



Investigation of the photoluminescence properties of composite optical resins containing high lanthanide content

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ABSTRACT

Novel composite optical resins with high lanthanide content have been synthesized through a free radical copolymerization of methacrylic acid (MA), styrene (St) and $\text{Eu}(\text{DBM})_3 \cdot \text{H}_2\text{O}$ nanocrystals. We characterized the structure, the thermal properties, dimensions and photoluminescence properties of $\text{Eu}(\text{DBM})_3 \cdot \text{H}_2\text{O}$ nanocrystals. Our results indicated that the diameters of the $\text{Eu}(\text{DBM})_3 \cdot \text{H}_2\text{O}$ nanocrystals were within the range of 30 to 300 nm. These materials exhibited characteristic europium ion luminescence. The europium-bearing nanocrystals were then incorporated into the copolymer systems of MA/St and luminescence functional optical resins with high lanthanide content (50 wt%) were obtained. The combination of these particles and optical resins is facile because the diameter of $\text{Eu}(\text{DBM})_3 \cdot \text{H}_2\text{O}$ is decreased. These copolymer-based optical resins not only possess good transparency and mechanical performance, but also exhibit an intense narrow band emission of lanthanide complexes and longer fluorescence lifetimes under UV excitation at room temperature.

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1. Introduction

New technologies for displaying applications require the development of advanced materials for the production of light [1]. A growing degree of research has been devoted to the study of the potential applications of luminescent nanoparticles. A significant amount of work has already been performed on Type II–VI semiconductors, whose synthesis through colloidal techniques leads to very good control of the particle diameters within the 2–10 nm range, and hence their luminescent color [2–5].

In recent years there has been intense research on the synthesis of photoactive lanthanide complexes [6]. The possibility of incorporating ligands into such species that function as light-harvesting units has been investigated. These units can act as antennas for light harvesting and can also transfer this energy to the lanthanide center, thus creating extensive photoluminescence. Coordination compounds of this type may be regarded as photoactive units for the fabrication of novel optical materials, namely as luminescent centers in host matrices. However, current research on lanthanide nanoparticles and nanowires has primarily concentrated on lanthanide oxides [7], lanthanide carbonate [8], lanthanide hydroxide [9] or lanthanide-doped nanoparticles [10]. Consequently, the research of composite materials

containing lanthanide nanoparticles and organic polymers has received little attention [11].

Composite materials of lanthanide metals and polymers are functional materials that combine the excellent luminescence characteristics of lanthanide ions with the excellent mechanical properties of plastics [12–15] such as their light weight, good transparency, impact resistance, low temperature processability and ability to accommodate dyes. These properties provide these systems with great potential for developing materials for optical, electrical, magnetic materials, as well as materials for lasers, catalysis and analysis. Therefore, the prospects of their development and applications are very promising. Currently, there are two methods to prepare the composite materials of lanthanide metals and polymers. These include (1) the Doping-method [16] and (2) the Bonding method [17]. However, these two methods have some drawbacks. Because of the presence of some water of hydration in the lanthanide complexes, they have poor compatibility with polymer matrices, which thus limits their doping content. Furthermore, the concentration induced quenching of lanthanide complex, leads to the difficulties of obtaining high lanthanide content and uniform dispersion within polymer matrices.

In this paper, we prepared nanocrystals of $\text{Eu}(\text{DBM})_3 \cdot \text{H}_2\text{O}$ [18] by chemical precipitation. Using elemental analysis, infrared spectroscopy, TGA-DSC, SEM and TEM analysis, we confirmed that the preparation of the target nanocrystals, and measured their thermal properties and diameters. In addition, fluorescence

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excitation and emission spectra, as well as UV–visible absorption spectra, were recorded. Subsequently, the nanocrystals were incorporated into a copolymer system of MA/St, yielding a luminescence functional optical resins with high lanthanide content (50 wt%). Our results indicated that the sizes of the $\text{Eu}(\text{DBM})_3 \cdot \text{H}_2\text{O}$ nanocrystals were within a range from 30 to 300 nm. Meanwhile, they exhibited characteristic europium ion luminescence. The optical resins could provide relatively stable environments for the $\text{Eu}(\text{DBM})_3 \cdot \text{H}_2\text{O}$ nanocrystals, while the $\text{Eu}(\text{DBM})_3 \cdot \text{H}_2\text{O}$ nanocrystals in return offered novel luminescent properties to the optical resins.

2. Experimental

2.1. Materials

Europium chloride ($\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$) was obtained by dissolving the lanthanide oxide Eu_2O_3 (99.99%, Yuelong chemical plant, Shanghai) in hydrochloric acid (HCl). Dibenzoyl-methane (DBM) (Aldrich, China), ammonium hydroxide ($\text{NH}_3 \cdot \text{H}_2\text{O}$), sodium hydroxide (NaOH), ethanol ($\text{CH}_3\text{CH}_2\text{OH}$), ammonium chloride (NH_4Cl), tris-(hydroxymethyl) aminomethane ($\text{NH}_2\text{C}(\text{CH}_2\text{OH})_3$) (TRIS) and silver nitrate (AgNO_3) were analytical grade (Shanghai Reagents Co. Ltd.). Styrene (St), methacrylic acid (MA), 2,2-azoisobutyronitrile (AIBN) and octadecanoic acid (OA) (analytical grade, Shanghai Polydex Industry Co., Ltd) were purified before use.

2.2. Syntheses of $\text{Eu}(\text{DBM})_3 \cdot \text{H}_2\text{O}$ nanocrystals and $\text{Eu}(\text{DBM})_3 \cdot 2\text{H}_2\text{O}$

The crude materials for the syntheses of the $\text{Eu}(\text{DBM})_3 \cdot \text{H}_2\text{O}$ nanocrystals included an aqueous solution of $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$, and an ethanol solution of DBM. The $\text{Eu}(\text{DBM})_3 \cdot \text{H}_2\text{O}$ [11,19,20] nanocrystals particles were prepared according to the methods described elsewhere [18]. In order to compare these nanocrystals, the $\text{Eu}(\text{DBM})_3 \cdot 2\text{H}_2\text{O}$ complex was prepared according to literature methods [20,21]. Briefly, the experimental procedure was as follows.

2.3. $\text{Eu}(\text{DBM})_3 \cdot \text{H}_2\text{O}$ nanocrystals

The synthesis of a series of $\text{Eu}(\text{DBM})_3 \cdot \text{H}_2\text{O}$ nanocrystals with different diameters is described below. An aqueous solution of europium chloride (15 mL, 0.01 M) was slowly added dropwise into an ethanol solution of DBM (50 mL, 0.01 M) with electromagnetic stirring. After mixing the two solutions, we added one of the four basic buffer solutions dropwise to adjust the pH of the solution to between 8 and 9, and continued stirring for 2.5 h. This induced the precipitation of different sizes of thin yellow $\text{Eu}(\text{DBM})_3 \cdot \text{H}_2\text{O}$ nanocrystals. The basic buffer solutions referred to above included four types of solutions. These included: (1) different solutions of ammonium hydroxide and water (v/v from 1:1 to 1:16), (2) a solution of ammonium hydroxide ($\text{pH}=13.75$, with a density of 0.9 kg L^{-1} , Assay (NH_3) is 28 wt% to 30 wt%), (3) $\text{pH}=9.2$ buffer solutions (5.4 g NH_4Cl solid, which was dissolved in 5 mL of water and added dropwise to ammonium hydroxide, and then diluted to 100 mL) and (4) $\text{pH}=8.2$ buffer solutions (2.5 g of TRIS solid was dissolved in 5 mL of water, and HCl (12 M) was then added dropwise to this solution until the desired pH was reached. This solution was then diluted to 100 mL). After the crude product was precipitated by the buffer addition, it was subsequently recrystallized from ethanol/water, and then evaporated under vacuum at 40°C for 12 h. Elemental analysis: calculated (found) for $\text{C}_{45}\text{H}_{38}\text{EuO}_7$: C 64.22% (64.13), H 4.56% (4.513).

2.4. $\text{Eu}(\text{DBM})_3 \cdot 2\text{H}_2\text{O}$

DBM (0.672 g, 3 mmol) was dissolved into 20 mL of hot ethanol and stirred. Subsequently, 3 mmol of NaOH was added to the resulting solution with stirring to adjust the pH to a value between 8 and 9. $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ (0.3665 g, 1 mmol) was dissolved in 2 mL of ethanol, and was then added dropwise to the mixture, which produced a thin yellow precipitate of $\text{Eu}(\text{DBM})_3 \cdot 2\text{H}_2\text{O}$. The crude product was recrystallized from ethanol/water, and then placed into a vacuum for evaporation at 40°C for 12 h. Elemental analysis: calculated (found) for $\text{C}_{45}\text{H}_{40}\text{EuO}_8$: C 62.79% (62.18), H 4.65% (4.62).

2.5. Syntheses of optical resins containing $\text{Eu}(\text{DBM})_3 \cdot \text{H}_2\text{O}$ or $\text{Eu}(\text{DBM})_3 \cdot 2\text{H}_2\text{O}$

After a certain amount of either of the $\text{Eu}(\text{DBM})_3 \cdot \text{H}_2\text{O}$ nanocrystals (or $\text{Eu}(\text{DBM})_3 \cdot 2\text{H}_2\text{O}$ particles) was dissolved into a solution of MA and St ($v/v=3:7$), 0.5 wt% AIBN was added as an initiator, and 0.3 wt% OA was added as a dispersant. The resulting mixture was then pre-polymerized at 60°C for 20 min. The contents were then cast into a mold consisting of two glass plates and a silicone rubber gasket. This system was sealed and maintained at a temperature of 57°C for 24 h. Subsequently, the reaction mixture was gradually heated to 95°C at a rate of $5^\circ\text{C}/15 \text{ min}$. This temperature (95°C) was then maintained for 2 h to complete the copolymerization. The resulting sheets were transparent, with a thickness of 3 mm.

2.6. Characterization

UV–visible spectra were obtained using a Shimadzu 3100 UV–vis–near-IR recording spectrophotometer. Visible light transmittance was recorded at a wavelength of 550 nm. FT-IR spectra were measured on a Nicolet AVATAR360 FT-IR Spectrometer in the $4000\text{--}400 \text{ cm}^{-1}$ regions. The far infrared spectra were recorded on a Magna 560 FT-IR Spectrometer in the $600\text{--}50 \text{ cm}^{-1}$ regions.

Elemental analysis (EA) was performed using a Perkin-Elmer 2400 series II analyzer. Thermogravimetric analysis (TGA) of the nanocrystals and the complex particles was performed using a Perkin-Elmer TGA7 at a heating rate of $10^\circ\text{C}/\text{min}$ under nitrogen atmosphere from 50 to 750°C . Differential scanning calorimetry (DSC) was performed on a NETZSCHDSC204 in nitrogen atmosphere at a heating rate of $10^\circ\text{C}/\text{min}$ from 0 to 350°C . The size and morphology of the nanocrystals and the complexes particles were determined at 200 kV by a Hitachi H-8100 transmission electronics microscope (TEM, Hitachi, Japan). The samples for TEM analysis were prepared from $\text{Eu}(\text{DBM})_3 \cdot \text{H}_2\text{O}$ nanocrystals as well as $\text{Eu}(\text{DBM})_3 \cdot 2\text{H}_2\text{O}$, which were dissolved into ethanol. A drop of the solution was placed onto a copper grid, and an ultrathin section of the optical resins with a thickness of 60–100 nm containing $\text{Eu}(\text{DBM})_3 \cdot \text{H}_2\text{O}$ nanocrystals particles was placed onto the copper grid. Scanning electron microscopy (SEM) images were recorded at a resolution better than 5 nm using a 5 keV electron beam.

Fluorescence excitation and emission spectra were measured using a RF-5301PC fluorescence spectrophotometer with a 450 W xenon lamp as the excitation source. Fluorescence lifetime measurements were performed at room temperature, using a tunable pulsed laser (OPO $\lambda_{\text{ex}}=300 \text{ nm}$) as the excitation source and a WPP500-2A monochromator to monitor the emission wavelength. The emitted light was acquired by a HR 3896 photomultiplier tube and the photocurrent was analyzed by a Tektronix Digital Oscilloscope (TDS) 620B operating at 500 Hz. The powder samples of the lanthanide complexes were directly pressed to form transparent powder plates, while the resin samples were

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