Electronic Supplementary Information

Enhanced upconversion luminescence and modulated paramagnetic performance in $NaGdF_4$: Yb, Er by Mg^{2+} tridoping

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Table S1 Nominal and ICP-AES results of cation mole ratios in the products

$NaGd_{(0.78-x)}F4$: 20%Yb, 2%Er, xMg	Na:Gd:Yb:Er:Mg	
	Nominal ratio	ICP-AES result
x=0	1.000:0.778:0.199:0.023	1.010: 0.778: 0.193: 0.019
x=3%	1.000:0.747:0.202:0.020:0.031	1.007: 0.770: 0.183:0.018: 0.039
x=7%	1.000:0.705::0.204:0.021:0.070	1.000: 0.719: 0.186: 0.018: 0.077
x=13.5%	1.000:0.638:0.205:0.022:0.135	1.006: 0.637: 0.186: 0.018: 0.159
x=25%	1.000:0.530:0.200:0.024:0.246	1.006: 0.523: 0.185: 0.019: 0.273
x=40%	1.000:0.354:0.207:0.023:0.416	1.057: 0.268: 0.200: 0.024: 0.508

As shown in Table S1, with increasing of Mg^{2+} doping concentrations in $NaGdF_4$, the molar percentages of Gd reduces gradually, and the value of Gd/Mg ratio is slightly lower than the nominal one, whereas Na/Yb/Er contents almost keep unchanged. These results confirmed the incorporation of Mg^{2+} into $NaGdF_4$ by substituting Gd^{3+} site and locating in interval position partially. When the value of x up to 40 mol%, due to the generation of $NaMgF_3$ phase, this can make the change of stoichiometry.

Table S2 Refined lattice constants of as-synthesized $NaGd_{(0.78-x)}F_4$: 20%Yb, 2%Er, xMg UCNCs

Value	x					
	0%	3%	7%	13.5%	25%	40%
a=b (Å)	6.03923(23)	6.04065(30)	6.03747(22)	6.03168(25)	6.02649(21)	6.01200(16)
c (Å)	3.57906(14)	3.57920(20)	3.57810(21)	3.57064(17)	3.56501(17)	3.54382(13)
Volume ($Å^3$)	113.0476	113.1060	112.9514	112.5000	112.1296	110.9274

Table S3 R-values and χ^2 of structure refined with the Rietveld method of six different Mg^{2+} doping concentration samples.

$NaGd_{(0.78-x)}F_4$: 20%Yb, 2%Er, xMg	Rp/%	Rwp/%	χ^2
x=0	3.86	4.84	1.328
x=3%	3.96	5.03	1.308
x=7%	4.25	5.36	1.301
x=13.5%	4.56	5.76	1.288
x=25%	4.72	5.97	1.398
x=40%	4.69	5.99	1.554

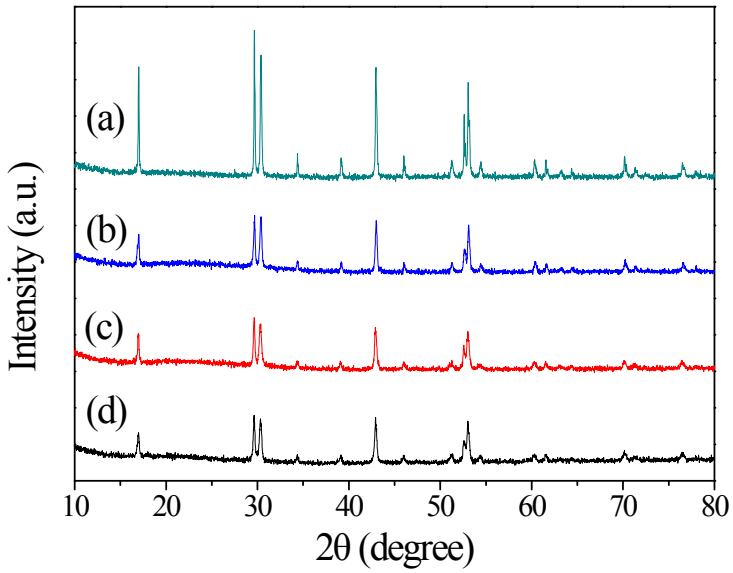

Figure S1 XRD patterns of 35% Mg^{2+}-doped $NaGdF_4$: 20%Yb^{3+}, 2%Er^{3+} at different times of Mg impurity injection. (a) 0 min, (b) 10 min, (c) 20 min, (d) 30 min. The unit length of intensity is fixed.

Experimental procedure: powder A (the mixture of Gd_2O_3, Yb_2O_3, Er_2O_3 and

NaOH) and powder B (MgO) were separately dissolved into the solution of CF_3COOH/deionized water and evaporated. Both powders were dissolved into OA and ODE at 150 °C for 30 min. The solution (from powder A) was injected into 320 °C of the mixture solution of OA and ODE, then the solution (from powder B) was injected into previous solution after 0 min, 10 min, 20 min, and 30 min respectively. Additionally, the injection time of 0 min was prepared in a similar fashion of $NaGdF_4$: Yb/Er/Mg nanocrystals (experimental section) *via* adjusting the quantities of MgO.

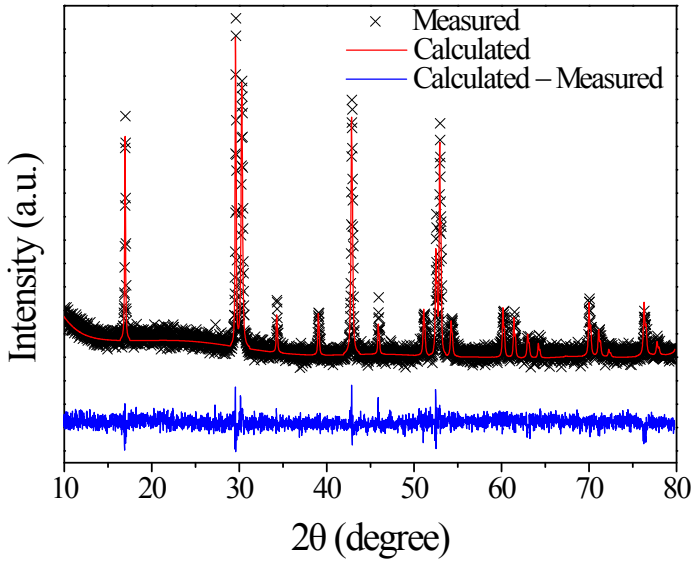

Figure S2 Rietveld fit of $NaGdF_4$: 20%Yb^{3+}, 2%Er^{3+}, 13.5%Mg^{2+} sample was shown as an example.

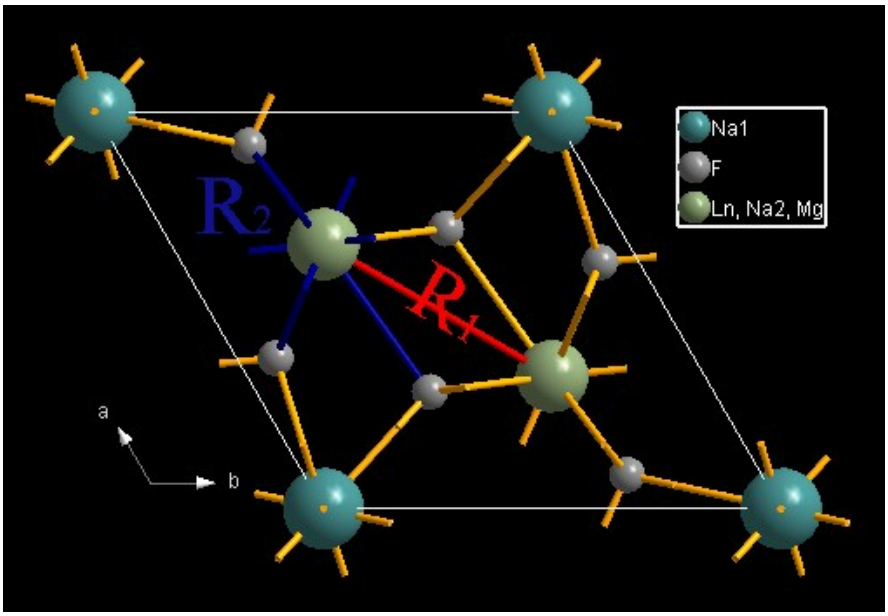

Figure S3 Crystal structure diagrammatic sketches. R_1 is the distance between Ln-Ln,

R_2 is the average bond length of Ln-F.

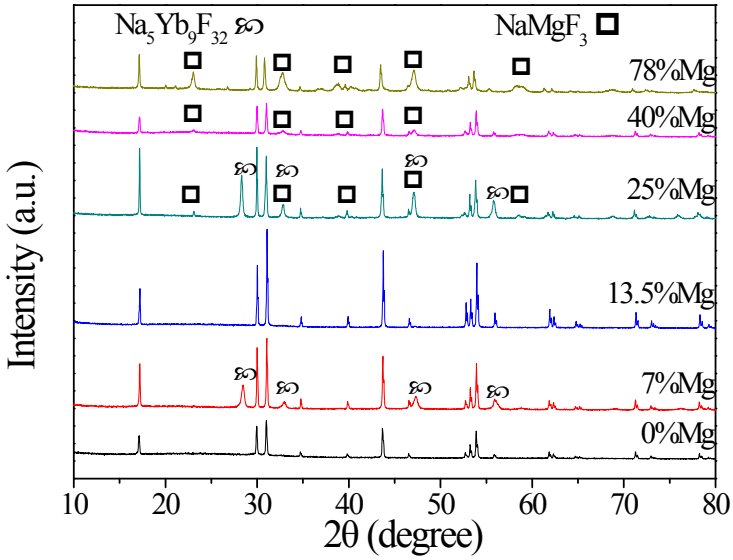

Figure S4 XRD patterns of as-prepared $NaYb_{(0.98-y)}F_4$: 2% Er^{3+}, yMg^{2+} samples, y=0, 7 mol%, 20 mol%, 25 mol%, 40 mol%, 78 mol%.

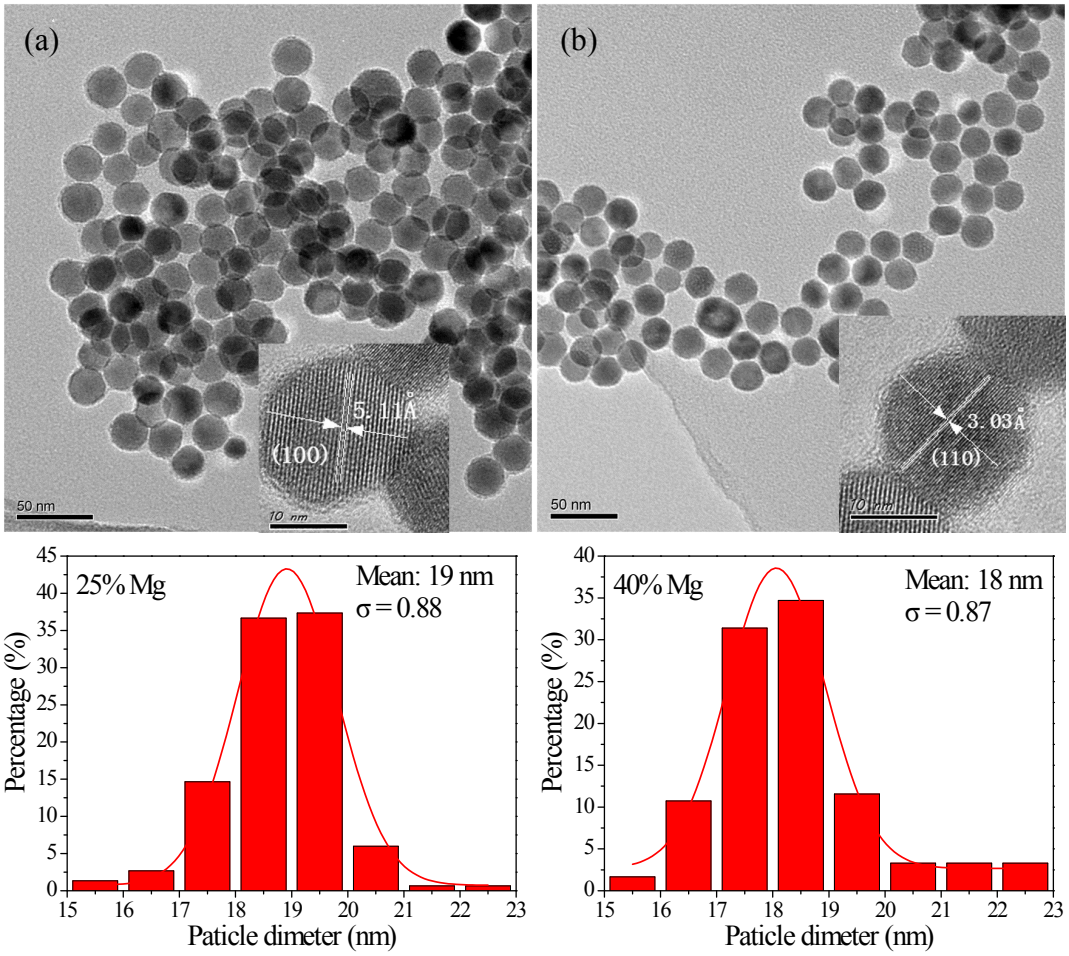

Figure S5 TEM images and corresponding size distribution of 25 mol% (a) and 40 mol% (b) Mg^{2+}-doped $NaGdF_4$:20%Yb^{3+}, 2%Er^{3+} nanocrystals. The insets are the

corresponding HRTEM images.

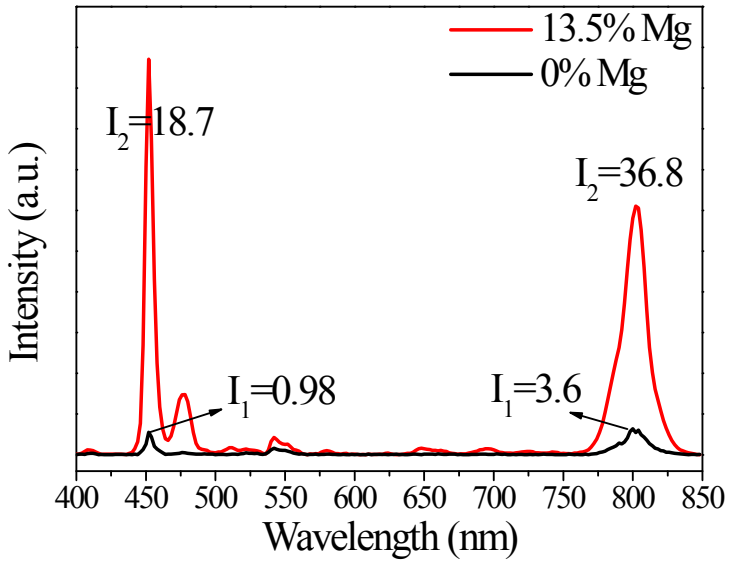

Figure S6 Upconversion emission spectra of Mg^{2+}-free and 13.5 mol% Mg^{2+}-doped $NaGdF_4$: 20%Yb^{3+}, 2%Tm^{3+}. I_1 and I_2 are the integral emission intensities of Mg^{2+}-free and Mg^{2+}-doped at 800 and 452 nm, respectively.

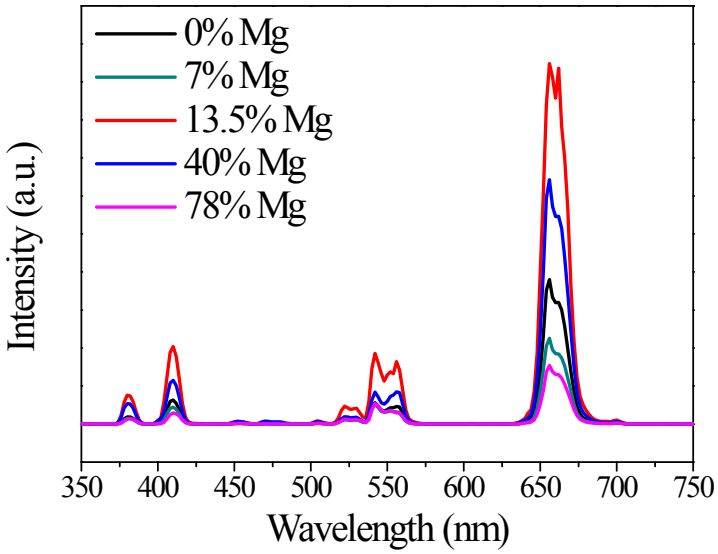

Figure S7 Upconversion emission spectra of $NaYbF_4$: 2%Er^{3+}, yMg^{2+}, y = 0, 7, 13.5, 40 and 78 mol%.

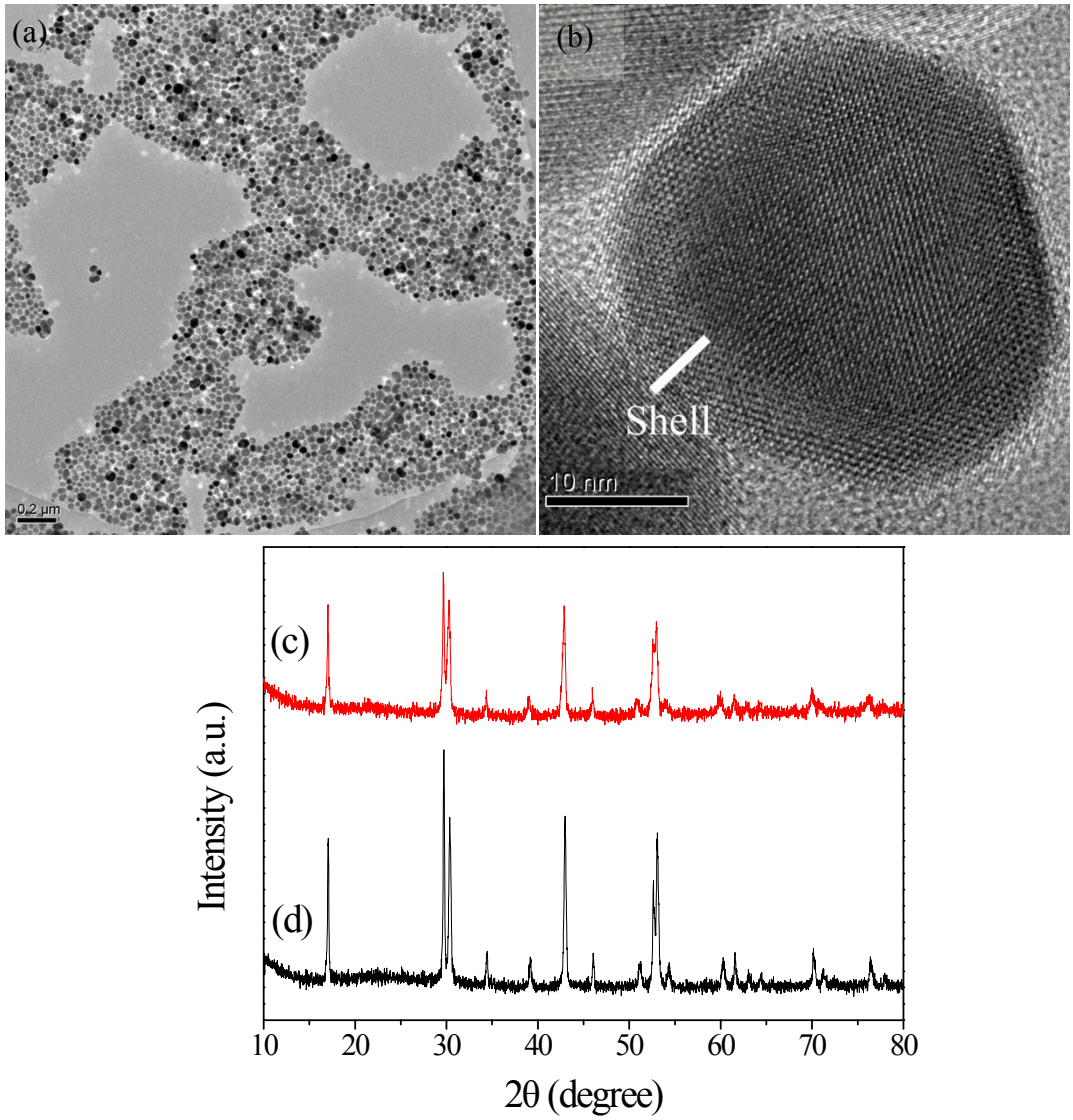

Figure S8 TEM (a), HRTEM (b) and XRD (c) of core-shell ($NaGdF_4$: 20%Yb^{3+}, 2%Er^{3+}@$NaGdF_4$). Core-shell UCNCs were prepared by the growth of $NaGdF_4$ shell according to the fabrication route of Mg^{2+}-doped core-shell (experimental section). XRD pattern of Mg^{2+}-doped core-shell was shown in (d). XRD patterns (c and d) indicate that the $NaGdF_4$ shells are of hexagonal-phase $NaGdF_4$.

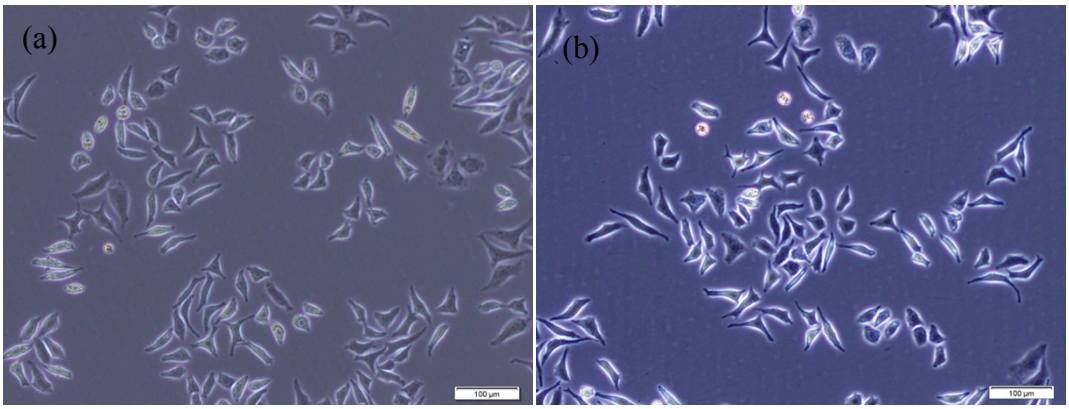

Figure S9 Cell microphotographs of (a) contrast group and (b) 0.1 $mg \cdot mL^{-1}$ water-soluble Mg-doped UCNCs after incubation for 24 h.