



Synthesis and characteristics of nanorods of gadolinium hydroxide and gadolinium oxide



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ABSTRACT

Stable and crystalline pure-phase gadolinium hydroxide ($\text{Gd}(\text{OH})_3$) with diameters of approximately 100–200 nm and lengths of 200–500 nm was synthesized using a surfactant (hexamethylenetetramine or polyvinylpyrrolidone) micelle solution in a hydrothermal process. The as-synthesized $\text{Gd}(\text{OH})_3$ nano-materials were subsequently sintered to form gadolinium oxide (Gd_2O_3) nanorods. X-ray diffraction, transmission electron microscopy, ultraviolet spectroscopy, and Fourier-transform infrared spectroscopy were used to examine the microstructures, morphologies, and optical characteristics of the sintered products. The results suggest that this hydrothermal process may be an effective and convenient approach to prepare $\text{Gd}(\text{OH})_3$ and Gd_2O_3 with one-dimensional nanostructures. The photoluminescence spectra were studied at excitation wavelengths of 210 and 230 nm, and the samples exhibited emission peaks indicating room-temperature photoluminescence.

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1. Introduction

Much attention has been focused on one-dimensional (1D) nanostructures such as nanobelts, nanotubes, nanowires, and nanorods because of their unique physical and chemical properties. These 1D nanostructures are expected to be critical to the function and integration of nanoscale devices [1,2]. Many techniques have been developed in recent years for the synthesis of nanorods, and significant efforts have been devoted to enhancing their optical properties.

The unique 4f electron configuration of rare-earth compounds has imparted them with magnetic, electrical, optical, and catalytic properties [3–6] that make these compounds -invaluable inorganic materials for lanthanide devices, fluorescence labels for biological

detection, magnetic materials, and other functional materials [7]. As these properties on the nanometer scale might be associated with the morphology of the materials, rare-earth compounds synthesized in the form of 1D nanostructures should be promising highly functionalized nanomaterials owing to both quantum confinement and shape-specific effects [8]. If the size of a rare-earth compound particle is smaller than the Bohr radius of the exciton, quantum confinement occurs. As a result, the bandgap of the particle increases and discrete energy levels are created at the edges of the valence and conduction bands [9]. Rare-earth hydroxides are of great importance because they can be directly converted to oxides through dehydration. Hydroxyl groups can also act as active sites for surface grafting through condensation of biological or organic reagents [10]. Because of these advantages, much attention has been paid to the synthesis and optical property studies of one-dimensional rare-earth hydroxide nanostructures [11–14]. Meanwhile, rare-earth oxides have also attracted the attention of many researchers as they have smaller phonon energies, which lead to reduced non-radiative losses and hence increased luminescence efficiency [15–18]. It has been reported that the nanoscale differences in electrical and optical characteristics of very small particles are caused by their high surface to volume ratio, which improves

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the surface and interfacial effects and increases the bandgap by reducing the number of allowable quantum states in the small particles [19].

Gadolinium-containing complexes are an extensively studied group of lanthanide metals because of their potential use in data storage, optoelectronic, sensor, and display applications [20–24]. To the best of our knowledge, very few phases of gadolinium oxide are produced when polyvinylpyrrolidone (PVP) or hexamethylenetetramine (HMT) is used as the surfactant for synthesis, and the products of hydrothermal synthesis are not uniform or well dispersed [17]. Here, we report a simple and effective method for growing gadolinium oxide nanorods from simple chemical reagents—gadolinium chloride hexahydrate ($\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$) and ammonia monohydrate ($\text{NH}_3 \cdot \text{H}_2\text{O}$). The synthesis of these nanomaterials was based on the preparation of gadolinium hydroxide as the precursor and subsequent sintering at designated temperatures for dehydration [25]. The hydrothermal method was used to prepare the uniform nanoprecursor because of its simplicity, low cost, and high efficiency: the cations (Gd^{3+}) were assembled with the template of the surfactant micelle in an aqueous solution. In addition to providing favorable sites for the growth of the precursor, the surfactant also affected the formation process, including nucleation, growth, and coagulation, and flocculation [26]. The surfactant thus plays an important role in the preparation of $\text{Gd}(\text{OH})_3$ and Gd_2O_3 nanorods, and the sintering temperature should not be too high in case of breakups.

2. Materials and methods

2.1. Synthesis of gadolinium hydroxide and gadolinium oxide nanorods

All chemical reagents used in the experiments were purchased from commercial sources as guaranteed-grade reagents and used without further purification. The purity of hexamethylenetetramine (HMT) and polyvinylpyrrolidone (PVP) were 99.9% and the purities of the precursors were not less than 99.90% respectively.

The synthesis of gadolinium hydroxide ($\text{Gd}(\text{OH})_3$) nanorods was based on the surfactant (HMT or PVP) and simple chemicals (gadolinium chloride hexahydrate, $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$, and aqueous ammonium hydroxide, $\text{NH}_3 \cdot \text{H}_2\text{O}$) as the reactants in a hydrothermal process. In brief, 5 mL of 0.1 mol/L $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$ was added to distilled water or 10 mL of a 0.1 mol/L HMT solution (or 0.1 mol/L PVP solution) under continuous stirring at room temperature. The mixture was stirred for 10 min, and 20 mL of a 0.1 mol/L $\text{NH}_3 \cdot \text{H}_2\text{O}$ solution was then added dropwise. The mixture was mixed uniformly for 40 min and then reacted in a reaction kettle at 120 °C for 10 h. The suspension was then cooled to room temperature, and the reaction products were recovered by centrifugation at 10,000 rpm for 20 min.

The collected materials were washed six times with ethyl alcohol and distilled water to remove the surfactant and other impurities, after which they were dried in an oven at 60 °C. The as-formed products were in the columnar $\text{Gd}(\text{OH})_3$ phase. After heat treatment at 350 and 600 °C for two successive 3-h periods according to the method reported by Dhananjaya et al., the materials were transformed to the gadolinium oxide (Gd_2O_3) phase. The product produced after calcination at 350 °C for 3 h could not be fitted with the data within the GdOOH system in JCPDS cards, indicating that a mixed phase was obtained [25].

2.2. Characterization of nanorods

In order to determine the crystal structures of the products, X-ray diffraction (XRD) patterns were obtained with a diffractometer

(Ultima-3, Rigaku, Tokyo, Japan) equipped with a rotating anode and a Cu K α radiation source (1.540562) at a scanning rate of 5° min⁻¹ ($2\theta = 10$ –85°). The X-ray tube voltage and current were set at 40 kV and 40 mA, respectively. Fourier-transform infrared spectroscopy (FTIR) spectra were recorded using an FTIR spectrometer (Vector-22, Bruker Daltonics, Billerica, MA, USA). Before the measurements, the background spectrum was obtained and it was later subtracted from the FTIR spectra of the samples. The as-synthesized samples were prepared for transmission electron microscopy (TEM) by loading several drops of an ethyl alcohol dispersion of the particles on amorphous-carbon-coated copper grids and drying the loaded grids at room temperature. Their size distribution and morphology were examined using a transmission electron microscope (JEM-2100, JEOL Ltd., Tokyo, Japan) equipped with an energy-dispersive analyzer. Ultraviolet–visible (UV–vis) measurements were made with a UV–vis spectrophotometer (Cary UV-2250, Agilent Technologies, Santa Clara, CA, USA). Room-temperature photoluminescence (RTPL) experiments were carried out on a fluorescence spectrophotometer (Varian Cary Eclipse, Agilent Technologies, Santa Clara, CA, USA) using a xenon lamp as the excitation source at room temperature. All products synthesized after hydrothermal reaction or annealing were analyzed, and all experiments were performed at room temperature.

3. Results and discussion

The structure and morphological characteristics of the nanoscale powder were studied by XRD and TEM analysis. The X-ray diffraction patterns of the samples prepared by hydrothermal synthesis, shown in Fig. 1a, could be readily indexed to a pure hexagonal phase. All of the diffraction peaks can be perfectly indexed to $\text{Gd}(\text{OH})_3$, and they agree well with the values in the corresponding JCPDS data (card NO. 83-2037). The materials showed diffraction from well-developed $\text{Gd}(\text{OH})_3$, without any indication of crystalline byproducts such as GdCl_3 or surfactants; no impurity peaks were detected, indicating the high purity of the products. The gadolinium hydroxides had the same hexagonal structure as the lighter gadolinium chloride (space group: group: C_{6h}^2 , $P6_3/m$), with the OH dipoles replacing the Cl^- ions and the dipole axis lying in the mirror planes perpendicular to the crystal hexagonal axis [27]. According to the characteristics of the crystal structure of $\text{Gd}(\text{OH})_3$, the atomic interactions along the *b*-direction are much weaker than those along the *a*- and *c*-axis, with those in the *a*-direction are equal to those in the *c*-direction; this means that the growth directions of the $\text{Gd}(\text{OH})_3$ nanostructures were largely confined to the $[1\ 0\ 0]$ and $[0\ 0\ 1]$ directions [27]. Fig. 2 displays typical TEM images of the as-synthesized hexagonal $\text{Gd}(\text{OH})_3$. It can be seen from Fig. 2a that the $\text{Gd}(\text{OH})_3$ particles synthesized without surfactants fused together to form agglomerates. However, when HMT or PVP was added to the hydrothermal progress, less agglomeration occurred and nanorods with more regular shapes and columnar ends were observed. The as-obtained $\text{Gd}(\text{OH})_3$ particles using surfactants (Fig. 2b and c) had shapes similar to those of nanorods with diameters of approximately 100–200 nm and lengths of 200–500 nm; the aspect ratio of the obtained nanorods was about 2.5. The growth process of $\text{Gd}(\text{OH})_3$ in the presence of HMT or PVP was different from that without surfactant; the surface tension of the solution was reduced owing to the existence of the surfactant, which lowered the energy needed for the formation of a new phase. In this crystallization process, surfactant molecules that were adsorbed on the crystal nuclei not only served as growth directors, but also as protectors for preventing product aggregation. When HMT or PVP was added, the crystals began to exhibit oriented growth and the morphology of the rods became regular, which resulted in increased XRD peak intensities and the lengths of

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