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A template-free solvothermal synthesis and photoluminescence properties of multicolor Gd_2O_2S:xTb^{3+}, yEu^{3+} hollow spheres

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ABSTRACT

The multicolor Gd_2O_2S:xTb^{3+}, yEu^{3+} hollow spheres were successfully synthesized *via* a template-free solvothermal route without the use of surfactant from commercially available Ln $(NO_3)_3 \cdot 6H_2O$ (Ln = Gd, Tb and Eu), absolute ethanol, ethanediamine and sublimed sulfur as the starting materials. The phase, structure, particle morphology and photoluminescence (PL) properties of the as-obtained products were investigated by X-ray diffraction (XRD), fourier transform infrared spectroscopy (FT-IR), field emission scanning electron microscopy (FE-SEM) and photoluminescence spectra. The influence of synthetic time on phase, structure and morphology was systematically investigated and discussed. The possible formation mechanism depending on synthetic time t for the Gd_2O_2S phase has been presented. These results demonstrate that the Gd_2O_2S hollow spheres could be obtained under optimal condition, namely solvothermal temperature $T = 220\ ^\circ C$ and synthetic time $t = 16$ h. The as-obtained Gd_2O_2S sample possesses hollow sphere structure, which has a typical size of about 2.5 μm in diameter and about 0.5 μm in shell thickness. PL spectroscopy reveals that the strongest emission peak for the Gd_2O_2S:xTb^{3+} and the Gd_2O_2S:yEu^{3+} samples is located at 545 nm and 628 nm, corresponding to $^5D_4 \rightarrow {}^7F_5$ transitions of Tb^{3+} ions and $^5D_0 \rightarrow {}^7F_2$ transitions of Eu^{3+} ions, respectively. The quenching concentration of Tb^{3+} ions and Eu^{3+} ions is 7%. In the case of Tb^{3+} and Eu^{3+} co-doped samples, when the concentration of Tb^{3+} or Eu^{3+} ions is 7%, the optimum concentration of Eu^{3+} or Tb^{3+} ions is determined to be 1%. Under 254 nm ultraviolet (UV) light excitation, the Gd_2O_2S:7%Tb^{3+}, the Gd_2O_2S:7%Tb^{3+},1%Eu^{3+} and the Gd_2O_2S:7%Eu^{3+} samples give green, yellow and red light emissions, respectively. And the corresponding CIE coordinates vary from (0.3513, 0.5615), (0.4120, 0.4588) to (0.5868, 0.3023), which is also well consistent with their luminous photographs.

1. Introduction

In recent years, hollow spheres have attracted considerable interest because of their singular properties and a wide range of potential applications [1,2]. Especially, inorganic hollow spheres represent a kind of attractive materials and have outstanding properties, including multi-aperture shell, favorable permeation, low density, high carrying capacity, controlled-release activity, enhanced catalysis viability, and excellent luminescent properties [3,4], making them a widespread range of potential applications in efficient catalysis, drug delivery carriers, biological imaging, diagnostic analysis, fluorescent labeling, and so on [5–8]. Accordingly, a great deal of effort has been devoted to the development of different methods for the design and manufacture of hollow structures. A variety of chemical and physicochemical methods such as template-assisted synthesis, kirkendall diffusion effects, Ostwald ripening, self-assembly technique, and chemically induced self-transformation have been employed for preparing hollow spheres [9–14]. So far, most methods for preparation of hollow spheres were based on template-assisted process, which is the most straightforward and versatile method [15]. However, this template directing strategy suffers from numerous challenges, including complex procedures, high cost and environmental pollution problems, etc. Thus, it is vital to study template-free methods for synthesising hollow structures.

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Gadolinium oxysulfide (Gd_2O_2S) is a promising host material with a wide band gap of 4.6 eV, and often exhibits favorable properties such as excellent chemical durability [16], high density (7.43 g/cm^3) [17], insolubility in water [18], innocuity [19], good scintillation and high luminescent efficiency [20], which have great potential and wide applications in host materials [21], X-ray intensifying screens [22], scintillator materials [23], X-ray computed tomography (X-CT) [24], up-conversion bioimaging [25], and so on. So, preparation and characterization of gadolinium oxysulfide have attracted more attention for many years. In previous reports, considerable efforts have been devoted to the synthesis of Gd_2O_2S nano/micromaterials, including solid-state reaction (SSR) method [26], gas sulfuration method [27], combustion method [28], emulsion liquid membrane (ELM) method [29], thermal decomposition method [30], precipitation method [31], and hydro/solvothermal method [32], etc. Methods as mentioned above, solvothermal method is very suitable to control morphology, dispersity and homogeneity of the products. Therefore, solvothermal methods have been gradually concerned, as they can successfully prepare rare earth oxysulfides with good morphologies and unique luminescence properties. Nevertheless, it still needs post annealing treatment to enhance the crystallinity and only can be used to prepare some middle rare earth oxysulfides. So, it is meaningful to find some simple and efficient ways to prepare the Gd_2O_2S products. To the best of our knowledge, solvothermal synthesis of the Gd_2O_2S hollow spheres *via* a template-free method has rarely been reported.

In this regard, multicolor Gd_2O_2S:xTb^{3+}, yEu^{3+} hollow spheres have been synthesized by one-pot solvothermal route and template-free method. Compared with the traditional template synthesis, this method is one of the most promising techniques because of its advantages such as environmental-friendly, simplicity, convenience and easily to control the product's shape. However, according to hard-soft acid-base theory (HSAB) [32], Gd^{3+} ions belong to hard acid and S^{2-} ions belong to soft base, which lead to a low affinity between them. For overcoming this shortcoming, we adopted ethanediamine as the main solvent and sublimed sulfur powder as sulfur source in order to increasing sulfur solubility in the ethanediamine solvent, which is very helpful to further improve the affinity between Gd^{3+} ions and S^{2-} ions and ensures the direct formation of Gd_2O_2S in the solvothermal autoclaves. Furthermore, phase, structure, morphology, formation process and PL properties of the product have been also investigated. It is expected that the multicolor Gd_2O_2S:xTb^{3+}, yEu^{3+} hollow spheres will enrich their family and further expand their promising applicable fields.

2. Experimental procedure

2.1. Preparation

Ln $(NO_3)_3\cdot 6H_2O$ (Ln = Gd, Tb and Eu, 99.99% purity), absolute ethanol, ethanediamine and sublimed sulfur powder (S_8) were used as the starting materials without further purification. Rare earth nitrate (Ln $(NO_3)_3\cdot 6H_2O$) were purchased from Jining Tianyi new material Co. Ltd. China. Ethanediamine ($C_2H_8N_2$) was purchased from Tianjin Zhiyuan Chemical Reagent Co. Ltd. China. The other reagents were purchased from Sinopharm Chemical Reagent Co. Ltd. Firstly, a certain amount of sublimed sulfur was dissolved in ethylenediamine to prepare 0.15 M ethylenediamine solution containing sulfur (A solution). Ln $(NO_3)_3$ (Ln = Gd, Tb and Eu) ethanol solution with Ln^{3+} ion concentration of 0.2 M was prepared by dissolving the corresponding Ln $(NO_3)_3\cdot 6H_2O$ in absolute ethanol. Then, A solution with volume of 65 mL was transferred to a para poly phenol (PPL) container of 100 mL. Accompanied with continuous stirring, 5 mL $Gd(NO_3)_3$ ethanol solution was added dropwise into the above solution by ZD-2A automatic potentiometric titration at a rate of 2 mL min^{-1}. The as-obtained suspension solution was heated in DZ-2A II vacuum drying oven for solvothermal synthesis at 220 °C for 2 h, 8 h and 16 h after sealed autoclave. After naturally cooled to room temperature, the products were collected by centrifugal cleaning with deionized water and absolute ethanol for several times and then dried at 80 °C overnight in order to obtain the final product. The Tb^{3+} and Eu^{3+} ions single doped and co-doped finalt products were also synthesized in the same procedure. The doping molar concentration of Tb^{3+} and Eu^{3+} ions were 1%, 3%, 5%, 7% and 10%, respectively.

2.2. Characterization

Phase and structure analyses were identified on X-ray powder diffraction (XRD, D8Advance) and Flourier transform infrared spectra (FT-IR) tools. The XRD pattern was operating at 40 kV and 30 mA with $Cu_{K\alpha} = 0.15406$ nm. Flourier transform infrared spectra (FT-IR) were recorded in the region of 4000-400 cm^{-1} using an Agilent Cary 660 FT-IR spectrophotometer by the KBr method. The particle morphologies were observed by field emission scanning electron microscopy (FE-SEM) using Hitachi SU8000 microscope operated at an acceleration voltage of 20 kV. PL spectra were obtained on a Hitachi F-7000 fluorescence spectrophotometer equipped with a 150 W Xenon lamp as the excitation source. The luminous photographs were obtained on a Boteng Ultraviolet Light Analyzer with the light power density of 0.8 mW mm^{-2}. The CIE coordinates were calculated from the spectra based on the 1931 CIE (Commission Internationale de L'Eclairage 1931 chromaticity) standard for colorimetry.

3. Results and discussion

3.1. Phase formation mechanism of the Gd_2O_2S

The $Gd(NO_3)_3\cdot 6H_2O$ dissolved in absolute ethanol can provide Gd^{3+} ions. Moreover, the reaction process of the crystal water in $Gd(NO_3)_3\cdot 6H_2O$ and ethylenediamine can release OH^- groups to provide oxygen ion (O^{2-}) in the final product. In addition, ethanediamine is also a good solvent for sublimed sulfur, then a large amount of S^{2-} ions are eventually produced by solubilization process to provide sulfur source in the final product. Generally, Gd^{3+} ions are hard acids and S^{2-} ions are soft bases. According to HSAB principle, hard acids prefer to bind to hard bases and soft acids prefer to bind to soft bases. Hence, it is very difficult to bond each other to form gadolinium compound containing sulfur in aqueous system. However, traditional HSAB theory can break through by adjusting the concentration and activity of reagent in solvent system. In this study, the ethylenediamine system possesses high concentration of S^{2-} ions and low concentration of OH^- groups. An excessive S^{2-} ions can overcome the low affinity of S^{2-} with Gd^{3+} ions to a great extent. Thus, it is helpful to bond each other for Gd^{3+}, S^{2-} ions and OH^- groups to form the $Gd_2(OH)_4S$ compound. XRD pattern exhibits two board peaks around $2\theta = 29.2°$ and 49.4°, which indicates that the $Gd_2(OH)_4S$ remains non crystalline structure. Furthermore, pure Gd_2O_2S sample can be obtained by the dehydroxylation of $Gd_2(OH)_4S$. The possible phase formation mechanism of the Gd_2O_2S can be found in Fig. 1.

3.2. Phase and structure analysis

Phase and structure of the as-obtained products were first examined by XRD. Fig. 2 shows XRD patterns of the products with various times and the standard data of Gd_2O_2S with JCPDS card No.