

NaYF₄:Er³⁺, Yb³⁺/SiO₂ Core/Shell Upconverting

Nanocrystals for Luminescence Thermometry up to 900

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A. Experimental Methods

Chemicals. All chemicals were used without further purification. The following chemicals were purchased from Sigma-Aldrich: Cyclohexane (99.5%, CH), oleic acid (90%, OA), ethanol (>99.8%, EtOH), methanol (>99.85%, MeOH), sodium hydroxide (>97%, NaOH), ammonium fluoride (>98%, NH₄F), ammonium hydroxide (28 wt% in H₂O, ammonia) lanthanide acetate hydrates (99.9%, Ln(Ac)₃), tetraethyl orthosilicate (99.999%, TEOS) and IGEPAL CO-520 ((C₂H₄O)_n-C₁₅H₂₄O with n ~ 5, average Mn = 441 g mol⁻¹, NP-5). 1-octadecene (90%, ODE) was purchased from Acros Organics.

Synthesis of NaYF₄ nanocrystals. The NaYF₄:Er³⁺, Yb³⁺ NCs are prepared via a co-precipitation method based on the work of Li and Zhang⁴² with some adjustments based on the work of Wang and coworkers.⁴³ Furthermore, we have improved the protocol to obtain a higher fraction of ligands on the

NP surface in order to increase the colloidal stability. This enhancement in colloidal stability is required for the shell growth with silica as explained below.

The synthesis of NaYF₄ NCs is performed in two steps - nucleation and growth. During the nucleation phase the reaction mixture is kept at room temperature to prevent the production of hazardous byproducts *e.g.* gaseous HF. These byproducts are formed at elevated temperatures due to the low decomposition temperature of the fluoride precursor, NH₄F. Once all the fluoride precursor has been used to prepare small nuclei of cubic NaYF₄, the temperature is increased and growth is initiated. The small nuclei are unstable at elevated temperatures and larger hexagonal NaYF₄ crystals are formed via Ostwald ripening-like growth,⁴⁴ resulting in the desired NCs.

The synthesis is performed in a Schlenk line to work under N₂ atmosphere and vacuum. During the reaction the reactants are stirred vigorously. First, 0.5 mmol of Ln(Ac)₃, with an Y:Yb:Er ratio of 80:18:2, is added to a mixture of 3 mL OA and 8.5 mL ODE. The resulting white, turbid dispersion is then degassed at 120 °C under vacuum for 90 min, to give a clear, slightly yellowish solution. Afterwards, the reaction mixture is flushed three times with vacuum and N₂ before cooling down to room temperature. This flushing is performed to remove any residual oxygen or water. Second, a mixture of NaOH and NH₄F in MeOH is prepared and added to the reaction mixture. These Na and F precursors are prepared by dissolving 1.25 mmol NaOH and 2 mmol NH₄F in 1.25 mL and 3.75 mL MeOH, respectively. The precursors are mixed just before the addition to the reaction mixture. This addition was done quickly to suppress the formation of unwanted NaF in the mixed precursor solution. The resulting white, turbid reaction mixture is subsequently stirred for *ca.* 16 h to form small (sub-10 nm) cubic NaYF₄ NCs.

Before the growth step is initiated, the excess MeOH is removed. This is done by heating the sample to 100 °C under vacuum for 30 min. Afterwards, the mixture is flushed with vacuum and N₂ - as described above - before further heating the reaction mixture to 300 °C for 110 min, resulting in larger hexagonal NCs. Although the reaction mixture is flushed throughout the synthesis extensively, there are always trace amounts of oxygen left in the reaction mixture. Consequently, a small fraction of the organic materials present in the reaction mixture can be oxidized, resulting in a light brown discoloration of the clear solution. After cooling down to room temperature, the reaction mixture becomes slightly turbid.

After the synthesis, the reaction mixture is washed to remove excess reagents and solvents. This is done by adding 1 equivalent of EtOH, centrifuging with a relative centrifugal force (RCF) of 840 for 8 min and removing the supernatant. The resulting sediment is redispersed in 5 mL CH. This washing step is repeated two more times to obtain a clear, colorless dispersion of NCs in 5 mL CH.

In the last step of the synthesis the ligand density is increased in order to enhance the colloidal stability of the NCs for the subsequent silica growth. This is done by adding 5 mL of OA and sonication for 15 min, resulting in a turbid dispersion. Afterwards 10 mL of EtOH is added and the dispersion is centrifuged at 840 rcf for 8 min. Finally, the sediment is redispersed in 5 mL CH to obtain a clear, slightly yellowish dispersion.

Synthesis of NaYF₄@SiO₂ nanocrystals. A micro-emulsion method optimized in our group⁴⁵ is used to grow an inert SiO₂ layer around the NCs. In short, *ca.* 10 mg of NCs dispersed in CH is added to a mixture of 3 mmol NP-5 in 12 mL CH. Subsequently, 80 μL of TEOS and 150 μL of ammonia is added to the mixture, while stirring for at least 15 min between injections to ensure sample homogeneity. After the last addition, the sample is stirred for 1 min and kept for *ca.* 24 h to allow for the silica growth.

After the synthesis, excess precursors, apolar solvents and surfactants are removed. This is done by addition of 3 mL EtOH to break up the micelles and afterwards centrifuging at 15000 rcf. The supernatant is removed and the sediment is redispersed in 10 mL EtOH. The dispersion is centrifuged and the sediment is washed two more times with EtOH to obtain a slightly turbid dispersion of NaYF₄@SiO₂ NCs in EtOH.

Setups. Transmission electron microscopy (TEM) characterization was performed using a FEI Tecnai20F and a FEI Talos F200X (in combination with a heating holder from DENSSolutions) both operating at 200 kV for *ex situ* and *in situ* measurements, respectively. At least 100 NCs were used to determine the average diameter of the NCs in a sample and the standard deviation in the size distribution. Energy dispersive X-ray spectroscopy (EDX) measurements were performed using an ultrathin window EDAX-detector and subsequently analyzed using Tecnai Imaging and Analysis software.

Ex situ Powder X-ray diffraction (XRD) measurements were performed on a Bruker D2Phaser using Co K α radiation with a wavelength of 1.79 Å. *In situ* XRD measurements were performed on a Bruker-AXS D8 in combination with an X-ray reactor chamber of Anton Paar for temperature control using Co K α radiation with a wavelength of 1.79 Å.

Emission spectra and photoluminescence (PL) decay curves were recorded using an Edinburgh Instruments FLS920 spectrofluorometer equipped with a 450W xenon lamp and a Hamamatsu R928 photomultiplier tube. For upconversion emission spectra, a 980 nm 2W continuous wave laser was used for excitation in the ²F_{5/2} level of Yb³⁺. For PL decay measurements an optical parametric oscillator system, Opotek He 355 II, was used, with a pulse width of 10 ns, a repetition rate of 20 Hz and pulse energy of *ca.* 3 mJ. To control the temperature during luminescence measurements, a Linkam THMS600 Microscope Stage was used.

B. Figures

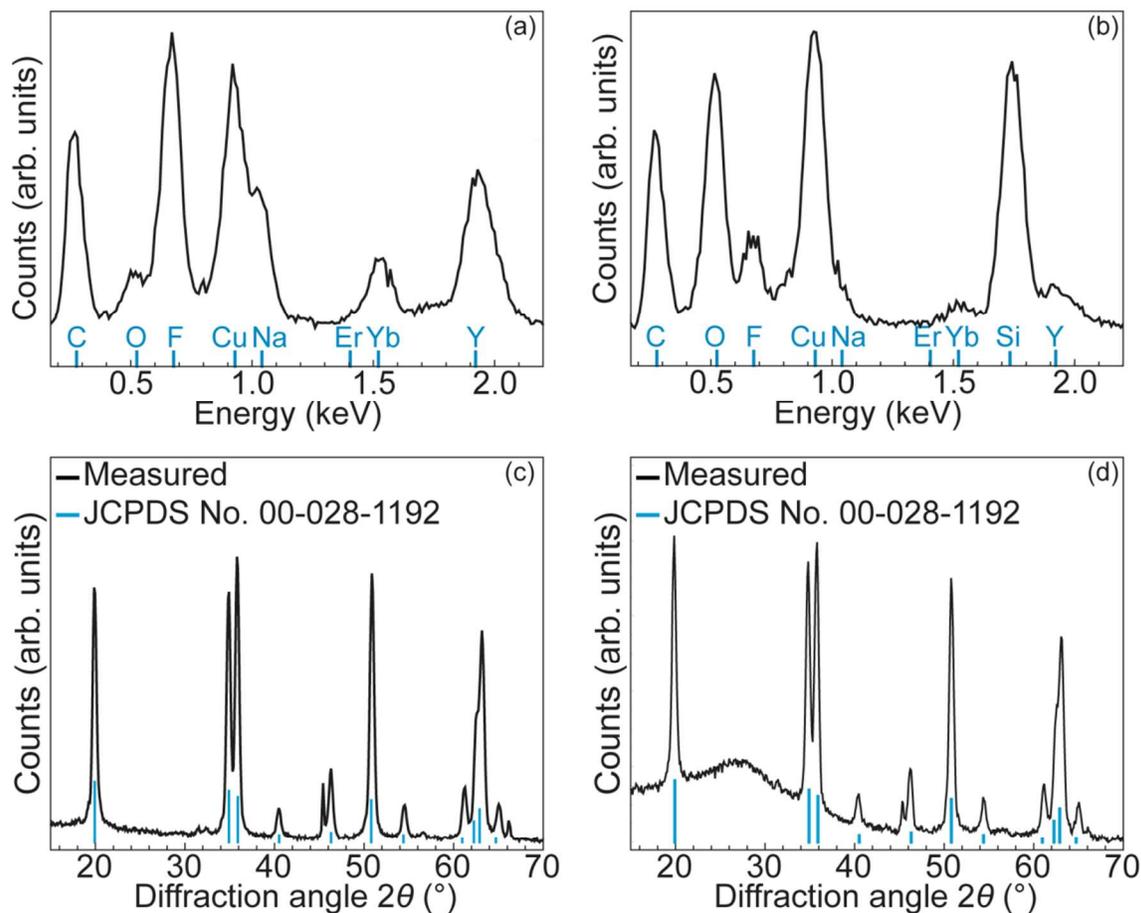


Figure S1. XRD diffractograms of NaYF₄ NCs and NaYF₄@SiO₂ NCs (a and b, respectively). The cyan lines are reference values for hexagonal NaYF₄ (JCPDS No. 00-028-1192), the extra peaks are due to low impurity levels of NaF (JCPDS No. 00-036-1455). EDX spectra of NaYF₄ and NaYF₄@SiO₂ (c and d, respectively).

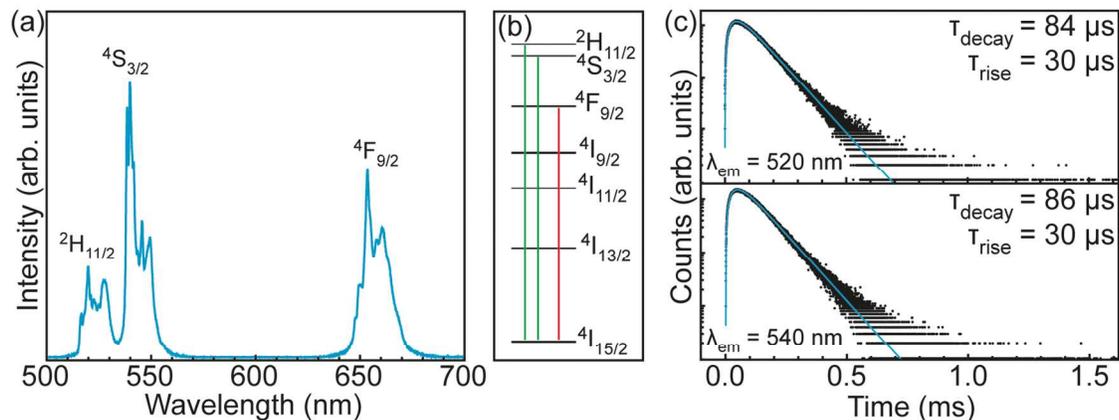


Figure S2. Emission spectrum of prepared NaYF₄@SiO₂ NCs between 500 nm and 700 nm while exciting Yb³⁺ at 980 nm (a) The energy diagram of Er³⁺ (b). The time-resolved luminescence measurements of the corresponding ²H_{11/2} and ⁴S_{3/2} excited states upon excitation at 980 nm (c).

C. Equations

The equation used to calculate the weighted average wavelength of the emission peaks of the ²H_{11/2}-⁴I_{15/2} (520 nm) and ⁴S_{3/2}-⁴I_{15/2} (545 nm) transitions is as follows.

$$\bar{\lambda} = \frac{\sum \lambda_i I_i}{\sum I_i} \quad (S1)$$

From Figure 2a, the weighted average wavelengths of the ²H_{11/2}-⁴I_{15/2} and ⁴S_{3/2}-⁴I_{15/2} peaks were calculated by taking into account the wavelength ranges of 500-533 nm and 533-570 nm respectively.

References

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