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Research Article

A User-Friendly Method for Synthesizing High-Quality $NaYF_4$:Yb,Er(Tm) Nanocrystals in Liquid Paraffin

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Application of "green chemistry" concept to synthesize nanomaterials is the current goal in developing new techniques for producing materials in commercial scale. In this study, we reported a low-cost and convenient method for synthesizing high-quality $NaYF_4$:Yb,Er(Tm) nanocrystals (NCs) in liquid paraffin. Experimental results indicated that the as-prepared NCs possessed pure β-phase structure, narrow size distribution, as well as strong up-conversion fluorescence. By varying the doped lanthanides, Er or Tm, the emission color of up-conversion fluorescence was tunable. In comparison to other high-boiling-point organic solvents, liquid paraffin is cheaper and prolific in oil industry. Besides, 280°C was the optimal temperature for $NaYF_4$:Yb,Er(Tm) synthesis, which was lower than that in the previous reports using other high-boiling-point organic solvents. Accordingly, this user-friendly method will facilitate the synthesis of high-quality lanthanide-doped $NaYF_4$ NCs in commercial scale.

1. Introduction

During the past decade, significant attentions have been paid on up-conversion luminescent nanocrystals (NCs) owning to their unique property, which absorbs two or more lower energy exciting photons but emits one higher energy photon [1–4]. In contrast, conventional down-conversion organic dyes and quantum dots emit only through adsorbing higher energy exciting photon [5, 6]. Consequently, it is capable for up-conversion NCs to generate visible emission by near-IR (NIR) excitation. This property makes them applicable both in academic studies and technical applications, such as solid lasers, light emitting devices, bio-labeling, biological assays, high throughout screening, and low intensity IR imaging [1–5, 7]. In addition, due to the atomic like emissions, up-conversion NCs usually possess sharp luminescence bands and immunize to photo-bleaching [8–11]. Furthermore, NIR exciting sources are cheaper and easier to obtain in comparison to UV-visible ones [12]. These advantages make up-conversion NCs become alternatives to organic dyes and quantum dots, especially in biological applications [1, 13–17].

Among various up-conversion NCs, lanthanide-doped $NaYF_4$, such as Yb/Er or Yb/Tm codoped $NaYF_4$, is becoming the focus, because $NaYF_4$ host materials have low vibrational energy, low nonradiative decay rate, and high radiative emission rate, which are the prerequisites to achieve high luminescence [18–20]. To date, lanthanide-doped $NaYF_4$ NCs are prepared mainly via colloidal chemistry routes, including coprecipitation, thermal decomposition, hydrothermal, or solvothermal synthesis, and sol-gel processing [4, 5, 21–24]. The thermal decomposition strategy is the most successful method for synthesizing high-quality NCs, represented by the highly crystalline phase and narrow size distribution of the products [3, 25]. Since a separated nucleation and growth of NCs is achievable just through manipulating the reaction temperature, it further allows for controlling NC size, shape, as well as crystal structure [26–28]. However, the raw materials used in thermal decomposition method are expensive and air-sensitive, and the synthesis is operated at high temperature, such as at 320°C and generates toxic by-product [25, 29, 30]. For the synthesis of NCs in commercial scale, it requires to develop synthetic techniques close to "green chemistry" concept, such as using environment- and

user-friendly solvents, saving energy, and avoiding waste [31].

In this study, we demonstrated a nearly "green chemistry" and mild method for synthesizing high-quality $NaYF_4$:Yb,Er(Tm) NCs with pure β-phase crystal structure. A cheap and user-friendly solvent of liquid paraffin was chosen as the reaction medium. The as-prepared NCs exhibited strong NIR-to-visible up-conversion luminescence, which was tunable by varying the codoped lanthanides. Besides, experimental result indicated that 280°C was the optimal temperature for $NaYF_4$:Yb,Er(Tm) synthesis, lower than that in the previous reports using other high-boiling-point organic solvents.

2. Materials and Methods

2.1. Materials. Sodium hydroxide (NaOH), ammonium fluoride (NH_4F), ethanol, methanol, oleic acid (OA, technical grade, 90%), liquid paraffin, yttrium chloride hexahydrate ($YCl_3 \cdot 6H_2O$, 99.9%), ytterbium chloride hexahydrate ($YbCl_3 \cdot 6H_2O$, 99.99%), erbium chloride hexahydrate ($ErCl_3 \cdot 6H_2O$, 99.9%), and thulium chloride hexahydrate ($TmCl_3 \cdot 6H_2O$, 99.9%) were all commercial products and used as received.

2.2. Synthesis of $NaYF_4$:Yb,Er(Tm) NCs. $NaYF_4$:18%Yb, 2%Er NCs were synthesized following this project: $YCl_3 \cdot 6H_2O$ (0.2420 g), $YbCl_3 \cdot 6H_2O$ (0.0700 g), and $ErCl_3 \cdot 6H_2O$ (0.0076 g) were mixed with 6 ml OA and 15 ml liquid paraffin in a 100 mL three-necked flask and degassed at 100°C for 1 h under vacuum. After cooled down to room temperature, a solution of NaOH (0.1 g) and NH_4F (0.148 g) in 10 ml methanol was added and the mixture was degassed at 100°C for 30 min again under vacuum. With the protection of N_2, the mixture was gradually heated to 280°C and kept at this temperature for 1 h under vigorous magnetic stirring. Then the products were precipitated through the addition of ethanol and washed with ethanol/water (1 : 1 v/v) for three times at room temperature. Finally, the resultant mixture was separated by centrifugation, and the precipitates were collected without any size-selection process. The resultant NCs were redispersible in various nonpolar solvents, such as hexane and toluene. Following a similar procedure, except using $TmCl_3 \cdot 6H_2O$ instead of $ErCl_3 \cdot 6H_2O$, $NaYF_4$:Yb,Tm NCs were synthesized.

2.3. Characterization. Transmission electron microscopy (TEM) was conducted using a Hitachi H-800 electron microscope at an acceleration voltage of 200 kV with a CCD camera. High-resolution TEM (HRTEM) imaging was implemented by a JEM-2100F electron microscope at 300 kV. X-ray powder diffraction (XRD) investigation was carried out by using Siemens D5005 diffractometer. Up-conversion fluorescence spectra were performed with a Hitachi F-4500 fluorescence spectrophotometer with a 980 nm laser at room temperature.

3. Results and Discussion

In our method, liquid paraffin was used as the reaction medium for synthesizing $NaYF_4$:Yb,Er NCs. Figures 1(a) and 1(b) showed the TEM images of the as-prepared $NaYF_4$:Yb,Er NCs. Under TEM, isolated NCs with spherical morphology were observed, which suggested that the adsorption of the capping ligand of oleic acid on the crystal surface prevented the further aggregation of $NaYF_4$ toward macroscopic crystals, leading to the formation of NCs. NCs also possessed very narrow size distribution with an average diameter of 30 nm and the deviation less than 5%. HRTEM image indicated that the NCs were single crystal, with an interplanar distance of 0.52 nm (Figure 1(c)), which was consistent with the (100) plane of β-phase $NaYF_4$ bulk crystals (viz. 0.516 nm) [32]. The selected area electron diffraction pattern exhibited a series of diffraction rings, which was consistent with the (100), (110), (111), (201), (311), and (321) planes of β-phase $NaYF_4$ (Figure 1(d)) [2, 32, 33]. Furthermore, as shown in Figure 1(e), the XRD peak positions and relative intensities of the as-prepared NCs were well agreed with the corresponding values of β-phase $NaYF_4$ (JCPDS standard card no.028-1192) [30, 32–35].

The as-prepared NCs could be facilely separated from liquid paraffin by centrifugation and redispersible in nonpolar solvents, such as hexane and toluene, making it possible for spectral characterization. Figure 2 showed the up-conversion fluorescence spectrum of a hexane solution with 1wt% $NaYF_4$:Yb,Er NCs, which was excited by 980 nm NIR laser. Four emission peaks, respectively at 408, 520, 539, and 651 nm, were observed. These emissions were generated by the transitions between the energy levels $^4H_{9/2}$, $^4H_{11/2}$, $^4S_{3/2}$, and $^4F_{9/2}$ to $^4I_{15/2}$ of Er^{3+} (Figure 3) [1, 20, 36]. In this context, the transition between $^4S_{3/2}$ and $^4I_{15/2}$ was the strongest, corresponding to the 539 nm emission. As a result, the solution of $NaYF_4$:Yb,Er NCs presented a green emission under 980 nm excitation (Figure 2 inset). Note that the generation of the emission related to an up-conversion mechanism, namely, absorbing two 980 nm photons but emitting one higher energy photon. The efficiency of up-conversion fluorescence strongly depended on the crystal phase of the NCs. As reported previously, $NaYF_4$:Yb,Er NCs had two different crystal phases, α-phase and β-phase. The up-conversion efficiency of β-phase is greatly stronger than that of α-phase. In the current synthesis, moreover, the as-prepared NCs possessed a pure β-phase (Figure 1(e)), leading to the strong up-conversion fluorescence [37]. Overall, the highly crystalline structure, narrow size distribution, and strong up-conversion fluorescence of the products indicated that the $NaYF_4$:Yb,Er NCs synthesized in liquid paraffin possessed a high quality, which was comparable to the corresponding NCs synthesized in the conventional solvent of octadecene (ODE) [2, 3, 38].

The growth temperature greatly influenced the size monodispersity and the crystal phases of the as-prepared $NaYF_4$:Yb,Er NCs. As shown in Figure 1(b), NCs synthesized at 280°C possessed the best size monodispersity, whereas the increase of reaction temperature from 280

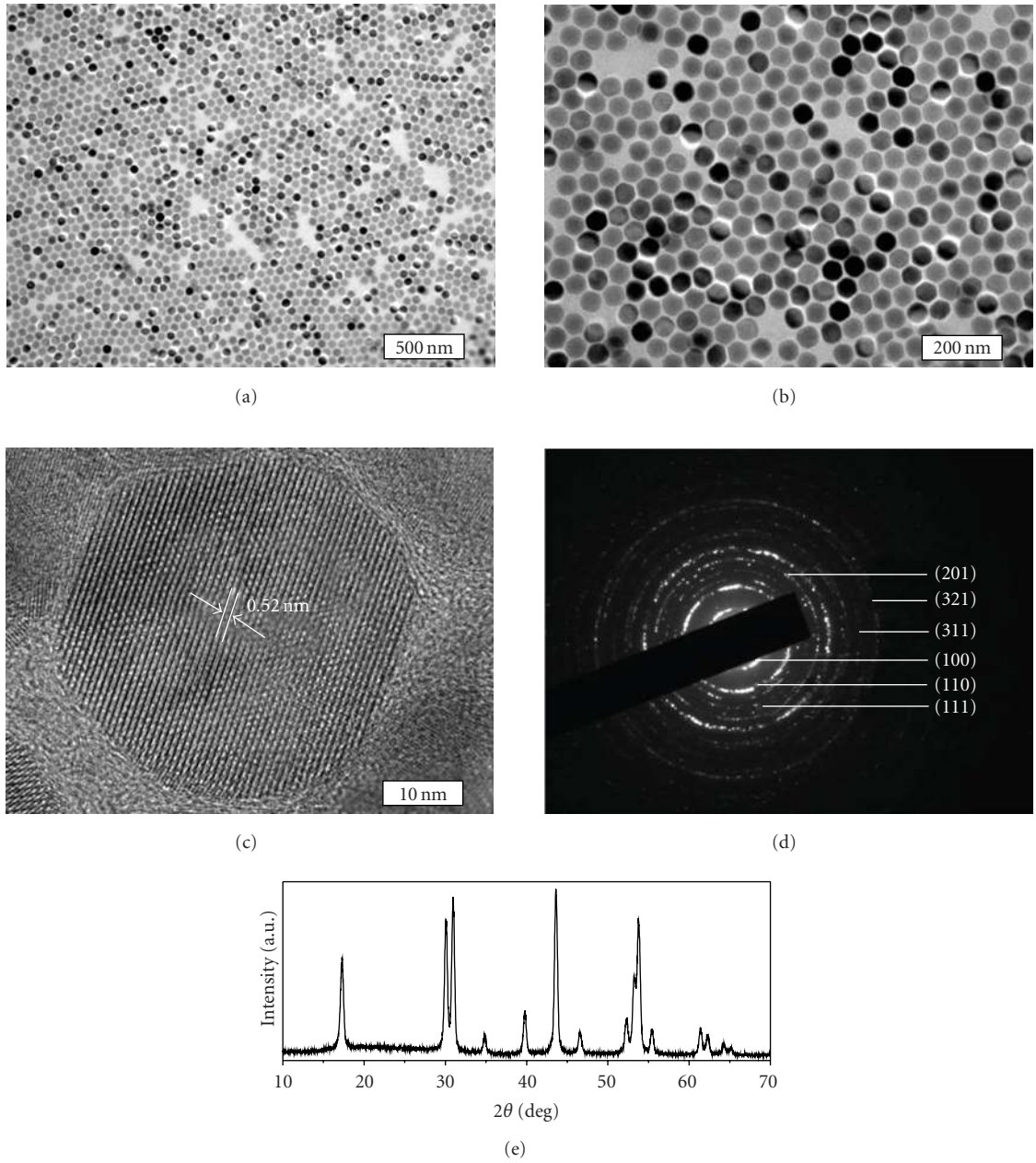


Figure 1: (a) Low- and (b) high-magnification TEM images, (c) HRTEM image, (d) selected area electron diffraction, and (e) XRD pattern of $NaYF_4$:Yb,Er NCs synthesized at 280°C.

to 320°C obviously decreased the size monodispersity (Figure 4). Besides spherical particles, anisotropic nanorods were also observed (Figure 4(b)). It should be mentioned that the optimal temperature for synthesizing monodisperse $NaYF_4$:Yb,Er NCs in ODE was 320°C, 40°C higher than in liquid paraffin. This difference was attributed to the different viscosity of them. The viscosity of liquid paraffin was lower than that of ODE due to the shorter alkyl chains of liquid paraffin, thus facilitating the diffusion of various atoms and molecules at a given temperature. According to the classical model of NC growth in high-boiling-point organic solvents, the growth rate, size distribution, and morphology were mainly dominated by a diffusion-limited process [1, 4, 39]. In brief, NC growth was the equilibrium of kinetics and thermodynamics. If atoms and molecules had lower diffusion rate, the deposition of them on NC surface would follow thermodynamics-favored process, namely, growth with less face selectivity. It led to quasispherical particles. In contrast, higher diffusion rate made the atom stacking have face selectivity via kinetics-favored process. The growth along high energy faces resulted in anisotropic NCs as well as poor size distribution [1, 34, 39]. Since the diffusion rate of atoms and molecules in liquid paraffin was higher than those in ODE at a given temperature, it was comprehensible that the

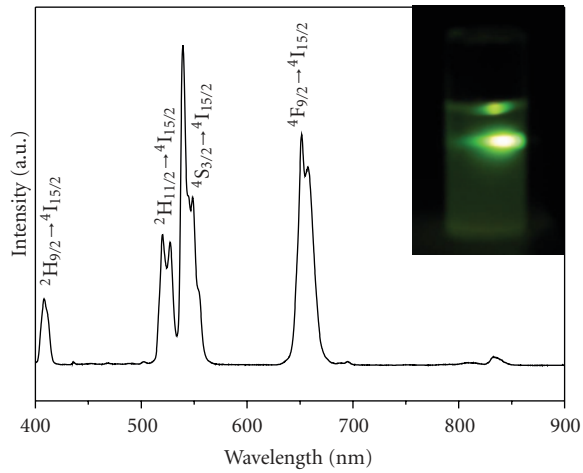


Figure 2: Up-conversion fluorescence spectrum of $NaYF_4$:Yb,Er NCs synthesized at 280°C. Inset: the corresponding fluorescent image.

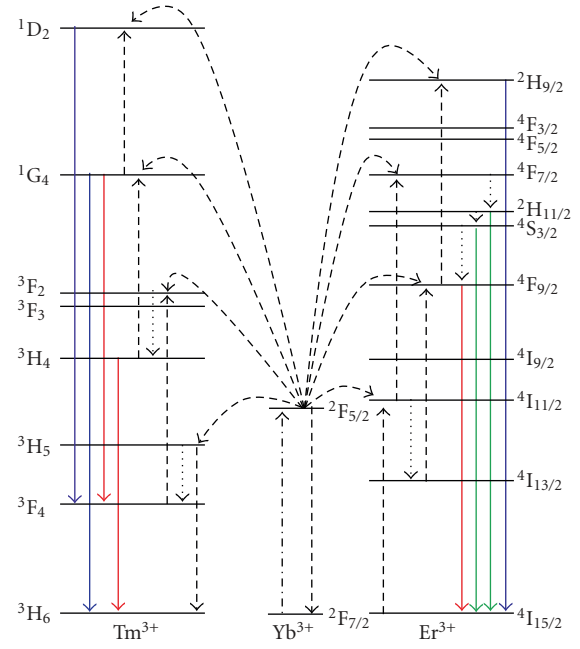
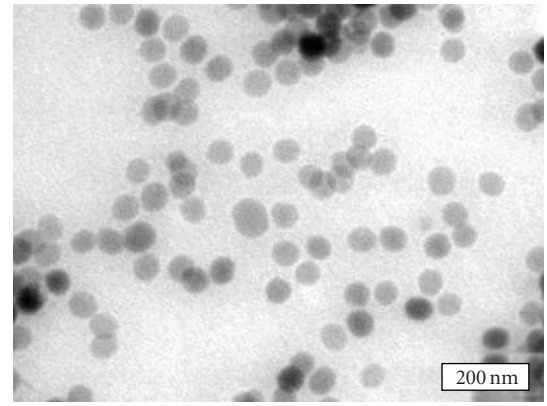


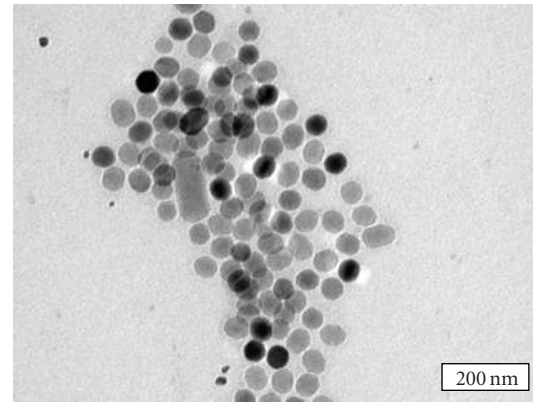
Figure 3: Schematic illustration of the transition energy levels of $NaYF_4$:Yb,Er and $NaYF_4$:Yb,Tm NCs.

optimal temperature for synthesizing $NaYF_4$:Yb,Er NCs in liquid paraffin should be lower than in ODE.

As indicated in the previous reports, high growth temperature facilitated the formation of β-phase $NaYF_4$:Yb,Er NCs. So, the conventional synthesis was operated at 320°C. However, in our method, the as-prepared $NaYF_4$:Yb,Er NCs synthesized at 280°C already had pure β-phase. Control experiment showed that below 280°C, the as-prepared NCs were the mixtures of α-phase and β-phase, indicating 280°C was the lower limit of temperature to obtain pure β-phase NCs. This result revealed an advantage using liquid paraffin



(a)



(b)

Figure 4: TEM images of $NaYF_4$:Yb,Er NCs synthesized at 300 (a) and 320°C (b).

as solvent, namely, the capability to synthesize high-quality NCs at relative low reaction temperature.

Current method was also extendable for synthesizing up-conversion NCs doped with other lanthanides, such as $NaYF_4$:Yb,Tm. As shown in Figure 5(a), $NaYF_4$:Yb,Tm NCs also possessed very narrow size distribution with an average diameter about 30 nm, which was similar to $NaYF_4$:Yb,Er NCs. HRTEM image indicated that the as-prepared NCs had highly crystalline structure, and corresponding to β-phase $NaYF_4$ crystals (Figure 5(b)) [32]. Figure 5(c) showed the up-conversion fluorescence spectrum and fluorescent image of $NaYF_4$:Yb,Tm NCs. Four emission peaks centered at 451, 475, 644, and 799 nm were observed, which were, respectively, attributed to the transition from the energy levels $^1D_2$ to $^3F_4$, $^1G_4$ to $^3H_6$, $^1G_4$ to $^3F_4$, and $^3H_4$ to $^3H_6$ of Tm^{3+} (Figure 3) [32, 33, 40]. Besides, the apparent emission color of $NaYF_4$:Yb,Tm NCs was blue, consistent with the $^1D_2$ to $^3F_4$ and $^1G_4$ to $^3H_6$ transitions (Figure 5(c) inset).

4. Conclusions

In summary, we demonstrated a low-cost and convenient method for synthesizing high-quality lanthanide-codoped

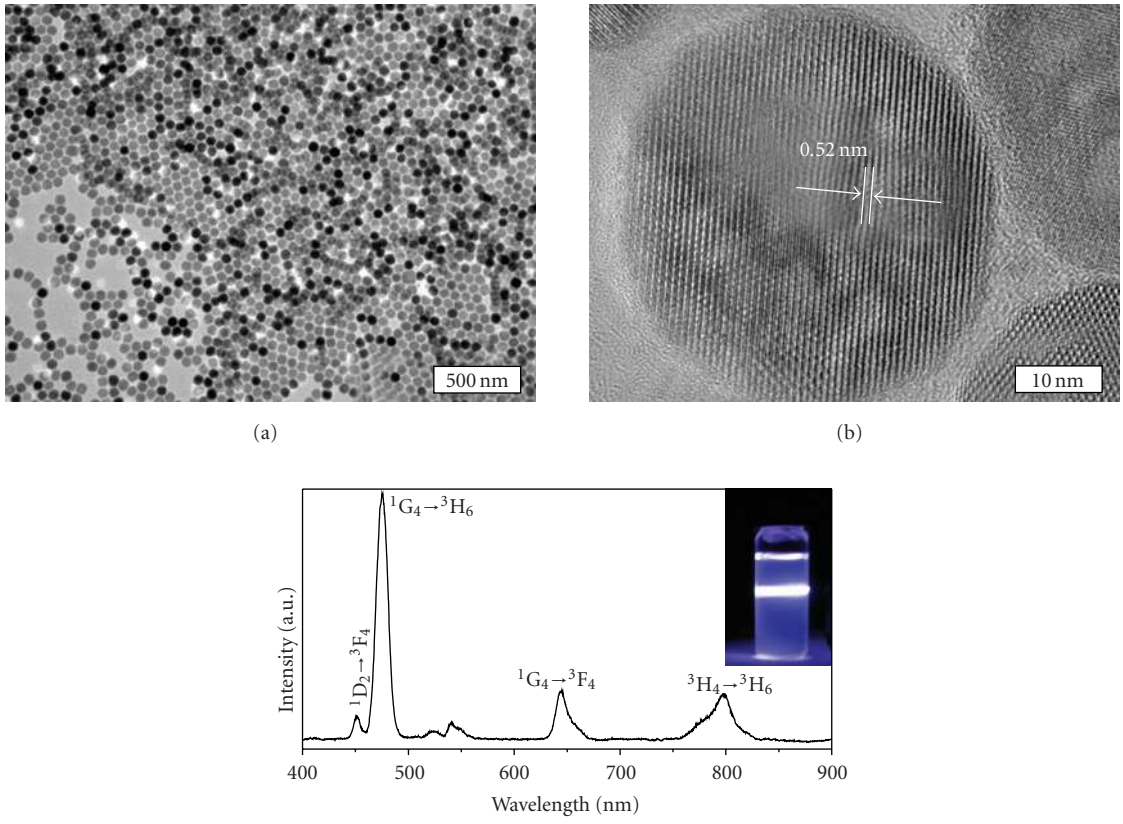


Figure 5: (a) TEM and (b) HRTEM images of $NaYF_4$:Yb,Tm NCs. (c) Up-conversion fluorescence spectrum of $NaYF_4$:Yb,Tm NCs. Inset: the corresponding fluorescent image.

$NaYF_4$ NCs in liquid paraffin. The as-prepared NCs possessed good crystalline structure, narrow size distribution, and strong up-conversion fluorescence. The color of up-conversion fluorescence was tunable by codoping different lanthanide, such as Yb/Er and Yb/Tm. In comparison to other high-boiling-point organic solvents, liquid paraffin is cheaper and prolific in oil industry. Besides, 280°C was the optimal temperature for the current synthesis, which was lower than that in the previous reports using other high-boiling-point organic solvents. Consequently, this user-friendly method will facilitate the synthesis of high-quality lanthanide-codoped $NaYF_4$ NCs in commercial scale. Further investigations are underway to synthesize various rare-earth fluoride NCs as well as control their morphologies in liquid paraffin.

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