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Multi modality of hollow tube $Gd_2O_3:Eu^{3+}$ nanoparticles by using nonpolar solvent

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ABSTRACT

$Gd_2O_3:Eu^{3+}$ is useful material in physics, chemical and biomedicine which can be applied to the magnetic resonance imaging (MRI) brightness, X-ray computed tomography (CT) as contrast agent and luminescence phenomenon as phosphor. In this paper, $Gd_2O_3:Eu^{3+}$ was synthesized by one-step low cost solvothermal reaction with different ratio of solvents (De-ionized water (DI)/toluene (TL)). The alteration of solvent ratios affects the morphology (rod to hollow tube shape) and size of $Gd_2O_3:Eu^{3+}$ which induce the property variation such as luminescence intensity, MR imaging and CT imaging brightness. The luminescence intensity of $Gd_2O_3:Eu^{3+}$ nanoparticles with DI 40/TL 0 is much higher than the 1.48, 1.68, 1.73 and 1.75 times by others (DI 0/TL 40, DI 10/TL 30, DI 20/TL 20 and DI 30/TL 10), MR images of $Gd_2O_3:Eu^{3+}$ with DI 0/TL 40 were shown to be 2.5 times brighter than that of the commercial contrast agent (Dotarem) and CT images of $Gd_2O_3:Eu^{3+}$ with DI 0/TL 40 was 1.68 times brighter than Dotarem. $Gd_2O_3:Eu^{3+}$ prepared with different solvent ratios can be selectively applied for potential applications as MRI, CT and FI multimodal imaging agent.

1. Introduction

The fabrication of inorganic nanoparticles with different morphology and size has received considerable attention because of the useful optical and magnetic properties. Specially, one-dimensional (1D) nanostructures such as rods, fibers and tubes are attracting attention due to their several applications for magnetic resonance imaging (MRI), X-ray computed tomography (CT) and optoelectronic devices [1–4].

These applications currently have been used single-modal technique. However, diagnostic and prognosis information obtained through the single-modal technique generally cannot satisfy the high requirement for efficiency and accuracy because of its limitations. For example, MRI and CT has the high resolution and anatomic information but low sensitivity. Fluorescence imaging (FI) has the high sensitivity but low spatial resolution to obtain anatomical and physiological information [5–11]. Therefore, the dual-modal technique combining both (MRI or CT) and FI, which have the high spatial resolution and sensitivity. It can be very useful biomedical applications to obtain the overall information.

The currently used fluorescent materials include organic dyes, quantum dots and lanthanide ions (Ln^{3+}) doped luminescence materials [12–14]. Ln^{3+} materials doped rare earth ion are attractive photoluminescence (PL) properties because of their good host role such as chemical durability, thermal stability, low phonon energy which is red emitting phosphors [15–17]. Gadolinium materials are one of the Ln^{3+} ions. Therefore, it is useful for fluorescence imaging and labels. The gadolinium materials also have been extensively researched for the biomedical imaging in MRI, drug delivery and CT [18–22]. The gadolinium materials are seven unpaired 4f electrons, paramagnetic T_1 agents and high spin magnetic moment ($s = 7/2$) (the largest value among the elements in the periodic table) and higher X-ray attenuation coefficient than iodine, which is useful for MRI and CT [23–25].

In this research, we report on the $Gd_2O_3:Eu^{3+}$ nanomaterials by using the solvothermal methods. The main aim of this research is to comprehend the effect of different ratios (De-ionized water (DI)/toluene (TL): 40/0, 30/10, 20/20, 10/30 and 0/40). To understand the effect by the control of the solvent ratios, the composition, particle shape, size, fluorescence, MR and CT properties of $Gd_2O_3:Eu^{3+}$ nanomaterials are investigated. $Gd_2O_3:Eu^{3+}$ nanomaterials at optimized DI/TL ratio are promising the dual-modal contrast agents.

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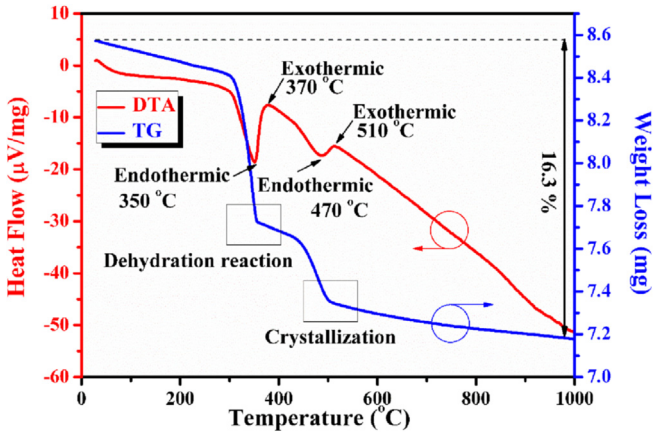

Fig. 1. TG-DTA curves of the $Gd(OH)_3:Eu^{3+}$ precursor in air.

2. Experimental section

2.1. Synthesis

The Eu^{3+} ions doped Gd_2O_3 nanoparticles were fabricated by the conventional solvothermal reaction method. Firstly, a stoichiometric amounts of high-purity gadolinium nitrate hexahydrate ($Gd(NO_3)_3 \cdot 6H_2O$) and 1 mol % europium nitrate hydrate ($Eu(NO_3)_3 \cdot xH_2O$) were dissolved in 40 mL solvents with different ratio of De-ionized water (DI) and toluene (TL) [C_7H_8]. In order to increase the ionization rate, ammonium hydroxide (NH_4OH) was added under vigorous stirring using a magnetic stirrer until the formation of a homogeneous solution. The solution was transferred into a stainless steel autoclave with a Teflon liner (80 mL capacity and 50% filling) and then heated to 180 °C at the rate of 1 °C/min, and maintained for 12 h with magnetic stirring at 180 rpm to make stable networks between the reactants. After gradually cooling down to room temperature the solution, the precipitates were separated through the centrifugation with 4000 rpm and washed several times with ethanol and DI. The obtained precipitates were dried at 80 °C in air for a day. The experiment was duplicated at different ratio of DI and TL interface (DI/TL: 40/0, 30/10, 20/20, 10/30, 0/40). Finally, $Gd_2O_3:Eu^{3+}$ nanoparticles were obtained by further calcination at 900 °C for 4 h.

2.2. Characterization

The X-ray diffraction (XRD) data were collected in the range of 15–70° for scanning rate of 2° per min by using Philips, X'Pert-MPD system X-ray diffractometer with 3 kW Cu-Kα radiation (λ = 1.54056 Å) X-ray tube. The morphology and size of the powders were examined by field emission scanning electron microscope (FE-SEM, JSM-6700, JEOL). Thermogravimetric (TG) and differential thermal analyses (DTA) were recorded using a thermal analysis system with temperature from 30 to 1000 °C at a heating rate of 10 °C/min. The room temperature photoluminescence excitation (PLE) and photoluminescence (PL) spectra of the $Gd_2O_3:Eu^{3+}$ were recorded on a PTI (Photon Technology International) fluorimeter using a Xe-arc lamp with a power of 60 W. The MR images was obtained by using a 3.0 T clinical MRI scanner (Philips, Achieva, Netherlands). A mount of dried $Gd_2O_3:Eu^{3+}$ powders prepared with different DI and TL ratios (40/0, 30/10, 20/20, 10/30 and 0/40) and various Gd^{3+} concentrations (0, 0.05, 0.1, 0.15 and 0.2 mM) were dispersed in DI through the sonication. And then, prepared materials were placed in a plastic vial. The plastic

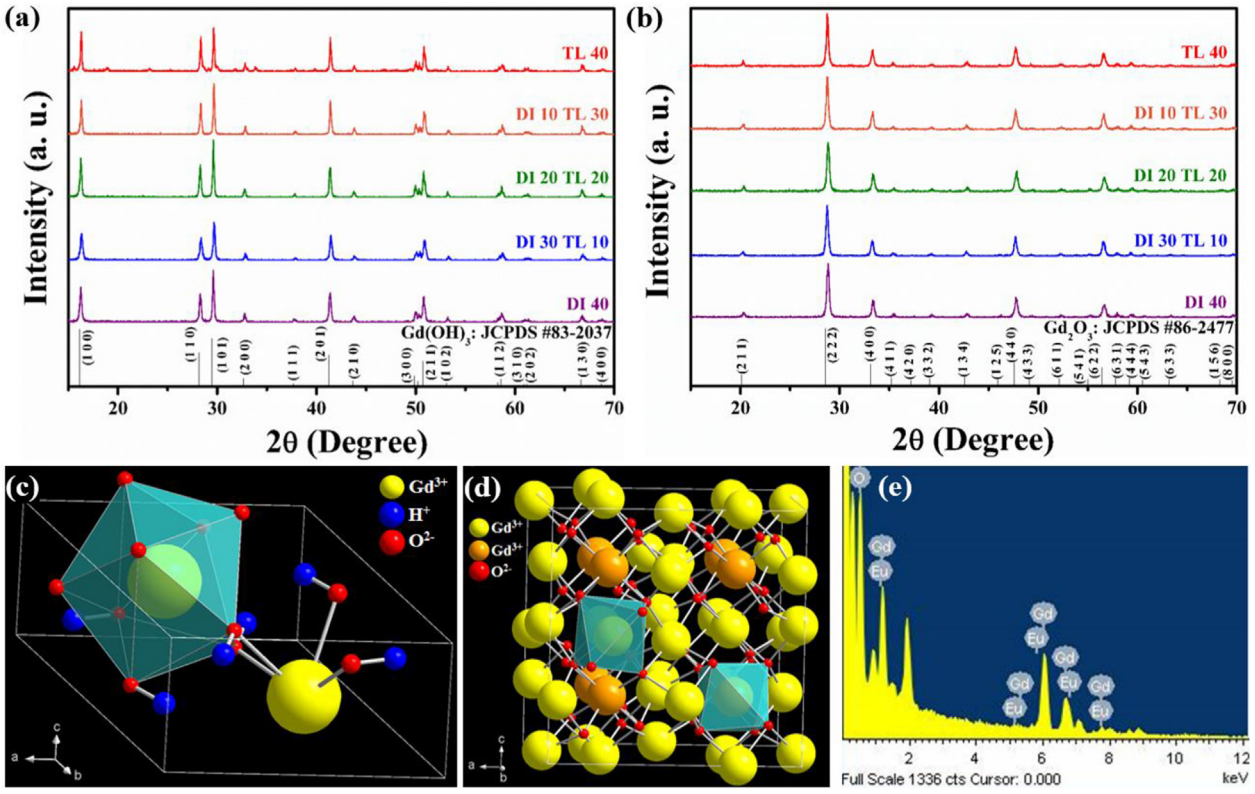

Fig. 2. XRD patterns of (a) $Gd(OH)_3:Eu^{3+}$ (b) $Gd_2O_3:Eu^{3+}$ samples with different DI/TL ratios (40/0, 30/10, 20/20, 10/30 and 0/40), (c) scheme of the hexagonal phase $Gd(OH)_3$, (d) cubic phase Gd_2O_3 structure and (e) EDS spectra of $Gd_2O_3:Eu^{3+}$ (DI 40/TL 0).