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COMMUNICATION

Synthesis of Water-soluble β -NaYF₄ Nanocrystals in a Green Way

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Pure β -NaYF₄ nanocrystals with hexagonal phase were synthesized in a novel way at low temperature using sparingly soluble rare-earth salts as precursors and ethanol/water as co-solvents. The phase of the products could be controlled by adjusting the water content. An up-converting aqueous colloidal solution and a transparent film were obtained through a simple post-treatment.

Up-converters excited by near-infrared (NIR) radiation are attractive because the efficient conversion of NIR to visible radiation offers an optical labelling technique in biological studies without those constraints associated with organic fluorophores and quantum dots.¹ For the rare-earth doped up-converters, the most studied case is hexagonal NaYF₄ (β -NaYF₄), as it shows the highest up-conversion efficiency when doped with Yb³⁺ and Er³⁺.² Many routes have been proposed to the preparation of NaYF₄ such as thermal decomposition of trifluoroacetates in high boiling solvents³ and liquid-solid-solution (LSS) solvothermal reactions.⁴ The advantages of the thermal decomposition method are the rapid formation of β -NaYF₄ and the uniformity of the as-prepared crystals. However the drawbacks include the requirements of high reaction temperatures and costly reagents, evaporation of toxic gases, and poor reproducibility,⁵ all of which will limit large scale practical applications of the method. As for solvothermal reactions, highly crystalline nanoparticles can be produced at relatively low temperature using common solvents. Unfortunately, mixtures of β -NaYF₄ and α -NaYF₄ (cubic phase) are often produced in the synthetic process. Moreover, the particles are usually quite large, making it difficult to form stable dispersions of colloids, which is important for enabling bio-applications and for fabricating thin film devices.⁶

For biological use, a general goal is to synthesize small up-converting nanocrystals with high luminescence efficiency that can form transparent solutions in water. There is therefore an urgent need for a simple, cost efficient and green way to water-soluble β -NaYF₄ with high luminescence efficiency. Since 2001, Peng et al

have reported alternative green routes to nanocrystals by using safer chemicals and slightly lower temperatures.⁷ Ozin et al proposed a new softer nanochemistry.⁸ The strategy was based on the use of sparingly soluble precursors, and has been applied to the synthesis of metal chalcogenide nanocrystals⁹ and rare-earth fluoride nanocrystals.¹⁰

Herein we report a green route to water-soluble β -NaYF₄ nanocrystals in a novel way employing a mixed solvent of ethanol and water at low temperature. The phase of the products could be readily controlled by adjusting the water content in the reaction system. The β -NaYF₄ nanocrystals can show distinct emission when doped with Eu³⁺. Bright green upconverting aqueous solution could also be achieved as Yb³⁺, Er³⁺ co-doped samples were post-treated by a solvothermal reaction, and transparent up-converting thin films were fabricated by dip-coating with the mixture of this solution and poly acrylic acid (PAA).

The reaction was carried out in a flask at 55 °C (see the Experimental section in ESI†). In the reaction, the total solvent volume was kept at 30 ml, different contents of ethanol and water were used to check the effect of the solvents on the phase-structure of the products. Figure 1 shows the powder X-ray diffraction (PXRD) patterns of the products obtained by stirring the mixture at 55 °C for

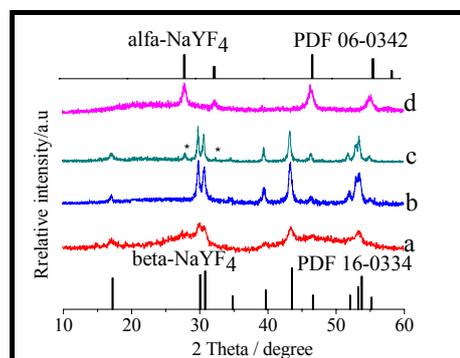


Fig. 1 Powder XRD patterns of the products grown from different mixed solvents with the total volume of ethanol and water of 30 ml: (a) 0.5 ml, (b) 2.5 ml (c) 5.0 ml and (d) 30 ml of H₂O, respectively.

2 h. The results show that the phase-structure of the products is sensitive to the content of water in the reaction system. When there is less water content (0.5ml) in the reaction system, the product shows very weak diffraction peaks of β -NaYF₄, (Fig. 1a). Increasing the water content to 2.5 ml, all diffraction peaks in Fig. 1b can be easily indexed to β -NaYF₄ (JCPDS 16-0334), which indicates a little more water in the reaction system could promote the formation of β -NaYF₄. However, when the water content increased to 5.0 ml, some peaks indexed to α -NaYF₄ (JCPDS 06-0342) appeared (starred marks in Fig. 1c), which indicated the products were mixtures of α - and β -NaYF₄. When pure de-ionized (DI) water was used as the solvent, the product was pure α -NaYF₄ (Fig. 1d).

From Thoma's YF₃-NaF phase equilibria,¹¹ β -NaYF₄ is the thermodynamically stable phase below 691 °C. However, most of the literature on the synthesis of NaYF₄ reported that the α -phase was formed at low temperature and β -phase at a higher temperature.¹² To investigate if there is a phase transformation in our system, the reaction was carried out in 27.5 ml of ethanol and 2.5 ml of DI water at room temperature. The PXRD patterns of the products formed after the reaction for different times are shown in Fig. 2. It can be observed that there are no obvious peaks in the PXRD pattern after 6 h (Fig. 2a). After 18 h, β -NaYF₄ seemed to appear according to the observation of weak diffraction peaks (Fig. 2b). The product was well crystallized after 24 h, all the peaks can be indexed to β -NaYF₄ (Fig. 2c). From 6 h to 24 h, there are no peaks indexed to α -NaYF₄ indicating there is no phase transformation from cubic to hexagonal in the reaction.

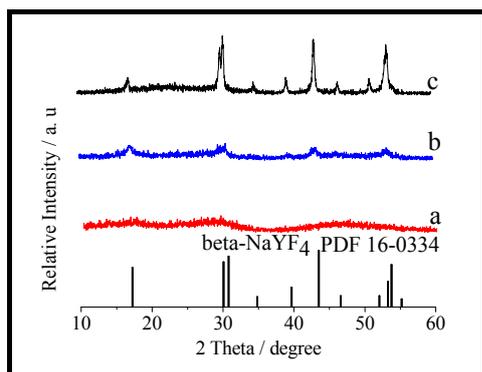


Fig. 2 PXRD patterns of the products collected for different growth time at room temperature: (a) 6 h, (b) 18 h, and (c) 24 h.

These results might have been caused by a different reaction mechanism. When yttrium oxalate reacts with fluoride in ethanol with a trace of water, the real precursor ion concentration (Ln^{3+}) in the solvent is quite low and the reaction proceeds slowly under thermodynamic control, and consequently β -NaYF₄ can be directly produced. With increasing water content, the precursor of free rare earth cations increase, leading to a kinetically controlled growth and consequently α -NaYF₄ is produced. The low solubility of the precursors in the solvent appears to play a vital role in promoting the growth of β -NaYF₄ at low temperature.

There was a report that NH₄F was necessary for the fast formation of NaYF₄ due to the high mobility of the ammonia gas produced in the reaction.¹⁰ In our previous study, NH₄F played an important role for the direct formation of β -NaYF₄.¹³ Here NaF was used instead of NH₄F in the reaction, and β -NaYF₄ can be obtained after 2 h even at low temperature of 55 °C. We attribute this disparity to the different

water content in the reaction system. When water was added, free Na⁺ and F⁻ from NaF could enter the reaction system easily, making the formation of NaYF₄ fast even in the absence of ammonia gas.

Doping has not much effect on the phase-structure of the products prepared at 55 °C. The PXRD patterns of samples doped with Eu³⁺, Yb³⁺, Er³⁺ are shown in Fig. S1, ESI†. The Eu³⁺ doped samples show characteristic emission under UV irradiation. The photoluminescence spectra are shown in Fig. 3.

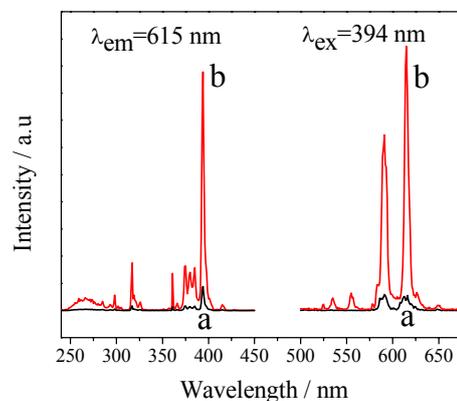


Fig. 3 Excitation and emission spectra of sample a: α -NaYF₄: Eu³⁺ (5 mol %) and sample b: β -NaYF₄: Eu³⁺ (5 mol %).

The excitation spectra of NaYF₄: Eu³⁺ (5 mol %) monitored at 615 nm shows that the strongest excitation band is around 394 nm which corresponds to the ⁷F₀ – ⁵L₆ transition of Eu³⁺. The emission of α -NaYF₄: Eu³⁺ (5 mol %) (sample a) is much weaker than that of β -NaYF₄: Eu³⁺ (5 mol %) (sample b) when excited by 394 nm, indicating β -NaYF₄: Eu³⁺ shows more efficient photoluminescence than α -NaYF₄: Eu³⁺. This phenomenon proves that β -NaYF₄ is a better host material than α -NaYF₄ not only for the up-conversion emission but also for down-conversion emission.

The as-prepared β -NaYF₄: Yb³⁺, Er³⁺ (20 mol %, 2 mol %, respectively) show weak up-conversion luminescence. To further improve the up-conversion efficiency, post heat-treatment was conducted by solvothermal reaction at 220 °C for 2 hours (see the Experimental details in ESI†). After solvothermal treatment, the product preserved its hexagonal phase-structure (Fig. S1d, ESI†) and particle sizes (Fig. S2, ESI†). This indicates that the size of the particles can be controlled in the range below 100 nm through such a post treatment. This is quite different with our previous works in which the direct autoclaving growth either in aqueous solution or organic solvents resulted in the production of larger crystals of β -NaYF₄ in the size range of micron.^{4,9b}

The solvothermally treated product can be dispersed in water directly. However, the nanoparticles (NPs) would re-precipitate after several washing procedures. This may be caused by the de-capping of ligand from the surface of the NPs. After mixed with PAA, a transparent colloidal solution re-formed due to the function of the free –COOH groups on the surface of the NPs, which was identified by FT-IR spectroscopy (Fig. S3, ESI†). The peak from OH become weaker (3381cm⁻¹) and peaks from –COOH (1567 and 1406 cm⁻¹) appeared, indicating the capping ethanol was replaced by PAA.

The colloidal aqueous solution shows its transparency under day

light (Fig. 4a, top), and bright green UC emission could be seen under 980 nm CW laser irradiation (Fig. 4b, top). The up-conversion luminescence spectrum is shown in Fig. 4c, top. The green emission band around 523 nm corresponds to the transition of $^2H_{11/2}(Er^{3+}) \rightarrow ^4I_{15/2}(Er^{3+})$ and that of 542 nm is from $^4S_{3/2}(Er^{3+}) \rightarrow ^4I_{15/2}(Er^{3+})$, and the red band around 652 nm is from the transition of $^4F_{9/2}(Er^{3+}) \rightarrow ^4I_{15/2}(Er^{3+})$, respectively.

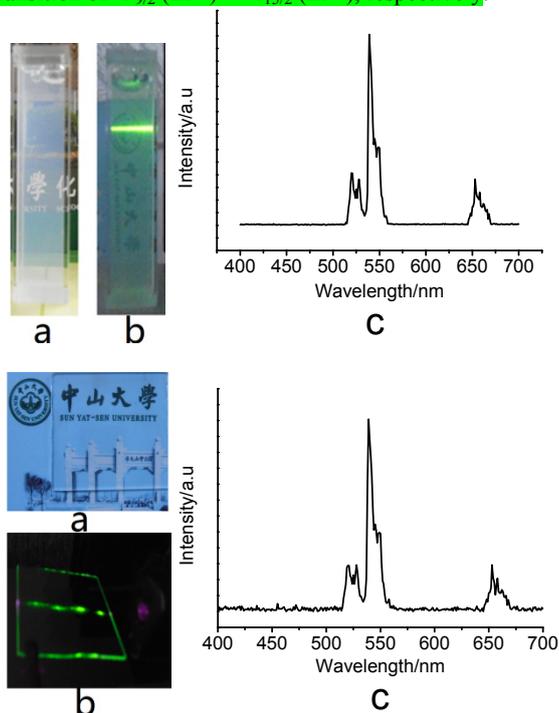


Fig. 4 Transparent aqueous colloidal solution (top) and transparent film (bottom) of β -NaYF₄: Yb, Er under (a) day light and (b) 980 nm CW laser irradiation. (c) Up-conversion spectrum of the solution (top) and the film (bottom).

Because of the nanoscale dimensions of the up-converting NPs and the PAAs on their surface, a transparent thin film could be produced on a glass substrate by dip-coating (see the Experimental details in ESI†). The film shows good optical transparency (Fig. 4a, bottom), and characteristic green emission under irradiation of 980 nm CW laser (Fig. 4b, bottom). The up-conversion spectrum of the film is shown in Fig. 4c, bottom, one can see that the bands position and the relative intensity of the UC emission do not change much compared with those of the colloidal solution (Figure 4c, Top). This transparent up-conversion thin film may find applications in the fields of displays, lighting or photonics.

Conclusions

In summary, small NaYF₄ nanoparticles of hexagonal phase have been prepared in a novel way using sparingly soluble precursors at low temperature in a mixed solvent of ethanol and water by controlling the amount of water. The as-prepared nanoparticles show efficient photoluminescence when doped with Eu³⁺. Bright up-conversion emission can also be achieved after the as-prepared nanoparticles doped with Yb³⁺, Er³⁺ are treated by solvothermal reaction. The post treated nanoparticles maintain their nanoscale dimensions and shape and can be dispersed in water directly as a

transparent stable colloidal solution. An optically transparent up-converting thin film was obtained by dip-coating a mixture of the NPs and PAAs on a glass substrate. Utility in display, lighting and photonic devices is anticipated.

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Notes and references

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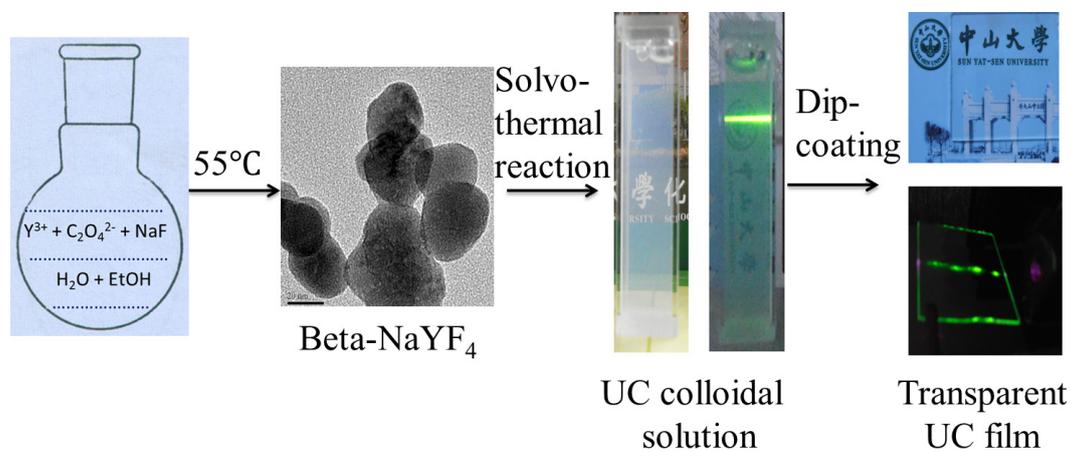
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TOC



Phase pure β - NaYF_4 nanocrystals and transparent UC colloidal solution and thin film could be made in a green way.