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Highly luminescent Cit/CaF₂: Ce³⁺, Tb³⁺ nanoparticles and detection of Cu²⁺ ions

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Abstract

Terbium doped calcium fluoride (CaF₂:Tb³⁺) and cerium co-doped CaF₂:Tb³⁺ (CaF₂:Ce³⁺, Tb³⁺) nanoparticles were synthesized by the hydrothermal method by using citric acid (Cit) as surfactant. The as-synthesized nanoparticles have good dispersibility in water to form an aqueous transparent dispersion at a concentration of 20 mg/mL. The nanoparticles have the CaF₂-type cubic structures. Photoluminescence (PL) investigation showed that energy transfer can be occurred effectively from Ce³⁺ ions to Tb³⁺ ions in Cit/CaF₂: Ce³⁺, Tb³⁺ nanoparticles. And the PL intensity of Cit/CaF₂: Ce³⁺, Tb³⁺ nanoparticles is very strong at a low concentration of 1 mg/mL, which is 16-fold as high as that of Cit/CaF₂: Tb³⁺ nanoparticles. The strong green emission from Cit/CaF₂: Ce³⁺, Tb³⁺ nanoparticles can selectively be quenched by Cu²⁺ ions in comparison to other metal ions and its detection limit is 1.02×10^{-5} M in an aqueous solution. The PL quenching is reversible by the addition of ethylenediaminetetraacetic acid disodium salt (EDTA-2Na) with the recovery of almost 80% of the original PL. The results revealed that Cit/CaF₂: Ce³⁺, Tb³⁺ nanoparticles could

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find a promising application for the detection of Cu^{2+} ions in an aqueous solution.

Keywords: Luminescence, Water-dispersible, Lanthanide, CaF2 nanoparticles, Detection

1. Introduction

Recently, lanthanide-doped nanoparticles attracted significant attention owing to their wide range of applications, such as phosphors, photocatalysts, sensors and optoelectronic applications [1-3]. The design and synthesis of lanthanide-based sensors are attracting increasing attention as lanthanide ions have sharp emission bands and long luminescence lifetimes (up to milliseconds). Numerous reports have demonstrated the good sensitivity and selectivity of lanthanide-doped upconversion nanoparticles (UCNPs) on detection of various metal ions [4-7]. In addition, lanthanide MOFs (metal-organic frameworks) are especially attractive due to their diversified coordination properties, unique luminescence and higher stability [8, 9], which can be used as luminescent sensors to detect metal ions [10, 11]. Although, the above mentioned lanthanide-based sensors are quite sensitive, they also suffer from some drawbacks. For lanthanide MOFs, they usually display low selectivity for detection of metal ions. For lanthanide-doped UCNPs, the up-conversion luminescence efficiency is usually low due to the existence of quenching groups. The luminescence efficiency of lanthanide doped down-conversion nanoparticles with visible luminescence is considerably higher if compared to lanthanide-doped UCNPs, especially for Ce³⁺ and Tb³⁺ co-doped nanoparticles.

The Cu²⁺ ion is a transition metal ion of the human body that is necessary for different physiological processes such as mitochondrial respiration, enzyme

oxidation-reduction reaction and so forth. Excessive copper intake can however cause neurodegenerative diseases [12-14]. In addition, the Cu²⁺ ion is also a common environmental pollutant that mainly comes from the mining, metal processing, machine manufacturing, organic synthesis and other industrial wastewater. The maximum allowance of Cu²⁺ ions in drinking water, given by the World Health Organization (WTO), is ~31.5 μ M [15]. It is therefore important to develop sensitive and selective sensors to detect Cu²⁺ ions in both the human body and in the environment.

The common methods for detecting Cu^{2+} ions are struggling to meet the rapid detection requirements because the methods are time-consuming, relatively expensive and involve complex operations [16-18]. A fluorescence analysis method has the advantages of high selectivity and sensitivity. Moreover it can release real-time and online detection. The fluorescence analysis methods are therefore extensively used in sensing heavy metal ions. A few fluorescence-based sensors have recently been designed and synthesized to detect Cu^{2+} ions. Most of these sensors are organic molecules, lanthanide-doped UCNPs, silver nanoparticles, gold nanoparticles and quantum dots [19-24]. To the best of the authors' knowledge, there are only a few reports on the detection of Cu^{2+} by using down-conversion lanthanide doped nanoparticles as a sensor [25-27].

Herein, the authors present a facile route to synthesize Cit/CaF_2 : Tb^{3+} and Cit/CaF_2 : Ce^{3+} , Tb^{3+} nanoparticles with higher water-dispersibility by using citric acid (Cit) as surfactants. The main effect of Cit is to hinder the growth of nanoparticles and to

make water-dispersible nanoparticles. The as-prepared nanoparticles can form an aqueous transparent dispersion with concentration up to 20 mg/mL. The PL intensity of Cit/CaF₂: Ce^{3+} , Tb^{3+} nanoparticles in water was very strong at a low concentration of 1mg/mL. The free hydroxyl groups on the surface of the Cit/CaF₂: Ce^{3+} , Tb^{3+} nanoparticles can coordinate with metal ions in water through electrostatic interaction. The luminescence of Cit/CaF₂: Ce^{3+} , Tb^{3+} nanoparticles was effectively quenched by Cu^{2+} ions in comparison with other metal ions in the experiment. Cit/CaF₂: Ce^{3+} , Tb^{3+} nanoparticles exhibited high selectivity and sensitivity towards Cu^{2+} ions.

2. Experiment

2.1 Preparation of the nanoparticles

The same process was used to prepare both the Cit/CaF₂: Tb³⁺ and Cit/CaF₂: Ce³⁺, Tb³⁺ nanoparticles. The doping content of Tb³⁺ was 5 mol% and the Ce³⁺, Tb³⁺ co-doped content was 5 and 5 mol%, respectively. The preparation of Cit/CaF₂: Ce³⁺, Tb³⁺ nanoparticles was taken as an example. 1.6g (8.3 mmol) Cit in 24 mL of deionized water was added to a three-necked flask. The pH of the Cit solution was adjusted to about 6.5 using ammonia. A 2 mL aqueous solution containing Ca(NO₃)₂·4H₂O (5.0 mmol), TbCl₃·6H₂O (0.28 mmol) and CeCl₃·7H₂O (0.28 mmol) was mixed with the Citrate solution. The mixture was stirred at 40 °C for about 10 min. The 2 mL aqueous solution of NH₄F (11 mmol) was added dropwise. The mixture was transferred into a Teflon autoclave (50 mL) after 20 min and then it was heated at 150 °C for 16 h. Moderate amounts of acetone were added to precipitate nanoparticles during cooling of the autoclave to room temperature. The nanoparticles

were separated with a centrifuge and washed with a solution of ethanol mixed with deionized water (volume ratio 3:1) by ultrasonication. Finally, the obtained nanoparticles were dried at 50 °C. The as-prepared nanoparticles can form transparent aqueous dispersions with the concentration up to 20 mg/mL. The pH adjustment is very important in the synthesis for the water-dispersion of Cit/CaF₂: Tb^{3+} and Cit/CaF₂: Ce^{3+} , Tb^{3+} nanoparticles. If the pH was not adjusted in the synthesis, the Cit/CaF₂: Tb^{3+} or Cit/CaF₂: Ce^{3+} , Tb^{3+} nanoparticles can hardly be dispersed in water.

2.2 Sample preparation for detecting metal ions

The stock solutions of the metal salts (MnCl₂·4H₂O, CdCl₂·H₂O, CuCl₂·2H₂O, NiCl₂·6H₂O, ZnCl₂, MgCl₂·6H₂O, CaCl₂, Pb(NO₃)₂, KCl and NaCl) with the concentration of 1×10^{-3} M and the dispersed solution of Cit/CaF₂: Ce³⁺, Tb³⁺ nanoparticles (5 mg/mL) were prepared in deionized water. 75 µL of different metal salt stock solutions were mixed with 1 mL solution of the dispersed nanoparticles, respectively, for the selective detection of metal ions. The mixtures were then diluted with deionized water to get a 5 mL solution. In order to analyze the detection sensitivity for Cu²⁺ ions, 1 mL of the nanoparticles' dispersed solution was added with different amounts of Cu²⁺ ions' stock solutions and diluted with deionized water to get a 5 mL mixed solution. The concentration of the Cu²⁺ ions is in the range of 2.0×10^{-6} M to 2.0×10^{-5} M.

2.3 Measurement technique

The crystal structure of the nanoparticles was identified by a powder X-ray diffractometer (XRD), Bruker D2 Phaser. The 2θ angles ranged from 15° to 80° . The

size and morphology of the nanoparticles were analyzed by a JEM-2100 transmission electron microscope (TEM). The infrared spectra in the range of 4000-500 cm⁻¹ were tested on a Nicolet iS50 fourier transform infrared (FTIR) spectrometer by using the KBr pellet method. The fluorescent properties of nanoparticles in an aqueous solution were measured at room temperature by a RF-5301PC spectrophotometer with 1 nm spectral resolution. The decay curves were recorded with a time-resolved spectrofluorometer (FLSP920). UV-vis absorption spectra were carried out by using a UV-2550 spectrophotometer in the 200-500 nm spectral range.

3. Results and discussion

3.1 Growth mechanism of the nanoparticles

During the synthesis process, the aqueous solution of NH_4F was added to the aqueous solution of the Citrates and metal ions (M^{n+}) drop by drop. The M^{n+} ions first formed complexes with Citrates because the mixed system contained a lot of Citrates. This was also reported in previous reports [28]. Subsequently, Cit-capped M^{n+} ions reacted with the added F ions to form nanocrystalline nuclei. The nanoparticles then grew gradually. The growth process ended as the Cit capped the nanoparticles' surface. According to the literature, the chelating agent is a key component to the sizes of particles [28, 29], the crystal growth can be accelerated by a small amount of chelating agent absorbed on the crystal surfaces. In our experiment, the content of Cit is enough for the formation of the nanoparticles with small sizes. Consequently, small nanoparticles were synthesized. The schematic diagram of growth process is shown in Scheme 1.

3.2 FTIR characterization of the nanoparticles

Fig. 1 shows the FTIR spectra of the nanoparticles in the spectral range of 4000-500 cm⁻¹. In the Cit spectrum, the broad peak from 2500 to 3750 cm⁻¹ was attributed to the hydroxyl stretching vibrations that formed from hydrogen bonds [30]. The stretching vibrations of C=O bonds in carboxyl groups were observed at 1732 cm⁻¹. The spectra for both the nanoparticles were similar because they had the same organic groups on the surface. The stretching band of C=O at 1732 cm⁻¹ was not observed from the main absorption bands for the nanoparticles. The symmetric and asymmetric vibration peaks of the carboxylate groups were observed at 1404 and 1631 cm⁻¹ [31]. The peak at about 3448 cm⁻¹ corresponded to hydroxyl stretching vibrations in alcoholic hydroxyls [30]. The results revealed that all of the carboxylate groups (-COO⁻) coordinated to the lanthanide ions at the surface of the nanoparticles. This means that there were no free carboxylic acid groups at the surface of the nanoparticles.

3.3 The XRD and TEM characterizations of the nanoparticles

Fig. 2 shows the XRD patterns for the two sets of nanoparticles compared to the standard pattern of cubic CaF_2 crystals (ICSD file 41413). The diffraction peaks of the nanoparticles were very broad and this is due to the very small size of the nanoparticles. The radius of Tb^{3+} and Ce^{3+} ions are bigger than that of Ca^{2+} , therefore doping with Tb^{3+} or Ce^{3+} increased the CaF_2 crystal lattice. The peak positions of the nanoparticles shifted towards lower angles compared to the pure cubic CaF_2 crystal due to the increased crystal lattice and no other impurity peaks were observed.

Fig. 3 shows the TEM images with no significant differences between the two nanoparticles samples' morphology and size. Each sample showed aggregation of small nanoparticles. According to FTIR spectra, the reason for the aggregation of the nanoparticles may be due to the hydrogen bonding effect between the hydroxyl groups of citric acid on the surface of nanoparticles.

3.4 Photoluminescence properties of the nanoparticles

Fig. 4 shows the broad PL excitation band centered around 261 nm for the Cit/CaF₂: Ce^{3+} , Tb^{3+} nanoparticles when the 543 nm (${}^{5}D_{4}-{}^{7}F_{5}$ for Tb^{3+}) emission peak was monitored. This broad excitation band was attributed mainly to energy transitions from the ${}^{2}F_{5/2}$ ground state to the 5d excited states of Ce³⁺ [32, 33]. Fig. 4 also shows the very weak forbidden f-f excited transitions of Tb^{3+} ions [33] in the 245 to 265 nm range for the Cit/CaF₂:Tb³⁺ nanoparticles. Fig. 5 shows the PL emission spectra for both the Cit/CaF₂: Ce³⁺, Tb³⁺ and the Cit/CaF₂: Tb³⁺ nanoparticles. The PL spectrum for the Cit/CaF₂: Ce³⁺, Tb³⁺ nanoparticles was divided into two parts. The first part included the 280-370 nm range and this mainly corresponded to the 5d-4f transitions of Ce³⁺ ions [34]. The second part included the bands located at about 489, 543, 585 and 621 nm that aroused from the ${}^{5}D_{4} \rightarrow {}^{7}F_{J}$ (J=6, 5, 4 and 3) transitions of Tb³⁺ ions [35, 36] with the green emission band at 543 nm as the strongest peak (close to the maximum range of the instrument). The Cit/CaF₂: Tb³⁺ nanoparticles showed only two weak emission peaks of Tb³⁺ ions at 489 and 543 nm. The PL intensity of the Cit/CaF₂: Ce³⁺, Tb³⁺ nanoparticles at 543 nm was 16-fold as high as that of the Cit/CaF₂: Tb³⁺ nanoparticles and this suggested that the energy transfer from

 Ce^{3+} ions to Tb^{3+} ions was very efficient. The proposed energy transfer process is shown in Fig 6. Energy transferred from the ground state to the 5d excited states of the Ce^{3+} ions and then to the ${}^{5}D_{1}$ level of Tb^{3+} ions. This was followed by nonradiative relaxation to the ${}^{5}D_{3}$ level, and from the the ${}^{5}D_{3}$ to the ${}^{5}D_{4}$ level of Tb^{3+} ions. Radiative relaxation then occurred from the ${}^{5}D_{4}$ level of Tb^{3+} ions to the ${}^{7}F_{J}$ (J=3, 4, 5 and 6) ground state levels [33].

The PL intensity of the Cit/CaF₂: Ce³⁺, Tb³⁺ nanoparticles at 543 nm will exceed the measurement range if the concentration is greater than 1mg/mL at 261 nm excitation wavelength. Fig. 7 (a) depicts the excitation bands of Cit/CaF₂: Ce³⁺, Tb³⁺ nanoparticles at a concentration of 5 mg/mL. The excitation spectrum shows three excitation peaks at 261, 302 and 326 nm. The excitation peak at 261 nm exceeded the measurement intensity range (1000). The PL spectra of Cit/CaF₂: Ce³⁺, Tb³⁺ nanoparticles at different concentrations (1, 5, 10 and 15 mg/mL) were therefore measured with 302 nm excitation. Fig. 7 (b) shows the increase in the PL intensity of the Cit/CaF₂: Ce³⁺, Tb³⁺ nanoparticles at 543 nm with an increase in solution concentration. The two peak intensities at 10 mg/mL and 15 mg/mL were very close and this suggested concentration quenching.

3.5 Detection of Cu^{2+} ions using Cit/CaF₂: Ce^{3+} , Tb^{3+} nanoparticles

In order to investigate the sensing properties of the Cit/CaF₂: Ce^{3+} , Tb^{3+} nanoparticles towards different metals, the PL properties of the Cit/CaF₂: Ce^{3+} , Tb^{3+} nanoparticles were monitored in the presence of different metal ions (for example, Ni²⁺ ions, Pb²⁺ ions, Ca²⁺ ions, Cu²⁺ ions, Cd²⁺ ions, Mg²⁺ ions, Mn²⁺ ions, Zn²⁺ ions,

Na⁺ ions and K⁺ ions). The PL spectra are shown in Fig. 8. The nanoparticles showed selective and sensitive response to Cu^{2+} ions, but the response to the other metal ions was not obvious. The PL of the Cit/CaF₂: Ce^{3+} , Tb^{3+} nanoparticles was selectively quenched in the presence of Cu^{2+} ions. The PL intensity at 543 nm of the nanoparticles showed a decrease of about 31% upon the addition of 1.5×10^{-5} M of Cu^{2+} . The maximum quenching effect of the 543 nm emission intensity was about 5.3% for all the other metal ions. In addition, the luminescent intensity of Ce^{3+} ions (5d-4f transition) was also decreased by addition of Cu²⁺ ions compared to the Cit/CaF₂: Ce³⁺, Tb³⁺ nanoparticles. Fig. 9 shows the decay curves of ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$ transition of Tb^{3+} for the Cit/CaF₂: Ce³⁺, Tb³⁺ nanoparticles and Cit/CaF₂: Ce³⁺, Tb³⁺ nanoparticles $+ Cu^{2+}$ ions. Biexponential decay was observed for the two samples. The Lifetime of 1.82 ms (24.24%) and 6.80 ms (75.76%) was obtained for the Cit/CaF₂: Ce³⁺, Tb³⁺ nanoparticles. The lifetime of the Cit/CaF₂: Ce³⁺, Tb³⁺ nanoparticles decreased to 1.05 ms (21.33%) and 4.80 ms (78.67%) upon addition of Cu^{2+} ions. The decay result was accorded with the fluorescence quenching of CaF₂: Tb^{3+} nanoparticles by Cu^{2+} ions.

Fig. 10 shows the UV-vis spectra of Cit/CaF₂: Ce³⁺, Tb³⁺ nanoparticles, Cu²⁺ ions and Cit/CaF₂: Ce³⁺, Tb³⁺ nanoparticles + Cu²⁺ ions. The Cu²⁺ ions have an absorption peak before 250 nm, and the Cit/CaF₂: Ce³⁺, Tb³⁺ nanoparticles exhibit two absorption peaks at 246 nm and 332 nm, respectively. The absorbance of the Cit/CaF₂: Ce³⁺, Tb³⁺ nanoparticles at 246 nm was increased with the addition of Cu²⁺ ions. The increased absorption is possibly responsible for the fluorescence quenching of Cit/CaF₂: Ce³⁺, Tb^{3+} nanoparticles by Cu^{2+} ions [37]. According to the FTIR spectrum, alcoholic hydroxyls were on the surface of the Cit/CaF₂: Ce³⁺, Tb³⁺ nanoparticles that can bond Cu^{2+} to the nanoparticles. Therefore, the reason of the fluorescence quenching was the charge transfer through the binding of Cu²⁺ ions to the alcoholic hydroxyls [38].

In order to measure the detection sensitivity of Cit/CaF₂: Ce³⁺, Tb³⁺ nanoparticles to Cu^{2+} ions, the PL spectra of the Cit/CaF₂: Ce^{3+} , Tb^{3+} nanoparticles were examined in the presence of Cu^{2+} ions with various concentrations upon excitation at 261 nm. Fig. 11 (a) shows that the PL intensity of the Cit/CaF₂: Ce^{3+} , Tb^{3+} nanoparticles at 543 nm gradually decreased with an increase in the Cu²⁺ ions' concentrations, in the 2×10^{-6} - 2.0×10^{-5} M range. A decrease of about 40.5%, in the 543 nm emission intensity, was achieved at the 2.0×10^{-5} M concentration. The corresponding Stern-Volmer plot for the Cu^{2+} ion is displayed in Fig. 11 (b) [26]. According to the plot of I_0/I with various concentration of Cu^{2+} ions, there is a good linear relationship (R²=0.99) between the intensity ratio and the Cu²⁺ concentration. The formula $3\sigma/S$ was used to calculate the detection limit [26]. In the formula, σ is the standard deviation of blank measurements and S is the slope of the plot, which can be obtained from Fig. 11 (b). The detection limit value was therefore calculated to be 1.02×10^{-5} M. This value is lower than the maximum Cu²⁺ ions concentration permitted in drinking water.

To check whether the fluorescence quenching is reversible, appropriate amounts of EDTA-2Na solution (10^{-2} M) was added to the Cu²⁺ quenched Cit/CaF₂: Ce³⁺, Tb³⁺ nanoparticles solution. Fig. 12 shows the recovery of the PL intensity at 543 nm by

the addition of the EDTA-2Na solution. Almost up to 80% of the initial PL intensity was recovered with 200 μ L of the EDTA-2Na solution. The response time was less than 1 min for both quenching and recovery of the PL intensity of Tb³⁺ ions.

4. Conclusions

Cit/CaF₂: Tb³⁺ and Cit/CaF₂: Ce³⁺, Tb³⁺ nanoparticles with high water-dispersibility have been prepared by hydrothermal method by using Cit as surface modification. A possible growth mechanism was given to explain the formation of the nanoparticles. The synthetic route presented in this work is very simple and it may easily be applied to synthesize other lanthanide ions doped in fluoride nanoparticles with water-dispersibility. The PL intensity of the Cit/CaF₂: Ce³⁺, Tb³⁺ nanoparticles at 543 nm was 16-fold as high as that of the Cit/CaF₂: Tb³⁺ nanoparticles in an aqueous dispersion at a low concentration of 1mg/mL. It is worth noting that Cit/CaF₂: Ce³⁺, Tb³⁺ nanoparticles can selectively detect Cu²⁺ ions in water among a number of metal ions with high sensitivity. The detection limit for the Cu²⁺ ions was obtained to be 1.02×10^{-5} M. The initial PL intensity was recovered to 80% with the addition of EDTA-2Na. The Cit/CaF₂: Ce³⁺, Tb³⁺ nanoparticles showed excellent PL properties for the application of detecting Cu²⁺ ions in the aqueous solution.

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Figure captions

Scheme 1 Schematic illustration for the formation process of Cit/CaF₂:Tb³⁺ and Cit/CaF₂: Ce^{3+} , Tb³⁺nanoparticles.

Fig. 1 FTIR spectra of the Cit/CaF₂:Tb³⁺ and Cit/CaF₂: Ce³⁺, Tb³⁺ nanoparticles and of Cit.

Fig. 2 XRD patterns of the Cit/CaF₂:Tb³⁺ and Cit/CaF₂: Ce³⁺, Tb³⁺ nanoparticles and for the CaF₂ (ICSD file 41413) standard pattern.

Fig. 3 TEM images of the (a) Cit/CaF_2 : Tb^{3+} and (b) Cit/CaF_2 : Ce^{3+} , Tb^{3+} nanoparticles.

Fig. 4 Excitation spectra of the Cit/CaF₂:Tb³⁺ and Cit/CaF₂: Ce³⁺, Tb³⁺nanoparticles in an aqueous dispersion at 1mg/mL concentration (λ_{em} =543 nm).

Fig. 5 Emission spectra of the Cit/CaF₂:Tb³⁺ and Cit/CaF₂: Ce³⁺, Tb³⁺ nanoparticles in an aqueous dispersion at 1mg/mL concentration (λ_{ex} =261 nm).

Fig. 6 Schematic diagram for the energy transfer process between Ce³⁺ and Tb³⁺ ions.

Fig. 7 (a) Excitation spectrum of the Cit/CaF₂: Ce³⁺, Tb³⁺nanoparticles in an aqueous dispersion at 5 mg/mL concentration (λ_{em} =543 nm) and (b) the emission spectra of the Cit/CaF₂: Ce³⁺, Tb³⁺ nanoparticles in an aqueous dispersion at different concentrations (λ_{ex} =302 nm).

Fig. 8 (a) PL spectra of the Cit/CaF₂: Ce³⁺, Tb³⁺nanoparticles in an aqueous dispersion (1mg/mL) after the addition of different metal ions (λ_{ex} =261 nm) and (b) the emission intensities of the Cit/CaF₂: Ce³⁺, Tb³⁺nanoparticles in an aqueous dispersion (1mg/mL) at 543 nm after the addition of different metal ions (λ_{ex} =261 nm). The concentration of the metal ions in the aqueous solution was 1.5×10⁻⁵ M.

Fig. 9 PL lifetime decay curves of Cit/CaF₂: Ce^{3+} , Tb^{3+} nanoparticles in the absence and presence of Cu^{2+} ions.

Fig. 10 UV-vis spectra of the Cit/CaF₂: Ce^{3+} , Tb^{3+} nanoparticles, Cu^{2+} ions and Cit/CaF₂: Ce^{3+} , Tb^{3+} nanoparticles + Cu^{2+} ions.

Fig.11 (a) PL spectra at 543 nm and (b) the corresponding Stern-Volmer plot of the Cit/CaF₂: Ce^{3+} , Tb^{3+} nanoparticles in the presence of the Cu^{2+} ions.

Fig. 12 PL spectra of Cit/CaF₂: Ce^{3+} , Tb^{3+} nanoparticles (Blank), Blank + Cu^{2+} ions, Blank + Cu^{2+} ions + 100 µL EDTA-2Na and Blank + Cu^{2+} ions + 200 µL EDTA-2Na at 543 nm.

Scheme 1











Fig. 5

















Fig. 10











• $CaF_2:Tb^{3+}$ and $CaF_2:Ce^{3+}$, Tb^{3+} nanoparticles were synthesized by using Citrate as the surface modification.

• The as-prepared nanoparticles formed a transparent aqueous dispersion with concentration up to 20 mg/mL.

• Cit/CaF₂: Ce³⁺, Tb³⁺ nanoparticles have strong green emission in an aqueous dispersion at a low concentration of 1 mg/mL.

• Cit/CaF₂: Ce³⁺, Tb³⁺ nanoparticles can selectively detect Cu²⁺ ions in water and detection limit is 1.02×10^{-5} M.

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Declaration of interests

 \square The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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