Supplementary Information

Mechanochemical synthesis of hexagonal $NaGdF_4$ nanoparticles: From the influence of stabilizing agents on hexagonal phase to the formation of core-shell structures

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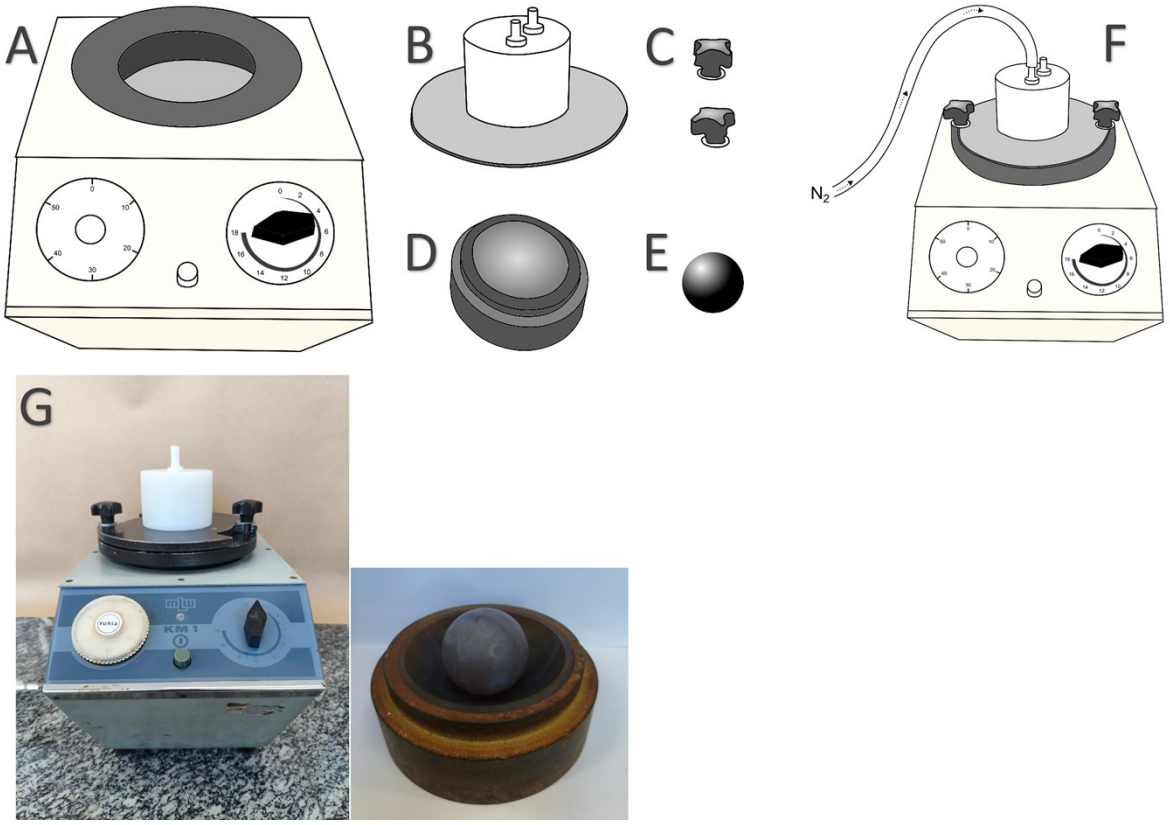

Fig. S1. Mill ball used in the experiments (a), consisting of an agate reaction vessel (d) and agata sphere (e), equipped with a Teflon lid (b) and sealing screws (c). On the right, a photographic representation of assembled system. (g) Photograph of the mechanochemical setup, including the agate jar and agate milling ball. The reactions were performed in an agate jar (volume: 100 mL; internal diameter: 92 mm), equipped with a Teflon cup (internal diameter: 78 mm; depth: 60 mm). A single agate milling ball (diameter: 52 mm; mass: 188 g) was used for all experiments.

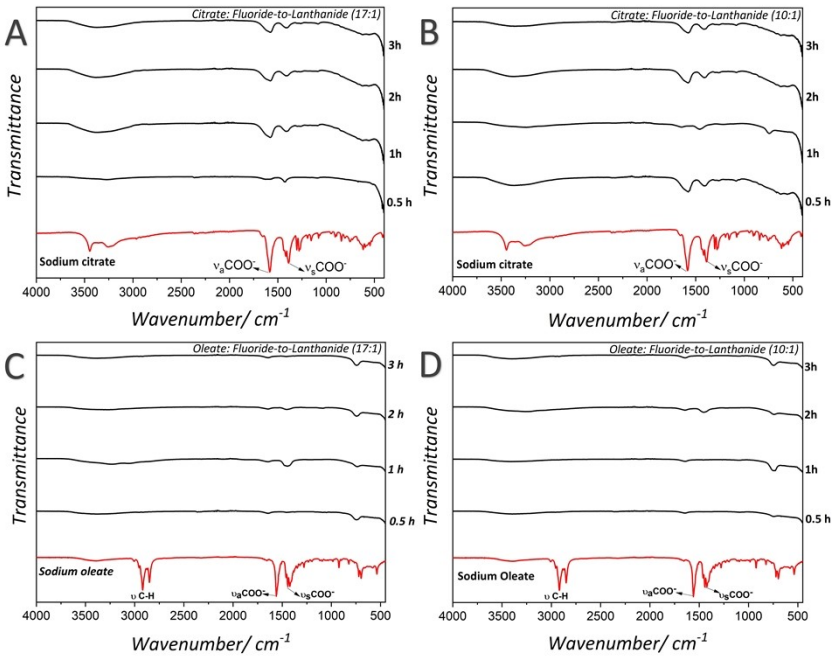

Fig. S2. FTIR spectra of nanoparticles containing eleate (a, b) and citrate (c, d), synthesized with fluoride:sodium molar ratios (17:1 and 10:1), at different reaction times (0.5, 1, 2 and 3h).

The citrate can be confirmed by bands in 1576 cm-1 and 1410 cm-1 related to the vibrational stretching asymmetric and symmetric of carboxylate groups (COO-), respectively, Fig. S2a. The presence of oleate attached of the nanoparticle was also confirmed by FTIR, through the bands associated to the (-CH2-), (COO^-) groups, as well as observed for oleate, Fig. S2b.

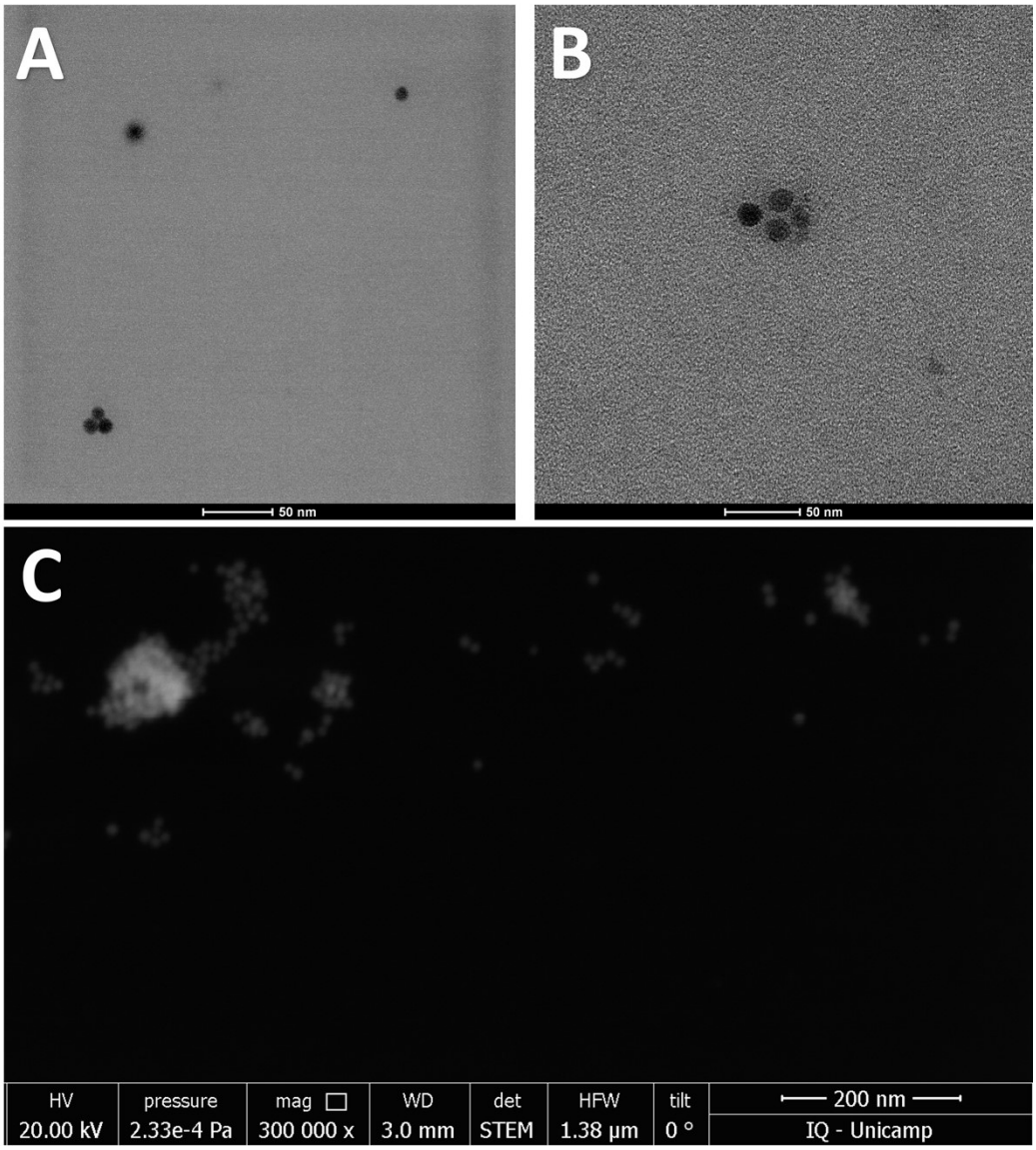

Fig. S3. Transmission Electron Microscospy (TEM) images of $NaGdF_4$:YbEr nanoparticles containing (a) oleate and (b) citrate, evidencing its shape and size. In (c) is shown the scanning electron microscope (SEM) image acquired to nanoparticle containing oleate using the STEM accessory.

Tab. S1. Lifetimes obtained for nanoparticles containing oleate and citrate, synthesized with fluoride:sodium molar ratios (17:1 and 10:1), at different reaction times (0.5, 1, 2 and 3 h). The nanoparticles were excited by a 980 nm laser, and the

lifetimes correspond to emission in the 520, 540 and 654 nm bands. The values were fitted using biexponential functions of the decay curves.

Nanoparticles	520 nm Lifetime 1/ µs	520 nm Lifetime 2/ µs	540 nm Lifetime 1/ µs	540 nm Lifetime 2/ µs	654 nm Lifetime 1/ µs	654 nm Lifetime 2/ µs
Oleate 17F 30 min	5.7	32	5.7	34.6	8.3	76.6
Oleate 17F 1h	9.5	57.8	9	58.2	85.6	296.5
Oleate 17F 2h	7.5	62.8	7.2	64	103.7	353.5
Oleate 17F 3h	5.4	73.3	5.6	76.6	6.8	193.8
Oleate 10F 30 min	7.3	25.2	7.5	26	12.7	50.7
Oleate 10F 1h	4.1	67.1	4.4	76.7	6.3	174
Oleate 10F 2h	5.4	61.4	5.4	64.9	98.3	369.1
Oleate 10F 3h	6.3	72.2	6.2	73.8	134.3	369
Citrate 17F 30 min	2.1	73.5	2.1	75	2.2	187.5
Citrate 17F 1h	6.1	73.1	82.9	452.1	73.7	234.7
Citrate 17F 2h	3.1	73.5	3.1	74.4	5	162.8
Citrate 17F 3h	2.8	59.9	2.8	61.2	3.2	102.7
Citrate 10F 30 min	79.2	339.9	79.6	341.9	165.4	755.3
Citrate 10F 1h	59.8	163.6	63.5	235.7	98.8	395.9
Citrate 10F 2h	1.7	76.4	1.3	77.1	1.8	165.4
Citrate 10F 3h	64	259.6	65.6	302.3	121	517.7
Core-shell Citrate 17F 2h	86	483	8.7	83	143	144

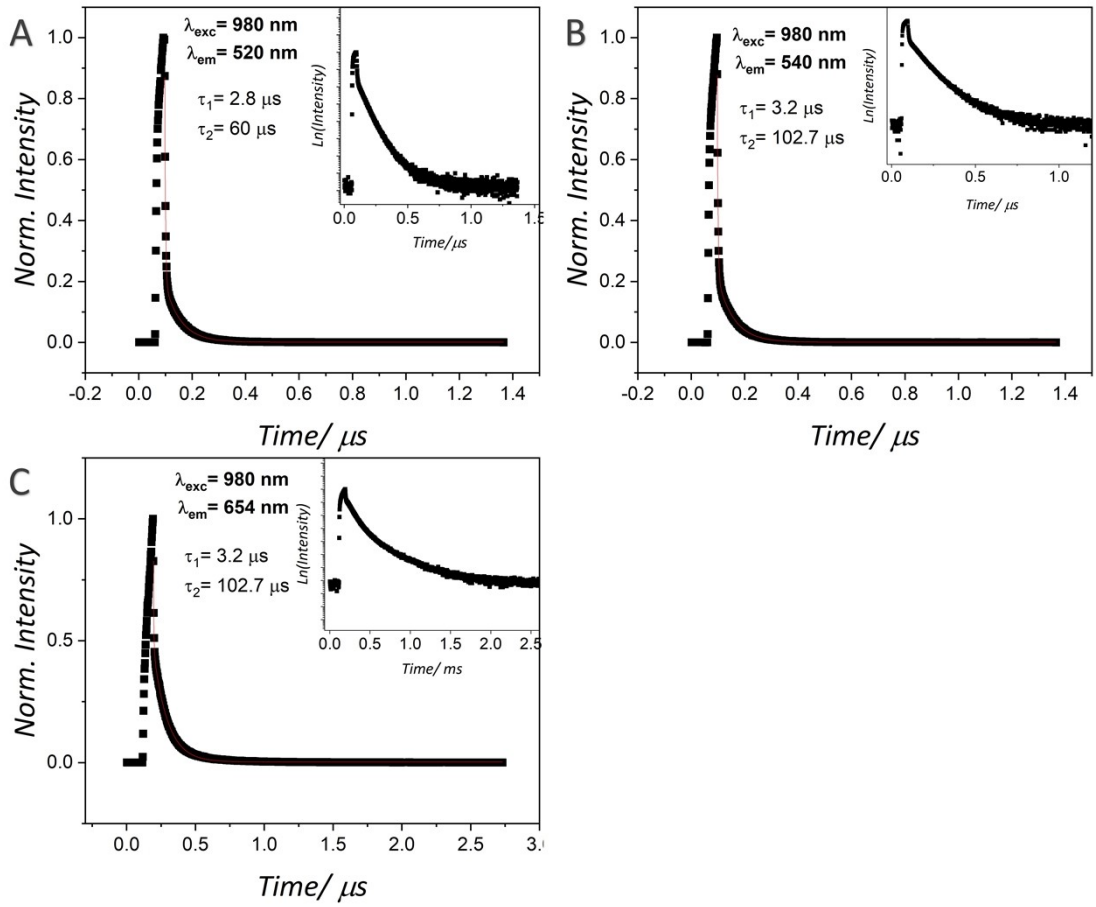

Fig. S4*. Decay curves of the excited state (representative example) for Er ion emission at 520, 540 and 654 nm, obtained from the $NaGdF_4$:Yb,Er nanoparticle containing cintrate (17F) synthesized in 3h, under excitation at 980 nm. The record time profile reflects the energy transfer upconversion (ETU) process.*

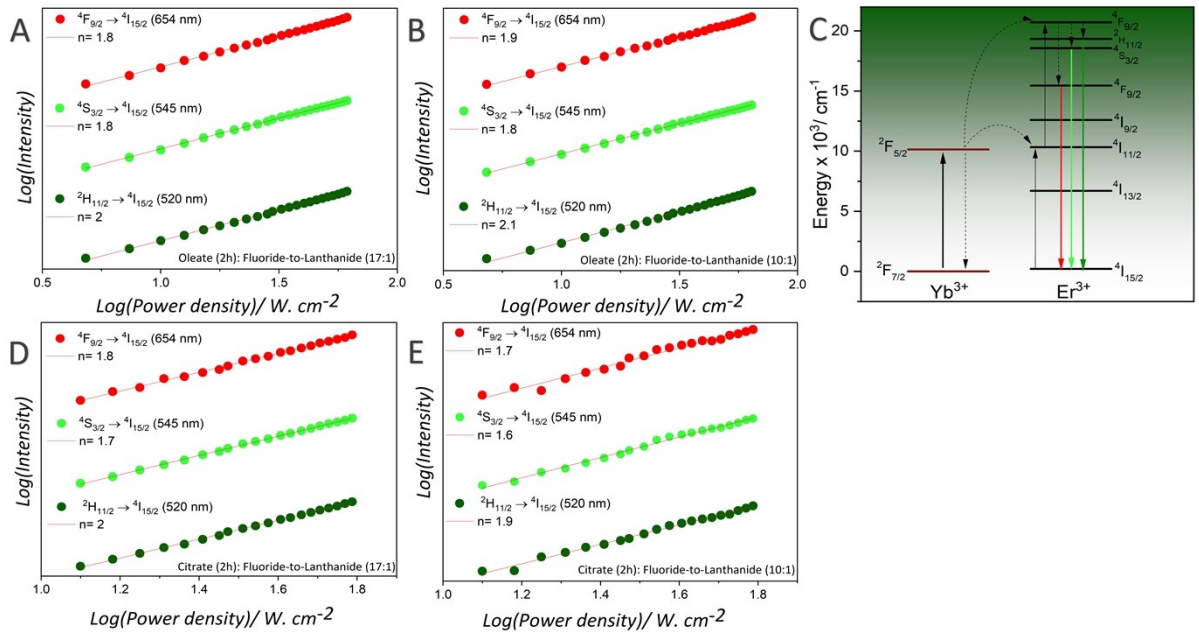

Fig. S5. Power law for nanoparticles containing oleate (a, b) and citrate (d, e), synthesized with a reaction time of 2 h. (c) Energy level diagram of Er and Yb ions, illustrating the possible energy transfer mechanism involved in the upconversion process.