Ionothermal synthesis of hexagonal-phase $NaYF_4$:Yb^{3+},Er^{3+}/Tm^{3+} upconversion nanophosphors†

Xiaomin Liu,[a] Junwei Zhao,[ab] Yajuan Sun,[a] Kai Song,[ab] Yi Yu,[a] Chuang Du,[a] Xianggui Kong*[a] and Hong Zhang*[b]

Received (in Cambridge, UK) 30th July 2009, Accepted 8th September 2009
First published as an Advance Article on the web 24th September 2009
DOI: 10.1039/b915517a

Water-soluble pure hexagonal-phase $NaYF_4$:Yb^{3+},Er^{3+}/Tm^{3+} nanoparticles were obtained by an ionothermal method for the first time which offers a new alternative in synthesizing such materials.

Rare-earth ions doped luminescence upconversion nanoparticles have attracted much attention in recent years owing to their superior spectroscopic properties, mainly arising from the existence of stable intermediate states, which may result in potential applications in many fields, especially in biology/biomedicine.[1–4] Among these materials, hexagonal-phase $NaYF_4$ is reported as one of the most efficient hosts for performing infrared-to-visible photon conversion in the doped rare-earth ions.[5–14] For their *in vivo* biological application, the prerequisites for an optimal universal bioprobe are water-solubility, small size and high luminescence efficiency. Up to now, the most general reported method to prepare pure hexagonal $NaYF_4$:Yb^{3+},Er^{3+}/Tm^{3+} upconversion nanocrystals (UP-NCs) with small size and good dispersibility has been the co-thermolysis of trifluoroacetate precursors at high temperature. However, these synthesized nanoparticles are hydrophobic and require further modification on their surfaces before biological applications. Although use of high temperature facilitates the formation of the thermally stable hexagonal phase, it requires rigorous experimental conditions and the decomposition of trifluoroacetate is highly toxic.[5–7] Just a few papers have reported that water-soluble and biocompatible hexagonal $NaYF_4$:Yb^{3+},Er^{3+}/Tm^{3+} UP-NCs with size around 50 nm could be obtained either hydrothermally or solvothermally.[8,9] It is, however, still difficult to control the size and phase purity. Hence, there is a challenge to develop a facile synthetic route to obtain small hydrophilic pure hexagonal $NaYF_4$:Yb^{3+},Er^{3+}/Tm^{3+} nanophosphors under relatively mild conditions.

In this communication we report our recent successful attempt in synthesizing such nanocrystals in ionic liquid (IL) media, which appear as "green solvents" due to their chemical stability, very low vapor pressure and non-flammability, and have been applied in many fields, ranging from synthesis, catalysis, separation and electrochemistry.[15,16] The syntheses hinge on the solvents being predominantly ionic. Thermal reactions using ionic liquids as reaction media are termed as "ionothermal" to distinguish from hydrothermal and solvothermal methods, which take place in a predominantly molecular solvent.[17] Recently, the synthesis of inorganic nanostructures in IL media has attracted extensive attention, including metals, metal oxides, metal alloys, metal fluorides, and so on.[18–21]

Based on the requested components and hydrophilic property of the ionic liquid, 1-butyl-3-methylimidazolium tetrafluoroborate, [Bmim][BF_4], was chosen as the solvent for manufacturing nanostructured hexagonal-phase $NaYF_4$:Yb^{3+},Er^{3+}/Tm^{3+} UP-NCs. The imidazolium cations provided the *in situ* capping reagent to prevent the $NaYF_4$ nucleation centers from growing up, while the tetrafluoroborate anions introduced a new fluorine source according to partial hydrolysis. Therefore, this IL could act as solvent and reaction agent, as well as template. Pure hexagonal-phase $NaYF_4$:Yb^{3+},Er^{3+}/Tm^{3+} nanoparticles with small size were obtained in this system at 160 °C. The as-prepared nanocrystals were water-soluble and displayed strong upconversion luminescence, suitable for biological applications. The ionothermal process reported here offers a new alternative in synthesizing $NaYF_4$:Yb^{3+},Er^{3+}/Tm^{3+} upconversion nanophosphors.

In a typical synthetic route, a given amount of sodium chloride and rare-earth nitrate were added into a beaker containing 10 ml of $BmimBF_4$ and stirred for 30 min at 80 °C; the above mixed solution was then transferred into a 23 mL Teflon-lined autoclave and kept at 160 °C for 18 h (see Fig. S1†), before being cooled to room temperature and diluted with absolute ethanol or acetone as appropriate. Finally, the precipitates were collected through centrifugation at a speed of 6000 rpm, washed with absolute ethanol, and dried in vacuum at 50 °C (see ESI†).

The characterization of $NaYF_4$:20%Yb,2%Er/Tm is summarized in Fig. 1. From the low-resolution micrograph, Fig. 1A, it is easily seen that the synthesized particles take on mixed morphologies (spherical, brick-like, hexagonal-shaped) and present some small holes. The corresponding HRTEM image, Fig. 1B, reveals the presence of clear crystal lattices from various directions, which means that the individual particles are polycrystalline. The fast Fourier transformation (FFT) pattern shown in Fig. 1C is composed of strong rings, pointing also to the polycrystalline nature of the particles.

---

[a] *Key Laboratory of Excited-State Processes, Changchun Institute of Optics Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033, P. R. China. E-mail: xgkong14@ciomp.ac.cn*
[b] *Van't Hoff Institute for Molecular Sciences, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WS Amsterdam, The Netherlands. E-mail: h.zhang@uva.nl*

† Electronic supplementary information (ESI) available: Experimental and instrumental details, IR and SEM images. See DOI: 10.1039/b915517a

The formation of the holes is suspected to arise from the aggregation growth mechanism of precursor particles during the precipitation process. In the aggregation model, the nuclei grow first, following a molecular addition mechanism, to form small primary particles, and then, these primary particles aggregate with one another (see Fig. S2, ESI†).[22] The relatively low temperature works against sufficient aggregation of the primary particles, leading to the formation of some holes. A histogram of the particle size distribution, deduced from several TEM images, is given in Fig. 1E. The particle sizes range from 25 to 70 nm. High crystallinity of the material is deduced from the X-ray diffraction (XRD) data given in Fig. 1F. The peak positions and intensities agree well with those calculated for the hexagonal $NaYF_4$ phase (line pattern PDF card No. 16-0334). From the line broadening of the diffraction peaks, the average crystallite size of the sample was determined to be approximately 23 nm using the Debye–Scherrer formula, which is smaller than the average particle size (55 nm) determined from the TEM data. This reflects the polycrystalline nature of the particles. The measured lattice spacing of region a of the HRTEM image is 0.505 nm, which also confirms the (100) plane of hexagonal $NaYF_4$ nanocrystals (Fig. 1D).

The ionothermal method reported here, differing from the other methods to obtaining $NaYF_4$:Yb^{3+},Er^{3+}/Tm^{3+} upconversion nanoparticles, lies in that the IL, [Bmim][BF_4], acts as solvent and reagent as well as template, which facilitates the formation of small hexagonal phase products. The fact that the [Bmim][BF_4] favors the formation of hexagonal $NaYF_4$ can be rationalized based on the phase transition condition from cubic to hexagonal. The phase transition behavior can be controlled by the environment or the energy barrier. It is reported, indeed, that the phase transition from cubic to hexagonal is mainly due to the modification of the environment of Y^{3+} occupation sites, including coordination numbers.[7] Analysis suggests that Y^{3+} or other cationic sites are conveniently coordinated by F^- with increasing the fluoride concentration, which decreases the energy barrier.[23] In this case, $[BF_4]^-$ hydrolyzes to form F^- under appropriate conditions.[21] Although no additional water was added into the system, the anions in the mixture were hydrolyzed because of the presence of trace water and hydration water of $Ln(NO_3)_3{\cdot}6H_2O$. Reaction in such a solvent is similar to a reaction in a pure "universal" fluoride source, which effectively reduces the energy barrier and facilitates the formation of the hexagonal phase even at relatively low temperature. The fact that small particles are obtained in this IL media can be explained by formation mechanism. In the case of [Bmim][BF_4], the $[BF_4]^-$ ion directs the hydrophilic property of the IL, while $[Bmim]^+$ greatly affects the physical and chemical properties, such as melting point, surface tension, polarity, solvency and viscosity, which directly influence the solvation and diffusion course of the lanthanide ions in the IL, further affecting the nucleation process. Moreover, [Bmim][BF_4] has low interface tension and in addition seems to adapt to other present phases ($\gamma \approx 38$ mN m^{-1} against air[24]) and molecular dynamic simulations have also been reported for the solvation of Ln^{3+} in ILs.[25] Based on these studies, it is believed that when Ln^{3+} ions are dissolved in [Bmim][BF_4], they are surrounded by the BF_4^- anions, and the first shell is surrounded by imidazolium cations. At the same time, the NO_3^- ions are surrounded by a rigid "cage" of imidazolium cations. Thus all the Ln^{3+} ions are in the same chemical environment and when the mixture is heated continuously, BF_4^- ions are degraded, leading to the formation of $NaYF_4$ grains. The IL acts as a coordinating solution and reaction in such a solvent is also similar to a reaction in pure "universal" ligands, which prevents the $NaYF_4$ nucleation centers from growing. Furthermore, the low interface tension of [Bmim][BF_4] leads to high nucleation rates, small particles can thus be generated which undergo Ostwald ripening only weakly.[18]

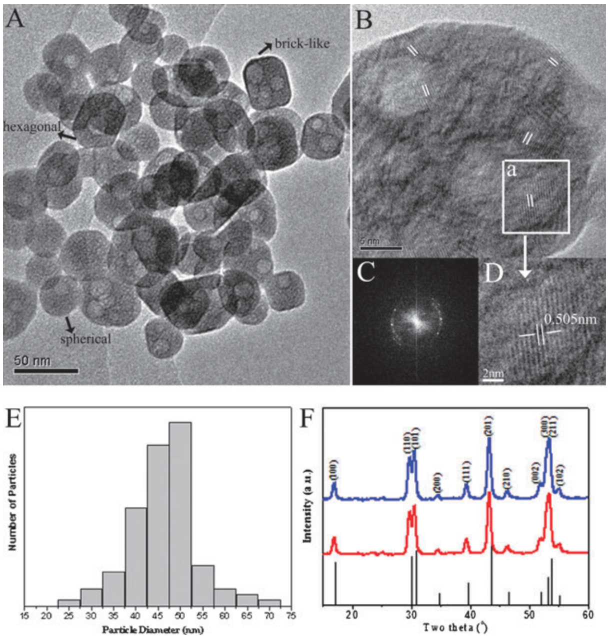

Fig. 1 Characterization data for $NaYF_4$:20%Yb^{3+},2%Er^{3+} nanocrystals. (A) TEM micrograph; (B) HRTEM and (C) FFT pattern of a single nanocrystal; (D) HRTEM image of region a; (E) histogram of the particle sizes obtained from TEM images of 400 nanocrystals; (F) experimental powder X-ray diffraction (XRD) pattern for $NaYF_4$:20%Yb^{3+},2%Er^{3+}(a), $NaYF_4$:20%Yb^{3+},2%Tm^{3+} (b), and the calculated line pattern for the hexagonal $NaYF_4$ phase.

In addition, the IL as a surfactant overlayer of the nanocrystals was identified by Fourier transform infrared (FTIR) spectroscopy (see Fig. S3, ESI†). Owing to the hydrophilic IL overlayer, these nanocrystals can be directly dispersed in water and present a strong positive charge (the zeta-potential of the nanoparticles is +42.3), which make them feasible for application in biological labeling and imaging.

The upconversion spectra of 1 wt% solutions of both $NaYF_4$:20%Yb^{3+},2%Er^{3+} and $NaYF_4$:20%Yb^{3+},2%Tm^{3+} nanocrystals in water are shown in Fig. 2, which were collected under 100 W cm^{-2} continuous excitation at 980 nm by a diode laser. The emission bands can easily be assigned to transitions within the 4f levels of the Er^{3+} and Tm^{3+} ions. The spectrum of the $NaYF_4$:20%Yb^{3+},2%Er^{3+} sample, as shown in Fig. 2A, exhibits three distinct Er^{3+} emission bands. The green emissions between 510 and 530 nm and between 530 and 570 nm are assigned to the ${}^2H_{11/2}$–${}^4I_{15/2}$ and ${}^4S_{3/2}$–${}^4I_{15/2}$ transitions, respectively. A dominant red emission is observed between 635 and 675 nm originating from the $^4F_{9/2}$–$^4I_{15/2}$ transition. Four upconverted Tm^{3+} emission bands are also observed in the $NaYF_4$:20%Yb^{3+},2%Tm^{3+} sample (Fig. 2B). The band observed between 440 and 500 nm is assigned to the $^1D_2$–$^3F_4$ and $^1G_4$–$^3H_6$ transitions, whereas a weak red emission between 630 and 670 nm and an intense NIR emission between 750 and 850 nm are assigned to the $^1G_4$–$^3F_4$ and $^3H_4$–$^3H_6$ transitions, respectively. The as-prepared samples are well dispersed in water to form clear colloidal solutions and are stable at least for one week. Fig. 2C shows their strong upconversion luminescence.

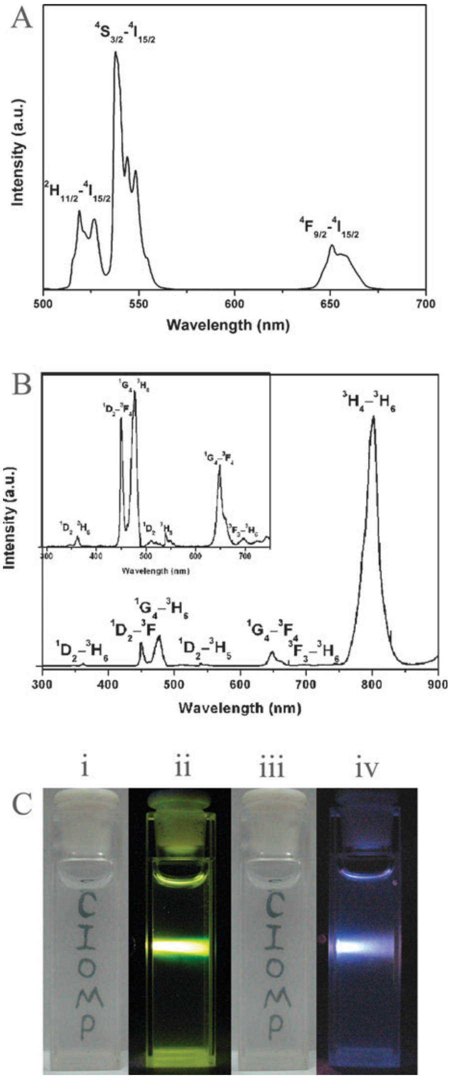

Fig. 2 Upconversion luminescence spectra of (A) $NaYF_4$:20%-Yb^{3+},2%Er^{3+} and (B) $NaYF_4$:20%Yb^{3+},2%Tm^{3+}. Inset: amplified spectra between 300 and 700 nm. (C) 1 wt% colloidal water solutions of $NaYF_4$:20%Yb^{3+},2%Er^{3+} (i and ii) and $NaYF_4$:20%Yb^{3+},2%Tm^{3+} (iii and iv) with (ii and iv) and without (i and iii) 980 nm excitation.

In summary, small, water-soluble and pure hexagonal phase $NaYF_4$:Yb^{3+},Er^{3+}/Tm^{3+} upconversion nanophosphors are successfully obtained for the first time by an ionothermal method. The key to this synthetical methodology is the use of ionic liquid, $BmimBF_4$, which acts as solvent and template, as well as fluorine source. Due to the overlayer of ILs on their surface, these nanocrystals can be directly dispersed in water and present strong positive charge. The new synthetic approach may facilitate biological application of these nanocrystals.

This work was financially supported by NSFC of China (20603035, 60601014, 10904142), the exchange program between CAS of China and KNAW of the Netherlands.

Notes and references

1 R. Kumar, M. Nyk, T. Y. Ohulchanskyy, C. A. Flask and P. N. Prasad, *Adv. Funct. Mater.*, 2009, **19**, 853.
2 P. Zhang, S. Rogelj, K. Nguyen and D. Wheeler, *J. Am. Chem. Soc.*, 2006, **128**, 12410.
3 Y. P. Li, J. H. Zhang, X. Zhang, Y. S. Luo, X. G. Ren, H. F. Zhao, X. J. Wang, L. D. Sun and C. H. Yan, *J. Phys. Chem. C*, 2009, **113**, 4413.
4 S. A. Hilderbrand, F. W. Shao, C. Salthouse, U. Mahmood and R. Weissledera, *Chem. Commun.*, 2009, 4188.
5 Y. Wei, F. Q. Lu, X. R. Zhang and D. P. Chen, *Chem. Mater.*, 2006, **18**, 5733.
6 G. S. Yi and G. M. Chow, *Adv. Funct. Mater.*, 2006, **16**, 2324.
7 H. X. Mai, Y. W. Zhang, R. Si, Z. G. Yan, L. D. Sun, L. P. You and C. H. Yan, *J. Am. Chem. Soc.*, 2006, **128**, 6426.
8 F. Wang, D. K. Chatterjee, Z. Q. Li and Y. Zhang, *Nanotechnology*, 2006, **17**, 5786.
9 J. H. Zeng, J. Su, Z. H. Li, R. X. Yan and Y. D. Li, *Adv. Mater.*, 2005, **17**, 2119.
10 J. C. Boyer, F. Vetrone, L. A. Cuccia and J. A. Capobianco, *J. Am. Chem. Soc.*, 2006, **128**, 7444.
11 J. Zhang, C. M. Shade, D. A. Chengelis and S. Petoud, *J. Am. Chem. Soc.*, 2007, **129**, 14834.
12 H. Schäfer, P. Ptacek, K. Kompe and M. Haase, *Chem. Mater.*, 2007, **19**, 1396.
13 C. Li, Z. Quan, J. Yang, P. Yang and J. Lin, *Inorg. Chem.*, 2007, **46**, 6329.
14 Y. Wang, L. P. Tu, J. W. Zhao, Y. J. Sun, X. G. Kong and H. Zhang, *J. Phys. Chem. C*, 2009, **113**, 7164.
15 P. Hapiot and C. Lagrost, *Chem. Rev.*, 2008, **108**, 2238.
16 K. Goossens, P. Nockemann, K. Driesen, B. Goderis, C. Görller-Walrands, K. Van Hecke, K. Binnemans and T. Cardinaels, *Chem. Mater.*, 2008, **20**, 157.
17 E. R. Cooper, C. D. Andrews, P. S. Wheatley, P. B. Webb, P. Wormald and R. E. Morris, *Nature*, 2004, **430**, 1012.
18 M. Antonietti, D. Kuang, B. Smarsly and Y. Zhou, *Angew. Chem., Int. Ed.*, 2004, **43**, 4988.
19 C. Burda, X. B. Chen, R. Narayanan and M. A. EI-Sayed, *Chem. Rev.*, 2005, **105**, 1025.
20 K. Biswas and C. N. R. Rao, *Chem.–Eur. J.*, 2007, **13**, 6123.
21 C. N. R. Rao, S. R. C. Viekchand, K. Biswas and A. Govindaraj, *Dalton Trans.*, 2007, 3728.
22 M. M. Xing, W. H. Cao, T. Pang and X. Q. Ling, *Solid State Commun.*, 2009, **149**, 911.
23 P. Ghosh and A. Patra, *J. Phys. Chem. C*, 2008, **112**, 3223.
24 P. Wasserscheid and W. Keim, *Angew. Chem., Int. Ed.*, 2000, **39**, 3772.
25 A. Chaumont and G. Wipff, *Phys. Chem. Chem. Phys.*, 2005, **7**, 1926.