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Synthesis of surface amino-functionalized $NaGdF_4$:Ce,Tb nanoparticles and their luminescence resonance energy transfer (LRET) with Au nanoparticles

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ABSTRACT

Luminescent/magnetic dual-functional $NaGdF_4$:Ce,Tb nanoparticles were first synthesized via a solvothermal method with rare earth stearate as the precursor, and the luminescence resonance energy transfer of $NaGdF_4$:Ce,Tb to Au nanoparticles was studied. The synthesized $NaGdF_4$:Ce,Tb were ellipsoidal nanoparticles, with pure hexagonal structure and an average size of 15 nm. The nanoparticles emit strong emission at 544 nm under the 246 nm excitation, and show good paramagnetic at room temperature. After surface amination by the typical Stöber method, the as-prepared $NaGdF_4$:Ce,Tb nanoparticles were served as the donor for the LRET with Au nanoparticles. Good linear relationships between the luminescence intensities of $NaGdF_4$:Ce,Tb (at 490 nm and 544 nm) and the concentration of Au nanoparticles were obtained, indicating a great potential application prospect of the LRET system in bioassays.

1. Introduction

Fluorescence resonance energy transfer (FRET) is a non-radiative process in which the electronic excitation energy of a donor chromophore is transferred to a nearby acceptor molecule via long-range dipole–dipole interactions [1]. To date, luminescent materials commonly used in FRET include organic dye [2], quantum dots [3,4] and rare earth doped down- or up-conversion nanoparticles [5,6], while, the FRET system with rare earth doped materials as the donor was commonly named as LRET [7]. Among them, the rare earth doped luminescent materials usually possess high quantum yield, long fluorescence lifetime and narrow emission peak. Especially, the rare earth doped upconversion nanoparticles are usually excited by near infrared light (NIR), the low excitation energy can effectively avoid auto-fluorescence from samples [8].

Among the rare earth doped luminescent materials, it is well known that Gd^{3+} ions doped nanoparticles always possess paramagnetism [9]. In recent years, nanomaterials that possess bifunctional properties have attracted more and more attention [10,11]. For example, nanomaterials exhibit optical and magnetic properties can realize the detection of samples by optical labeling or magnetic resonance image, and carry out separation and enrichment of samples at the same time [12]. Recently, researches on the synthesis and application of these bi-functional nanoparticles have become the hotspot, there are some reports dedicated on it. The hydrophobic oleic acid-capped Tm/Yb/Er co-doped $NaGdF_4$ nanoparticles were synthesized and applied as contrast agents for magnetic resonance imaging (MRI) in vivo [13]. The results indicated that these dual-functional nanoparticles exhibited excellent signal-to-noise ratio, low cytotoxicity, and can be served as a new platform for the detection of biological tissues.

Based on the recent research, the major approaches for the preparation of rare earth doped nanoparticles in solution phase, include co-precipitation [14,15], thermal decomposition [16], sol–gel [17], polyol-mediated process [18], hydro/solvothermal [19,20], micro-emulsion [21], and son on. However, with the rapid development of nanotechnology, rare earth doped materials have demonstrated broad prospects in application of optics, optoelectronics, and bioassays, etc. [22,23]. Above all, the synthesis of high quality nanocrystals possessing small size, uniform shape, both high luminescent and magnetic intensity with a simple and rapid method is still of important significance.

Recently, the analysis and detection based on the LRET system have been developed as a new kind of method with high sensitivity and selectivity. The method has been applied for the detection of nucleic acids [24], avidin [25], glucose [26] and immunoassay [27], etc. The lanthanides doped luminescent materials usually possess high quantum yield, long fluorescence lifetime and narrow emission peak [28,29], so that the signal to noise ratio can be greatly improved when lanthanides were used as the donor in LRET. Au nanoparticles itself cannot produce fluorescence, leading to avoid the interference from background. Moreover, the broad and

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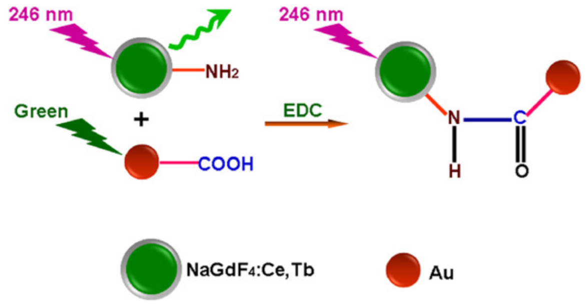

Scheme 1. The LRET diagram between $NaGdF_4$:Ce,Tb and Au nanoparticles.

continuous absorption of Au nanoparticles can ensure the high efficiency of a LRET process. Therefore, Au nanoparticles were usually used as the receptor in LRET system.

In this work, a novel method for the synthesis of luminescent/magnetic bi-functional $NaGdF_4$:Ce,Tb nanoparticles was developed via a two phase mechanism, with rare-earth stearate as the precursor, oleic acid, ethanol and water as the solvent. The nanoparticles possessed both optical and magnetic properties. After surface aminated modification through typical stöber method, the as-prepared nanoparticles were applied for the LRET with Au nanoparticles, and an effective LRET system was established through the covalent interaction of amino and carboxyl groups (Scheme 1).

2. Materials and methods

2.1. Materials

Rare earth oxides (RE_2O_3, RE = Gd, Ce and Tb) of 99.99% purity, sodium fluoride (NaF), oleic acid (OA), stearic acid, tetraethyl orthosilicate (TEOS), 3-aminopropyltrimethoxysilane (APTES), isopropanol, chloroauric acid, sodium citrate and absolute alcohol were of analytical grade. All chemicals above were purchased from National Medicines Corporation Ltd. of China and used as received without further purification. 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC) were purchased from Acros (USA). Triple-distilled water was used throughout the experiments.

2.2. Synthesis and modification of $NaGdF_4$:Ce,Tb nanoparticles

$NaGdF_4$:Ce,Tb nanoparticles were prepared referencing to a solvothermal method previously reported by our group [30], based on the solid–liquid two-phase reaction mechanism. First, the rare earth stearate were synthesized according to the reported method, and used as the precursor. To synthesize of $NaGdF_4$:Ce,Tb nanoparticles, 4 mL of oleic acid, 18 mL of ethanol and 8 mL of water were mixed together. Then, 0.2100 g NaF and 1 mmol of rare earth stearate $(C_{17}H_{35}COO)_3RE$ (RE = $Gd_{0.75}Ce_{0.10}Tb_{0.15}$) was added. The mixture was stirred to form a homogeneous solution, then transferred to a autoclave, solvothermally treated at 120 °C for 18 h. After finishing the reaction and cooling to room temperature, the product was purified by centrifugation and washing with ethanol for several times, dried at 60 °C for 12 h.

The modification of as prepared $NaGdF_4$:Ce,Tb nanoparticles was performed according to the typical stöber method [31]. First, 20 mg of $NaGdF_4$:Ce,Tb nanoparticles were dispersed in 70 mL of ethanol under sonication, then 20 mL H_2O and 2.5 mL $NH_3{\cdot}H_2O$ were added. After stirred for about 10 min at 35 °C, the aminated reaction was activated with the addition of TEOS and APTES, and kept at 35 °C for 5 h. Finally, the product was precipitated and washed with ethanol by centrifuging, and dried at 60 °C overnight.

2.3. Preparation of Au nanoparticles

In this experiment, sodium citrate was used as the reductant for the preparation of gold nanoparticles. During the specific experimental procedure, 1 mL of 1% chlorine gold acid and 79 mL water were first mixed together and heated to 60 °C, then 2 mL of 1% citric acid sodium solution was quickly added. After 30 min, Au colloid solution was obtained.

2.4. LRET between $NaGdF_4$:Ce,Tb and Au nanoparticles

The $NaGdF_4$:Ce,Tb nanoparticles were dispersed in water under sonication to form a 2 mg mL^{-1} colloidal solution. Then, a mixture of 200 μL 200 μg mL^{-1} EDC and different volumes (0–350 μL) of 48 μg mL^{-1} Au was added, the final solution was adjusted to 2 mL and oscillated at 37 °C for 2 h. After reaction, the solution was detected on a LS-55 luminescence spectrometer under the 246 nm excitation.

2.5. Characterization

The size and morphology of prepared $NaGdF_4$:Ce,Tb nanoparticles were observed on a H-7650 transmission electron microscope (TEM, HITACHI Co., Japan) operating at an accelerating voltage of 100 kV. X-ray powder diffraction (XRD) measurements were carried out by an X' Pert Pro diffractometer (PANalytical Co., Holand) equipped with Cu Kα radiation (λ = 0.15406 nm). The optical property was examined on a LS-55 luminescence spectrometer (PerkinElmer Co., USA). The hysteresis loop was measured on a vibrating sample magnetometer (VSM 7407, LakeShore, USA). Fourier transform infrared (FT-IR) spectra of the modified nanoparticles were measured on a Spectrum One (B) spectrometer (PerkinElmer Co., USA). The absorption spectra of Au nanoparticles were recorded on a UV-2100 UV–vis spectrometer (Ruili Analytical Instrument Company, Beijing, China).

3. Results and discussion

3.1. Morphology and structure characterization of $NaGdF_4$:Ce,Tb nanoparticles

In this experiment, a solid–liquid mechanism was applied for the preparation of $NaGdF_4$:Ce,Tb nanoparticles. Rare earth stearate was used as the precursor, a mixture of oleic acid, ethanol and water was the reaction medium. During the reaction, rare earth ions were slowly released from the precursor and reacted with F^- and Na^+ ions to form $NaGdF_4$:Ce,Tb nanoparticles. Meanwhile, during formation of the nanoparticles, oleic acid in the reaction system can be covered at the particle's surface, avoid their aggregation and play an important role for the size and morphology controlling. Fig. 1a shows the typical TEM image of the $NaGdF_4$:Ce,Tb nanoparticles. From the image it can be seen that, the nanocrystals were almost uniform ellipsoidal particles with an average size of about 15 nm.

The XRD patterns of $NaGdF_4$:Ce,Tb nanoparticles were represented in Fig. 1b. Compared with the standard pattern, it can be concluded that the nanoparticles possess pure hexagonal structure. All diffraction peaks of as prepared $NaGdF_4$:Ce,Tb nanoparticles are matched well with the peaks in standard pattern (Hexagonal JCPDS NO. 00-027-0699).

3.2. Luminescent properties of $NaGdF_4$:Ce,Tb nanoparticles

Fig. 2 represents the emission spectrum of $NaGdF_4$:Ce,Tb nanoparticles monitored at 246 nm. The seven peaks located in 381, 413, 435, 490, 544, 577 and 622 nm were all the typical emission of Tb^{3+} ions, which are corresponding to the $^5D_3$–^7F_J (J = 6, 5,