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A general strategy to fabricate ligand-free water-soluble up-conversion nanoparticles

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A B S T R A C T

It is a generally accepted method to synthesize the monodisperse $NaYF_4$:Yb^{3+}, Er^{3+} with uniform size and shape by using oleic acid (OA) as surfactant or solvent. However, the obtained oleate-capped up-conversion nanoparticles $NaYF_4$:Yb^{3+}, Er^{3+} (Ln-UCNPs, Ln = Yb^{3+}, Er^{3+}) have inherent hydrophobia properties, which should be processed by complicated post-treatments to render them water dispersible before used in biomedicine. Herein, we introduce a facile approach, ultrasonic separation, to obtain water-soluble and ligand-free Ln-UCNPs by analyzing the capping effect between Ln^{3+} and the carboxy group of oleate anions. After ultrasonic separation, the ligand-free of Ln-UCNPs disperse in water and ethanol easily, which are characterized by transmission electron microscopy (TEM), fourier transform infrared spectroscopy (FTIR), thermogravimetric analyses (TGA), nuclear magnetic resonance (NMR) and zeta potential. The experiments demonstrate that the present method is simple and effective to remove oleate layers from the surface of $NaYF_4$:Yb^{3+}, Er^{3+}, and worthy of being generalized.

1. Introduction

Up-conversion nanoparticles (UCNPs) have attracted more attention in recent years, and because of their unique 4f or 5f electron structure, some nanocrystals are doped with the rare-earth activator ions Er^{3+}, Tm^{3+} and Ho^{3+} exhibit upconversion luminescence (UCL) [1], which allows application in solid-state lasers [2], optical-fiber-based telecommunications [3], lamps for illumination [3], flat-panel displays [2,4], optical storage [5], increasing the conversion efficiency of photovoltaic cells [6], and especially in biomedical applications such as biosensing and multitargeting, or diagnostics [7–10]. Being excited by near-infrared (NIR) light, UCNPs demonstrate special advantages such as high chemical stability, low toxicity, the avoidance of autofluorescence from biological samples [11], deep tissue penetration and no photobleaching [7,12]. $NaYF_4$:Yb^{3+}, Er^{3+} is the most famous one of the UCNPs materials, which has been accepted as one of the most promising classes of luminescent labels for bioimaging in vitro and in vivo [13,14]. Acting as bioimaging agents, the UCNPs also require uniform size (normally less than 100 nm considering penetrating membranes) and shape, high crystallinity and water-soluble properties. In order to achieve the above applications, we can run two aspects: the first is to obtain the high quality UCNPs with ideal size and shape by the controlling synthesis protocol precisely; the second is that the as-prepared UCNPs should disperse into water easily.

To date, hydrothermal synthesis, solvothermal method and co-thermolysis are considered as the efficient approaches for the fabrication of the ideal size and shape of $NaYF_4$:Yb^{3+}, Er^{3+} nanoparticles (NPs) after numerous efforts in devoting to the exploration of controlling synthesis of $NaYF_4$:Yb^{3+}, Er^{3+} by scientists. Organic molecules, especially OA are known to either promote or inhibit crystal growth through modifying crystal growth dynamically. So, the use of organic additives or organic media as the controller of shape and size is a popular strategy to fabricate the desired products. However, the as-prepared $NaYF_4$:Yb^{3+}, Er^{3+} NPs are hydrophobic due to the OA-coating on the surface. It is well known that the biological fluids are aqueous solution. So, for these NPs to be used as bio-labeling, they must be dispersible and colloidally stable in biological media while at the same time they retain their high efficiencies. In order to meet the biomedical application, the subsequence complicated surface modifications are required, such as polymer capping [15], surface silanization [16], OA-capped $NaYF_4$:Yb^{3+}, Er^{3+} NPs coating by hydrophilic group [14,17], ligand exchange [18], ligand oxidation [19–21], and hydrochloric acid [22]. All of the post-treatments are time-consuming and may lead to aggregation. Given this, many ways for improvements are attempted to obtain OA-free $NaYF_4$:Yb^{3+}, Er^{3+} NPs directly, and

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eventually some water-soluble $NaYF_4:Yb^{3+}$, Er^{3+} NPs have been obtained by using a water-soluble ligand or polymer as a surfactant instead of OA [23–27]. However, the as-prepared $NaYF_4:Yb^{3+}$, Er^{3+} NPs synthesized by these methods always show irregular shape and size. So, it is imperative to explore an safe, simple and cost-effective approach to obtain water-soluble uniform $NaYF_4:Yb^{3+}$, Er^{3+} NPs.

It is known that the surface of $NaYF_4:Yb^{3+}$, Er^{3+} NPs synthesized using OA as surfactant exists in a fair amount of electron-poor metal atoms Y, which can coordinate with the carboxy groups of oleate anions. The capping effect of oleate falls in between chemical absorption and physical absorption, which can be broken by high power external force. Herein, we report a simple and easily-operated physical method, ultrasonic separation, to remove the oleate ligand from the surface of oleate-capped $NaYF_4:Yb^{3+}$, Er^{3+} NPs.

2. Experimental section

All of the commercially available reagents are purchased and unpurified. Rare-earth oxide (Y_2O_3, Yb_2O_3, Er_2O_3, 99.9%, Sigma), OA (90%, Sigma), 1-octadecene (ODE, >90%, Sigma), absolute ethanol (>99.5%, Sigma), cyclohexane (>90%, Sigma), and rare earth chlorides ($LnCl_3·6H_2O$, Ln = Y, Yb, Er, Y:Yb:Er = 80:18:2 in molar ratio) are prepared by ourselves.

2.1. Synthesis of oleate-capped $NaYF_4:Yb^{3+}$, Er^{3+} NPs

In this initial step 0.212 g of $LnCl_3$ (Ln = Y, Yb, Er, Y:Yb:Er = 80:18:2 in molar ratio) is weighed and added to a mixed solution of 6 ml OA and 15 ml ODE in a 50 ml flask. The mixture is stirred and heated to 160 °C to form a homogeneous solution, and then is cooled to room temperature. Then 10 ml of methanol solution containing NaOH (0.1 g) and NH_4F (0.148 g) is slowly added into the flask and stirred for 30 min. Subsequently, the solution is slowly heated to remove methanol, degassed at 100 °C for 10 min, and then heated to 325 °C at a rate of 20 °C/min and maintains at this temperature for 60–120 min under argon protection. After the solution has cooled naturally to room temperature, nanocrystals are centrifuged from the solution with ethanol. The nanocrystals are precipitated without any size selection and washed several times with ethanol/cyclohexane (v/v = 1:1), and can be easily re-dispersed in various nonpolar organic solvents (e.g., hexane, cyclohexane, toluene).

2.2. Synthesis of ligand-free Ln-UCNPs

In the typical experiment, the as-prepared nanocrystals solutions of cyclohexane (3 mg/mL) are treated with high power sonication (400 W) for 20 min, and then separated to get the precipitation by centrifuge. The ligand-free NaYF4:Yb, Er NPs are obtained after the above repeated operations three times, which are dispersed in ethanol and water easily.

2.3. Characterization

X-ray diffraction: The samples are characterized by X-ray powder diffractometer (XRD) through using a Brucker D8-advance X-ray Diffractometer with Cu Kα radiation (λ = 1.5418 Å), the operation voltage and current are respectively 40 kV and 40 mA. The 2θ range scan is swept from 10° to 70° in 0.02° steps with a count time of 0.2 s.

TEM: Particle sizes and shapes are characterized by transmission electron microscopy (TEM) (JEOL, 100CX, Japan). Samples are prepared by drying a drop of nanocrystal dispersion in cyclohexane/toluene (1/1) or ethanol on amorphous carbon coated copper grids.

TGA: Thermogravimetric analyses are recorded on a TA Instrument SDT 2960 simultaneous DTA–TGA at the heating rate of 10 °C/min under N_2.

FTIR: The IR spectrum is obtained by using Brucker TENSOR Infrared Spectrometer.

NMR: The NMR measurement is carried out on Bruker BioSpin GmbH spectrometer.

Emission spectra: The UC emission spectra are measured by using a self-regulating spectrophotometer and a pulsed 980 nm laser as the excitation source.

Zeta-potential: The zeta potential measurements are carried out on a Zeta PALS zeta potential analyzer (Brookhaven Instruments Corporation) at room temperature.

3. Results and discussion

In a typical investigation, the as-prepared 40 nm $NaYF_4:Yb^{3+}$, Er^{3+} NPs is employed as an example. Fig. 1 shows the XRD spectra and TEM images of as-prepared $NaYF_4:Yb^{3+}$, Er^{3+} NPs and OA-free $NaYF_4:Yb^{3+}$, Er^{3+} NPs, respectively. As can be seen, the XRD spectra (Fig. 1A) indicate that the as-prepared $NaYF_4:Yb^{3+}$, Er^{3+} NPs crystallize with the β-phase of $NaYF_4$ (all of the diffraction peaks are lined with the data of JCPDS No. 16-0334). The calculated size of the

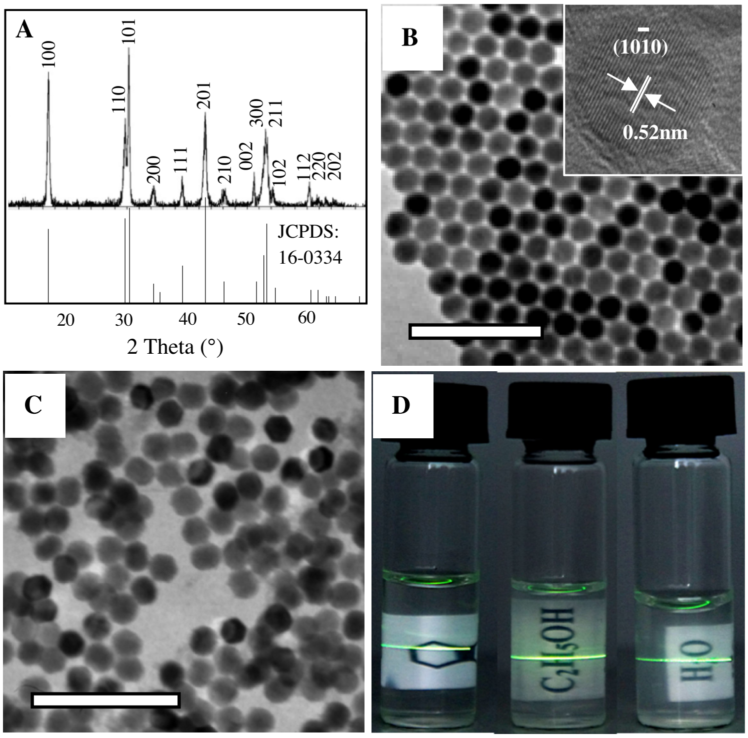

Fig. 1. XRD pattern, TEM and digital images of Ln-UCNPs. (A) XRD of as-prepared Ln-UCNPs, (B) and (C) are the TEM images of OA-capped Ln-UCNPs, OA-free Ln-UCNPs dispersed into cyclohexane, ethanol, respectively and (D) is the digital pictures of OA-capped Ln-UCNPs dispersed into cyclohexane, OA-free Ln-UCNPs dispersed into ethanol and deionized water, respectively. The scale bar is 200 nm.