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# Synthesis, characterization, and photoluminescence properties of Gd:Tb oxysulfide colloidal particles

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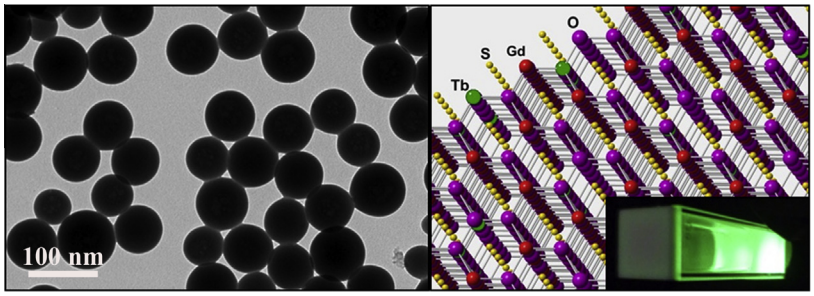
## HIGHLIGHTS

- The size and shape of the $Gd_2O_2S:Tb^{3+}$ can be modulated by the synthesis parameters.
- The $Tb^{3+}$ dopant ions were dispersed uniformly in the host matrix.
- The quenching of luminescence depends of $Tb^{3+}$ ion concentration in the host matrix.
- The electrophoretic mobility and the optical behavior rely on the medium pH.

## GRAPHICAL ABSTRACT

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## ABSTRACT

Terbium-doped gadolinium oxysulfide ($Gd_2O_2S:Tb^{3+}$) nanoparticles were synthesized by using a hydrothermal method followed with a sulfur reaction. We studied parameters such as precursor concentration, stock solutions temperature, reaction time, and reaction temperature to obtain well defined homogeneous particles with specific shape and size. The chemical evolution of the formed particles was followed by the Infrared Spectroscopy (FTIR), thus showing the removal of the hydroxycarbonate precursors at different stages of synthesis. X-ray analysis (WAXD) confirmed that the calcination and sulfidation processes produced cubic ($Gd_2O_3:Tb^{3+}$) and hexagonal ($Gd_2O_2S:Tb^{3+}$) crystalline structures. The photoluminescent (PL) properties were evaluated as a response to UV light excitation in both solid phase and colloidal suspension; we determine the maximum emission intensity as a function of the $Tb^{3+}$ ion dopant concentration and determine the limiting amount in the material before quenching occurs. In colloidal suspensions, the emission spectra of both $Gd_2O_3:Tb^{3+}$ and $Gd_2O_2S:Tb^{3+}$ were compared, and we observed that the sulfidation process increased the integrated emission intensity seventyfold with respect to the former. To evaluate the particles behavior in aqueous media for possible uses in medical applications, an electrophoretic mobility study was carried out, thus observing that the fluorescence emission depends on the pH of the solution, which in turn correlates with the electrophoretic mobility of the particles.



*Abbreviations:* $Gd_2O_2S:Tb3^+$, terbium-doped gadolinium oxysulfide; $Gd_2O_3:Tb^{3+}$, terbium-doped gadolinium oxide; ssT, stock solution temperature; pC, precursor concentrations; rT, reaction temperature; rt, reaction time; RT, room temperature; EM, electrophoretic mobility.

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## 1. Introduction

In the last two decades, a large number of lanthanides compounds such as hydroxides, oxides and rare-earth (RE) doped oxysulfides ($RE_2O_2S$:RE) have been extensively studied due to their usefulness as magnets, catalysts, and safety indicators (scintillators for X-ray detection) [1–4]. Moreover, $RE_2O_2S$:RE have received particular attention for their high performance as fluorescent materials [5–7] which have allowed the development of optical devices, for example as solid state lasers, optical amplifiers, and color displays [8–10]. Furthermore, their high efficiency in converting UV photons into visible light, broad excitation band, wide-band gap (4.6–4.8 eV), and high chemical and thermal stability [11,12] make them a good alternative in biological applications versus organic dyes and quantum dots; both of which have serious limitations for *in vivo* applications [13]. In this area, the compatibility of $RE_2O_2S$:RE phosphors with biological systems have been studied with the idea of using them as fluorescent labels, contrast agents, components in the multiplexed immunoassays, and in the fabrication of hybrid materials between long-term luminescent core with organic coating [14–16]. Therefore, the synthesis and characterization of these materials with controlled size and shape, are crucial [17]. However, the production of monodisperse $RE_2O_2S$ nanoparticles still remains a great challenge for researchers to date, because there is not an effective synthetic route to obtain particles with a narrow size distribution and specific shape [18,19]. A great variety of methods such as the sol–gel method [20], the combustion process [21], or the hydrothermal method [22] have been widely used, but they often do not give a good particle size distribution in the nanoscale regime with a well-defined morphology [18,23,24]. The thermal decomposition of molecular precursors has been reported as an effective method to synthesize colloidal nanoscale metals/alloys and metallic chalcogenides, including ternary compounds [21,25]. This methodology has been widely used but unfortunately the process includes a great variety of initial precursors and is extremely vulnerable to the formation of relatively large amorphous aggregates [26–29]. Hence, in this work we proposed some modifications to the hydrothermal method that will simplify the reported methodology [30], our study is based on the precise control of the synthesis parameters that allow the production of stable and homogeneous terbium doped gadolinium oxysulfide ($Gd_2O_2S:Tb^{3+}$) colloidal particles. The advantage of this method is that unlike previous reports [20–25,30] it employs a limited number of reagents, which reduces the preparation time and the production of secondary sub-products, as well as to obtain a sample free of impurities. In addition, we evaluate the optical properties of oxysulfide particles in solid and colloidal solution, determining the highest emission intensity, by changing the $Tb^{3+}$ ion dopant concentration up to a concentration in the material before quenching occurs. Additionally, for potential application in biological systems, an electrophoretic mobility study was carried out, showing for first time the photoluminescence emission intensity behavior of $Gd_2O_2S:Tb^{3+}$ particles in colloidal solution as a function of the particle surface charge.

## 2. Experimental section

### 2.1. Synthesis of $Gd_2O_2S$:Tb

Gd $(NO_3)_3{\cdot}6H_2O$, Tb $(NO_3)_3{\cdot}6H_2O$ and urea reagents with 99.999% and 98% of purity respectively were purchased from Sigma–Aldrich and used accordingly. The $Gd_2O_2S:Tb^{3+}$ particles were prepared following a three-stage synthesis method. The first step was the nucleation and growth of hydroxycarbonate particles in aqueous solution by using our modified hydrothermal precipitation method, which promotes the complexation reaction of carbonates and lanthanides ions ($Gd^{+3}$ and $Tb^{+3}$) by controlling the rate of ions hydroxylation in the solution. The second step was the production of lanthanides oxide ($Gd_2O_3:Tb^{3+}$) by annealing the hydrocarbonates samples at high temperature, and the third step was the sulfidation reaction to obtain the oxysulfide ($Gd_2O_2S:Tb^{3+}$) particles. In addition, the following parameters were systematically modified: precursor concentrations (pC), reaction temperature (rT), temperature of the stock solutions (ssT) and reaction time (rt). These parameters were optimized until we obtained nanoparticles with well-defined shape. The reaction mixture was made up of two solutions: Solution A was obtained by mixing the selected concentration of Gd and Tb nitrates salts in 100 ml of deionized water. Solution B was produced by dissolving an appropriated amount of urea in 100 ml of deionized water, the overall concentration of lanthanides and urea in these solutions is presented in Table 1. Before mixing, both solutions were brought to the preheating temperature for 15 min. The reaction was carried out by adding the solution B into solution A with a volumetric rate of 3 ml/min under vigorous stirring. Details of the reaction parameters and the concentrations of the precursors are given in Table 1. It is important to mention that during the reaction, the color of the solution turned blue-white after 15 min and white after 45 min, indicating the formation of the hydroxycarbonates particles. Once the precipitates were obtained, the suspension was let to cool down slowly to room temperature (RT). The solid phase was separated by centrifugation (5000 rpm for 10 min) and the samples were washed with deionized water to remove impurities; the cleansing process was repeated several times by re-suspending the precipitate in deionized water and introducing the sample 5 min in an ultrasonic bath between each washing. Afterward, the composed Gd and Tb hydroxycarbonates samples ($Gd(OH)CO_3{\cdot}H_2O$:Tb) were dried in an oven at 50 °C for 12 h. Then, the $Gd(OH)CO_3{\cdot}H_2O$:Tb particles were annealed at 800 °C in air for 2 h to eliminate the organic precursors and produce the $Gd_2O_3:Tb^{3+}$. The oxysulfide particles ($Gd_2O_2S:Tb^{3+}$) were obtained through a sulfidation reaction carried out in a two-holder quartz tube. The first holder was used as reservoir of sulfur powders (Fermont 100%) and the second to place the oxide powders. The reactor was introduced into the furnace leaving the second holder in the center and the first holder in the inlet of the furnace, the later was also covered with an electrical heating appliance (see Scheme S1) and heated at 350 °C to obtain sulfur gas which was brought inside the furnace by high purity nitrogen that was used as a carrier. The sulfidation reaction was produced by annealing the oxide powders at 900 °C for 180 min under the sulfur–nitrogen gas stream. After that, the sample was cooled at room temperature maintaining the constant the $N_2$ flow through the system.

The $Tb^{+3}$ doping percentage was achieved by modifying the Gd and Tb ratio, thus, an appropriate amount of $Tb(NO_3)_3{\cdot}6H_2O$ was added in the solution A to obtain the required Tb concentration in the material (0.01, 0.1, 1.5, 3.0, 4.5, 6.0, 7.0 or 9.0% mol). The effect of lanthanides total concentration was evaluated at 1.9, 6.0, and 11.2 mM concentrations (see Table 1).

### 2.2. Characterization

The particle size and shape were examined by Transmission Electron Microscopy (TEM – Jem Joel 1230) operated at 200 KV and equipped with an EDS accessory (Oxford INCA-STEAM 019A2) for chemical analysis. The samples were prepared by suspending the particles in ethanol and placing a small drop on the carbon grid. The analysis of chemical bonding was performed by Fourier Transform Infrared Spectroscopy (FTIR), using a Bruker Vector 22 instrument coupled with a diamond crystal ATR accessory. The samples were dried and prepared as powders.