Controlled synthesis of lanthanide-doped NaYF₄ upconversion nanocrystals via ligand induced crystal phase transition and silica coating

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(Received 26 June 2007; accepted 21 August 2007; published online 18 September 2007)

Upconversion nanocrystals (NCs) of NaYF₄:Yb,Ln (Ln=Er and Tm) in cubic and hexagonal phases were synthesized in oleic acid (OA) and/or trioctylphosphine (TOP) with octadecene (ODE) via a thermolysis method. Only cubic-phase NCs were obtained in OA/ODE and TOP/ODE solvents; on the other hand, the hexagonal-phase NCs resulted in OA/TOP/ODE. The phase transition from cubic to hexagonal was induced by a ligand formed between oleate and TOP at high temperature. Moreover, the addition of OA/TOP in high and low ratios produced hexagonal nanoparticles and nanorods, respectively. The formed NCs were coated by SiO₂ using microemulsion reactions for further biofunctionalization in biological applications. © 2007 American Institute of Physics. [DOI: 10.1063/1.2783476]

The lanthanide ion (Ln³⁺, Ln=Er, Tm, and Ho) doped near-IR (NIR)-to-visible upconversion nanocrystals (UC-NCs) have attracted significant interest in recent years due to their many potential biological and security applications. Compared with conventional downconversion fluorescent labels, these UC-NCs convert two or more photons of lower energy (e.g., 980 nm) into one higher energy photon in the visible light range and benefit from the availability of low cost and high power infrared lasers, which allows deeper light penetration in tissue and lower photodamage to living organisms. In addition, the UC process from NIR also significantly increases the signal-to-noise ratio due to the absence of autofluorescence and the reduction of light scattering. Furthermore, the lanthanide ions are inherently resistant to photobleaching and photochemical degradation, which gives additional advantages over organic dye markers and quantum dots for biolabeling and bioassays. To achieve these goals, synthesis of rare-earth-doped UC-NCs with high UC quantum efficiency is the key. To date, NaYF₄ in cubic (α) and hexagonal (β) phases has been reported as one of the most efficient host matrices, and the β-phase NaYF₄ has a higher efficiency than the α-phase one. Several previous studies have been conducted to synthesize NaYF₄:Yb,Ln nanoparticles using water-soluble lanthanide salts and sodium fluorides (or NaF made from sodium precursors and ammonium fluoride). Unfortunately, these methods usually produce either less efficient small α-phase NCs (Refs. 3, 14, and 15) or large β-phase NCs (>50 nm) that are difficult to functionalize. Recently, methods for the synthesis of colloidal NaYF₄:Yb,Ln NCs by thermolysis of lanthanide and sodium trifluoroacetic precursors in high boiling point coordination and/or noncoordination solvents, such as oleic acid (OA), oleylamine, and octadecene (ODE), have been developed. These organic ligand capped NCs could be further functionalized for various applications such as those of quantum dots. It was found that the ratios of precursors, reaction temperature and time, and coordination property of solvents played synergistic roles in controlling the particle size, morphology, and UC efficiency. For example, at synthesis conditions of unity Na/Ln molar ratio and 300 °C, it was reported that the as-synthesized NCs were α phase by using OA/ODE solvents. In order to obtain β-phase NCs, Na/Ln ratios needed to be over 2.1, and the temperature had to be raised to 330 °C, the solvents’ boiling point, which made it difficult to control the synthesis. Recently, small (<20 nm), monodisperse, and pure β-phase UC-NCs were obtained by the authors by introducing the trioctylphosphine oxide (TOPO) ligand in the thermolysis method. Unfortunately, the use of TOPO made it difficult to grow large particles above 20 nm and to control the particle size distribution. In addition, the solubility of the TOPO-capped lanthanide-doped NCs was low in organic solvents, so the direct silica coating to make the particles hydrophilic via reverse micelles in microemulsion systems was very difficult. Thus, it is still a challenge to find a facile way to synthesize β-phase UC-NCs with a broader and controllable size range, making further functionalization easier. Therefore, with the goal of synthesizing β-phase NCs in a broader size range (20–200 nm) and improving the functionality for biofunctionalization, trioctylphosphine (TOP) ligand was investigated in this work.

Similar to TOPO, TOP is another ligand which has been widely used to synthesize quantum dots. However, there is no literature available for the synthesis of colloidal NaYF₄:Yb,Ln NCs by using TOP. To further understand the ligand effect on the NC growth and crystallinity, TOP was compared with OA and dissolved in a noncoordination ODE solvent. The phase transition from an α phase to a β phase was examined by varying the OA/TOP ratios in the ODE solvent. To demonstrate the functionality of these NCs for the biological application, the synthesized hydrophobic α- and β-phase NaYF₄:Yb,Ln NCs were made hydrophilic by coating with a thin layer of silica through reverse micelles via metal alkoxide hydrolysis and condensation in a microemulsion system.

In this work, the Na/Ln molar ratio was fixed at 1.6. Experiments were conducted for various OA/TOP/ODE solvents by varying the OA/TOP ratios. The experimental procedures were reported elsewhere, except results from the different solvent systems that were used in this work. With the total solvent volume of 20 ml, the volumes of the OA/TOP/ODE solvents used for synthesis were (a) 10/10/0, (b) 8/2/10 (OA/TOP=4:1), (c) 2/2/16 (OA/TOP=1:1), (d)
The fact that the ODE to mixed phases and pure groups from oleate and TOP. All NMR analyses demonstrated the shifted phosphine peaks. Furthermore, $^1$H NMR spectra analysis on NCs confirmed the coexistence of alkyl position was most probably caused by a ligand formed between in the OA/TOP ratio of unity suggested that the phase transition was most probably caused by a ligand formed between the OA and the Lewis base TOP, which produced totally reduced the energy barrier for the phase transition. It is also interesting to note that at the OA/TOP ratio of 1:4, the $\alpha \rightarrow \beta$ phase transition led to the formation of more dynamic stable rod-shape NCs, which indicated that the excess TOP ligand changed the NC surface energy of facets and caused anisotropic growth. A schematic mechanism for the phase transition due to the change of energy barrier via the oleate-TOP ligand formation is depicted in Fig. 3. Further studies are still needed to achieve better understanding of the detailed physical-chemical process of phase transition.

The coexistence of the small $\alpha$-phase NCs with the large $\beta$-phase NCs in Fig. 1(b) indicates that the phase transition occurred at the same time as the Ostwald ripening. To confirm the occurrence of the Ostwald-ripening process, the samplings at the reaction time of 30 min were collected from solvents at OA/TOP ratios of 1:1 and 1:4. The corresponding TEM images of these samples are shown in Fig. 4. In Fig. 4, it is seen that fewer large particles were formed by consuming many small ones, which is the typical Ostwald-ripening process for large particle growth. At the OA/TOP ratio of 1:1, the $\beta$-phase hexagonal nanoparticles were obtained in a broad range from 50 to 200 nm. A further increase of the TOP/OA ratio led to the formation of the rod-shape NCs. Therefore, an addition of TOP ligand into OA provided a different pathway other than changing precursor ratios to synthesize the $\beta$-phase NCs with tunable size and shape. NaYF$_4$:Yb,Tm and NaYF$_4$:Yb,Ho UC-NCs have been prepared in the same method in our work.

The NCs synthesized in the OA/ODE and OA/TOP/ODE solvents had an excellent solubility in organic solvents such as hexane. However, for potential biological applications, these NCs need to be modified to be hydrophilic. Therefore, surface coating of a thin layer of silica onto these NaYF$_4$:Yb,Ln NCs was reported recently, there were no reports available on coating the hydrophobically ligated $\alpha$- and $\beta$-phase UC-NCs. By using the method for silica coating onto oleate-capped PbSe quantum dots, in
the present study a silica layer was coated onto the oleate and oleate/TOP capped α- and β-phase NCs.

Figure 5 shows the TEM images of the silica coated NCs: (a) the α-phase NaYF₄:Yb,Er synthesized in OA/ODE and (b) the β-phase NaYF₄:Yb,Er synthesized in OA/TOP/ODE solvents at unity OA/TOP ratio. UC emission spectra of the corresponding NCs before and after coating were also shown under the TEM images. It is seen that for small NCs in the α phase, silica coating leads to a dramatic reduction of luminescence intensity. However, for the β-phase NCs, silica coating almost does not affect the luminescence intensity and spectra, except in the green region. The reason for the luminescence reduction for small NCs was evaluated by the volume ratio of the SiO₂ coating layer to the particle. For samples (a) and (b), the average thickness of the silica layers is 17 and 8 nm, and the approximate volume ratios between the coating layers and particles are 50 and 1.5, respectively. The much larger silica to crystal volume ratio in sample (a) indicates that the ion density is decreased significantly when the outside coating thickness is comparable to the particle diameter, which results in the significant reduction of luminescence. For sample (b), the small silica to crystal volume ratio causes less change in ion density, and thus the silica layer has less effect on luminescence intensity. The emission peaks at 520.8, 545, and 658.8 nm of the Er doped NCs were due to \(^4H_{11/2} \rightarrow ^4I_{15/2}, ^4S_{3/2} \rightarrow ^4I_{15/2}, \) and \(^4F_{9/2} \rightarrow ^4I_{15/2} \) transitions for Er³⁺, respectively. However, it is interesting to note that for β-phase NCs of sample (b), the luminescence intensity of green emission was reduced more significantly than that of red emission before and after the silica coating. The reason is because the green emission is a three-photon process which is more sensitive to the reduction of the excitation intensity than the two-photon red emission. The emission intensities for green and red emissions are, respectively, proportional to the cubic and square of the excitation intensity. In addition, the quantum efficiency of UC-NCs strongly depends on the particle crystal size. Large particles will deliver stronger luminescence. To demonstrate the improvement of luminescence intensity via phase transition, the UC emission spectra of the uncoated α- and β-phase NCs are compared in Fig. 5(c). It is clearly seen that the large β-phase NCs have much stronger emission intensity than that of the α-phase NCs. After coating with silica, both α- and β-phase NCs could be suspended in polar solvents such as ethanol for a very long time, which would be suitable for further biofunctionalization and is currently underway.

In summary, the \(\alpha \rightarrow \beta \) phase transition of NaYF₄:Yb,Ln (Ln=Er and Tm) UC-NCs was observed by adding TOP and OA into a noncoordination solvent. More efficient β-phase nanoparticles were obtained at OA/TOP ratios near unity. A further increase of TOP in OA/TOP ratios led to the formation of nanorods. The results showed that the large β-phase nanoparticles and nanorods were formed via the Ostwald-ripening process. A ligand formed between OA and TOP molecules was proposed for the phase transition. By adjusting the reaction time and OA/TOP ratios, a broad range of particle sizes from 50 to 200 nm can be controlled. Both α- and β-phase UC-NCs were directly coated with a layer of silica by using the microemulsion reactions. The effect of coating on the UC luminescence intensity was strongly dependent on the volume ratio between the coating layer and particles and on the emission wavelength. Synthesis of the β-phase UC-NCs in a broad size range and the coating of a silica layer provided a great potential for the future biofunctionalization and biological application.


29JCPDS File No. 6-0342.

30JCPDS File No. 28-1192.

