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The synthesis and luminescent properties of novel water-soluble $\text{CaF}_2:\text{Tb}^{3+}$ nanoparticles

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ABSTRACT

Novel water-soluble $\text{CaF}_2:\text{Tb}^{3+}$ nanoparticles were synthesized using benzoimidazole-5-carboxylic acid (Ligand) as surfactant. The particle size of the nanoparticles is below 10 nm. The investigation of fluorescence properties showed that there exists energy transfer from the surface coating of nanoparticles to Tb^{3+} leading to the sensitized fluorescence emission of Tb^{3+} . The luminescence lifetimes of Tb^{3+} were 937.56 μs (37.41%) and 2.78 ms (62.59%). It is more important that Cu^{2+} and Fe^{3+} can give rise to emission quenching to the Tb^{3+} of nanoparticles, especially Cu^{2+} . In the region of 2.5×10^{-5} – 5×10^{-4} M, the higher the concentration of Cu^{2+} or Fe^{3+} is, the stronger fluorescence quenching to the Tb^{3+} is. Additionally, the possible mechanisms of the luminescence quenching were also discussed.

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1. Introduction

Trivalent lanthanide ions (Ln^{3+}) doped nanomaterials have been widely used in fields of illumination, laser, display, optical communication, optoelectronic devices, solar cells, biology and medicine due to the unique luminescence properties such as superior photostability, large Stoke's shift and long luminescence lifetime [1–6]. Recent interest in Ln^{3+} doped nanomaterials has been to explore new methods of preparing Ln^{3+} doped nanoparticles and improve the dispersion of nanoparticles in solvents [7–9]. Calcium fluoride (CaF_2) is known to be an excellent host for Ln^{3+} due to its low phonon energy ($\sim 328 \text{ cm}^{-1}$), adequate thermal and environmental stability, and large solubility for all lanthanide ions without deleterious effects [10,11]. So many different methods such as co-precipitation [12], hydrothermal [13], reverse micelle [14], fluorolytic sol-gel process [15], miniemulsion [16], and combustion synthesis [17] were reported to synthesize Ln^{3+} doped CaF_2 nanoparticles. The coordination of a monolayer of (charged) ligands on the surface of nanoparticles can reduce the aggregation between nanoparticles and improve its dispersibility in solvents. In order to obtain water-soluble Ln^{3+} doped nanoparticles for detection and bio-application, most investigations have focused on Ln^{3+} doped nanoparticles coated with hydrophilic ligands such as chitosan (CS) [18], peptide [19], poly-(acrylic acid) (PAA) [20], poly(amino acid) [21] and so on.

Herein, we report the synthesis, structural and luminescent properties of novel water-soluble $\text{CaF}_2:\text{Tb}^{3+}$ nanoparticles capped with benzoimidazole-5-carboxylic acid (Ligand) using co-precipitation method. Ligand was used as the surfactant to ensure water-solubility of the nanoparticles. It is interesting that Cu^{2+} and Fe^{3+} can give rise to emission quenching to the Tb^{3+} of the as-prepared nanoparticles. Fe^{3+} and Cu^{2+} are essential trace elements for human health. Their excess or deficiency may cause several abnormalities in human health [22,23]. In this paper, the effect of Cu^{2+} and Fe^{3+} on the luminescence of $\text{CaF}_2:\text{Tb}^{3+}$ nanoparticles was also studied and the possible mechanism of Cu^{2+} or Fe^{3+} -induced luminescence quenching of the nanoparticles was discussed.

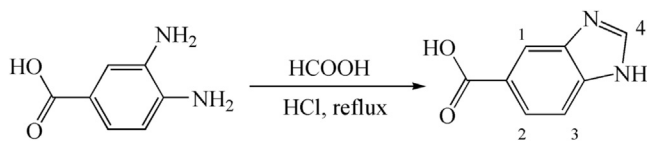
2. Experimental

2.1. The synthesis of benzoimidazole-5-carboxylic acid (ligand)

Ligand was synthesized according to the literature [24] and its reaction equation was shown in Scheme 1. 3,4-Diaminobenzoic acid (1.52 g, 10 mmol) and 2 mL formic acid were dissolved in 30 mL HCl (5 mol/L) in a round bottom flask. The mixture was refluxed under 110 °C for 5 h and then cooled to room temperature. The pH value was adjusted to about 5 with 30% NaOH solution. The mixture was then cooled in refrigerator and collected by filtration. The product was washed with water twice and dried in vacuum. $^1\text{H-NMR}$ (DMSO-d_6) δ =8.36 (1 H, s, H_1), 8.08 (1 H, d, J = 8.4 Hz, H_2), 7.91 (1 H, d, J = 8.4 Hz, H_3), 8.15 (1 H, s, H_4).

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Scheme 1. The reaction equation of Benzoimidazole-5-carboxylic acid.

2.2. The synthesis of $\text{CaF}_2:\text{Tb}^{3+}$ nanoparticles

The $\text{CaF}_2:\text{Tb}^{3+}$ nanoparticles were prepared as follows and the doping concentrations of Tb^{3+} was 5 mol%. Benzoimidazole-5-carboxylic acid (0.4135 g, 2.550 mmol), $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (0.6022 g, 2.550 mmol), and $\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$ (0.0501 g, 0.134 mmol) were dissolved in 90 mL of anhydrous ethanol. After being stirred for about 10 min at 75 °C, then a solution of NH_4F (0.1889 g, 5.100 mmol) in 1 mL of water was added dropwise. The mixture was stirred for 3 h and then cooled to room temperature. The precipitate was separated by centrifugation and was washed with 95% ethanol by ultrasonication for three times. Finally, the particles were dried in a vacuum.

2.3. Sample preparation for the investigation of the effect of metal ions on the luminescence of $\text{CaF}_2:\text{Tb}^{3+}$ nanoparticles

A certain amount of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, NaCl , $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{CdCl}_2 \cdot \text{H}_2\text{O}$ was respectively dissolved in deionised water to prepare metal salt solutions of 1×10^{-3} M. $\text{CaF}_2:\text{Tb}^{3+}$ nanoparticles were dissolved in deionised water to prepare a stock solution of 10 mg/mL. For detection of metal ions, moderate metal salt solutions were mixed with 2.5 mL stock solution and the mixtures were diluted with water to get 5 mL solution. All the experimental solutions contain same amount of nanoparticles at a concentration of 5 mg/mL.

2.4. Measurements

^1H NMR spectra were obtained on a NMR spectrometer (GY-PNMR12-6). The phase of the nanoparticles was determined by A Bruker D2 Phaser X-Ray Diffractometer with Ni filtered Cu K α radiation. The morphology of the nanoparticles was characterized by a transmission electron microscopy (TEM, FEI TECNAI, 200 KV). The infrared spectra were obtained from KBr pellet using a Fourier transform spectrometer (TENSOR27). The room-temperature excitation and emission spectra were measured by a fluorescence spectrophotometer (RF-5301PC). The decay curves were recorded with a time-resolved spectrofluorometer (FLSP920). UV–vis absorption spectra were obtained by using a UV spectrophotometer (T6 new century) in the wavelength region of 200–500 nm.

3. Results and discussions

3.1. FT-IR characterization of the $\text{CaF}_2:\text{Tb}^{3+}$ nanoparticles

Fig. 1 displays the IR spectra of Ligand and $\text{CaF}_2:\text{Tb}^{3+}$ nanoparticles. In the spectrum of Ligand, the broad peak between 2150 and 2700 cm^{-1} demonstrated the intra-molecular hydrogen bonding and molecular packing [25,26]. The intense band at 1717 cm^{-1} is attributed to C=O stretching vibrations in COOH groups. The peak at 1577 cm^{-1} was assigned to NH in-plane bending vibration and the peak at 1308 cm^{-1} was associated with C–N stretching vibration. Two bands at 931 and 757 cm^{-1} could be ascribed to C–H out-of-plane bending vibrations [27,28]. For $\text{CaF}_2:\text{Tb}^{3+}$ nanoparticles, the typical asymmetric and symmetric vibration of $-\text{COO}^-$ group peaks were detected at 1387

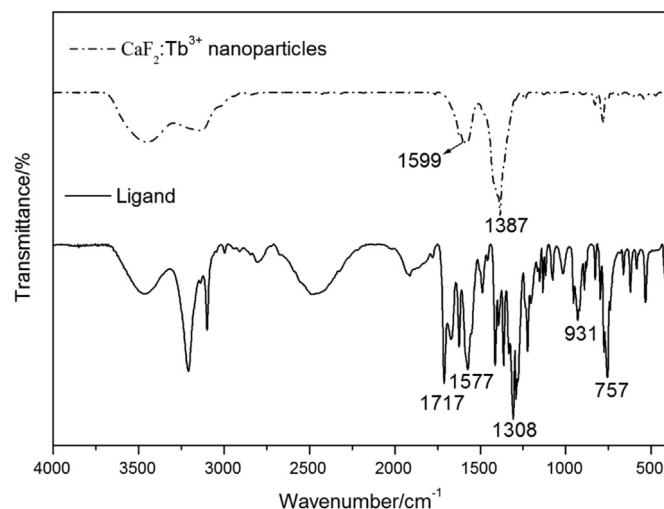


Fig. 1. FT-IR spectra of the $\text{CaF}_2:\text{Tb}^{3+}$ nanoparticles and Ligand.

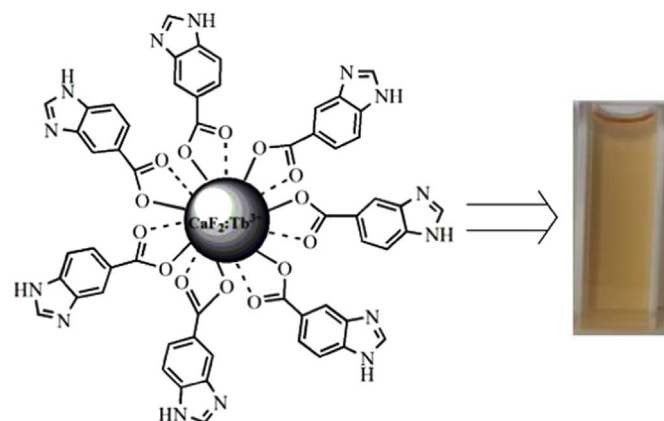


Fig. 2. Schematic diagram showing structure of the nanoparticles and picture of the nanoparticles at a concentration of 10 mg/mL in water.

and 1599 cm^{-1} , which reveals the presence of carboxylate anions on the $\text{CaF}_2:\text{Tb}^{3+}$ surface. Meanwhile, the lack of C=O stretching band at 1717 cm^{-1} also confirmed carboxylate formation on the surface of the nanoparticles.

3.2. Schematic diagram of the structure of $\text{CaF}_2:\text{Tb}^{3+}$ nanoparticles

According to the IR spectrum of $\text{CaF}_2:\text{Tb}^{3+}$ nanoparticles, Ligand was bonded to the surface of nanoparticles by coordination interactions between carboxylate and nanoparticles. Fig. 2 shows schematic diagram of the structure of the nanoparticles. Due to the surface of the nanoparticles contains hydrophilic groups, the dispersion of the composite nanoparticles was enhanced in water. Therefore, the $\text{CaF}_2:\text{Tb}^{3+}$ nanoparticles can be well dispersed in water to form a transparent solution (Fig. 2).

3.3. Structure and morphology of $\text{CaF}_2:\text{Tb}^{3+}$ nanoparticles

Fig. 3 shows the XRD pattern of the $\text{CaF}_2:\text{Tb}^{3+}$ nanoparticles. The peak positions agree well with the data of pure cubic CaF_2 crystals (ICSD file 41413), and no impurity peaks are observed. Thus it can be concluded that the original structure of CaF_2 can be retained after the modification and doping. From the XRD pattern, the nanoparticles size can be estimated using the Debye–Scherrer formula: $d = 0.89\lambda / B \cos\theta$, where d is the particle size; λ is the wavelength of $\text{CuK}\alpha_1$ (0.15406 nm) line; B is the full-width at

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