Electronic Supplementary Material (ESI) for Nanoscale

Electronic Supplementary Information

The impact of shell host ($NaYF_4$/CaF_2) and shell deposition method on the up-conversion enhancement in Tb^{3+}, Yb^{3+} codoped colloidal α-$NaYF_4$ core-shell nanoparticles

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Table S1. A list of all the synthesized samples as well as the type of synthesis and concentration of the shell.

shell	synthesis method	shell:core molar ratio			
		1 layer	2 layers	3 layers	4 layers
$NaYF_4$ CaF_2	shell by shell	0.2	0.5	0.8	1.0
		1.2	1.5	1.8	2.0
		2.2	2.5	2.8	3.0
	one step coating	1.0			
		1.5			
		2			
		3			

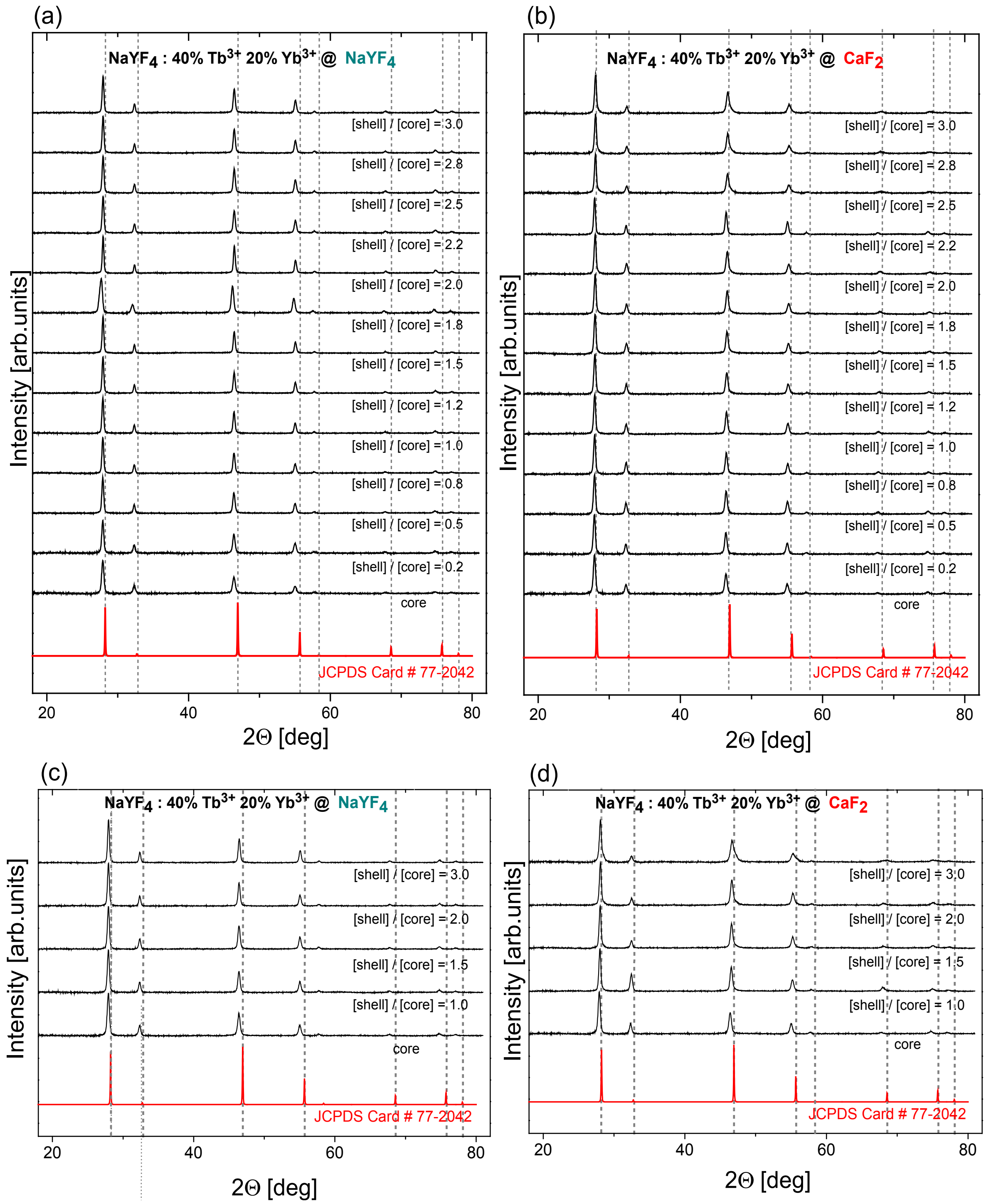

Fig. S1 XRD pattern of cubic $NaYF_4$: 40% Tb^{3+}, 20% Yb^{3+} core nanocrystals and the corresponding core coated with $NaYF_4$ (a, c) and CaF_2 (b, d) shell with different shell:core molar ratio for samples obtained by shell by shell (a, b) and one step coating method (c, d).

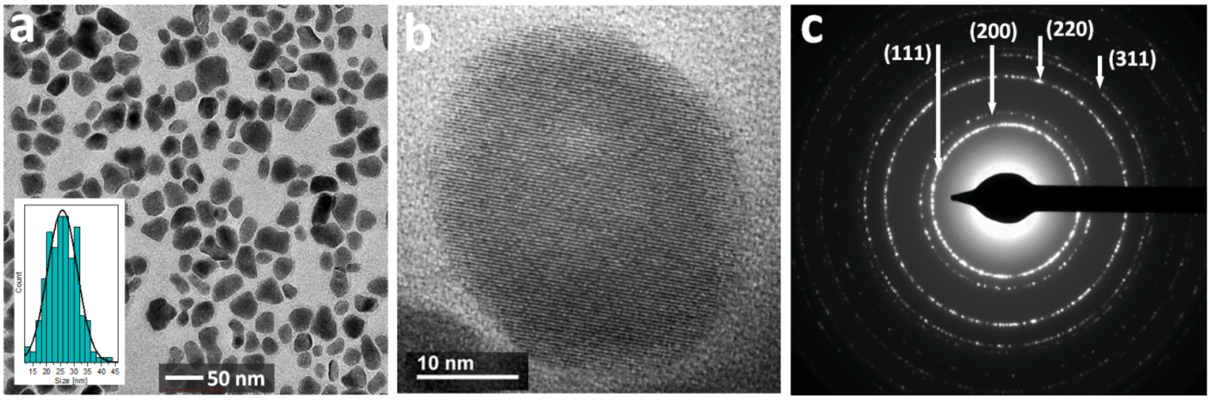

Fig. S2 (a) TEM images of $NaYF_4$:40%Tb^{3+}, 20%Yb^{3+} core nanoparticles; (b) HRTEM image of a single crystallite. Inset in (a) displays a histogram of the size distribution; (c) SEAD pattern of the $NaYF_4$:40%Tb^{3+}, 20%Yb^{3+} nanoparticles.

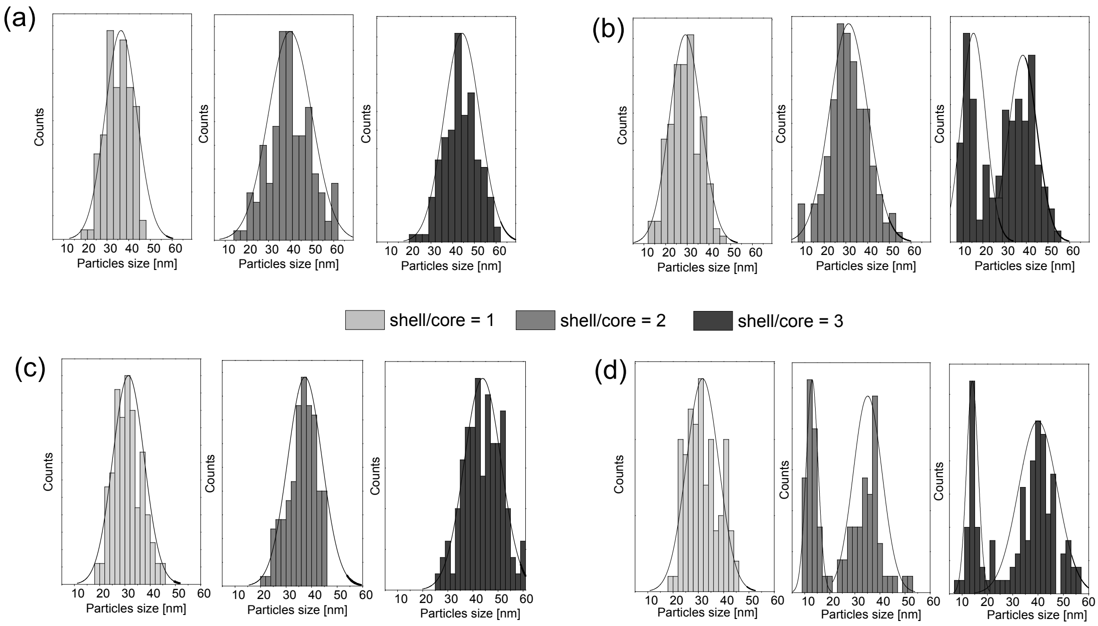

Fig. S3 Size distribution of $NaYF_4$:40%Tb^{3+},20%Yb^{3+} core coated with $NaYF_4$ (a, b) and CaF_2 (c, d) shell with different shell:core molar ratio. The core/shell nanoparticles were obtained by shell by shell (a, c) and one step coating (b, d) method.

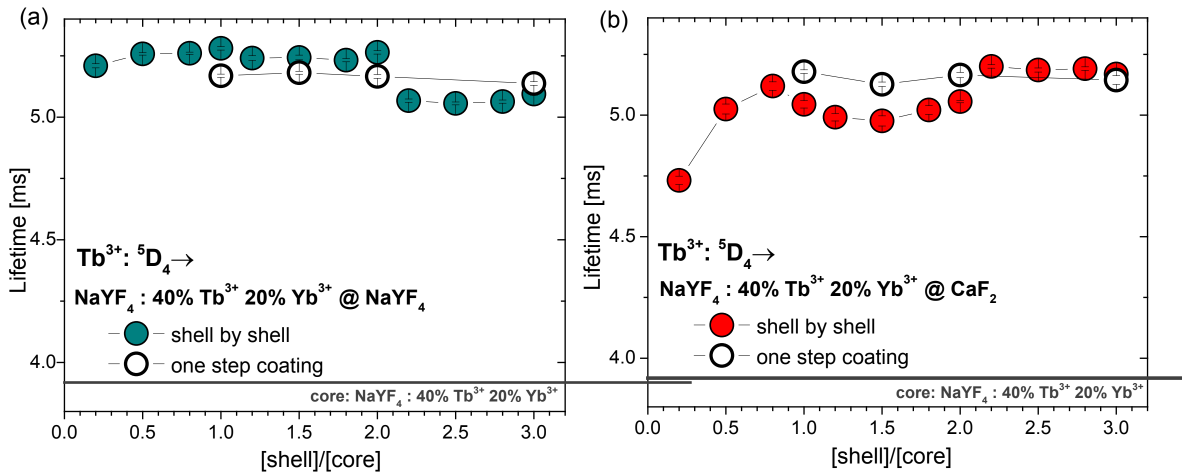

Fig. S4 Dependence of luminescence lifetimes of Tb^{3+} versus shell:core molar ratio for both $NaYF_4$ (a) and CaF_2 (b) shells. Shell by shell (filled circles) and one step (open circles) coating samples was compared. The $^5D_4$ terbium ions level was excited either through the cooperative energy transfer from ytterbium ions (under 976 nm).

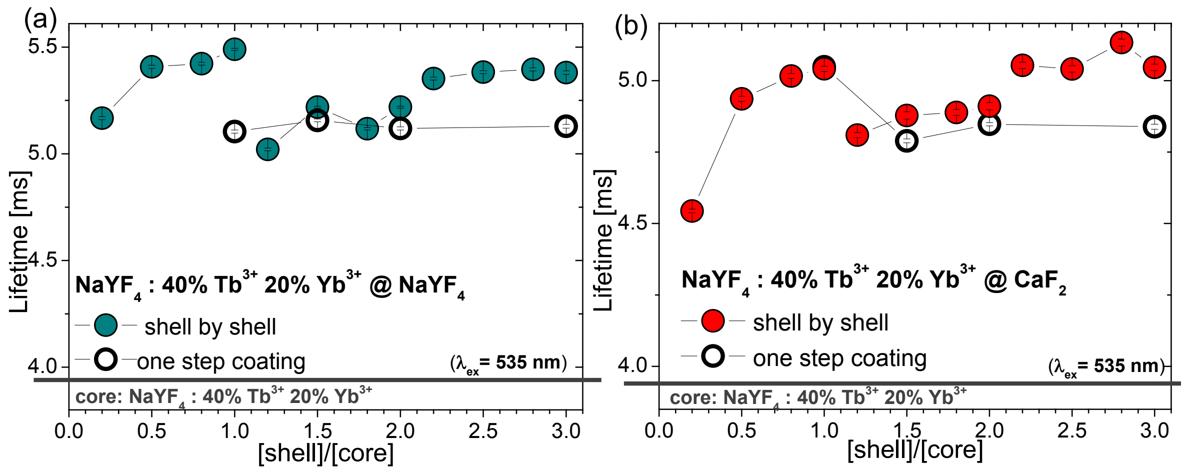

Fig. S5 Dependence of luminescence lifetimes of Tb^{3+} versus shell:core molar ratio for both $NaYF_4$ (a) and CaF_2 (b) shells. Shell by shell (filled circles) and one step (open circles) coating samples was compared. The $^5D_4$ terbium ions level was excited by direct excitation of terbium ions (under 532 nm).

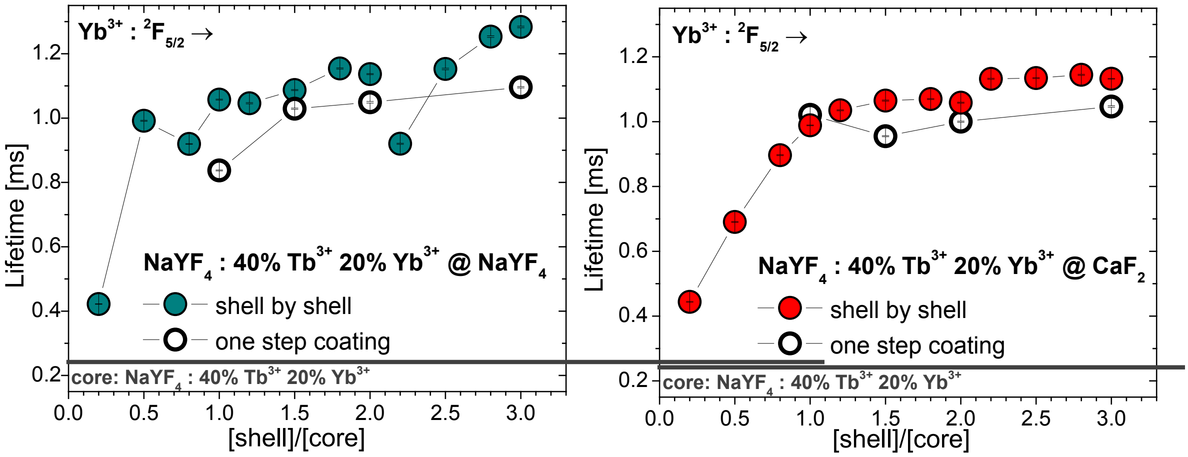

Fig. S6 Dependence of luminescence lifetimes of Yb^{3+}: $^2F_{5/2}$ versus shell:core molar ratio for both $NaYF_4$ (a) and CaF_2 (b) shells. Shell by shell (filled circles) and one step (open circles) coating samples was compared.

Table S2 contains intentional and experimental relative concentrations found from spectra deconvolution of 27 mixtures of three different (Yb^{3+}/Er^{3+}, Yb^{3+}/Tm^{3+}, and Yb^{3+}/Tb^{3+}) luminophores. Although the same experimental conditions (e.g. excitation geometry, power density etc.) were used along all the measurements, the corresponding numbers in both columns (intentional vs. experimental) cannot be directly compared. This is because no absolute NPs concentrations per unit volume was known or these chloroform dispersed colloidal solutions of NPs were drying in slightly different way forming layers of different thickness. However, the samples of the same composition, e.g. $[w_{Er}, w_{Tb}, w_{Tm}]$ = [1,1,1] = [3,3,3] = [5,5,5] = [33%,33%,33%] (where 1, 3 and 5 describe relative unit volumes of Er^{3+}, Tb^{3+} and Tm^{3+} colloidal solutions used to form a mixture) led to very similar experimental weights, here $[w_{Er}, w_{Tb}, w_{Tm}]$ = [55,19,26] % = [54,20,26] % = [53, 20, 27] %. This confirms reliability of data deconvolution and capability to distinguish numerous spectral fingerprints. Number of possible spectral fingerprints is much higher, since both concentration variability C may increase (here C=5 concentration levels, which may rise to e.g. C=10 levels) and more possible taggants T may be used (beside Yb^{3+}/Tm^{3+}, Yb^{3+}/Tb^{3+} and Yb^{3+}/Er^{3+} also Yb^{3+}/Dy^{3+} and Yb^{3+}/Ho^{3+} thus T=5). Therefore, the number of possible spectral coed rises to $N = C^T = 10^5$.

Table S2. Intentional and experimental relative concentrations found from spectra deconvolution of 27 mixtures of three different (Yb^{3+}/Er^{3+}, Yb^{3+}/Tm^{3+}, and Yb^{3+}/Tb^{3+}) luminophores.

Sample number	Intentional relative concentrations [%]			Experimental relative concentrations [%]		
	[Er]	[Tm]	[Tb]	[Er]	[Tm]	[Tb]
1	33	33	33	55	19	26
2	20	20	60	40	31	29
3	14	14	71	32	49	19
4	20	60	20	48	18	34
5	14	43	43	38	27	35
6	11	33	56	32	36	32
7	14	71	14	36	11	53
8	11	56	33	30	24	47
9	9	45	45	25	31	44
10	60	20	20	67	14	19
11	43	14	43	64	22	15
12	33	11	56	56	31	13
13	43	43	14	55	12	33
14	33	33	33	54	20	26
15	27	27	45	50	27	23
16	33	56	11	51	10	38
17	27	45	27	48	17	35
18	23	38	38	42	25	33
19	71	14	14	77	12	11
20	56	11	33	70	18	11
21	45	9	45	66	24	10
22	56	33	11	67	10	22
23	45	27	27	65	15	20
24	38	23	38	58	23	20
25	45	45	9	62	9	30
26	38	38	23	57	14	29
27	33	33	33	53	20	27