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Controlled synthesis and luminescent properties of different morphologies $GdBO_3:Eu^{3+}$ phosphors self-assembled of nanoparticles

Zhihua Leng, Yali Liu, Nannan Zhang, Linlin Li, Shucai Gan*

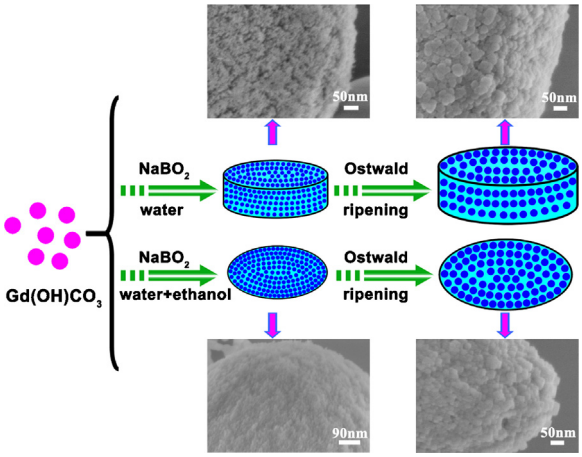
College of Chemistry, Jilin University, Changchun 130026, PR China

HIGHLIGHTS

- Cake-like and olive-like $GdBO_3$ self-assembled of nanoparticles were synthesized.
- This method used $Gd(OH)CO_3$ and $NaBO_2{\cdot}4H_2O$ as the precursors for the first time.
- When a small amount of ethanol was added, different morphologies can be obtained.

GRAPHICAL ABSTRACT

Small amount of ethanol has a favorable effect on controlling the products' morphology. The formation of cake-like and olive-like $GdBO_3$ microcrystals self-assembled of nanoparticles can be assigned to the Ostwald ripening process.



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ABSTRACT

Uniform cake-like and olive-like $GdBO_3$ samples have been successfully synthesized for the first time via a simple solution-based hydrothermal method using $Gd(OH)CO_3$ colloid spheres and $NaBO_2{\cdot}4H_2O$ as the precursors. It was found that small amount ethanol in the hydrothermal process was responsible for determining the shape of products. The FT-IR analysis indicates that vaterite-type $GdBO_3$ can be synthesized by this method. The obtained cake-like and olive-like $GdBO_3$ with rough surfaces have similar mircostructures which are composed of numerous nanoparticles. Time-dependent experiments were employed to study the possible formation mechanism. The formation of cake-like and olive-like $GdBO_3$ mircostructures self-assembled of nanoparticles can be ascribed to the Ostwald ripening process. A detailed investigation on the photoluminescence (PL) properties of $GdBO_3:Eu^{3+}$ samples with different morphologies indicates that the PL properties of as-obtained $GdBO_3:Eu^{3+}$ phosphors are dependent on their morphologies. The effect of Eu^{3+} doping concentration on PL intensity was also investigated and the quenching concentration of $GdBO_3:Eu^{3+}$ is 20%.

* Corresponding author. Tel.: +86 431 88502259; fax: +86 431 88502259.
E-mail address: gansc@jlu.edu.cn (S. Gan).

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1. Introduction

In recent years, controlled synthesis of inorganic functional nano-/micro-materials with well-defined morphology has been an important goal of modern materials chemistry not only because of their esthetic appearances but also their shape-dependent properties [1–3]. Among various morphologies and structures, self-assembly of inorganic nanobuilding blocks into one-dimensional (1D), two-dimensional (2D), and three-dimensional (3D) ordered hierarchical nanostructures is fascinating because the variation of the arrangements of the building blocks provides a means to tune the properties of the materials. Up to now, great interests and tremendous efforts have been progressively devoted to the exploration of various convenient and efficient approaches to fabricate different kinds of lanthanide compounds with the controlled shape, size distribution, and dimensionality [4–6].

Lanthanide orthoborates belong to a group of traditional phosphors, which were widely used in the plasma display panels, the Hg-free fluorescence lamps and bioimaging materials [7]. Among a variety of borate phosphors, $GdBO_3$:Eu^{3+} is one of the excellent and efficient phosphors available for the red primary of the color picture in plasma display panels due to its special optical properties, high stability, low synthesis temperature, and high ultraviolet and optical damage threshold [8]. Compared with bulk materials, lanthanide compounds nanocrystals have better shape tailoring ability to improve nanodevice fabrication [9]. Furthermore, most of the previous works about rare earth orthoborates were mainly concentrated on using H_3BO_3 as boron source to obtain different structures via hydrothermal process [10–13], and few studies used $NaBO_2{\cdot}4H_2O$ as boron source [14,15].

Recently, $Ln(OH)CO_3$ colloid spheres as precursors have been widely used to fabricate different kinds of lanthanide compounds [16–19]. In our previous work, $Y(OH)CO_3$ colloid spheres have been used as precursors treated with $Na_2B_4O_7{\cdot}10H_2O$ to fabricate ellipsoid-like YBO_3 [20]. In this paper, for the first time, large-sized cake-like and olive-like $GdBO_3$ self-assembled of nanoparticles was synthesized via a simple solution-based hydrothermal method using $Gd(OH)CO_3$ colloid spheres and $NaBO_2{\cdot}4H_2O$ as the precursors.

2. Experimental

2.1. Materials

$Ln(NO_3)_3$ (Ln = Gd and Eu) aqueous solutions was obtained by dissolving the corresponding metal oxide in dilute HNO_3 solution under heating, respectively. All the other reagents are of analytical grade and used directly without further purification. Distilled water was used throughout.

2.2. Preparation of monodisperse $Gd(OH)CO_3$ colloid spheres

The monodisperse colloid spheres of $Gd(OH)CO_3$ were prepared via a urea-based homogeneous precipitation process [21]. 10 ml of $Gd(NO_3)_3$ (0.1 M) and 2 g urea were dissolved in distilled water, and the total volume of the solution was about 67 ml to keep the Gd^{3+} constant at 0.015 M and the urea constant at 0.5 M. The above solution was first homogenized under magnetic stirring at room temperature. After that, the resultant solution was heated at 90 °C for 2 h in the water bath. The obtained suspension was separated by centrifugation and collected after washing with distilled water several times.

2.3. Preparation of cake-like and olive-like $GdBO_3$

In a typical procedure for the preparation of cake-like $GdBO_3$, the as-obtained 1 mmol of $Gd(OH)CO_3$ was firstly redispersed into distilled water by ultrasonic treatment. 10 ml of $NaBO_2{\cdot}4H_2O$ (0.4 M) aqueous solution was dripped into the dispersion followed by further stirring. After that, the resultant mixture was subsequently diluted to 40 ml with distilled water and transferred into a 50 ml Teflon-lined autoclave. The hydrothermal reaction was conducted at 180 °C for 24 h. After the autoclave was cooled to room temperature, the obtained white products were washed with distilled water and ethanol several times and then dried in vacuum at 60 °C. Olive-like $GdBO_3$ was prepared in similar manner to that for cake-like $GdBO_3$, except that 5 ml anhydrous ethanol instead of equal volume of distilled water was added in the hydrothermal process.

A similar process was employed to prepare $GdBO_3$:Eu^{3+} using a stoichiometric amount of $Eu(NO_3)_3$ aqueous solution instead of $Gd(NO_3)_3$ solution for the precursors at the initial stage as described above.

2.4. Characterization

All the samples were investigated by X-ray diffraction (XRD) measurements performed on a Rigaku D/max-II B X-ray diffractometer with monochromatic Cu K_α radiation. The morphology and composition of the samples were characterized by field-emission scanning electron microscopy (FE-SEM, S-4800, Hitachi), employing the accelerating voltage of 10 kV. The infrared spectra of the samples were taken in KBr pressed pellets on a NEXUS 670 infrared Fourier transform spectrometer (Nicolet Thermo, Waltham, MA). The photoluminescence excitation and emission spectra were recorded with a Hitachi F-7000 spectrophotometer equipped with a 150 W Xe lamp as the excitation source. All the measurements were performed at room temperature.

3. Results and discussion

3.1. Phase identification and morphology

Fig. 1 shows the XRD patterns of the products obtained when the amorphous $Gd(OH)CO_3$ colloid spheres were treated with $NaBO_2{\cdot}4H_2O$ at 180 °C for 24 h in the hydrothermal process. All of the diffraction peaks can be indexed to pure phase $GdBO_3$ (PDF #

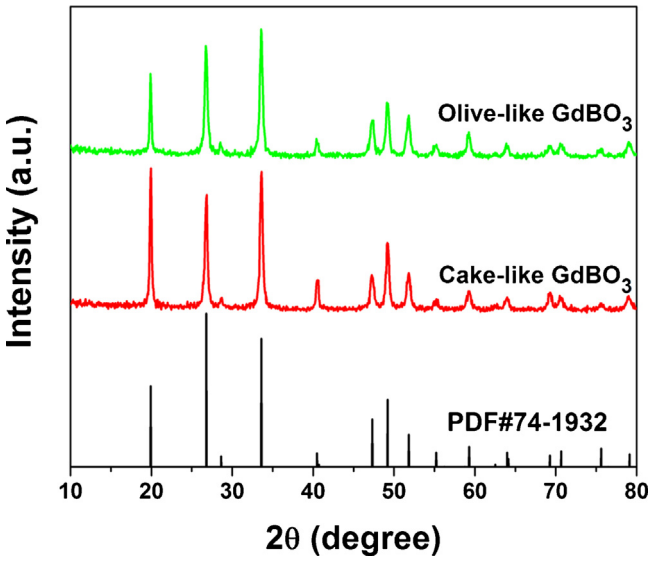

Fig. 1. XRD patterns of the as-obtained $GdBO_3$ samples.