

Supporting Information

Ultrafast Synthesis and Coating of High Quality

β -NaYF₄:Yb³⁺,Ln³⁺ Short Nanorods

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Synthesis of the Up-converting nanorods

All chemicals were purchased from Sigma-Aldrich and used as received. The purity of yttrium, ytterbium, erbium, thulium and terbium acetates were 99.9%. Sodium fluoride, benzyl alcohol and polyvinylpyrrolidone (PVP) were of analytical grade. Oleic acid (OA) is 70-80% of purity. Water MilliQ was used throughout the experiments. The stoichiometry of the samples was $\text{NaY}_{0.8-x}\text{Yb}_{0.2}\text{Ln}_x\text{F}_4$ (with x : 0.005 for Tm^{3+} and 0.02 for Tb^{3+} and Er^{3+} samples). The samples were labelled as UCNR(Tm), UCNR(Tb) and UCNR(Er), respectively. The protocol is described for UCNR(Tb), and the synthesis for the other two samples is similar but introducing the stoichiometric amount of $\text{Tm}(\text{Ac})_3$ or $\text{Er}(\text{Ac})_3$ instead of $\text{Tb}(\text{Ac})_3$.

MICROWAVE SYNTHESIS

In a typical synthesis of UCNRs(Tb), 0.415 g of $\text{Y}(\text{Ac})_3$, 0.140 g of $\text{Yb}(\text{Ac})_3$ and 0.014 g of $\text{Tb}(\text{Ac})_3$ were dispersed in 2.25 mL of benzyl alcohol (BA) by stirring at 60 °C until good homogenization. In the meanwhile, 0.084 g of NaF were dissolved in 750 μl of MilliQ water (18.2 M Ω). Both solutions were mixed in a microwave tube and sonicated for few seconds. Then, the tube containing the mixture was inserted in a CEM Discovery SP-X microwave reactor. The microwave treatment is a two-step process: (1) the mixture was heated from room temperature to 60 °C and hold it for 5 minutes in order to completely dissolve the precursor mixture, and (2) a heating from 60 to 180 °C and keep it for 10 minutes. During this second step, the nucleation and growth of the nanorods take place. After the MW treatment, a N_2 flow was first used to fast cool down the solution (reaching 50 °C) and then left until reaching room temperature. **The bare or "fresh" UCNRs were**

collected by centrifugation (5000 rpm for 10 min) after the addition of absolute EtOH to the reaction tube. The product was washed four times with EtOH to remove the excess of organics and recovered by centrifugation (5000 rpm for 10 min). The reproducibility of the synthesis protocol has been confirmed has been repeated 5 times and the results were similar reproducible. The yield of the synthesis was estimated to be around 85%.

COATING

For PVP and OA coating, the reaction tubes were kept at 80 °C to avoid gelling of the solution and to maintain a certain degree of reactivity. Then, a diluted PVP water solution (100 mg in 500 µl) or 300 µl of OA were directly introduced into the reaction tubes. In both cases, the mixtures were sonicated for few minutes. To collect the final products, the particles were washed four times with EtOH to remove the excess of organics and recovered by centrifugation (5000rpm for 10 min). Finally, they were air dried to remove the EtOH and re-dispersed in the appropriate solvent, i.e. water or cyclohexane for PVP- and OA-coated UCNRs, respectively.

CHARACTERIZATION TECHNIQUES

The crystalline phase of powdered samples was analyzed using the X-ray diffraction technique with a Bruker AXS diffractometer equipped with a copper anode. The XRD patterns were measured from 2θ 15° to 80°, with a step of 0.05° and 1.5 s per step. The goniometer was controlled with the D4 Endeavor software from Bruker AXS.

TEM micrographs and electron diffraction (ED) images to analyze morphologies and crystalline phase were obtained with a JEOL JEM-1210 electron microscope, operating at

120 kV. The mean diameter and polydispersity of each system were determined by counting and sizing over 100 rods from TEM images. One drop of the nanorods dispersion was placed in a carbon film copper grid at -140 °C by the use of liquid nitrogen during the imaging.

The luminescence measurements were performed on a Jasco FP-8300 spectrofluorimeter using 3 mL quartz cuvettes with 10 mm path-length and a sample concentration of 5 mg of UCNRs in 5 mL of the appropriate solvent (water or cyclohexane). The infrared laser diode RLTM DL-980-2W module (980 nm \pm 5nm, 2 W cw, stability <5%, laser head 141x46x73 mm) from Roithner LaserTechnik was used as the pump source. The laser was focalized in the cuvette to increase the output power up to 105 Wcm⁻² optical power density on the sample.

PRELIMINARY WORK

Various essays were made in order to obtain pure hexagonal phase nanocrystals of Ln,Yb:NaYF₄. Within the attempts performed, precursor salts, mixture of solvents, microwave conditions (which were based on the solvent mixture, in order to avoid fast boiling of solvents and change reactants concentrations) and post-synthetic coating of the resulting UCNPs were performed, including particles with no coatings, to verify particles reactivity after microwave irradiation. Table SI.1 summarizes the essayed reaction and the crystalline phase obtained.

Table SI.1: Samples prepared in order to obtain pure hexagonal up-converting nanoparticles. St stands for Stearate anion and Ac for Acetate anion. W, EG and BA stand for water, ethylene glycol and benzyl alcohol, respectively. PST is the acronym of post – synthetic treatment performed in order to coat nanoparticles.

Sample Code	Precursors +NaF	Solvent mixture composition	V (mL)	MW parameters	PST	Crystal phase
S1	Y,Yb,Ln(St) ₃	W:EtOH 1:4	3	30',300W, 80°C,12 bar	1. OA 2.No PST 3.Cytrate	Fm-3m (α)
S2	Y,Yb,Ln(St) ₃	W:EG 1:4	3	30',300W, 150°C,12 bar	1. OA 2.No PST	Fm-3m (α)
S3	Y,Yb,Ln(St) ₃	W:BA 1:4	3	300W, 5',60°C/10',180°C, 12 bar	1. OA 2.No PST	Fm-3m (α)
S4	Y,Yb,Ln(Ac) ₃	W:EtOH 1:4	3	30',300W, 80°C,12 bar	1. OA 2.No PST	Fm-3m (α)
S5	Y,Yb,Ln(Ac) ₃	W:EG 1:4	3	30',300W, 150°C,12 bar	1. OA 2.No PST	Fm-3m (α)
S6	Y,Yb,Ln(Ac) ₃	W:BA 1:4	3	300W, 5',60°C/10',180°C, 12 bar	1. OA 2. No PST 3. PVP	P-6 or P6 ₃ /m (β)

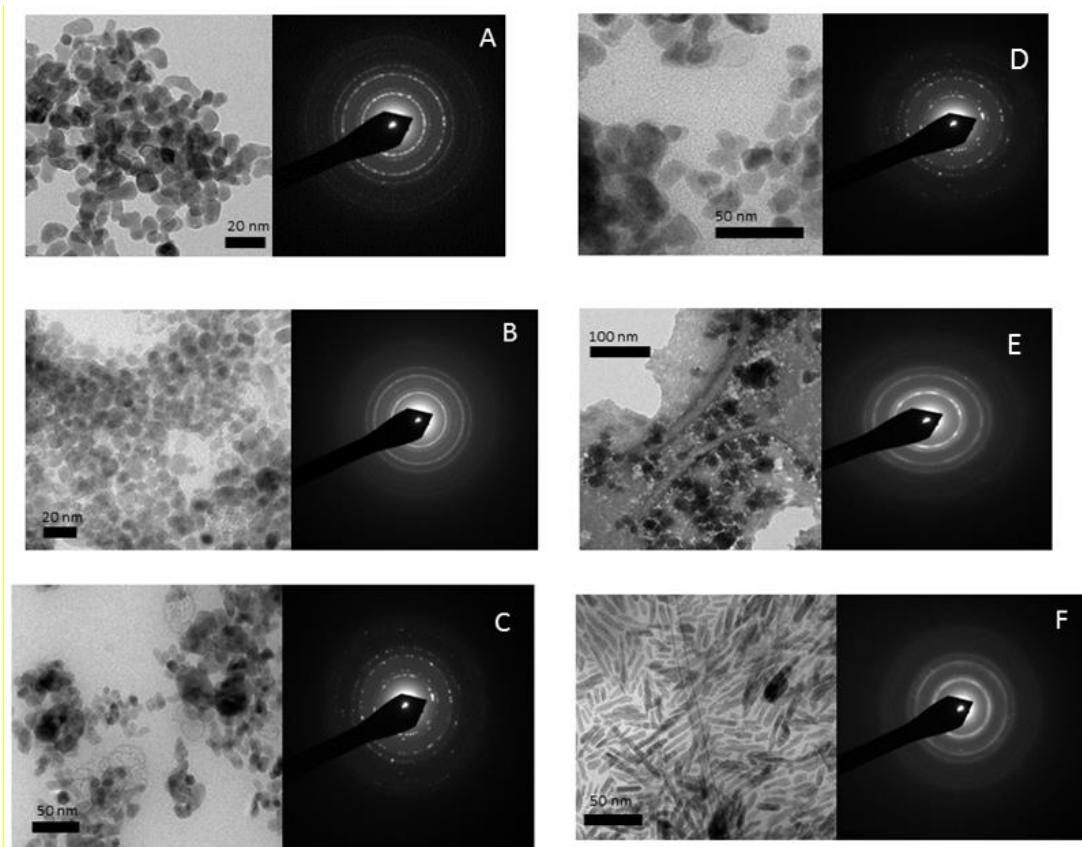


Fig. S11: TEM micrographs and SAED patterns of the Tb,Yb:NaYF₄ nanocrystals synthesized by microwave treatment: A) S1, B) S2, C) S3, D) S4, E) S5, F) S6 samples from Table SI.1. SAED diffractograms were indexed to cubic structures from A to E, and only pure hexagonal crystal configuration in F.

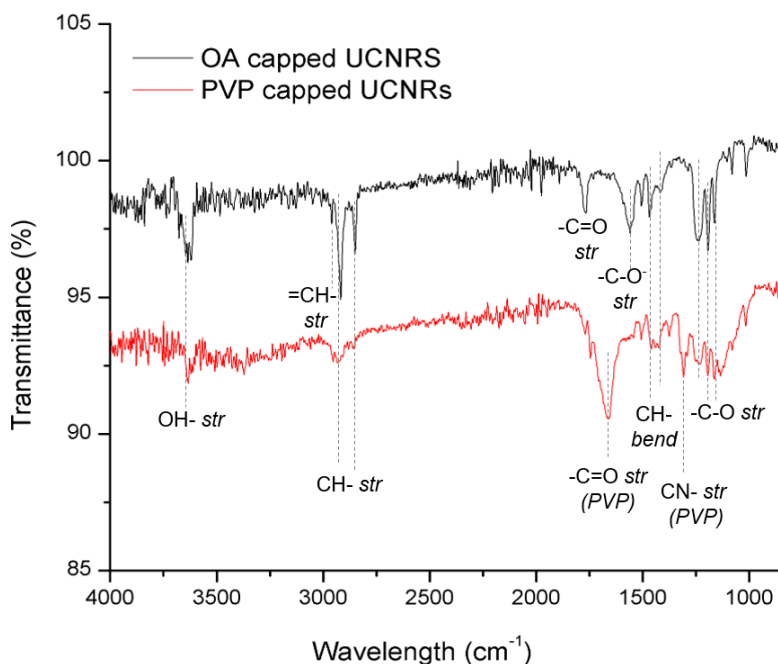


Fig. SI2: FTIR spectra of the PVP- and OA-UCNRs samples.

Fig. SI2 shows the FTIR spectra of the PVP- and OA-coated UCNRS samples. The band located at around 3670 cm^{-1} assigned to OH- stretching reveals the presence of residual water or alcohol species in both nanocrystals. In the spectrum of the PVP-coated sample, the bands appearing between 2920 and 2850 cm^{-1} are associated to the antisymmetric (ν_{as}) and symmetric (ν_s) CH stretching of $-\text{CH}_2$ groups, respectively. The intense peak at 1658 cm^{-1} belongs to the C=O group of PVP. Scissoring bending vibrations of CH_2 groups are found around 1450 cm^{-1} . The band at 1308 cm^{-1} is due to C-N stretching vibration of PVP. The C-O stretches from the carbonyl group is also detected at 1158 and 1230 cm^{-1} .

Characteristics of the OA can also be seen in the FTIR spectrum, which relates to the long alkyl chain, the double bond between carbon atoms and the carboxylic group. The band at 3006 cm^{-1} is assigned to the stretching vibration of =CH. The bands at 2916 and 2850 cm^{-1} are respectively associated to the antisymmetric (ν_{as}) and symmetric (ν_s) CH stretching of methylene ($-\text{CH}_2$) in the long alkyl chain. The CH_2 deformation vibration appears at 1468 cm^{-1} . The bands at 1767 and 1561 cm^{-1} correspond to the stretching vibration of CO in carboxylic groups from non-coordinated oleic acid (residual free oleic acid) and carboxylate (capped oleate ligand) groups, respectively. The band at 1561 cm^{-1} demonstrates presence of oleate ligands on the surface of the UCNRS.