

Research Article

A User-Friendly Method for Synthesizing High-Quality NaYF₄: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 NaYF₄: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 NaYF₄: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 NaYF₄ NCs in commercial scale.

1. Introduction

During the past decade, significant attentions have been paid on up-conversion luminescent nanocrystals (NCs) owing 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 throughput 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 NaYF₄, such as Yb/Er or Yb/Tm codoped NaYF₄, is becoming the focus, because NaYF₄ 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 NaYF₄ 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 NaYF₄: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 NaYF₄: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 (NH₄F), ethanol, methanol, oleic acid (OA, technical grade, 90%), liquid paraffin, yttrium chloride hexahydrate (YCl₃·6H₂O, 99.9%), ytterbium chloride hexahydrate (YbCl₃·6H₂O, 99.99%), erbium chloride hexahydrate (ErCl₃·6H₂O, 99.9%), and thulium chloride hexahydrate (TmCl₃·6H₂O, 99.9%) were all commercial products and used as received.

2.2. Synthesis of NaYF₄:Yb,Er(Tm) NCs. NaYF₄:18%Yb, 2%Er NCs were synthesized following this project: YCl₃·6H₂O (0.2420 g), YbCl₃·6H₂O (0.0700 g), and ErCl₃·6H₂O (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 NH₄F (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 N₂, 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 TmCl₃·6H₂O instead of ErCl₃·6H₂O, NaYF₄: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 NaYF₄:Yb,Er NCs. Figures 1(a) and 1(b) showed the TEM images of the as-prepared NaYF₄: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 NaYF₄ 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 NaYF₄ 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 NaYF₄ (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 NaYF₄ (JCPDS standard card no.028-1192) [30, 32–35].

The as-prepared NCs could be facily separated from liquid paraffin by centrifugation and redispersible in non-polar 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% NaYF₄: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 Er³⁺ (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 NaYF₄: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, NaYF₄: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 NaYF₄: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 NaYF₄: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

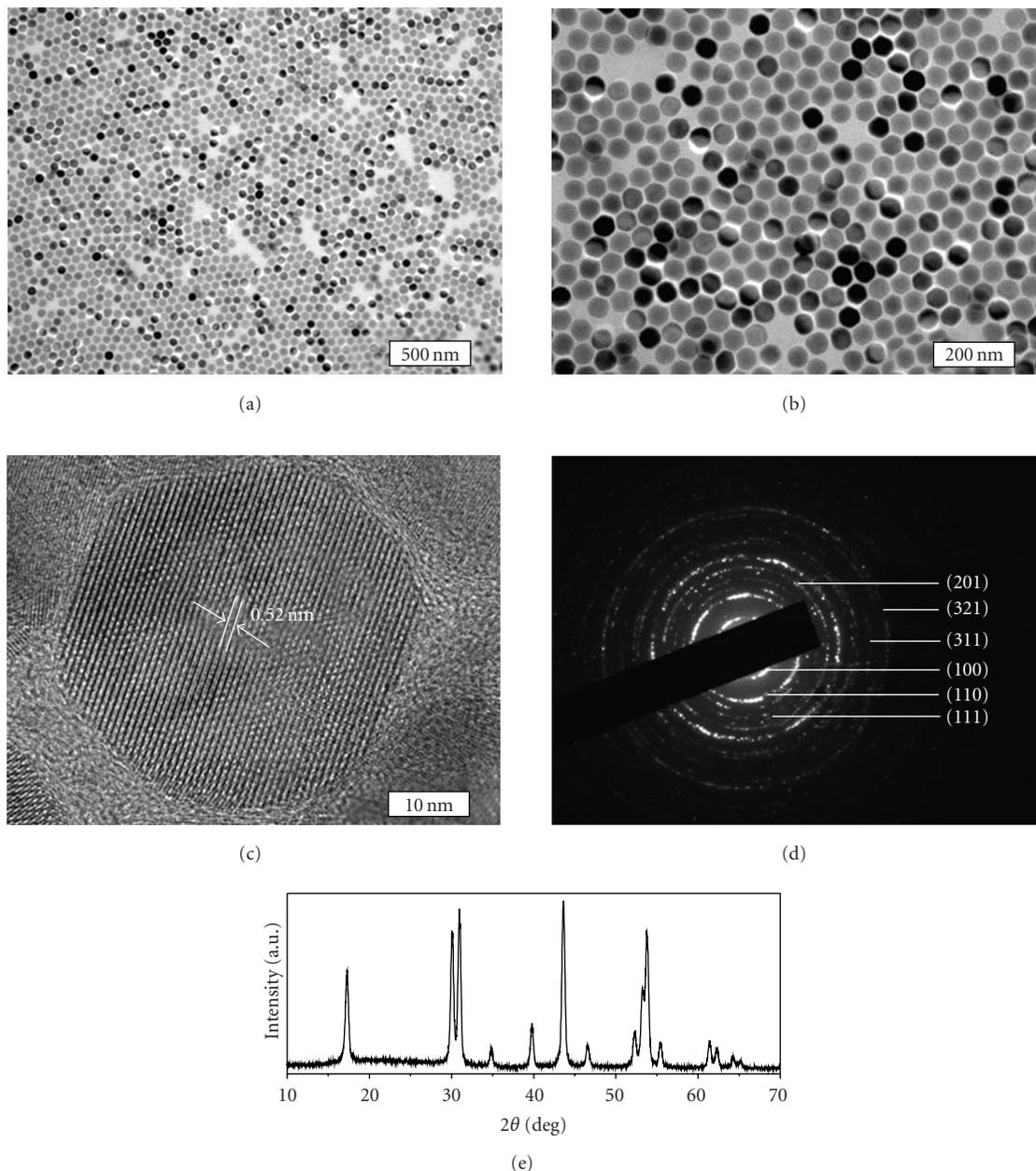


FIGURE 1: (a) Low- and (b) high-magnification TEM images, (c) HRTEM image, (d) selected area electron diffraction, and (e) XRD pattern of $\text{NaYF}_4:\text{Yb,Er}$ NCs synthesized at 280°C .

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 $\text{NaYF}_4:\text{Yb,Er}$ 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

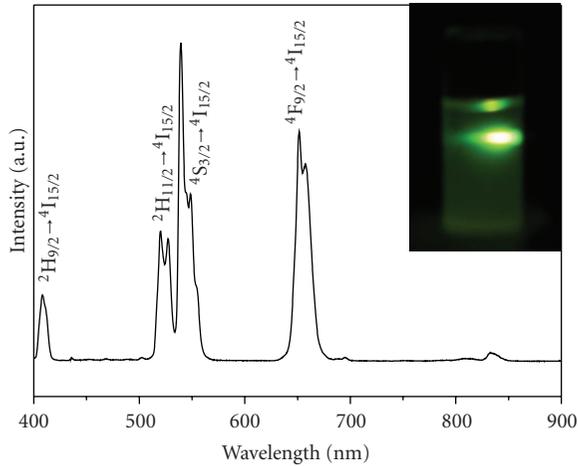


FIGURE 2: Up-conversion fluorescence spectrum of NaYF₄:Yb,Er NCs synthesized at 280°C. Inset: the corresponding fluorescent image.

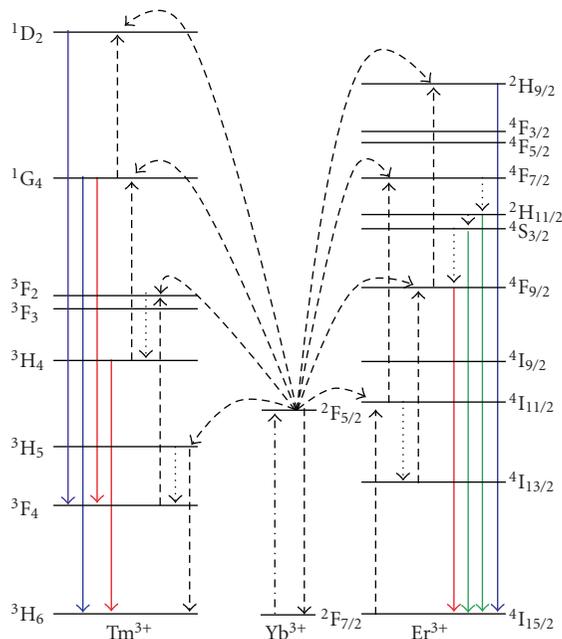
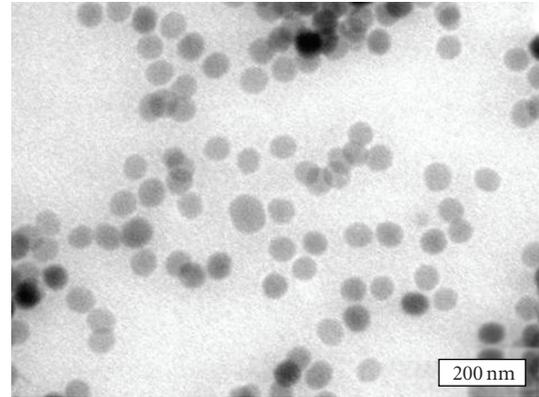


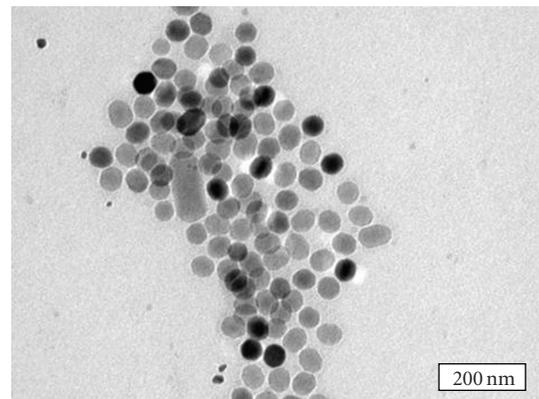
FIGURE 3: Schematic illustration of the transition energy levels of NaYF₄:Yb,Er and NaYF₄:Yb,Tm NCs.

optimal temperature for synthesizing NaYF₄: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 NaYF₄:Yb,Er NCs. So, the conventional synthesis was operated at 320°C. However, in our method, the as-prepared NaYF₄: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 NaYF₄: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 NaYF₄:Yb,Tm. As shown in Figure 5(a), NaYF₄:Yb,Tm NCs also possessed very narrow size distribution with an average diameter about 30 nm, which was similar to NaYF₄:Yb,Er NCs. HRTEM image indicated that the as-prepared NCs had highly crystalline structure, and corresponding to β -phase NaYF₄ crystals (Figure 5(b)) [32]. Figure 5(c) showed the up-conversion fluorescence spectrum and fluorescent image of NaYF₄: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 Tm³⁺ (Figure 3) [32, 33, 40]. Besides, the apparent emission color of NaYF₄: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

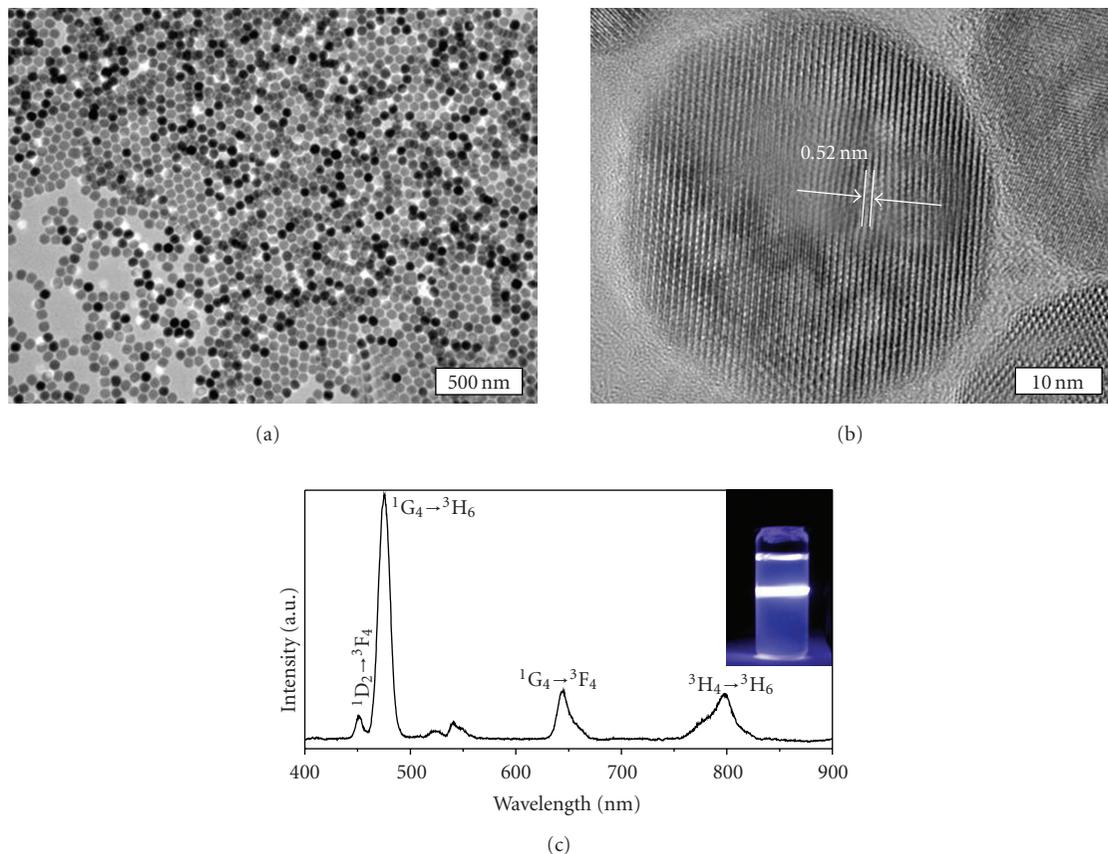


FIGURE 5: (a) TEM and (b) HRTEM images of $\text{NaYF}_4:\text{Yb,Tm}$ NCs. (c) Up-conversion fluorescence spectrum of $\text{NaYF}_4:\text{Yb,Tm}$ NCs. Inset: the corresponding fluorescent image.

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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References

- [1] F. Wang and X. Liu, "Recent advances in the chemistry of lanthanide-doped upconversion nanocrystals," *Chemical Society Reviews*, vol. 38, no. 4, pp. 976–989, 2009.
- [2] J.-C. Boyer, L. A. Cuccia, and J. A. Capobianco, "Synthesis of colloidal upconverting $\text{NaYF}_4:\text{Er}^{3+}/\text{Yb}^{3+}$ and $\text{Tm}^{3+}/\text{Yb}^{3+}$ monodisperse nanocrystals," *Nano Letters*, vol. 7, no. 3, pp. 847–852, 2007.
- [3] S.-Z. Zhang, L.-D. Sun, H. Tian, Y. Liu, J.-F. Wang, and C.-H. Yan, "Reversible luminescence switching of $\text{NaYF}_4:\text{Yb,Er}$ nanoparticles with controlled assembly of gold nanoparticles," *Chemical Communications*, no. 18, pp. 2547–2549, 2009.
- [4] L. Wang and Y. Li, "Controlled synthesis and luminescence of lanthanide doped NaYF_4 nanocrystals," *Chemistry of Materials*, vol. 19, no. 4, pp. 727–734, 2007.
- [5] Z. Li and Y. Zhang, "Monodisperse silica-coated polyvinylpyrrolidone/ NaYF_4 nanocrystals with multicolor upconversion fluorescence emission," *Angewandte Chemie International Edition*, vol. 45, no. 46, pp. 7732–7735, 2006.
- [6] M. Wang, C.-C. Mi, W.-X. Wang et al., "Immunolabeling and NIR-excited fluorescent imaging of HeLa cells by using $\text{NaYF}_4:\text{Yb,Er}$ upconversion nanoparticles," *ACS Nano*, vol. 3, no. 6, pp. 1580–1586, 2009.
- [7] J. Shan, X. Qin, N. Yao, and Y. Ju, "Synthesis of monodisperse hexagonal $\text{NaYF}_4:\text{Yb, Ln}$ ($\text{Ln} = \text{Er, Ho}$ and Tm) upconversion nanocrystals in TOPO," *Nanotechnology*, vol. 18, no. 44, Article ID 445607, 2007.

- [8] P. Li, Q. Peng, and Y. D. Li, "Synthesis of NaYF₄ nanocrystals with predictable phase and shape," *Advanced Materials*, vol. 21, pp. 1945–1948, 2009.
- [9] J. Shan and Y. Ju, "A single-step synthesis and the kinetic mechanism for monodisperse and hexagonal-phase NaYF₄:Yb, Er upconversion nanophosphors," *Nanotechnology*, vol. 20, no. 27, Article ID 275603, 2009.
- [10] M. Yu, F. Li, Z. Chen et al., "Laser scanning up-conversion luminescence microscopy for imaging cells labeled with rare-earth nanophosphors," *Analytical Chemistry*, vol. 81, no. 3, pp. 930–935, 2009.
- [11] G. Chen, H. Liu, G. Somesfalean, H. Liang, and Z. Zhang, "Upconversion emission tuning from green to red in Yb³⁺/Ho³⁺-codoped NaYF₄ nanocrystals by tridoping with Ce³⁺ ions," *Nanotechnology*, vol. 20, no. 38, Article ID 385704, 2009.
- [12] M. Zhang, S. Shi, J. Meng et al., "Preparation and characterization of near-infrared luminescent bifunctional core/shell nanocomposites," *Journal of Physical Chemistry C*, vol. 112, no. 8, pp. 2825–2830, 2008.
- [13] D. K. Chatterjee, L. S. Fong, and Y. Zhang, "Nanoparticles in photodynamic therapy: an emerging paradigm," *Advanced Drug Delivery Reviews*, vol. 60, no. 15, pp. 1627–1637, 2008.
- [14] M. Nyk, R. Kumar, T. Y. Ohulchanskyy, E. J. Bergey, and P. N. Prasad, "High contrast in vitro and in vivo photoluminescence bioimaging using near infrared to near infrared up-conversion in Tm³⁺ and Yb³⁺ doped fluoride nanophosphors," *Nano Letters*, vol. 8, no. 11, pp. 3834–3838, 2008.
- [15] N. M. Idris, Z. Li, L. Ye et al., "Tracking transplanted cells in live animal using upconversion fluorescent nanoparticles," *Biomaterials*, vol. 30, no. 28, pp. 5104–5113, 2009.
- [16] M. Kumar, Y. Guo, and P. Zhang, "Highly sensitive and selective oligonucleotide sensor for sickle cell disease gene using photon upconverting nanoparticles," *Biosensors and Bioelectronics*, vol. 24, no. 5, pp. 1522–1526, 2009.
- [17] F. Wang and X. Liu, "Upconversion multicolor fine-tuning: visible to near-infrared emission from lanthanide-doped NaYF₄ nanoparticles," *Journal of the American Chemical Society*, vol. 130, no. 17, pp. 5642–5643, 2008.
- [18] S. Schietinger, T. Aichele, H.-Q. Wang, T. Nann, and O. Benson, "Plasmon-enhanced upconversion in single NaYF₄:Yb³⁺/Er³⁺ codoped nanocrystals," *Nano Letters*, vol. 10, no. 1, pp. 134–138, 2010.
- [19] X. Yu, M. Li, M. Xie, L. Chen, Y. Li, and Q. Wang, "Dopant-controlled synthesis of water-soluble hexagonal NaYF₄ nanorods with efficient upconversion fluorescence for multicolor bioimaging," *Nano Research*, vol. 3, no. 1, pp. 51–60, 2010.
- [20] C.-J. Carling, J.-C. Boyer, and N. R. Branda, "Remote-control photoswitching using NIR light," *Journal of the American Chemical Society*, vol. 131, no. 31, pp. 10838–10839, 2009.
- [21] F. Wang, Y. Han, C. S. Lim et al., "Simultaneous phase and size control of upconversion nanocrystals through lanthanide doping," *Nature*, vol. 463, no. 7284, pp. 1061–1065, 2010.
- [22] L. W. Qian, J. T. Zai, Z. Chen, J. Zhu, Y. P. Yuan, and X. F. Qian, "Control of the morphology and composition of yttrium fluoride via a salt-assisted hydrothermal method," *CrystEngComm*, vol. 12, pp. 199–206, 2010.
- [23] Y. Y. Zhang, L. W. Yang, C. F. Xu, J. X. Zhong, and C. Q. Sun, "Sensitized deep-ultraviolet up-conversion emissions of Gd³⁺ via Tm³⁺ and Yb³⁺ in hexagonal NaYF₄ nanorods," *Applied Physics B*, vol. 98, no. 2-3, pp. 243–247, 2010.
- [24] L. Gao, X. Ge, Z. Chai, G. Xu, X. Wang, and C. Wang, "Shape-controlled synthesis of octahedral α -NaYF₄ and its rare earth doped submicrometer particles in acetic acid," *Nano Research*, vol. 2, no. 7, pp. 565–574, 2009.
- [25] C. Lin, M. T. Berry, R. Anderson, S. Smith, and P. S. May, "Highly luminescent NIR-to-visible upconversion thin films and monoliths requiring no high-temperature treatment," *Chemistry of Materials*, vol. 21, no. 14, pp. 3406–3413, 2009.
- [26] Z. Li and Y. Zhang, "An efficient and user-friendly method for the synthesis of hexagonal-phase NaYF₄:Yb, Er/Tm nanocrystals with controllable shape and upconversion fluorescence," *Nanotechnology*, vol. 19, no. 34, Article ID 345606, 2008.
- [27] H.-X. Mai, Y.-W. Zhang, R. Si et al., "High-quality sodium rare-earth fluoride nanocrystals: controlled synthesis and optical properties," *Journal of the American Chemical Society*, vol. 128, no. 19, pp. 6426–6436, 2006.
- [28] H.-X. Mai, Y.-W. Zhang, L.-D. Sun, and C.-H. Yan, "Size- and phase-controlled synthesis of monodisperse NaYF₄:Yb,Er nanocrystals from a unique delayed nucleation pathway monitored with upconversion spectroscopy," *Journal of Physical Chemistry C*, vol. 111, no. 37, pp. 13730–13739, 2007.
- [29] K. W. Krämer, D. Biner, G. Frei, H. U. Güdel, M. P. Hehlen, and S. R. Lüthi, "Hexagonal sodium yttrium fluoride based green and blue emitting upconversion phosphors," *Chemistry of Materials*, vol. 16, no. 7, pp. 1244–1251, 2004.
- [30] S. J. Budijono, J. Shan, N. Yao et al., "Synthesis of stable block-copolymer-protected NaYF₄:Yb³⁺, Er³⁺ up-converting phosphor nanoparticles," *Chemistry of Materials*, vol. 22, no. 2, pp. 311–318, 2010.
- [31] J. Han, H. Zhang, H. Sun, D. Zhou, and B. Yang, "Manipulating the growth of aqueous semiconductor nanocrystals through amine-promoted kinetic process," *Physical Chemistry Chemical Physics*, vol. 12, no. 2, pp. 332–336, 2010.
- [32] C. Liu, H. Wang, X. Li, and D. Chen, "Monodisperse, size-tunable and highly efficient β -NaYF₄:Yb,Er(Tm) up-conversion luminescent nanospheres: controllable synthesis and their surface modifications," *Journal of Materials Chemistry*, vol. 19, no. 21, pp. 3546–3553, 2009.
- [33] G. S. Yi and G. M. Chow, "Synthesis of hexagonal-phase NaYF₄:Yb,Er and NaYF₄:Yb,Tm nanocrystals with efficient up-conversion fluorescence," *Advanced Functional Materials*, vol. 16, no. 18, pp. 2324–2329, 2006.
- [34] C. Li, J. Yang, Z. Quan, P. Yang, D. Kong, and J. Lin, "Different microstructures of β -NaYF₄ fabricated by hydrothermal process: effects of pH values and fluoride sources," *Chemistry of Materials*, vol. 19, no. 20, pp. 4933–4942, 2007.
- [35] J. Zhang, C. M. Shade, D. A. Chengelis, and S. Petoud, "A strategy to protect and sensitize near-infrared luminescent Nd³⁺ and Yb³⁺: organic tropolonate ligands for the sensitization of Ln³⁺-doped NaYF₄ nanocrystals," *Journal of the American Chemical Society*, vol. 129, no. 48, pp. 14834–14835, 2007.
- [36] S. Heer, K. Kömpe, H.-U. Güdel, and M. Haase, "Highly efficient multicolour upconversion emission in transparent colloids of lanthanide-doped NaYF₄ nanocrystals," *Advanced Materials*, vol. 16, no. 23-24, pp. 2102–2105, 2004.
- [37] D.-K. Ma, S.-M. Huang, Y.-Y. Yu, Y.-F. Xu, and Y.-Q. Dong, "Rare-earth-ion-doped hexagonal-phase NaYF₄ nanowires: controlled synthesis and luminescent properties," *Journal of Physical Chemistry C*, vol. 113, no. 19, pp. 8136–8142, 2009.
- [38] H. P. Zhou, C. H. Xu, W. Sun, and C. H. Yan, "Clean and flexible modification strategy for carboxyl/aldehyde-functionalized upconversion nanoparticles and their optical applications," *Advanced Functional Materials*, vol. 19, pp. 3892–3900, 2009.

- [39] X. Liang, X. Wang, J. Zhuang, Q. Peng, and Y. Li, "Synthesis of NaYF₄ nanocrystals with predictable phase and shape," *Advanced Functional Materials*, vol. 17, no. 15, pp. 2757–2765, 2007.
- [40] X. Liu, J. Zhao, Y. Sun et al., "Ionothermal synthesis of hexagonal-phase NaYF₄:Yb³⁺,Er³⁺/Tm³⁺ upconversion nanophosphors," *Chemical Communications*, no. 43, pp. 6628–6630, 2009.



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