

Supporting information

Ultra-Sensitive Water Detection Based on NaErF₄@NaYF₄

High-Level-Doping Upconversion Nanoparticles

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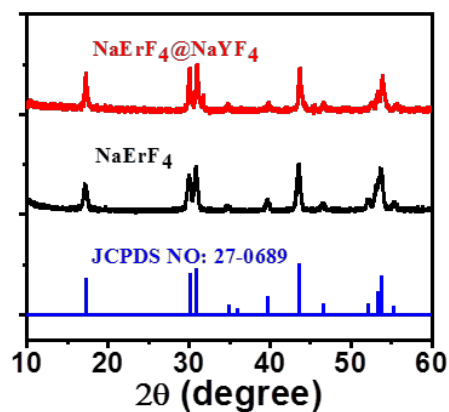


Figure S1 The X-ray powder diffraction of NaErF₄ bare core and NaErF₄@NaYF₄ core-shell nanoparticles. All the peaks accord with the standard hexagonal structure of NaYF₄ nanoparticles (Joint Committee on Powder Diffraction Standards file number 27-0689).

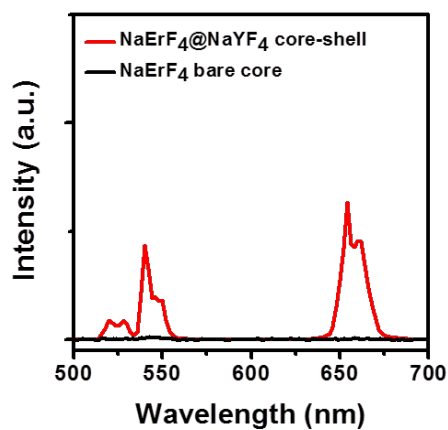


Figure S2 The upconversion emission spectra of NaErF₄ bare core and NaErF₄@NaYF₄ core-shell nanoparticles in DMF solvent (the NaYF₄ shell thickness is 2 nm, excitation is at 800 nm with a power density 5 W/cm²).

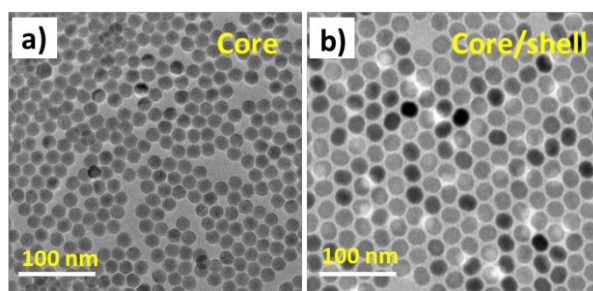


Figure S3 The TEM images of (a) NaYF₄: 20% Yb, 2% Er bare core nanoparticle (diameter ~18 nm) and (b) the NaYF₄: 20% Yb, 2% Er@NaYF₄: 10% Yb, 20% Nd core-shell nanoparticle.

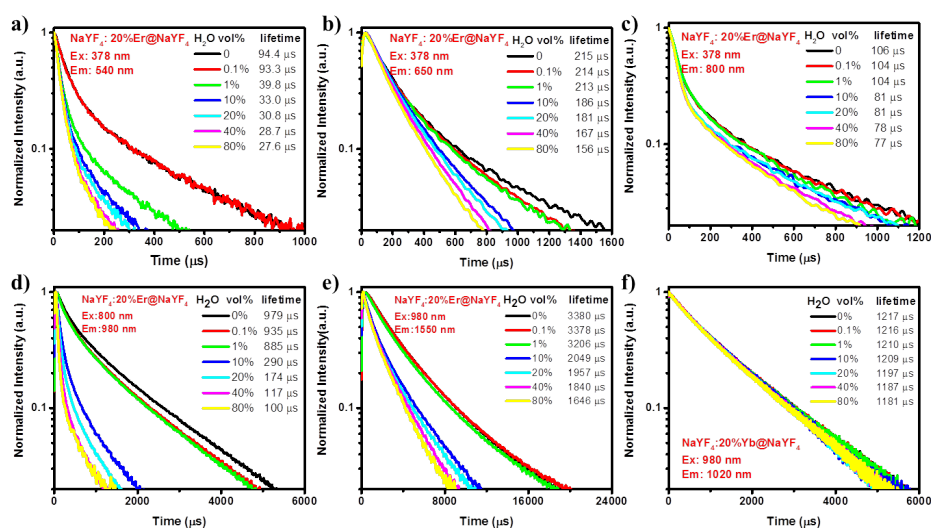


Figure S4 Luminescence decay curves of ligand-free NaYF₄: 20% Er@NaYF₄ (a-e) and NaYF₄: 20% Yb@NaYF₄ (f) nanostructures dispersed in DMF solvent containing different water contents, a) ⁴S_{3/2} energy state, b) ⁴F_{9/2} energy state, c) ⁴I_{9/2} energy state, d) ⁴I_{11/2} energy state, e) ⁴I_{13/2} energy state, f) ²F_{5/2} energy state. The excitation and emission wavelengths are marked in the figure. All these two samples were constructed with a 20 nm core and 2 nm thick shell.

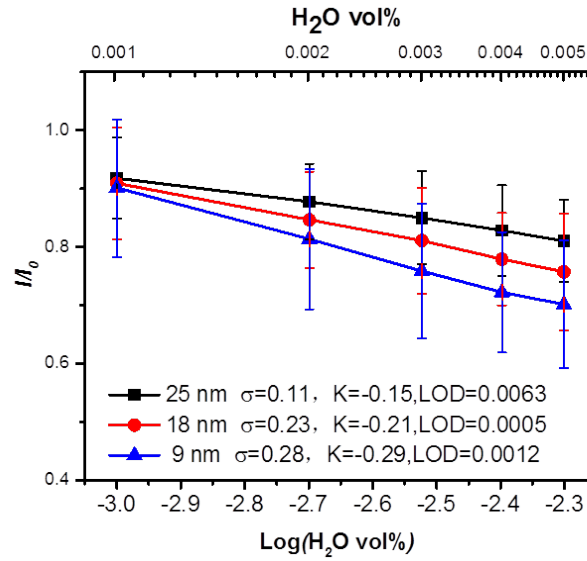


Figure S5 The testing results of core size-dependent LOD results (the NaErF₄ core diameters are marked in the figure. All the competitors have the same amount of Er³⁺ ions, *i.e.*, 0.02 mmol/mL NaErF₄ inner core, and the NaYF₄ shell thickness is fixed to 2 nm, the 800 nm excitation power density is 5 W/cm²). Theoretically, for ultra-sensitive detection, increasing the core size will bring in two positive effects: (1) decreased σ value, (2) increased adsorbed water molecules at each particle surface, and one negative effect (longer energy migration distance to connect the inner Er³⁺ and adsorbed water molecules). Our results indicate that within our testing range, with the increase of core size, the LOD value will first decrease and then increase. Therefore, the optimized core size is determined to 18 nm.

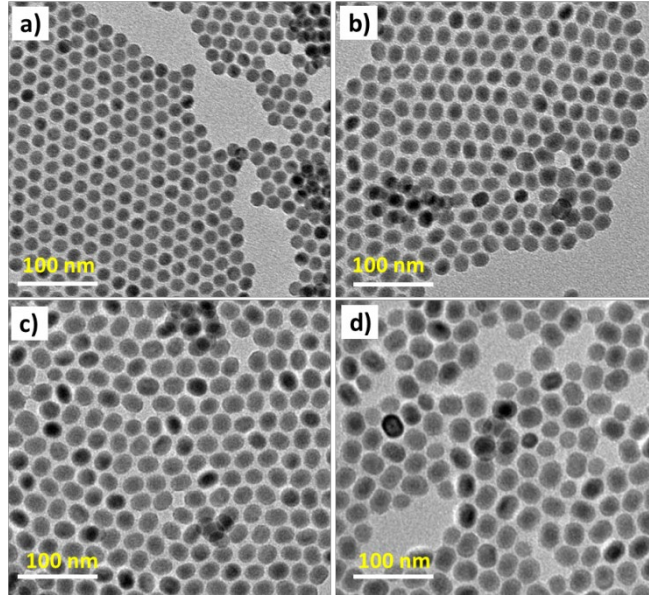


Figure S6 The TEM images of (a) the NaErF₄ bare core (~ 18 nm) and NaErF₄@NaYF₄ core-shell nanoparticles with different shell thicknesses: (b) 2 nm, (c) 4 nm, and (d) 5.5 nm.

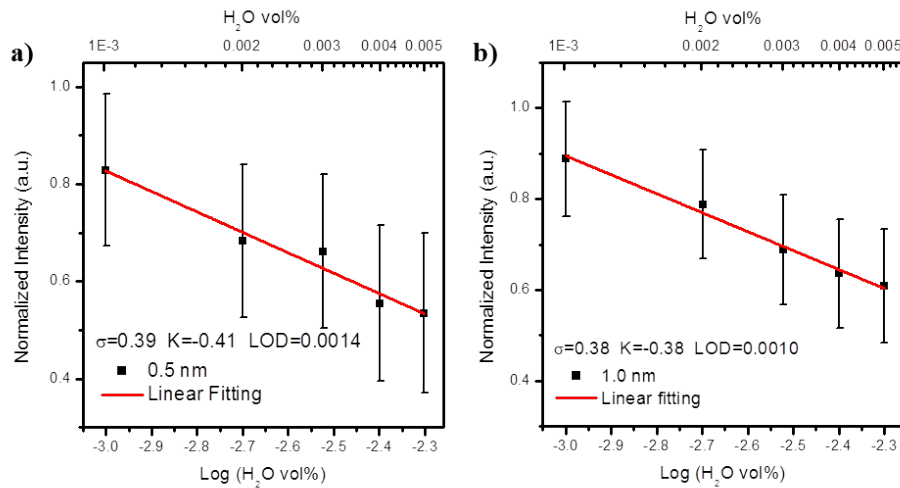


Figure S7 Water content dependence of the red UC emission intensity for NaErF₄@NaYF₄ core-shell nanoparticles, a) shell-thickness of 0.5 nm, b) shell-thickness of 1.0 nm. The emission intensity is the integration area from 580 to 700 nm. Excitation is at 800 nm with a power density of 5 W/cm².

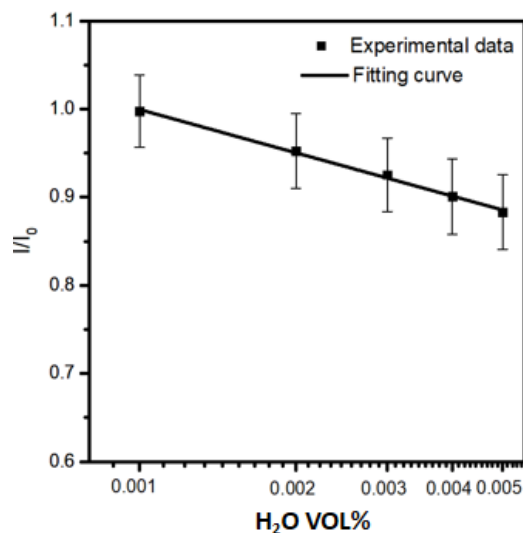


Figure S8 Water dependence of the red UC emission intensity for NaYF₄: 20% Yb, 2% Er@NaYF₄: 10% Yb, 20% Nd structure (excitation is at 800 nm with a power density 5 W/cm², $\sigma \approx 0.048$, $K \approx -0.07$, LOD = 0.0085%).

Table S1 Luminescence decay lifetimes of ⁴S_{3/2}, ⁴F_{9/2}, ⁴I_{9/2}, ⁴I_{11/2} and ⁴I_{13/2} energy states of Er³⁺ in the NaErF₄@NaYF₄ nanostructure.

H ₂ O content (vol%)	Lifetime of ⁴ S _{3/2} energy state (μs)	Lifetime of ⁴ F _{9/2} energy state (μs)	Lifetime of ⁴ I _{9/2} energy state (μs)	Lifetime of ⁴ I _{11/2} energy state (μs)	Lifetime of ⁴ I _{13/2} energy state (μs)
0	42.2	86.7	118.7	233.3	569.1
0.01	35.2	77.5	98.3	231.2	568.1
0.1	33.3	74.2	96.9	223.1	559.3
1	32.1	67.6	91.1	204.6	526.3
10	31.2	57.8	85.6	178.4	410.5
20	29.2	52.1	79.9	161.1	360.7
40	26.7	41.5	70.3	134.5	302.8
60	25.9	37.7	68.2	121.9	274.9
80	23.1	35.4	60.1	119.1	260.7

Table S2 The measured water impurities from two purchased DMF solvents (I/I_0^* is measured from 100 μL original solvent mixed with 900 μL anhydrous DMF).

DMF	Bought from	From factory's instruction (vol%)	Experimental I/I_0^*	Calculated H_2O vol%
Sample 1	Fuyu Fine Chemical Co., Ltdj	<0.1	0.75907	0.05
Sample 2	Tiantai Chemical Co., Ltdj	<0.1	0.71479	0.08