Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information

Inflection in Size-dependence of Thermally Enhanced Up-conversion Luminescence of UCNPs

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S1. Calculation on the enhancement factor of thermo-enhanced up-conversion luminescence resulted from decrease in the efficiency of EM-induced SQ by means of lattice thermal expansion:

The following calculation is based on the assumption that EM-induced SQ can be able to dominate the whole nonradiative deexcitation of UCNPs. The efficiency of EM process through the cascade ET of n pairs of Yb^{3+} ions can be described by the following equation:

$$\gamma_{ET}(r_n) = \frac{C}{(r^6)^n} \tag{S1}$$

Where *r* is the distance of the donor and acceptor, the parameter C is the "energy-transfer strength" prefactor, the value of which depends on the energy match of transitions in the lanthanide center to the vibrational energies of the solvent, as well as on the oscillator strengths of the donor and acceptor transitions involved. In our work, the element doping concentration and synthetic solvent are consistent. So, we can reasonably simplify C to a constant.

Upon heating, the efficiency for EM can be expressed as:

$$\gamma^*_{ET}(r_n) = \frac{C}{(r^{*\,6})^n} \tag{S2}$$

$$r^* = (1 + I_T) \cdot r \tag{S3}$$

Where $I_T = \Delta d/d_{303\ K}$, $\Delta d = d_T - d_{303\ K}$.

And the Equation S2 can be reduced to:

$$\gamma^*_{ET}(r_n) = \frac{C}{\left(\left((1 + I_T) \cdot r\right)^6\right)^n} = \frac{C}{C} \cdot (1 + I_T)^{-6 \cdot n} \cdot \gamma_{ET}(r_n) \tag{S4}$$

Therefore,

$$\gamma^{*}{}_{ET}(r_n) = (1 + I_T)^{-6 \cdot n} \cdot \gamma_{ET}(r_n) \quad \text{(S5)}$$

According to the temperature-dependent XRD results, the interplanar spacing expansion factor I_T(T=423K) can be reasonably taken as 1.0×10^{-3}. Averagely, we make n=5. Accordingly, $\gamma^*_{ET} = (1+0.001)^{-30}\,\gamma_{ET} = 0.9705\,\gamma_{ET}$, which means the efficiency for EM-induced SQ is reduced by around 3%.

As is known to all, the upconversion quantum yield of nanoparticles is usually well below 1% at ambient condition. Therefore, it is reasonable to hypothesize that 99% of the total excitation energy is consumed via EM-induced SQ at room temperature and 1% of excitation energy is supposed to enable the upconversion luminescence. Upon heating to 423K, efficiency for EM-induced SQ is reduced by around 3%, which causes a increase in percentage of excitation energy for upconversion luminescence to 3.921% (1%+99%*(1-97.05%)). One can equate this to increase in pumping power by 392.1%.

Upconversion luminescence obey the power law:

$$I = P^m \quad \text{(S6)}$$

Where m represents the pumping photon number.

Upon 980nm excitation, the $^1G_4 \rightarrow {}^3H_6$ transition of Tm belongs to three-photon process. **Therefore, $I^* = (3.921)^3\, I = 60.28\, I$, which means a 60.28-fold enhancement of up-conversion luminescence can be obtained via heating.**

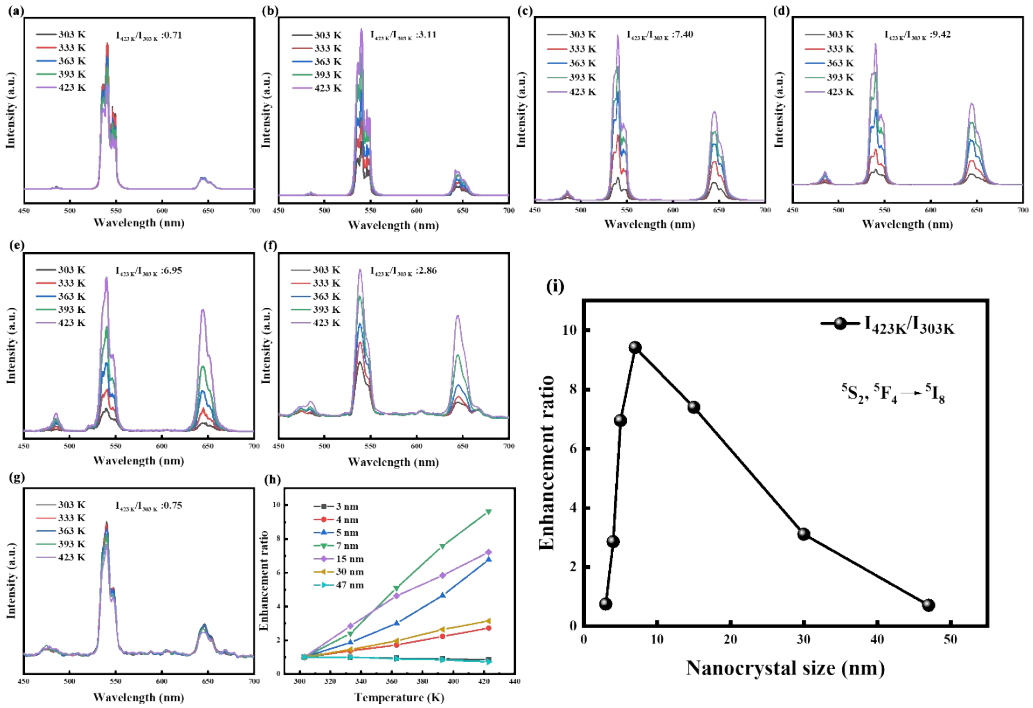

Figure S1. Temperature-dependent UCL emission spectra of all seven $NaGdF_4$:Yb/Ho (20/2 mol%) samples. (a) 3 nm, (b) 4nm, (c) 5 nm, (d) 7 nm, (e) 15 nm, (f) 30 nm and (g) 46nm are tested. The power density of the 980 nm was constant at 0.55 W/cm^2. (h) Integrated UCL intensities of samples with different size as a function of temperature. Integrated intensities at various temperatures have been normalized to that at 300K for each sample. (i) Plot of the integrated intensity ratio for the $^5S_2$,$^5F_4$ to $^5I_8$ transition ($I_{423\ K}/I_{303\ K}$) against the $NaGdF_4$:Yb/Ho (20/2 mol%) size.

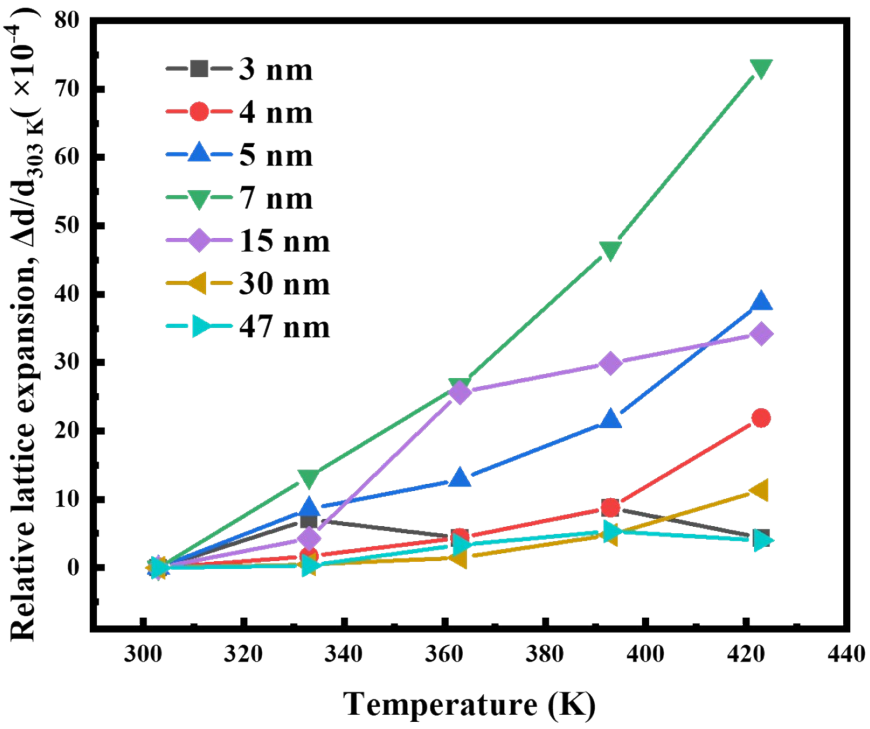

Figure S2. Relative lattice expansion of different-sized particles as a function of temperature.

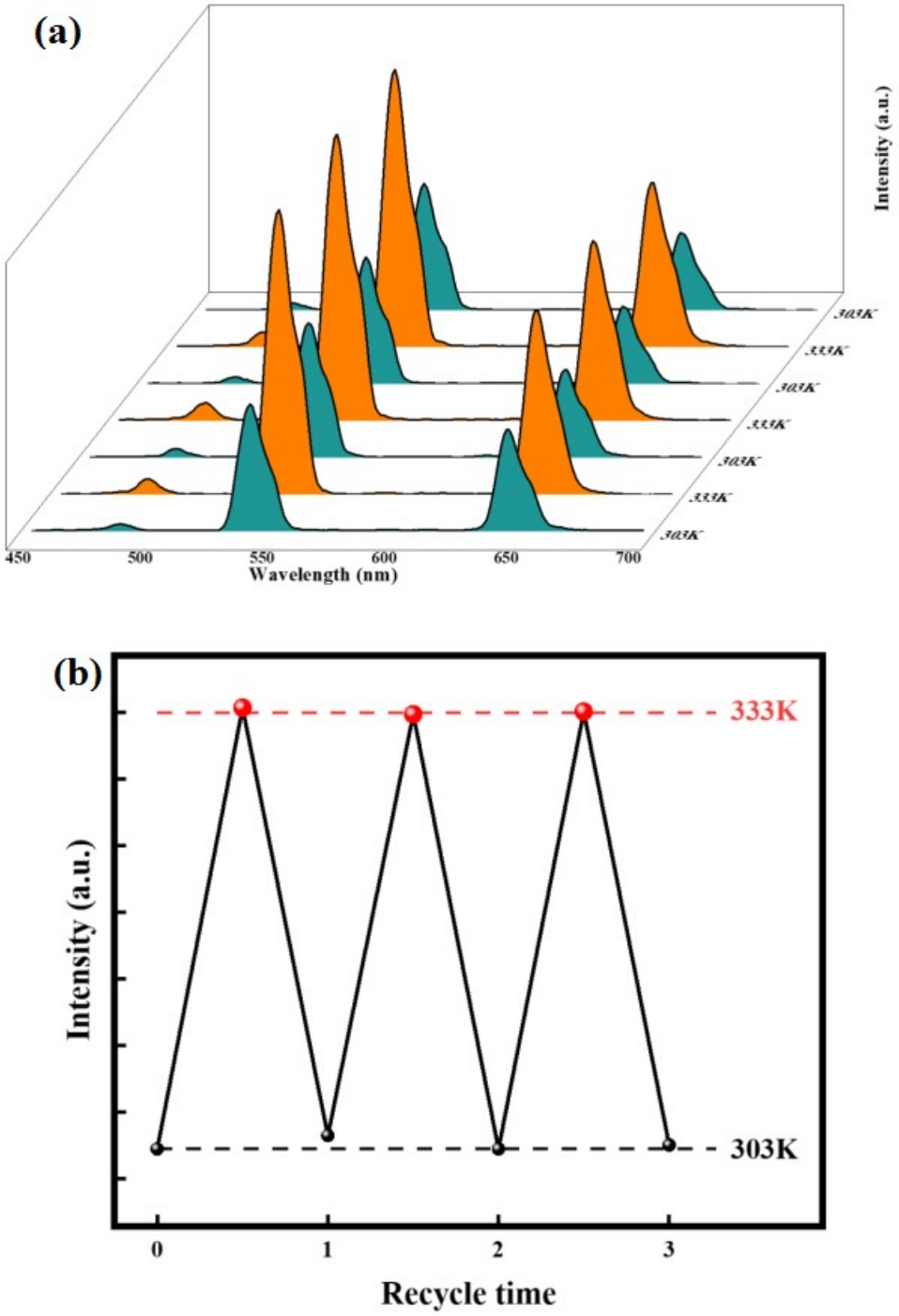

Figure S3. (a) UCL emission spectra of NaGdF4:Yb/Ho nanoparticles sized ~7nm in the dehydrated ODE solution at room temperature and 60℃respectively. Since the heating of ODE solution was carried out in ambient environment, for safety consideration the heating temperature was controlled at 60℃. Evidently, the sample at 60℃ yielded stronger UCL than that at room temperature. (b) Temperature-recycle measurements of temperature-dependent UCL confirm the good repeatability.

Table S1. The value of d and Δd/d for each sample measured at different temperatures.

Sample name / Temperature	Sample a			Sample b			Sample c			Sample d		
	2θ	d(Å)	Δd/d(×10⁻⁴)	2θ	d (Å)	Δd/d(×10⁻⁴)	2θ	d (Å)	Δd/d(×10⁻⁴)	2θ	d (Å)	Δd/d(×10⁻⁴)
303 K	29.8081	2.9760	0	29.6740	2.9760	0	30.1036	2.9760	0	29.6204	2.9760	0
333 K	29.8071	2.9761	0.33	29.6731	2.9761	0.47	30.0905	2.9773	4.26	29.5811	2.9799	13.33
363 K	29. 8037	2.9764	1.47	29.6642	2.9770	3.33	30.0249	2.9836	25.63	29.5398	2.9839	26.67
393 K	29.7938	2.9774	4.80	29.6582	2.9775	5.33	30.0117	2.9849	29.92	29.4807	2.9898	46.67
423 K	29.7962	2.9772	4.00	29.6403	2.9793	11.33	29.9986	2.9862	34.21	29.3989	2.9979	73.33
	Sample e			Sample f			Sample g					
	2θ	d (Å)	Δd/d(×10⁻⁴)	2θ	d (Å)	Δd/d(×10⁻⁴)	2θ	d (Å)	Δd/d(×10⁻⁴)			
303 K	29.9198	2.9760	0	30.0249	2.9760	0	29.8804	2.9760	0			
333 K	29.8935	2.9786	8.59	30.0198	2.9765	1.68	29.8593	2.9781	7.07			
363 K	29.8804	2.9798	12.88	30.0117	2.9773	4.38	29.8673	2.9773	4.38			
393 K	29.8541	2.9824	21.49	29.9986	2.9783	8.77	29.8543	2.9785	8.75			
423 K	29.8016	2.9875	38.75	29.9592	2.9824	21.91	29.8673	2.9773	4.38			

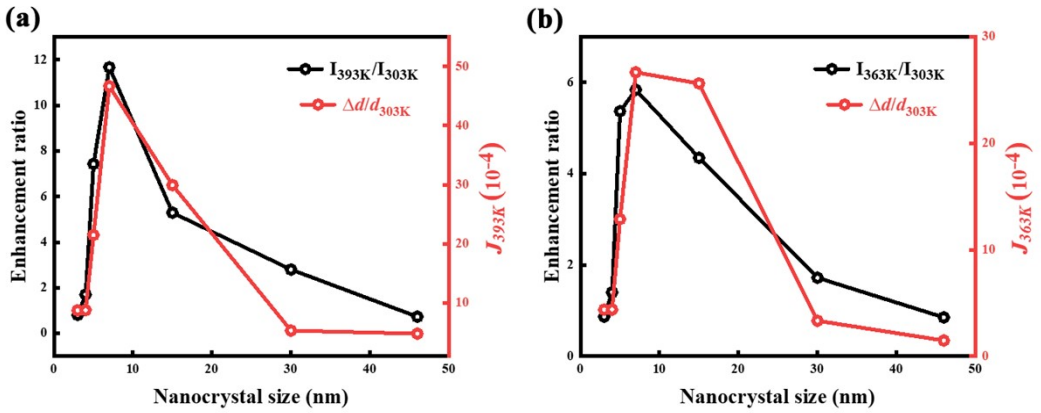

Figure S4. (a) Plot of the integrated intensity ratio for the $^5D_0 \rightarrow {}^7F_2$ transition (I_{363K}/I_{303K}, black line) and spacing expansion factor J_{363K} for the (101) plane (red line) against the nanocrystal size. (b) Plot of the integrated intensity ratio for the $^5D_0 \rightarrow {}^7F_2$ transition (I_{393K}/I_{303K}, black line) and spacing expansion factor J_{393K} for the (101) plane (red line) against the nanocrystal size.

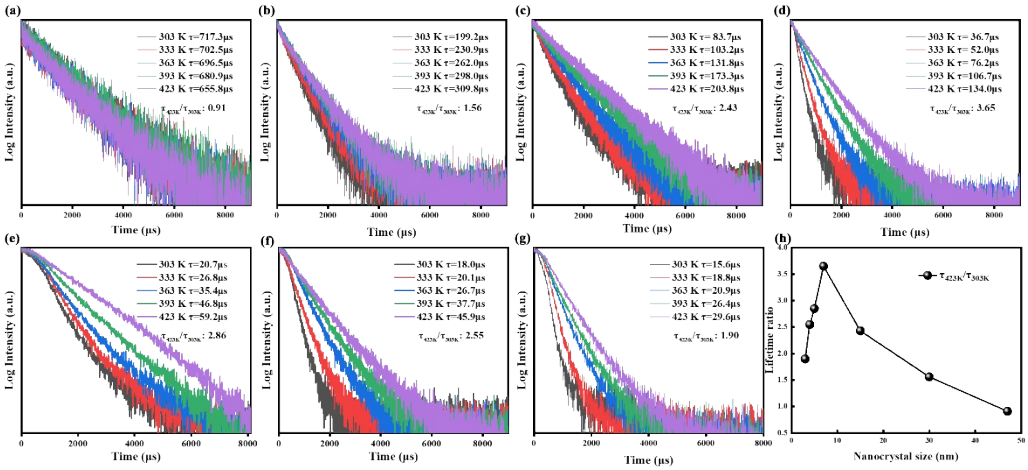

Figure S5. Temperature-dependent Yb^{3+} DCL lifetime of $^2F_{5/2} \rightarrow {}^2F_{7/2}$ (λ_{ex} =980 nm, λ_{em} = 1020 nm) in $NaGdF_4$: Yb/Tm (20/1 mol%) UCNPs with different sizes of (a) 47 nm, (b) 30 nm, (c) 15 nm, (d) 7 nm, (e) 5 nm, (f) 4 nm and (g) 3 nm. (h) Lifetime ratio (define as τ_{423K}/τ_{303K}) as a function of nanocrystal size.

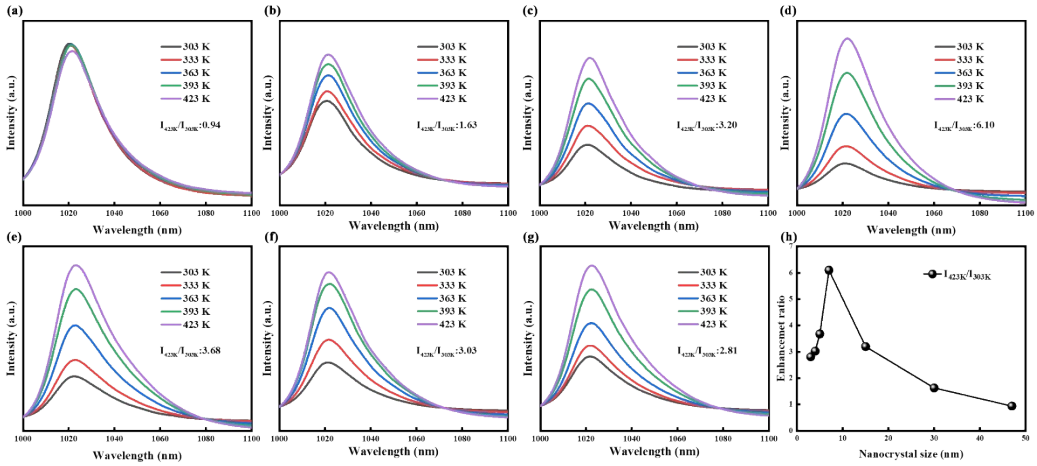

Figure S6. Temperature-dependence DCL emission spectra of $NaGdF_4$: Yb/Tm (20/1 mol%) UCNPs with different sizes of (a) 47 nm, (b) 30 nm, (c) 15 nm, (d) 7 nm, (e) 5 nm, (f) 4 nm and (g) 3 nm. (h) Enhancement ratio (define as I_{423K}/I_{303K}) as a function of nanocrystal size.