



## Full Length Article

## Highly uniform up-converting nanoparticles: Why you should control your synthesis even more



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## ABSTRACT

Luminescent  $\beta$ -NaYF<sub>4</sub>:Yb<sup>3+</sup>,Er<sup>3+</sup> ( $x_{Yb}$ : 0.17,  $x_{Er}$ : 0.03) nanomaterials were synthesized for use as labels for biomedical applications with high temperature co-precipitation synthesis in 1-octadecene and oleic acid. The effect of the synthesis conditions (e.g. argon flow, cooling and stirring rates) on the products' up-conversion luminescence intensity, particle size and morphology were studied. The factors contributing to these properties were analysed. It was observed that an efficient inert gas flow is essential to the formation of the preferred highly-luminescent hexagonal structure. Furthermore, the flow rate, together with the stirring rate, crucially affect the Er:Yb molar ratio of the products. The optimization of this ratio is essential when strong up-conversion emission is required from small particles, whereas the morphology and uniformity of the nanoparticles can be controlled with the cooling rate. These results emphasize the importance of controlling the synthesis conditions, especially when nanoparticles need to have a specific morphology because of their use e.g. as luminescent labels in medical diagnostics.

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## 1. Introduction

Up-conversion luminescence is a unique type of luminescence where low energy radiation (usually near infra-red, NIR) is converted into higher energy radiation, usually in the UV–vis range (300–700 nm) [1,2]. Different combinations of R<sup>3+</sup> ions (R: rare earth, e.g. Yb–Er or Yb–Tm) as the sensitizer and activator, respectively, in selected hosts can produce up-conversion luminescence with different colours. This phenomenon has many potential applications such as enhancement of photosynthesis [3], wavelength conversion in solar cells [4], pH and ion sensors [5–7], biomedical assays [8], and medical imaging [9]. For example, in biomedical assays and applications, up-conversion luminescence nanomaterials are a highly attractive label group because of there is no autofluorescence at the visible wavelengths where the near-infrared excited anti-Stokes shifted emission is detected. This eliminates the need for time-resolved measurements required with conventional fluorescence labels [10,11]. NIR radiation also

enables the use of challenging sample matrices such as whole blood which absorbs light strongly below 600 nm [12]. When the up-converting nanophosphors are used as luminescent labels in biomedical assays they need to be uniform and monodisperse to produce efficient and equal binding sites for the biomolecules – for this reason using spherical particles would be ideal.

The NaYF<sub>4</sub> material has been found to be among the best hosts for up-conversion luminescence [13–15]. It is reported to have three different structures (low-temperature cubic, hexagonal and high-temperature cubic) [16,17] in which the cubic structures have only one cation site while in the hexagonal structure two [16] or three [12,18,19] possible sites have been reported for the rare earths. Of these structures, the hexagonal form ( $\beta$ -NaRF<sub>4</sub>; P63/m (#176), Z: 1.5 [13,20]) has proven to be superior for the up-conversion luminescence [21]. This is thought to be due to low phonon energy in the  $\beta$ -NaYF<sub>4</sub> lattice (max. 350 cm<sup>-1</sup> [22]) and ca. 0.4 Å shorter R–R distance when compared to the cubic form which favours the energy transfer from Yb<sup>3+</sup> to Yb<sup>3+</sup> and Er<sup>3+</sup> [16]. It is also thought that the non-centrosymmetric coordination of R<sup>3+</sup> ions in the  $\beta$ -NaYF<sub>4</sub> enhances the luminescence promoting more the 4f–4f transitions than the centrosymmetric coordination of the R<sup>3+</sup> site in the cubic  $\alpha$ -NaYF<sub>4</sub> [13,21]. The desired hexagonal form can be obtained by introducing necessary thermal energy

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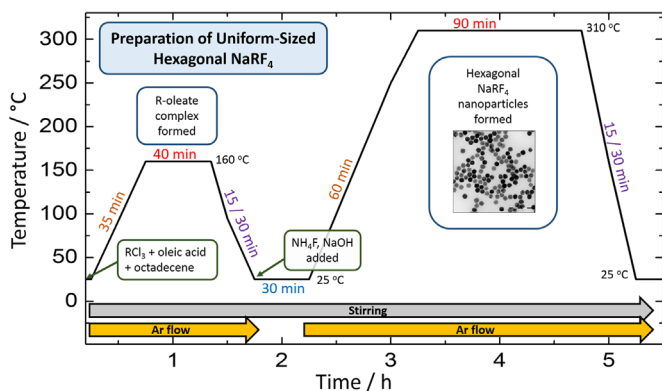


Fig. 1. Schematic presentation of the synthesis protocol for obtaining uniform-sized hexagonal  $\text{NaRF}_4$  nanoparticles.

into the lattice to drive the irreversible phase transition from cubic to hexagonal [23,24]. This, however, results in significant increase in the crystallite size of the material. One-pot, single stage preparation method leads to loss of intimate control of the morphology of these materials, as well.

This work was carried out to investigate the synthesis conditions of the modified [25] high temperature co-precipitation method using 1-octadecene and oleic acid [26] (Fig. 1) and how the conditions affect the particle morphology and up-conversion luminescence. It is possible to achieve the requirement of high reproducibility of the prepared materials with an automation robot [27] but it is obvious that the availability of this kind of robot in common laboratory experiments is not always an option and thus investigating the synthesis parameters is crucial. This method is used as such for the synthesis of  $\text{NaRF}_4$  nanoparticles, but also its variations are reported. These include tests of different ways of introducing rare earth ions into the synthesis and the influence of reaction temperatures [28–30].

This synthesis route is also employed in the preparation of core-shell structures [31] or other host materials such as  $\text{KMnF}_3$  [32]. However, to the authors' knowledge the impact of the parameters studied in the present work have not been reported previously.

In this study it was important to produce uniformly sized nanoparticles with desired morphology – in most cases spherical – to be used as luminescent labels in biomedical assays [8,9]. The protective inert gas flow (argon), duration of cooling period, and stirring rate during the synthesis (Fig. 1) were studied for their effect on the nanomaterial properties. Moreover, as the increase in the nanoparticle size strengthens significantly up-conversion luminescence [33], an appropriate compromise between these properties was investigated.

## 2. Materials and methods

### 2.1. Materials preparation

The  $\text{NaYF}_4:\text{Yb}^{3+},\text{Er}^{3+}$  nanomaterials were prepared with the synthesis procedure reported previously [25] using selected dopant concentrations ( $x_{\text{Yb}}: 0.17$  and  $x_{\text{Er}}: 0.03$ ) (Fig. 1). In the synthesis, methanol solutions ( $0.2 \text{ mol dm}^{-3}$ ) of  $\text{RCl}_3$  (R: Y, Yb, Er,  $6 \text{ cm}^3$  in total) were added to a  $250 \text{ cm}^3$  flask containing 1-octadecene and oleic acid ( $21$  and  $9 \text{ cm}^3$ , respectively). This solution was then heated to and maintained at  $160 \text{ °C}$  for  $40 \text{ min}$  and further cooled down (in  $15$  or  $30 \text{ min}$ ) to room temperature under argon atmosphere ( $1\text{--}3 \text{ dm}^3 \text{ h}^{-1}$  flow).

Then, a methanol solution containing  $\text{NH}_4\text{F}$  and  $\text{NaOH}$  ( $0.18$  and

$0.12 \text{ g}$ , respectively, in total  $15 \text{ cm}^3$ ) was added into the mixture described above and stirred for  $30 \text{ min}$  at room temperature ( $125$  to  $625 \text{ rpm}$ ). The solution was subsequently heated and maintained at  $310 \text{ °C}$  for  $90 \text{ min}$  under argon flow and again cooled down (in  $15$  or  $30 \text{ min}$ ) to room temperature. Both cooling times were kept the same during the same synthesis. The products were eventually precipitated by the addition of ethanol and collected by centrifugation. The products were washed several times with absolute ethanol and dried at room temperature in a vacuum desiccator for characterization. When the specific parameter was not under investigation the values for argon flow rate, cooling time and stirring rate were  $2 \text{ dm}^3 \text{ h}^{-1}$ ,  $30 \text{ min}$  and  $375 \text{ rpm}$ , respectively.

All chemicals used were of analytical grade. Yttrium, ytterbium and erbium chloride hexahydrate ( $\text{RCl}_3 \cdot 6\text{H}_2\text{O}$ , 99.99% purity with respect to other rare earths), ammonium fluoride ( $\text{NH}_4\text{F}$  99.99%), sodium hydroxide ( $\text{NaOH}$ , 99.99), 1-octadecene (90) and oleic acid (90) were all purchased from Sigma-Aldrich. Absolute ethanol and methanol were used as received.

### 2.2. Characterization

The particle morphologies were determined with a Tecnai 12 Bio Twin transmission electron microscope equipped with a CCD camera. The acceleration voltage was  $120 \text{ kV}$  giving the resolution of  $0.49 \text{ nm}$ . Before measurements, the samples were prepared dispersing the up-converting nanomaterials into diluted toluene and then drying a drop on the surface of a carbon coated copper grid. Average particle diameters were calculated with the ImageJ software version 1.43 s [34] (<http://rsb.info.nih.gov/ij>) from 100 particles.

The XPD measurements were used to probe the structure and phase purity of the nanomaterials. The patterns were collected at room temperature with a Huber G670 image plate Guinier camera ( $\text{Cu K}\alpha_1$  radiation,  $1.5406 \text{ Å}$ ) with the  $2\theta$  range between  $4$  and  $100^\circ$  (step  $0.005^\circ$ ). Data collection time was  $30 \text{ min}$  and  $10$  data reading scans of the image plate.

The crystallite sizes of the  $\text{NaYF}_4:\text{Yb}^{3+},\text{Er}^{3+}$  nanomaterials were estimated also from the diffraction data using the Scherrer formula (Eq. (1)) [35]. In this equation,  $d$  is the mean crystallite size (m),  $\lambda$  the X-ray wavelength (m),  $\beta$  (rad) the full width at half maximum (FWHM) of the chosen reflection and  $\theta$  ( $^\circ$ ) half of the Bragg's angle ( $2\theta$ ). Reflection broadening due to the diffractometer was eliminated from the  $\beta_s$  value by using a microcrystalline reference ( $\beta_r$ ; Eq. (2)). The commercial, microcrystalline  $\text{NaYF}_4:\text{Yb}^{3+},\text{Er}^{3+}$  (PTIR 550/F, Phosphor Technology, Stevenage, England) was then used. The (002) and (200) reflections were used to calculate the thickness of the hexagonal plates and the width of the hexagonal faces, respectively, thus giving an estimate of the anisotropy of the size and morphology of the nanocrystallites.

$$d = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

$$\beta^2 = \beta_s^2 - \beta_r^2 \quad (2)$$

The elemental compositions of the products were probed with X-ray fluorescence spectroscopy (XRF) using the PANalytical epsilon 1 apparatus using the internal Omnic calibration.

The up-conversion luminescence and its behaviour with different excitation power densities was studied with NIR laser excitation at  $976 \text{ nm}$ . This excitation is in a good resonance with the  $^2\text{F}_{5/2}$  and  $^4\text{I}_{11/2}$  energy levels of  $\text{Yb}^{3+}$  and  $\text{Er}^{3+}$ , respectively. This enables the efficient energy transfer up-conversion process (ETU) of the  $\text{Yb}^{3+}\text{--Er}^{3+}$  pair (Fig. 2) that has been well described in the

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