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Process intensification for scalable synthesis of ytterbium and erbium co-doped sodium yttrium fluoride upconversion nanodispersions

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ABSTRACT

Rare-earth doped $NaYF_4$ upconversion nanomaterials have found many applications from biosensing through photoelectric conversion to luminescent anti-counterfeiting. However, the scalable synthesis methods of ultrasmall $NaYF_4$ nanoparticles are still challenging. Herein, We demonstrated that the intensified mixing of the precursor by a high-gravity rotating packed bed (RPB) reactor before the hydrothermal synthesis process enabled the preparation of ultrasmall $NaYF_4$:Yb^{3+}/Er^{3+} upconversion nanoparticles, with much smaller size, more uniform distributions and higher Er^{3+}-doping level than those obtained in the stirred tank reactor (STR) route. In stark contrast to conventional synthetic techniques that require stringent control over several experimental variables for controlling morphologies and sizes, the process intensification approach presented here requires modification of only a single variable while enabling tremendous improvements to control the formation of $NaYF_4$ based UCNPs with small feature size. The UCNPs dispersed well in various organic solvents (e.g. ethanol, acetone, toluene, cyclohexane, etc.), forming transparent nanodispersions with upconversion luminescence under 980 nm NIR light irradiation. The preliminary applications of $NaYF_4$:Yb^{3+}/Er^{3+} nanodispersions for upconversion luminescent transparent hybrid films and anti-counterfeiting were also demonstrated.

1. Introduction

Rare-earth doped upconversion nanoparticles (UCNPs) that convert longer wavelength NIR light into shorter wavelength ultraviolet/visible/NIR light have attracted extensive scientific attention in recent years [1–4]. After several decades of technological developments, UCNPs have found many applications in many fields such as anti-counterfeiting [5–7], optoelectronic devices [8], bioimaging [9,10] and cancer treatment [11,12]. For instance, both theoretically and experimental studies have demonstrated that the power conversion efficiency of a solar cell would be significantly increased by using an ideal upconverter, such as transparent hybrid films embedded with UCPNs [13–15]. In addition, UCNPs have recently shown great potential to satisfy the demands for anti-counterfeiting applications due to their small size, low power density NIR excitation, high chemical stability, good wetting properties and compatibility with transparent security inks [5–7,16]. Since the traditional anti-counterfeit technologies are easily infringed [17], an advanced anti-counterfeit technology is therefore urgently needed in many important fields, especially for anti-counterfeit of paper documents or certificates, such as checks, passports, and even banknotes [16,18]. The efforts of chemical engineers are to develop solutions for some important problems, including but not limited to design, operation, control, optimization, and intensification of chemical, physical, and biological processes for sustainable development [19]. Upconversion luminescence based anti-counterfeiting is one of the most promising directions in moving toward UCNPs for large-scale production and commercial applications. It has been generally accepted that ultrasmall UCNPs are beneficial for hybrid optoelectronic devices and anti-counterfeiting ink. Therefore, the development of scalable methods for the synthesis sub-10 nm UCNPs is one of key materials challenge.

UCNPs are typically composed of an inorganic host lattice and rare-earth dopant ions embedded in the host lattice [4]. Sodium yttrium fluoride ($NaYF_4$) is among the most effective host materials for upconverison luminescence process due to its lowest phonon energy (phonon cutoff ~350 cm^{-1}), low nonradiative decay rates, and high radiative emission rates, especially doping with Yb^{3+}/Er^{3+} and Yb^{3+}/Tm^{3+} [3]. One common synthetic method for $NaYF_4$:Yb^{3+}/Er^{3+} nanoparticles is based on the thermal decomposition of trifluoroacetate precursors in high boiling noncoordinating solvents [20,21]. However, the thermal decomposition approach requires expensive precursors and

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high energy consumption, which limited the scale-up production of UCNPs. Another approach for preparation of $NaYF_4$:Yb^{3+}/Er^{3+} nanoparticles is based on liquid precipitation reaction between soluble rare-earth salts and alkali fluorides along with post hydrothermal process [22,23], which has been regarded as an effective method for mass production of UCNPs due to the low-cost and ease of scale-up. However, it is a common problem that the rare-earth doped $NaYF_4$ sample prepared shows two distinct particle morphologies that include small nanocubes and large nanorods, making it hard to obtain products with uniform size and well-proportioned distribution. The conventional precipitation process is usually performed in a batch-type stirred tank reactor (STR), in which the nucleation of UCNPs does not take place uniformly due to the low efficiency of mass transfer and fluid mixing in STR [24,25]. In 2010, Wang et al. reported a route for synthesis of ultra-small $NaYF_4$ based UCNPs with uniform morphology by doping Gd^{3+} ions, making a breakthrough in this field [26]. Simultaneous phase and size control of $NaYF_4$ based UCNPs through lanthanide doping lead to another issue, namely the additional of extra reactants and ions in the nanocrystal, raising the costs of raw materials and reducing the performance of the products.

Herein, we propose a route for the synthesis of $NaYF_4$:Yb^{3+}/Er^{3+} UCNPs by utilizing a high gravity rotating packed bed (RPB) reactor for nucleation of UCNPs along with post hydrothermal process. The high gravity environment and tiny droplets generated by the RPB lead to significant intensification of mass transfer and micromixing, which are of great benefit for the homogeneous nucleation and growth of particles [27,28]. Detailed studies on the effects of operating parameters and comparison with those obtained via a traditional STR route. The morphology, structure and upconversion luminescence property of the $NaYF_4$: Yb^{3+}/Er^{3+} nanoparticles were investigated by transmission electron microscope (TEM), power X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectrophotometry and luminescence spectra measurements. The upconversion luminescence behaviors of $NaYF_4$:Yb^{3+}/Er^{3+} nanoparticles dispersed in various organic solvents were investigated. Furthermore, transparent hybrid films of $NaYF_4$:Yb^{3+}/Er^{3+} and polyvinyl butyral (PVB), which has been among the most widely used binders for inks, were prepared by solution blending method. The $NaYF_4$:Yb^{3+}/Er^{3+} nanoparticles were also transferred into aqueous phase and used as the ink to draw anti-counterfeiting watermarks in paper. Upconversion luminescence properties of the hybrid films and the papers under the irradiation of 980 nm NIR laser were also investigated, demonstrating the potential of the $NaYF_4$:Yb^{3+}/Er^{3+} nanodispersions for anti-counterfeiting.

2. Experimental section

2.1. Materials

Yttrium chloride hexahydrate ($YCl_3{\cdot}6H_2O$, 99.9%), ytterbium chloride hexahydrate ($YbCl_3{\cdot}6H_2O$, 99.9%), erbium chloride hexahydrate ($ErCl_3{\cdot}6H_2O$, 99.5%), were purchased from Macklin Biochemical Co., Ltd. (Shanghai, China). Oleic acid, sodium hydroxide, ammonium fluoride (NH_4F) and organic solvents were purchased from Sinopharm Chemical Reagent Co., Ltd. (Beijing, China). 1,2-distearoylsn-glycero-3-phosphoethanolamine-N-[methoxy(polyethyleneglycol)-5000] (PEG) was purchased from Creative PEGWorks, Inc. The polyvinyl butyral (PVB) resin was obtained from the Sigma Aldrich. All the chemicals were used without any additional purification unless otherwise mentioned. Deionized water prepared by a Hitech Laboratory Water Purification System DW100 (Shanghai Hitech Instruments Co., Ltd.) was used for all experiments.

2.2. Synthesis of $NaYF_4$: Yb^{3+}/Er^{3+} by STR route

For the synthesis of $NaYF_4$:Yb^{3+}/Er^{3+} nanodispersions in a common STR reactor, 6 mL of NaOH aqueous solution (0.01 mol/mL) was mixed with 40 mL of oleic acid under vigorous stirring, forming oil-water mixture solution A. The solution B which is 22 mL of aqueous solution containing 2.56 mmol of $YCl_3{\cdot}6H_2O$, 0.576 mmol of $YbCl_3{\cdot}6H_2O$, and 0.064 mmol of $ErCl_3{\cdot}6H_2O$, was added into the solution A under vigorous stirring, followed by the addition of 16 mL of solution C (i.e. aqueous solution of NH_4F with concentration of 1 mol/L). After stirring at room temperature for 15 min, the mixed solution was sealed into a Teflon-lined autoclave and heated at 200 °C for 2 h. As the solution cooled to room temperature, the paste of $NaYF_4$:Yb^{3+}/Er^{3+} was collected by centrifugation and washing for 4 times with water and ethanol, respectively. The $NaYF_4$:Yb^{3+}/Er^{3+} nanodispersions were then obtained by re-dispersing the paste in organic solvents (e.g. ethanol, acetone, ethyl acetate, toluene, cyclohexane, etc.) under ultrasonic treatment.

2.3. Synthesis of $NaYF_4$: Yb^{3+}/Er^{3+} by RPB route

In order to investigate the effect of process intensification of high-gravity technology on the preparation of $NaYF_4$:Yb^{3+}/Er^{3+} nanodispersions, a RPB reactor was used to mix the three kinds of formulated solution (solution A, B, and C) instead of mixing them in a STR. The RPB reactor consists of a rotator with stainless packing, two liquid inlets, an outlet, a casing, and a motor, and the detailed setup information on the RPB reactor can be found in our previous work [29]. The dosage and the volume of reactants were the same as those of the STR experiment. The solution A, containing 0.06 mol of NaOH, 6 mL of water, 40 mL of ethanol, and 40 mL of oleic acid, were pumped into RPB reactor through one feed inlet. The solution B (22 mL of aqueous solution containing 2.56 mmol of $YCl_3{\cdot}6H_2O$, 0.576 mmol of $YbCl_3{\cdot}6H_2O$, and 0.064 mmol of $ErCl_3{\cdot}6H_2O$) and solution C (16 mL of 1 mol/L NH_4F aqueous solution) were pumped into the RPB reactor through the other feed inlet. The post hydrothermal process of the RPB route was the same as the STR experiment. In our experiment, we explored the influence of the different high-gravity level on the particle size of the UCNPs nanoparticles by changing the rotation speeds of the RPB from 1000 to 2500 rpm. As calculated by Eq. 1 [28], the high gravity levels (β) of the RPB routed at various rotation speeds (1000, 1500, 2000, and 2500 rpm) were determined to be 70 g, 157 g, 279 g, and 436 g, respectively.

$$\beta = \frac{\omega^2 r}{g} \tag{1}$$

where β is the high gravity level. The ω is he angular speed of the RPB reactor. The r is the geometric average radius of the rotator and g represents the gravitational acceleration speed (i.e. 9.8 m/s^2).

2.4. Phase-transfer of $NaYF_4$: Yb^{3+}/Er^{3+} nanoparticles

The phase-transfer $NaYF_4$:Yb^{3+}/Er^{3+} nanoparticles into aqueous solution was performed by a simple phase inversion method as reported in the previous work with some modifications [30]. Briefly, 2 mL of $NaYF_4$:Yb^{3+}/Er^{3+} nanodispersions in chloroform (10 mg/mL) and 2 mL of PEG solution in chloroform (10 mg/mL) were mixed. The mixture solution was gently heated at 50 °C in a rotary evaporator to evaporate the chloroform. Next, 5 mL of water was added to the solid mass followed by ultrasonic treatment for 5 min. The excess PEG molecules were removed by centrifugal separation and the final product of PEG coated $NaYF_4$:Yb^{3+}/Er^{3+} nanoparticles were re-dispersed in 10 mL of water for further use.

2.5. Characterization

XRD patterns of the samples were measured by a Shimadzu XRD-6000 diffractometer. The FTIR spectra of solid samples were measured by a PerkinElmer spectrum GX Fourier system. The morphology studies of the nanoparticles were performed using a Hitachi H-9500 TEM. The