

Study on the structure and luminescent properties of the coordinated Eu_2O_3 ethanol colloids

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ABSTRACT

This work reports the synthesis of the coordinated Eu_2O_3 ethanol colloids by focused pulsed laser ablation at the interface of solid Eu_2O_3 target and a flowing liquid containing thenoyltrifluoroacetone (TTA) and 1,10-phenanthroline (Phen). The high resolution transmission electron microscopy, X-ray diffraction and infrared spectroscopy results show the coordinated Eu_2O_3 nanoparticles have the structure of an inner core of crystal Eu_2O_3 and an outer layer of ligands, TTA and Phen, coordinated to the surface europium ions of the Eu_2O_3 nanoparticles. Thermal stability analysis shows the mass of ligands in coordinated Eu_2O_3 clusters is 14.36%. The coordinated Eu_2O_3 ethanol colloids can irradiate intense red light under ultraviolet radiation, and their fluorescence spectrum presents typical characteristic emission peaks of Eu^{3+} ions.

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1. Introduction

Rare earth elements have various photo-, electro-, and magnetic characteristic for its unique electronic structure, and become more and more important in research and application of functional materials [1,2]. Materials containing lanthanide ions have been used as phosphors, laser materials [3] and heterogeneous chemical catalysis [4].

Nanoparticles have attracted much attention because of their excellent optical-, magnetic-, catalytic properties, etc. [5–7]. Nanocrystalline Tb_2O_3 [1] and Eu_2O_3 [2] prepared by colloidal methods can emit green and red light under ultraviolet irradiation due to defect free, respectively. Patra et al. [8] used nanoparticles of oxides of europium and terbium to coat the submicron size spheres of silica and alumina, and obtained phosphors with high luminescence intensity. The luminescence of Eu^{3+} is particularly interesting because Eu_2O_3 is one of the most important oxide phosphors and the major emission band is centered near 612 nm (red), which is one of the tricolor (red, blue, and green) from which a wide spectrum of colors, including white, can be generated by appropriate mixing. For this reason, Eu^{3+} has been thoroughly investigated as a luminescent activator in many host lattices, such as MCM-41 [9], barium strontium titanate (Ba, Sr) TiO_3 ceramics [10], PbWO_4 crystals [11], and

$\gamma\text{-Al}_2\text{O}_3$ [12]. And Eu^{3+} doped in Y_2O_3 is a commercially available phosphor with extremely high quantum efficiency [9].

Many methods including colloidal precipitation [1,2], sol-gel electrophoresis deposition [13], solid-state reaction [14], pulsed laser ablation [15] are used to prepare materials containing Eu_2O_3 nanoparticles. Especially, pulsed laser ablation has attracted much attention recently because of its high-energy output, the ability to adjust the power of the laser, and the purity of the final product [16]. Recently, more and more researchers use pulsed laser ablation at vacuum or inert atmosphere [17], static liquid [18], flowing liquid [15,19] to prepare nanoparticles colloids. As compared to laser ablation at static liquid, laser ablation at flowing liquid can successively synthesis the nanoproducts, however, the nanoparticles are highly active because many dangling bonding on its surface and easily react to solvent or aggregate together.

In this paper, the ligands are used to coordinate to the surface metal ions of the naked Eu_2O_3 nanoparticles that produced by the pulsed laser ablation at flowing liquid. The structure, thermal stability and luminescence property of the coordinated Eu_2O_3 nanoethanol colloids are discussed through Fourier transform infrared spectroscopy (FT-IR), thermogravimetry and differential scanning calorimetry (TG/DSC), high resolution transmission electron microscopy (HRTEM) and fluorescence spectrum.

2. Experimental methods and materials

The ethanol solutions containing TTA and Phen were used as flowing liquid, which submerged the Eu_2O_3 target (>99.99%). The concentrations of TTA and Phen in flowing liquid were 4.2×10^{-4} M and 1.4×10^{-4} M, respectively. The Eu_2O_3 target was irradiated by the focused output of 532 nm light from a DCR-3G Nd:YAG laser

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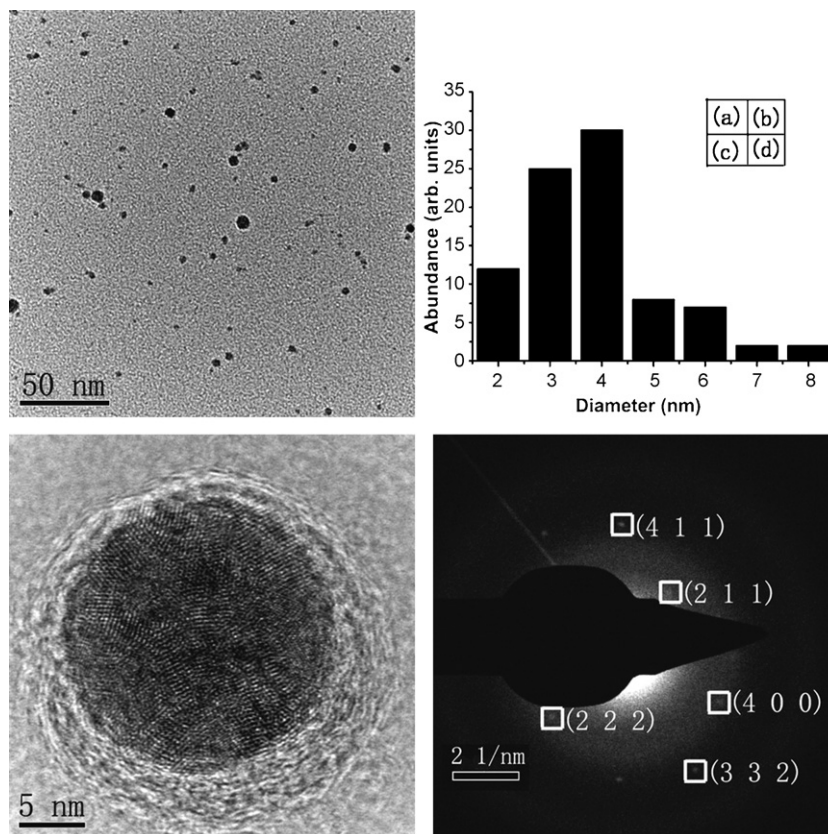


Fig. 1. HRTEM image (a) and size distribution (b) of the coordinated Eu_2O_3 clusters, single nanoparticles images (c) and (d) is the select-area electron diffraction (SEAD) pattern of (a). The scales bars in (a), (c), and (d) are 50 nm, 5 nm and 2 nm^{-1} , respectively.

(Spectra Physics Inc.), operating at 10 Hz at the fluence of $300 \text{ mJ pulse}^{-1}$ with the width of 8 ns. The spot size of the laser beam on the surface of target was less than 1 mm, and the flowing liquid was flowing over the target with the speed of approximately 0.05 mL s^{-1} and the submerging depth of 1–2 mm. The whole preparation process was done in high pure nitrogen atmosphere at room temperature.

The coordinated Eu_2O_3 clusters can be obtained from the coordinated Eu_2O_3 ethanol colloids by centrifugal settling and removing supernatant liquid. The obtained deposit was washed by ethanol (repeated eight times), finally a powder was obtained and used for characterization of FT-IR, XRD and TG/DSC after being dried in vacuum. Approximately 0.88 mg of samples was used for TG/DSC characterization.

The HRTEM photographs and SEAD were obtained on the FEI F20 transmission electron microscope (Philips Company). Electron micrographs were recorded using eight drops of colloids onto a copper mesh coated with an amorphous carbon film. The particle size distribution was determined by the Getdata software (Version 2.21) and Origin (Version 7.0, Originlab Corporation). A Philips X'pert-MPD powder X-ray diffractometer (Philips Holland) using $\text{Cu K}\alpha 1$ radiation was used to study the crystal structure of sample powder with Si as an external standard and the scan velocity of $1.2^\circ \text{ min}^{-1}$. Data analysis used MDI JADE 4 software package: Lattice parameter refinement was performed with search/match process and Rietveld refinement with the pattern fitting structure refinement program, data were collected in a constant scan mode over the range $5^\circ < 2\theta < 90^\circ$. FT-IR was performed on an AVATA 360 FTIR spectrometer. The photo of the coordinated Eu_2O_3 ethanol colloids under ultraviolet irradiation was recorded with a FinePix A500 digital camera (Fujifilm). The deposits were analyzed by thermogravimetry (TG) and differential scanning calorimetry (DSC) using a Netzsch STA 449 C simultaneous TG/DSC instrument, respectively. TG measurements were performed at a $10^\circ \text{ C min}^{-1}$ scanning rate, employing a 20 mL min^{-1} flow of argon as a purge gas and reference cells. The fluorescence spectra of obtained Eu_2O_3 ethanol colloids were measured by an Edinburgh FL/FS 920 fluorophotometer at room temperature with 450 W xenon lamp as excited source (input slits width = 0.5 nm, output slits width = 1.5 nm).

3. Results and discussion

3.1. HRTEM analysis

Fig. 1 (a) shows the HRTEM micrograph of the coordinated Eu_2O_3 clusters after being prepared for 1 h. Fig. 1(b) shows the particle

size distribution as determined by surveying the micrograph. The average diameter is approximately 4 nm (3.8 nm calculated average) with an 87% distribution within $\pm 2 \text{ nm}$. Because the limitation of the used apparatus, stable HRTEM images of smaller particles cannot be obtained. In order to study the microstructure of the nanoparticles, a bigger nanoparticle is selected; in addition, the bigger particles and the smaller particles have the same microstructure. Fig. 1(c) shows the microstructure of the bigger particle. From Fig. 1(c), it is found that the particle consists of an inner core with obvious crystal lines and an outer layer of amorphous materials, and the crystal lines with different directions indicate the inner core of the particles was consisted by many smaller crystals, and the size of crystal is very small. The diameter of the particle is about 30 nm and the inner core is about 19 nm. The inner core is Eu_2O_3 crystal and the outer layer is composed of organic ligands of TAA and Phen. Fig. 1(d) shows the SEAD pattern of the particle in Fig. 1(c). It is found that the SEAD pattern of the particle has several diffractive points and the numbers indicates the particular diffracting planes. The interplanar spacing and diffracting planes together with that of JCPDS card (86-2476) are listed in Table 1. From Table 1, it is found

Table 1

The interplanar spacing and diffracting planes together with that of JCPDS card (86-2476).

Diffracting planes	Interplanar spacing (nm)	
	Eu_2O_3 (JCPDS card 86-2476)	The coordinated Eu_2O_3 particle
(2 1 1)	0.443317	0.4336
(2 2 2)	0.313472	0.3234
(4 0 0)	0.271475	0.2888
(4 1 1)	0.255949	0.2543
(3 3 2)	0.231515	0.2328

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