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Phase-, shape- and size-controlled synthesis of $NaYF_4:Yb^{3+},Er^{3+}$ nanoparticles using rare-earth acetate precursors

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Abstract: Hexagonal-phase $NaYF_4:Yb^{3+},Er^{3+}$ upconversion nanoparticles (UCNPs) with a uniform size distribution were synthesized using rare-earth acetates as precursors. The effects of reaction temperature and time on the phase transition process of the UCNPs were systematically studied. Based on the evolution of particle morphology and phase with temperature and time, it could be concluded that the transition from cubic phase to hexagonal phase for $NaYF_4:Yb^{3+},Er^{3+}$ UCNPs was consistent with a dissolution/recrystallization process. In addition, the shape and size of the UCNPs could be controlled by adjusting the solvent ratio and the precursor ratio, respectively.

Keywords: $NaYF_4:Yb^{3+},Er^{3+}$; chemical synthesis; crystal growth; upconversion luminescence; rare earths

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Over the past few decades, upconversion nanoparticles that can convert a near-infrared (NIR) excitation into a visible emission have attracted considerable attention for their potential applications in various fields including solid-state lasers[1], three-dimensional color displays[2], solar cells[3] and biomedical imaging[4]. As luminescent probes in biomedical field, UCNPs have distinct advantages over the conventionally used fluorescent dyes and quantum dots, such as low autofluorescence background, improved signal-to-noise ratios, high resistance to photobleaching and great penetration depth.

Among various upconversion materials, β-$NaYF_4:Yb^{3+},Er^{3+}$ (hexagonal phase) has been shown to be the most efficient upconversion material. Numerous efforts have been devoted to synthesize high quality β-$NaYF_4:Yb^{3+},Er^{3+}$ UCNPs. For example, Ma et al.[5] and Sun et al.[6] have reported the synthesis of β-$NaYF_4:Yb^{3+},Er^{3+}$ UCNPs with various sizes and morphologies via a hydrothermal or solvothermal method. Unfortunately, these approaches still remain a big challenge in the synthesis of UCNPs with high crystallinity and good monodispersity. Thermo-decomposition of trifluoroacetates precursors is considered to be a promising approach to the preparation of β-$NaYF_4:Yb^{3+},Er^{3+}$ UCNPs with a narrow size distribution and high monodispersity[7,8]. However, a very high reaction temperature is needed (above 330 ºC) for this method to obtain hexagonal-phase nanoparticles, which is very close to the boiling points of the solvents. The narrow reaction temperature window (less than 10 ºC) and the complex decomposition process of trifluoroacetates make the experimental conditions difficult to precisely control. In addition, the decomposition of trifluoroacetates would produce various toxic fluorinated and oxyfluorinated carbon gases, and thus all the experiments must be carefully carried out to avoid the health hazards. Rare-earth acetates are considered to be an excellent alternative of trifluoroacetates for the synthesis of β-$NaYF_4:Yb^{3+},Er^{3+}$ UCNPs without any toxic products or high temperature requirements. A few studies have been reported on the synthesis of β-$NaYF_4:Yb^{3+}$, Er^{3+} UCNPs using rare-earth acetates as precursors[9,10]. However, to the best of our knowledge, the effects of synthesis conditions on the size, shape and phase of $NaYF_4:Yb^{3+},Er^{3+}$ UCNPs have not been systemically studied. The growth mechanism and the relationship between preparation parameters and the size/shape/phase of $NaYF_4:Yb^{3+}$, Er^{3+} UCNPs are not fully understood.

Herein, pure β-$NaYF_4:Yb^{3+},Er^{3+}$ UCNPs were successfully synthesized in high boiling-point solvents using rare-earth acetates as precursors. Effects of the reaction temperature and time on the phase transition of $NaYF_4:Yb^{3+},Er^{3+}$ UCNPs were studied and the growth mechanism was also discussed. In addition, the size and shape control of UCNPs were achieved by changing the precursor ratio and the solvent ratio, respectively.

1 Experimental

All the chemicals, including yttrium(III) acetate hydrate (99.9%), ytterbium(III) acetate tetrahydrate (99.9%),

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erbium(III) acetate hydrate (99.9%), oleic acid (90%), 1-octadecene (90%), ammonium fluoride (99.8%) and sodium hydroxide (99.8%) were purchased from Sigma-Aldrich and used without further purification. NaYF$_4$:Yb^{3+},Er^{3+} UCNPs were synthesized using a modification of a previously reported procedure[9].

In a typical synthesis of NaYF$_4$:Yb^{3+},Er^{3+} UCNPs, 1 mmol rare-earth acetates (Y/Yb/Er=78:20:2) with 6 mL of oleic acid (OA) and 15 mL of 1-octadecene (ODE) were added to a 100 mL flask to form a mixed solution under vigorous stirring. The solution was heated to 100 ºC for 30 min and then cooled to 50 ºC. A solution of 4 mmol of NH$_4$F and 2.5 mmol of NaOH in 20 mL of methanol was added, and kept at 50 ºC for 30 min. After methanol was evaporated, the solution was heated to 300 ºC under an argon atmosphere for 90 min and then cooled to room temperature. The nanoparticles were precipitated by the addition of ethanol and isolated via centrifugation. UCNPs of different sizes, morphologies and structures were synthesized following the similar procedures by varying the experimental conditions such as reaction temperature (280–310 ºC), time (0–90 min), the components of solvent and the amount of NH$_4$F. When an experimental parameter was changed, all the other parameters remained the same as the typical synthesis.

Powder X-ray diffraction (XRD) was performed on a Shimadzu XD-3A X-ray diffractometer equipped with a Cu Kα radiation. The particle morphology was recorded on a Tecnai G2 transmission electron microscope (TEM). The upconversion luminescence (UCL) spectra were obtained by a Hitachi F-7000 fluorescence spectrophotometer using a commercial 980 nm NIR laser as the excitation source.

2 Results and discussion

2.1 Effects of reaction temperature

Fig. 1 shows TEM images and XRD patterns of NaYF$_4$:Yb^{3+},Er^{3+} UCNPs synthesized at different temperatures. In the synthesis, the reagents Ln(CH$_3$COO)$_3$ (Ln=Y, Yb, Er) were first dissolved in mixed OA/ODE at 100 ºC to form a transparent solution and then the solution was cooled down to 50 ºC. After the NH$_4$F and NaOH were added into the solution, the reaction started immediately and a yellow turbid solution was formed. The TEM analysis shows that at 50 ºC quite small nanoparticles were formed in the solution (Fig. 1(a)). The polycrystalline diffraction rings in their SAED (selected area electron diffraction) pattern (Fig. 1(a)) could be indexed to an α-NaYF$_4$ (cubic phase) crystal structure, which was further confirmed by the XRD pattern (Fig. 1(b)). When the reaction temperature was increased to 280 ºC and kept for 90 min, nanoparticles with a bigger size were produced. The XRD pattern reveals that the as-prepared UCNPs were still of pure cubic phase, which means that there is no change in crystal structure from 50 to 280 ºC. When the reaction was carried out at 290 ºC, the as-obtained samples were not uniform in size distribution and consisted of spherical nanoparticles and irregular-shape nanoparticles. The high-resolution TEM (HRTEM) and XRD analysis indicate that spherical nanoparticles were hexagonal phase and irregular nanoparticles were cubic phase. At 295 ºC, the amount of irregular nanoparticles (cubic phase) obviously decreased and simultaneously that of spherical nanoparticles (hexagonal phase) increased (Fig. 1(a)). SAED and XRD patterns show that pure β-NaYF$_4$:Yb^{3+}, Er^{3+} UCNPs were obtained at 300 ºC, and no cubic-phase UCNPs could be observed (Fig. 1(a) and (b)). The spherical UCNPs were uniform in size distribution with a diameter of 26 nm. Further elevating the reaction temperature to 305 ºC, the size of UCNPs increased to 34 nm in diameter (Fig. 1(a) and the crystallinity was also improved (Fig. 1(b)).

2.2 Effects of reaction time

Fig. 2 presents TEM images and XRD patterns of

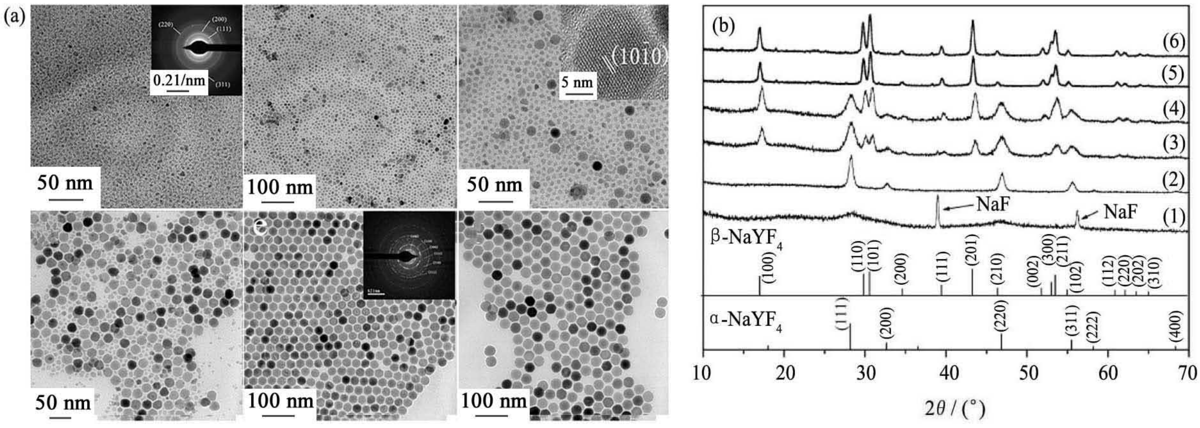

Fig. 1 (a) TEM image of the UCNPs synthesized at different reaction temperatures (1) 50 ºC for 30 min, Inset: corresponding SAED pattern; (2) 280 ºC for 90 min; (3) 290 ºC for 90 min, Inset: corresponding HRTEM image of the spherical nanoparticles; (4) 295 ºC for 90 min; (5) 300 ºC for 90 min, Inset: corresponding SAED pattern; (6) 305 ºC for 90 min, and (b) corresponding XRD patterns (Other synthesis conditions: 6 mL OA/15 mL ODE, NH$_4$F-to-Ln^{3+} ratio of 2.5)