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Synthesis of $\text{NaYF}_4:\text{Yb}^{3+}$, Er^{3+} upconversion nanoparticles in normal microemulsions

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Abstract

An interface-controlled reaction in normal microemulsions (water/ethanol/sodium oleate/oleic acid/*n*-hexane) was designed to prepare $\text{NaYF}_4:\text{Yb}^{3+}$, Er^{3+} upconversion nanoparticles. The phase diagram of the system was first studied to obtain the appropriate oil-in-water microemulsions. Transmission electron microscopy and X-ray powder diffractometer measurements revealed that the as-prepared nanoparticles were spherical, monodisperse with a uniform size of 20 nm, and of cubic phase with good crystallinity. Furthermore, these nanoparticles have good dispersibility in nonpolar organic solvents and exhibit visible upconversion luminescence of orange color under continuous excitation at 980 nm. Then, a thermal treatment for the products was found to enhance the luminescence intensity. In addition, because of its inherent merit in high yielding and being economical, this synthetic method could be utilized for preparation of the UCNPs on a large scale.

Introduction

The synthesis and spectroscopy of $\text{NaYF}_4:\text{Yb}^{3+}$, Er^{3+} upconversion nanoparticles (UCNPs) have attracted a tremendous amount of attention because of their potential use in bioanalysis and medical imaging recently [1-5]. Upconversion was first recognized and formulated by Auzel in the mid-1960s [6], which is a process where low energy light, usually near-infrared (NIR) or infrared (IR), is converted to higher energies, ultraviolet (UV) or visible, via multiple absorptions or energy transfers. Up to now, several synthetic paths have been reported to obtain UCNPs, such as co-precipitation [2], hydrothermal, or solvothermal processing [7-11], liquid-solid two-phase approach [12], co-thermolysis of trifluoroacetate [13-17], decomposition of carbonate [18], diffusion-limited growth [19], and ionic liquid-assisted technique [20].

It is known that an important prerequisite for the applications of UCNPs is the availability of small and monodisperse nanoparticles [1]. Recently, the synthesis of various inorganic nanoparticles in normal microemulsions attracts our attention [21]. In the normal microemulsions, reactions are taking place at the interface of the normal micelles. Owing to the polarity inverse caused by the neutralization, the particles can be

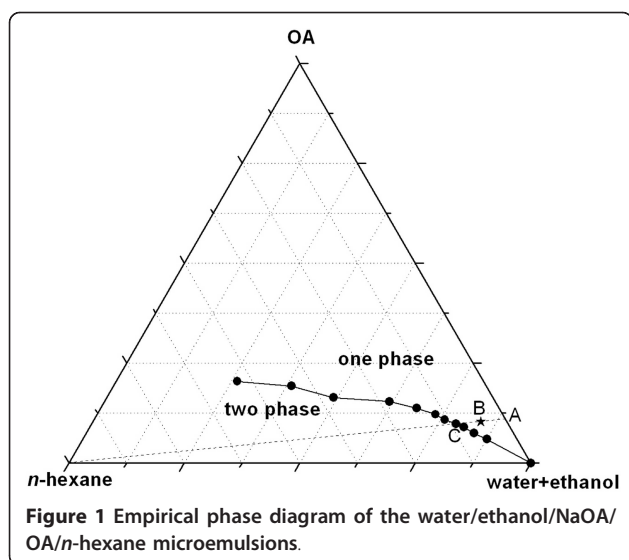
transferred from water phase to the oil phase. However, to the best of our knowledge, there is no study about the synthesis of $\text{NaYF}_4:\text{Yb}^{3+}$, Er^{3+} UCNPs by this method. Therefore, we designed an oil/water interface-controlled reaction in normal microemulsions (water/surfactant/*n*-hexane) to produce $\text{NaYF}_4:\text{Yb}^{3+}$, Er^{3+} UCNPs. The products are small, monodisperse, and high-yielding. They show good dispersibility in nonpolar organic solvents and emit visible upconversion luminescence under 980 nm excitation. Moreover, this synthetic strategy is very facile and less costly, which could be applied to mass-production.

Results and discussion

First, the phase behavior of the system was studied to obtain the appropriate microemulsions. Figure 1 shows the empirical phase diagram of the water/ethanol/sodium oleate (NaOA)/oleic acid (OA)/*n*-hexane mixtures at 298 K. Because of the complexity of the five-component system, the phase diagram was simplified to a ternary phase diagram, which is composed of total OA (including the part to generate NaOA with sodium hydroxide), water plus ethanol, and *n*-hexane. The composition is described using volume fractions. The water/ethanol ratio is always 1:1. The NaOA/OA molar ratio is always 2:3, and the total volume of OA is considered as the surfactant volume. The phase diagram is determined by gradual addition of *n*-hexane to a one-phase

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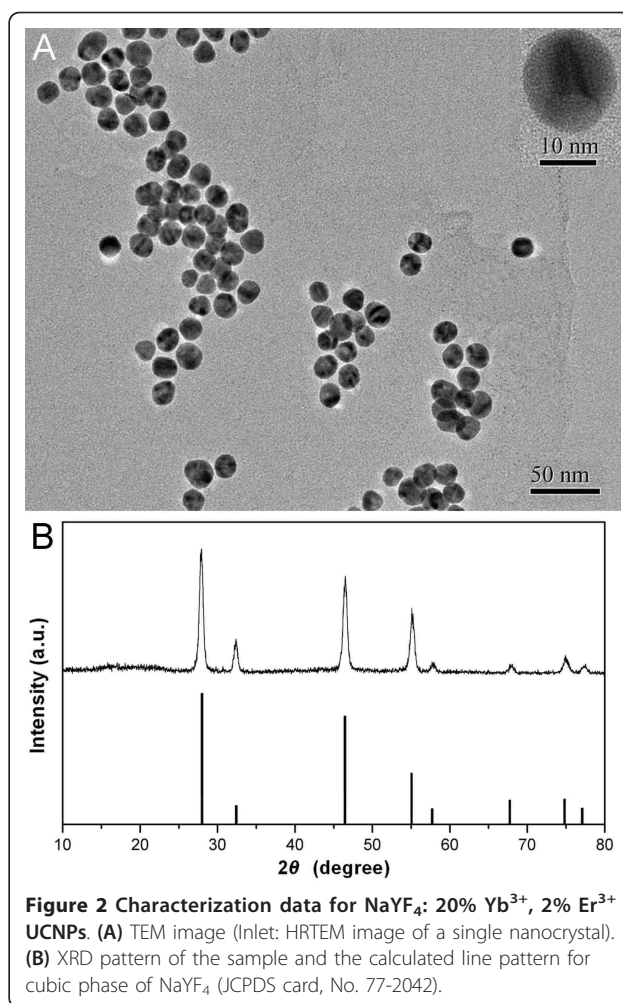


water/ethanol/NaOA/OA mixture with a constant volume fraction. For example, we begin from point A, and reach a critical point C where the solution starts showing a two-phase character.

The result shows that the one-phase/two-phase envelope extends from the point at 100% water plus ethanol to the point at 26.23% water plus ethanol, 20.45% OA, and 53.32% *n*-hexane, and the two-phase part is located in the lower OA region. Obviously, with an increase of the ratio of OA/(water plus ethanol), more *n*-hexane can be dissolved into their mixtures to form a stable system. The actual point (point B) we used is located in the right-bottom region, where the oil-in-water microemulsions are formed.

Figure 2 shows the characterization data for the NaYF₄:20% Yb³⁺, 2% Er³⁺ sample. The TEM image (Figure 2A) demonstrates that the synthesized particles are roughly spherical, monodisperse with the size uniformity of about 20 nm in diameter. The X-ray powder diffractometer (XRD) pattern (Figure 2B) shows well-defined peaks, indicating the high crystallinity of the synthesized material, and the peak positions and intensities from the experimental XRD pattern match closely with the calculated pattern for cubic phase of NaYF₄ (JCPDS card, No. 77-2042). From the line broadening of the diffraction peaks, the crystallite size of the sample was determined to be approximately 18 nm using the Debye-Scherrer formula, which corresponds to the particle size determined from the TEM result.

The NaYF₄:Yb³⁺, Er³⁺ UCNPs can easily be dispersed in nonpolar solvents (such as *n*-hexane, cyclohexane) to form homogenous colloidal solutions. Figure 3A shows images of a 1 wt.% solution of NaYF₄:20% Yb³⁺, 2% Er³⁺ UCNPs in *n*-hexane, demonstrating its transparency. The visible upconversion luminescence can be observed



when the solution is excited at 980 nm with a power density of 1.2 kW/cm² (Figure 3B). The corresponding upconversion luminescence spectrum is also shown in Figure 3C. There are three major emission bands at 520-530 nm (green light), 540-550 nm (green light), and 650-670 nm (red light), which are assigned to the ²H_{11/2} to ⁴I_{15/2}, ⁴S_{3/2} to ⁴I_{15/2}, and ⁴F_{9/2} to ⁴I_{15/2} transitions of Er³⁺ ion, respectively. Under 980 nm excitation, the absorption of the first photon can elevate Yb³⁺ ion to the ²F_{5/2} level from ground state, and then it can transfer the energy to the Er³⁺ ion. This energy transfer can promote Er³⁺ ion from ⁴I_{15/2} level to the ⁴I_{11/2} level and from the ⁴I_{11/2} level to the ⁴F_{7/2} by another energy transfer upconversion process (or a second 980 nm photon) if the ⁴I_{11/2} level is already populated. Then, the Er³⁺ ion can relax nonradiatively to the ²H_{11/2} and ⁴S_{3/2} levels, and the green emissions occur (²H_{11/2} → ⁴I_{15/2} and ⁴S_{3/2} → ⁴I_{15/2}). Alternatively, the ion can further relax and populate the ⁴F_{9/2} level leading to the red emission (⁴F_{9/2} → ⁴I_{15/2}) [8,22]. The curve also shows that red emissions are much stronger than green

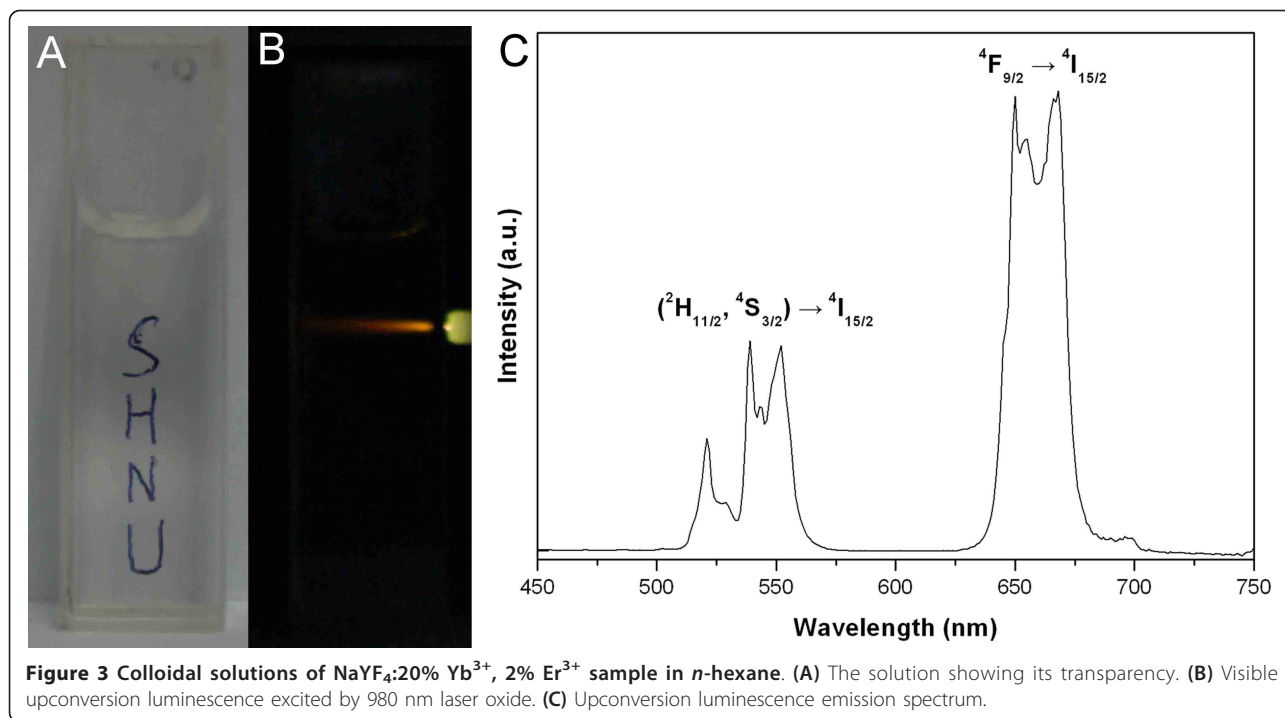


Figure 3 Colloidal solutions of $\text{NaYF}_4:20\% \text{Yb}^{3+}$, $2\% \text{Er}^{3+}$ sample in *n*-hexane. (A) The solution showing its transparency. (B) Visible upconversion luminescence excited by 980 nm laser oxide. (C) Upconversion luminescence emission spectrum.

emissions, so the products present light of orange color on the whole (Figure 3B).

It is noted that the as-prepared nanoparticles are cubic phase, whose fluorescence efficiency is at least one-order of magnitude less than that of the hexagonal phase [8]. A thermal treatment at ca. 400-600°C was reported to transform the cubic phase to the hexagonal phase, but which led to undesirable particle growth and agglomeration [2]. We carried out the annealing of the as-prepared nanoparticles under N_2 atmosphere by heating them to 600°C, and maintaining this temperature for 5 h. After annealing, the particles aggregated into larger clusters (Figure 4A), and the XRD pattern (Figure 4B) shows that hexagonal $\text{NaYF}_4:\text{Yb}^{3+}$, Er^{3+} phase emerged in addition to the already existing cubic pattern (marked with asterisks), which implies that the particles transformed partially from cubic phase to hexagonal phase by annealing. In addition, upconversion luminescence emission spectrum (Figure 5) was obtained after ultrasonic dispersion of a 1 wt.% solution of the products in *n*-hexane, compared with the spectrum of nanoparticles before annealing, its green emission plays a dominant role, and the overall emissions are much stronger than those for cubic phase products.

Conclusions

In summary, we designed a method of normal microemulsions to prepare $\text{NaYF}_4:\text{Yb}^{3+}$, Er^{3+} UCNPs, which are small, monodisperse, and have good dispersibility in nonpolar organic solvents. Besides, the products

exhibited visible upconversion luminescence under 980 nm excitation and a thermal treatment was proved to be able to strengthen the luminescence intensity. This method has its inherent merit in high yielding and being economical. Further study is currently underway to functionalize these synthesized UCNPs for their applications in biolabel and medical imaging.

Materials and methods

All reagents used in this study, including sodium hydroxide, oleic acid, ethanol, *n*-hexane, sodium fluoride, and $\text{Ln}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ($\text{Ln} = \text{Y}$, Yb , and Er , 99.99%) salt, were of analytical grade from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). These chemicals were used without further purification. Water used in the experiment was double distilled.

In a typical synthetic route, sodium hydroxide (400 mg) was dissolved in a mixture of water (20 mL) and ethanol (30 mL), followed by the addition of oleic acid (7.4 mL) and *n*-hexane (4 mL); this formed a bright yellow transparent solution. Then, two separate aqueous solutions (5 mL) of $\text{Ln}(\text{NO}_3)_3$ (0.8 mmol, $\text{Y}:\text{Yb}:\text{Er} = 78:20:2$) and sodium fluoride (3.2 mmol) were added to the above microemulsions one after the other with vigorous stirring. Then, the solution was transferred to a Teflon-lined stainless steel autoclave and heated at 180°C for 6 h. When the autoclave was cooled down to room temperature, the products were found deposited at the bottom. Then, *n*-hexane (30 mL) was added to destroy the one-phase solution and form a two-phase

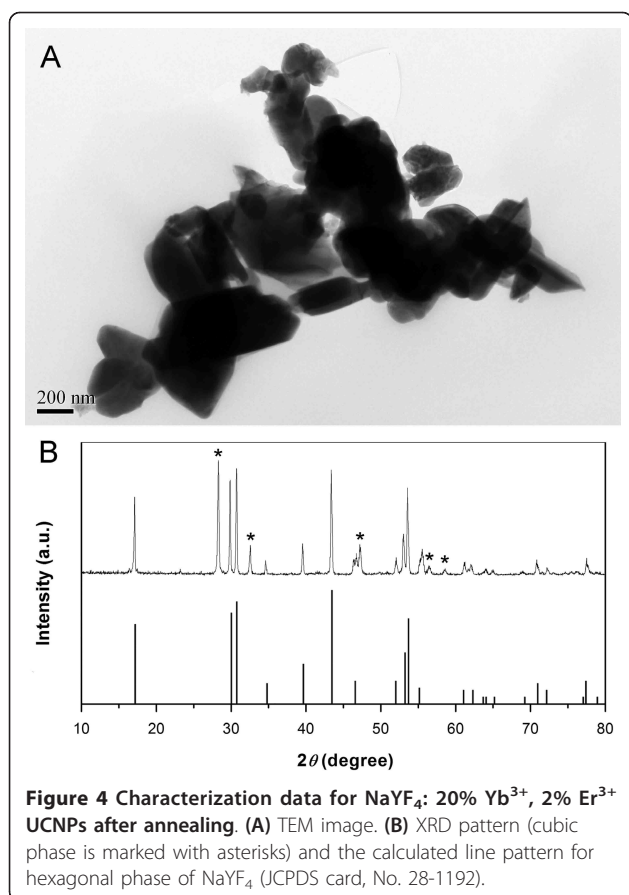


Figure 4 Characterization data for NaYF₄: 20% Yb³⁺, 2% Er³⁺ UCNPs after annealing. (A) TEM image. (B) XRD pattern (cubic phase is marked with asterisks) and the calculated line pattern for hexagonal phase of NaYF₄ (JCPDS card, No. 28-1192).

mixture, so the hydrophobic colloidal NaYF₄:20% Yb³⁺, 2% Er³⁺ UCNPs were extracted into the upper layer (*n*-hexane region). With precipitation by additional ethanol, and highspeed centrifugation, the white products (yield: 85%) were re-dispersed in *n*-hexane to bring out a transparent colloidal solution.

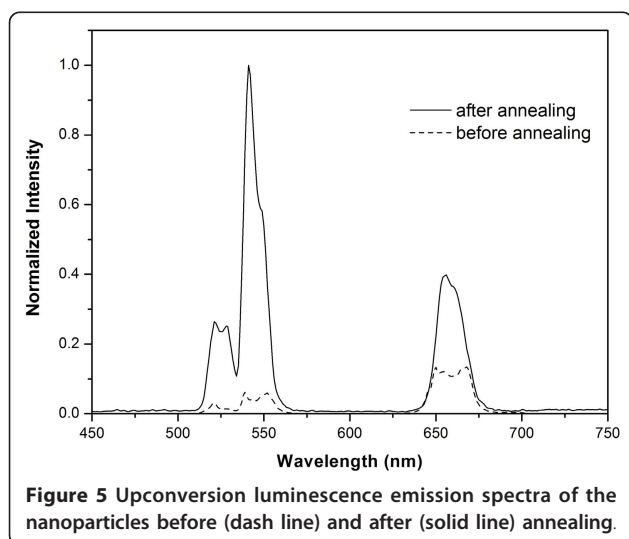


Figure 5 Upconversion luminescence emission spectra of the nanoparticles before (dash line) and after (solid line) annealing.

The structure and morphology of NaYF₄:20% Yb³⁺, 2% Er³⁺ UCNPs were characterized by XRD and TEM. The obtained samples were characterized by XRD using a Bruker D8-advance X-ray diffractometer with Cu_{Kα} radiation ($\lambda = 1.5418 \text{ \AA}$). The low- and high-resolution transmission electron microscopy (HRTEM) was performed on a JEOL JEM-3010 electron microscope operated at 300 kV. The upconversion emission spectra of NaYF₄:20% Yb³⁺, 2% Er³⁺ UCNPs were acquired using a Jobin-Yvon Fluorolog-3 fluorescence spectrometer system equipped with an external 0-1300 mW adjustable laser (980 nm, Beijing Hi-Tech Optoelectronic Co., China) as the excitation source, instead of the Xenon source in the spectrophotometer, and with an optic fiber accessory.

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Authors' contributions

SNS and XYW carried out the phase diagram studies. SNS participate in the sequence studies and drafted the manuscript. NJQ conceived of the study, and participated in its design and coordination and helped to draft and revise the manuscript.

Competing interests

The authors declare that they have no competing interests.

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