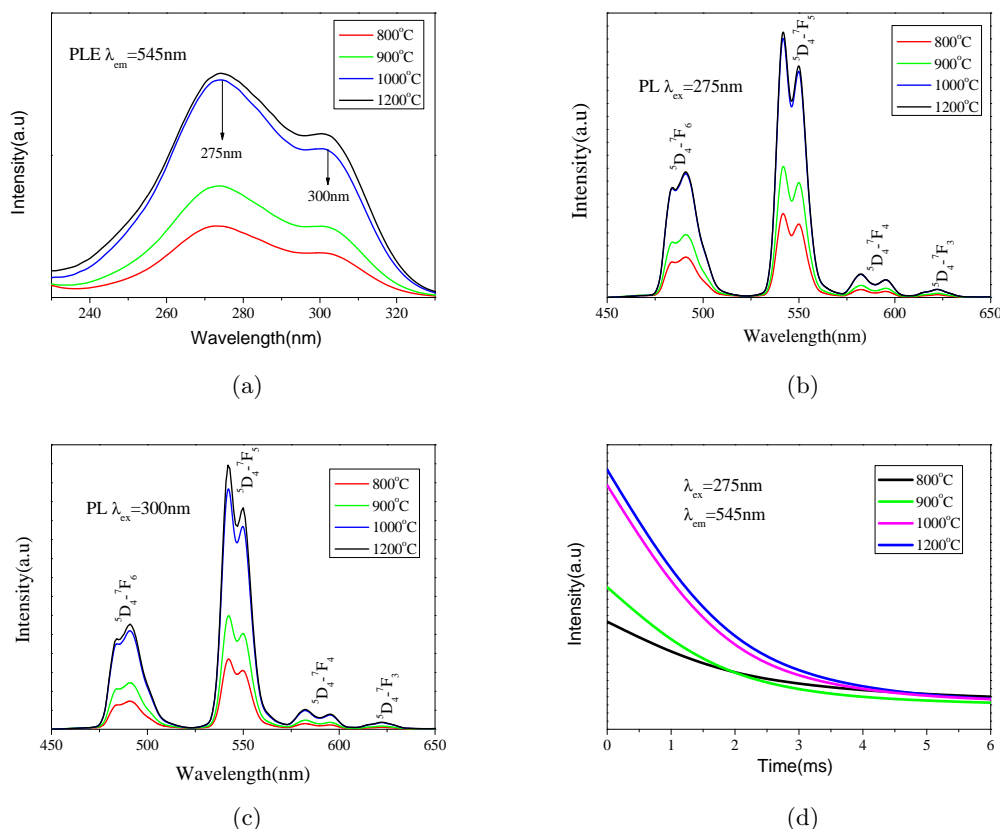


Fig 4. Photoluminescence spectrum of Tb^{3+} -doped Y_2O_3 nanospheres annealed at different temperature: (a) PLE spectra monitoring at $\lambda_{\text{em}}=545\text{nm}$; (b) PL spectra under $\lambda_{\text{ex}}=275\text{nm}$; (c) PL spectra under $\lambda_{\text{ex}}=300\text{nm}$; (d) PL decay curve corresponding to $^5\text{D}_4 \rightarrow ^7\text{F}_5$.

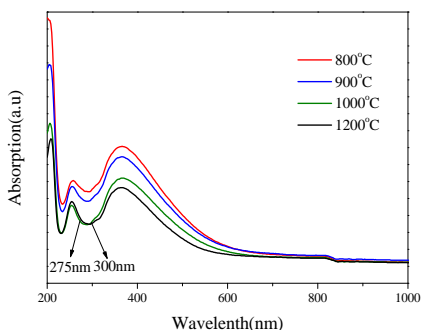


Fig 5. Absorption spectrum of Tb^{3+} -doped Y_2O_3 nanospheres annealed at different temperature.

d phosphors can be excited by either 275nm or 300nm ultraviolet light Fig 4.(a), where Tb^{3+} ($4f^8$) are excited to higher $4f^75d^1$ levels and then nonradiatively relaxe to $^5\text{D}_4$ excited states[6]. Obviously the PL intensity excited by 275nm is higher than 300nm from Fig 4.(a). Due to the relatively large energy gap between $^5\text{D}_4$ and $^7\text{F}_j$ ground states this relaxation process occurs radia-

tively and we get the spectra in the visible range. Among all the transitions of Tb^{3+} , the predominance one is $^5\text{D}_4 \rightarrow ^7\text{F}_5$ at 545nm 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 275nm and 300nm. 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 200nm to 600nm decreases with the raising of annealing temperature. Two peaks near to 275nm and 300nm, the intensity the latter is higher than the former, contribute to PL spectrum excited by 275nm and 300nm. This is in line with the PLE spectrum and PL spectrum, the intensity the latter is lower

than the former.

4 CONCLUSIONS

Tb³⁺-doped Y₂O₃ 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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