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Excitation wavelength-dependent anti-thermal quenching of upconversion luminescence in hexagonal $NaGdF_4$:Nd^{3+}/Yb^{3+}/Er^{3+} nanocrystals

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Supporting materials

I. Rate equations for UC luminescence dynamics

To simplify the problem, several unimportant processes are omitted, such as the radiative transition of $^4I_{13/2}$ to $^4I_{15/2}$. Therefore, according to a simple six-level model (see Figure S2), the luminescence dynamics process is described as follows:

$$\frac{dN_0}{dt} = A_{50}N_5 + A_{40}N_4 - W_{ET2}N_{Yb1}N_0 \qquad (1)$$

$$\frac{dN_1}{dt} = W_{21}N_2 - W_{ET4}N_{Yb1}N_1 \qquad (2)$$

$$\frac{dN_2}{dt} = W_{ET2}N_{Yb1}N_0 - W_{ET3}N_{Yb1}N_2 - W_{21}N_2 \qquad (3)$$

$$\frac{dN_4}{dt} = W_{54}N_5 + W_{ET4}N_{Yb1}N_1 - W_{43}N_4 - A_{40}N_4 \qquad (4)$$

$$\frac{dN_5}{dt} = W_{ET3}N_{Yb1}N_2 - A_{50}N_5 - W_{54}N_5 \qquad (5)$$

where $N_0, N_1, N_2, N_3, N_4, N_5, N_{Yb1}$ are populations of levels $^4I_{15/2}$ (Er^{3+}), $^4I_{13/2}$ (Er^{3+}), $^4I_{11/2}$ (Er^{3+}), $^4I_{9/2}$ (Er^{3+}), $^4F_{9/2}$ (Er^{3+}), $^2H_{11/2}/^4S_{3/2}$ (Er^{3+}), and $^2F_{5/2}$ (Yb^{3+}), respectively, $W_{ET2}, W_{ET3}, W_{ET4}$ are energy transfer rates from Yb^{3+} to Er^{3+}, W_{21}, W_{43}, and W_{54} are the multiphonon relaxation rates of levels $^4I_{11/2}$ (Er^{3+}), $^4F_{9/2}$ (Er^{3+}), and $^4S_{3/2}$ (Er^{3+}).

At steady state ($dN_i/dt = 0$), from Eqs. (3) and (5) we obtain

$$N_5 = \frac{W_{ET2} W_{ET3} N_{Yb1}{}^2 N_0}{(A_{50} + W_{54})(W_{ET3} N_{Yb1} + W_{21})} \qquad (6)$$

Further, according to Eqs. (2), (3), (4) and (6) we obtain

$$N_4 = \frac{1}{W_{43} + A_{40}} \left[\frac{W_{ET2} W_{ET3} W_{54} N_0 N_{Yb1}{}^2}{(A_{50} + W_{54})(W_{ET3} N_{Yb1} + W_{21})} + \frac{W_{ET2} N_0 W_{21}}{W_{ET3} + W_{21} / N_{Yb1}} \right] \qquad (7)$$

Taken together, N_4 and N_5 are both increasing function of N_{Yb1}. Upon 808 nm excitation with low pump power, N_{Yb1} takes the form

$$N_{Yb1} = \frac{W_{ET1} N_{Yb0} N_{Nd1}}{W_{ET2} N_0 + W_{ET3} N_2 + W_{ET3} N_1} \approx \frac{W_{ET1} N_{Yb} \rho_{808} \sigma_{Nd} N_{Nd}}{W_{ET2} N_{Er}} \qquad (8)$$

In contrast, under 980 nm excitation with low pump power, N_{Yb1} is re-written as follows:

$$N_{Yb1} = \frac{\rho \sigma N_{Yb0}}{W_{ET2} N_0 + W_{ET3} N_2 + W_{ET3} N_1} \approx \frac{\rho_{980} \sigma_{Yb} N_{Yb}}{W_{ET2} N_{Er}} \qquad (9)$$

where W_{ET1} are energy transfer rates from Nd^{3+} to Yb^{3+}, ρ_{808} and ρ_{980} are the output power of lasers, σ_{Nd} is the absorption cross-section of Nd^{3+} ions at 808 nm, σ_{Yb} is the absorption cross-section of Yb^{3+} ions at 980 nm, N_{Yb0} and N_{Nd1} are populations of $^2F_{7/2}$ (Yb^{3+}) and $^4F_{5/2}$ (Nd^{3+}), respectively, N_{Er} , N_{Yb} and N_{Nd} are the concentration of Er^{3+}, Yb^{3+} and Nd^{3+} ions, respectively.

II. Figures

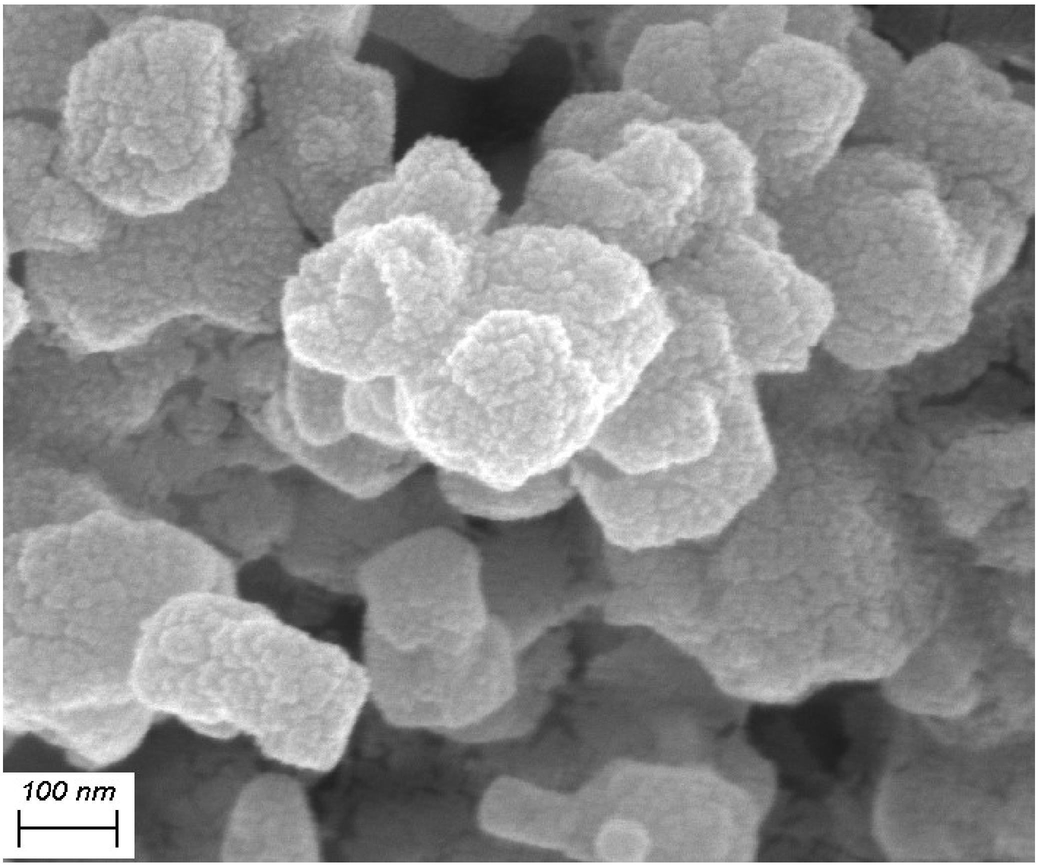

Figure S1 High resolution SEM image of the sample with 1%Nd^{3+}

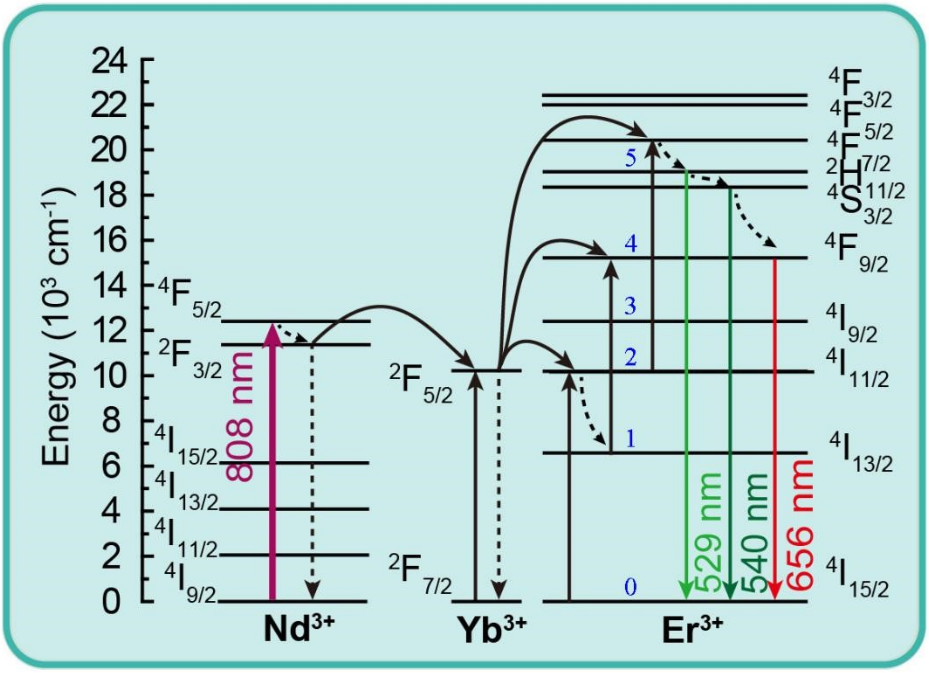

Figure S2 Proposed population pathways for upconversion luminescence of Nd^{3+}, Yb^{3+} and Er^{3+} tri-doping

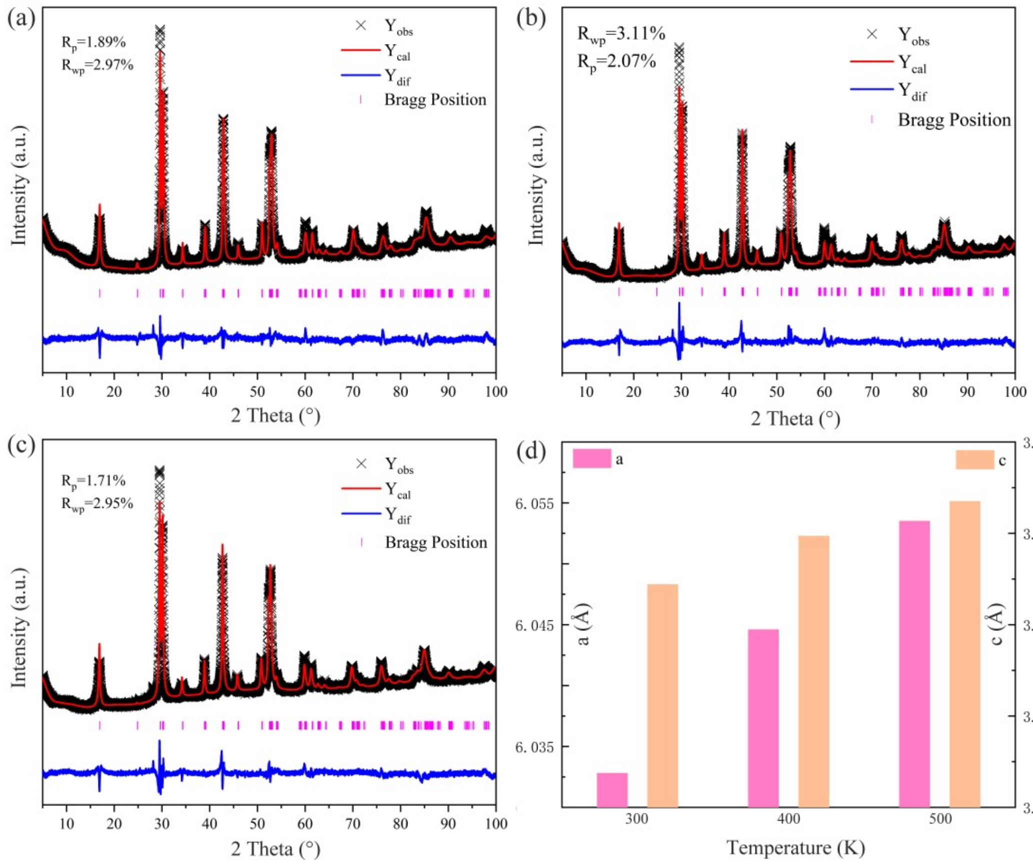

Figure S3 Rietveld refinement of XRD pattern at three representative temperatures. (a) 300 K; (b) 400 K; (c) 500 K; (d) cell parameters at various temperatures.

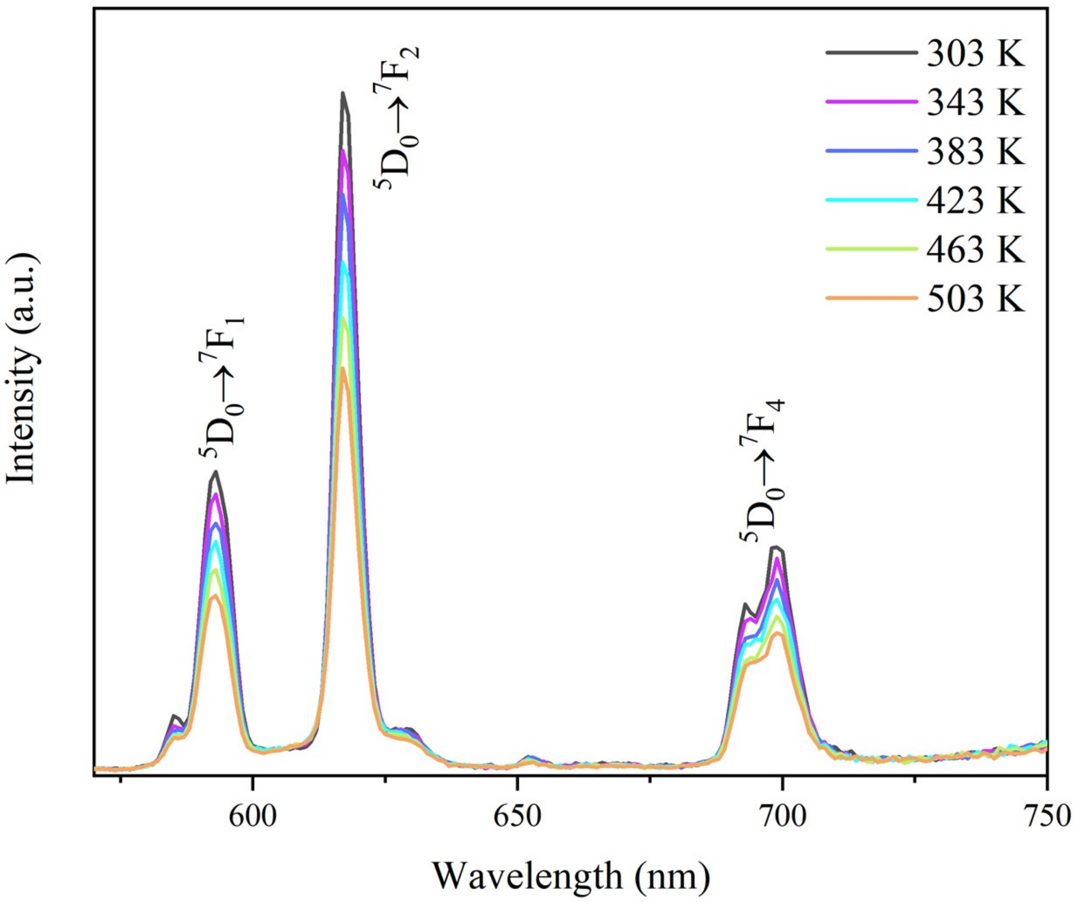

Figure S4 394 nm-responsive PL spectra of $NaGdF_4$:5%Eu^{3+} at various temperatures

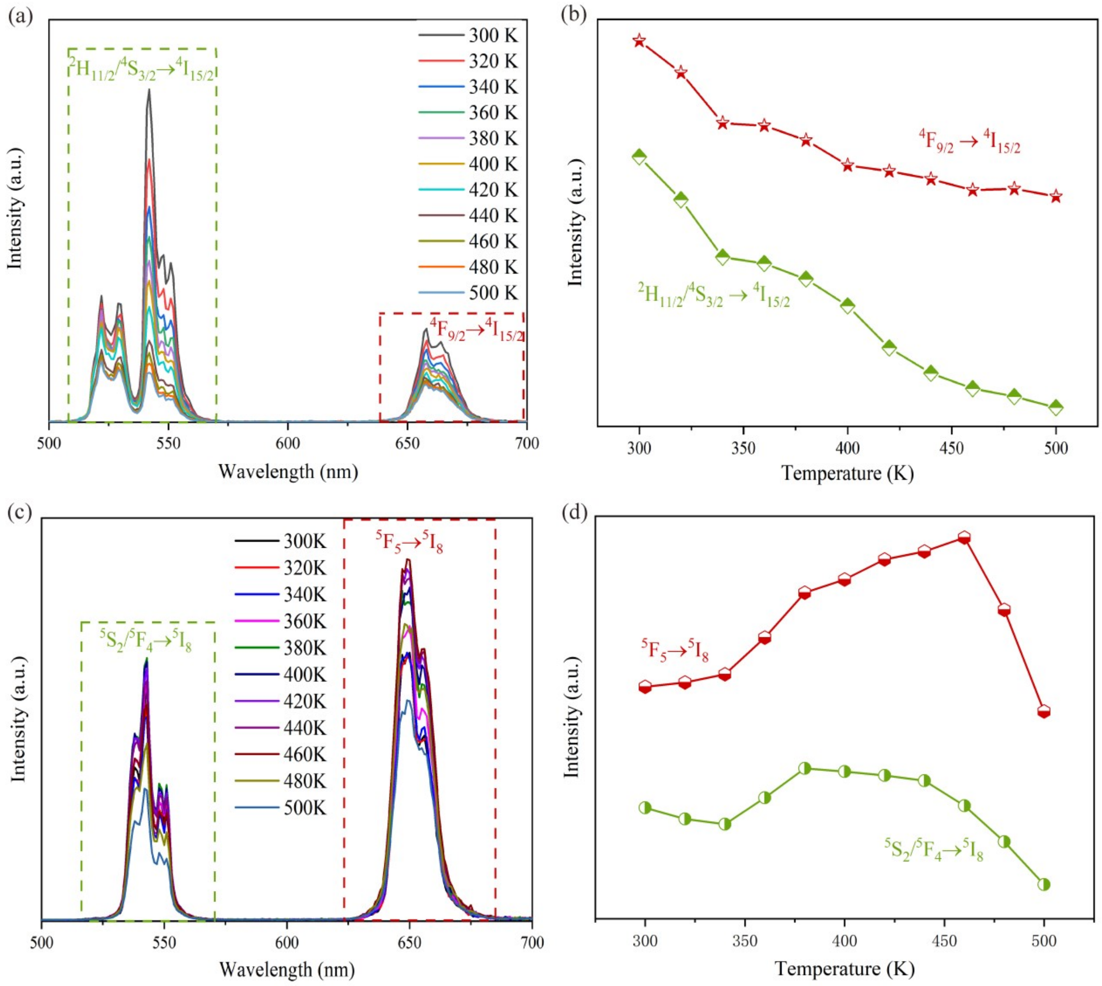

Figure S5 Upconversion luminescence properties at various temperature. (a) Upconversin spectra of $NaGdF_4$:Yb^{3+}/Er^{3+} under 980 nm excitation; (b) Dependence of emission intensity originated from Er^{3+} on temperature; (c) Upconversin spectra of $NaGdF_4$:Yb^{3+}/Ho^{3+} under 980 nm excitation; (b) Dependence of emission intensity originated from Ho^{3+} on temperature

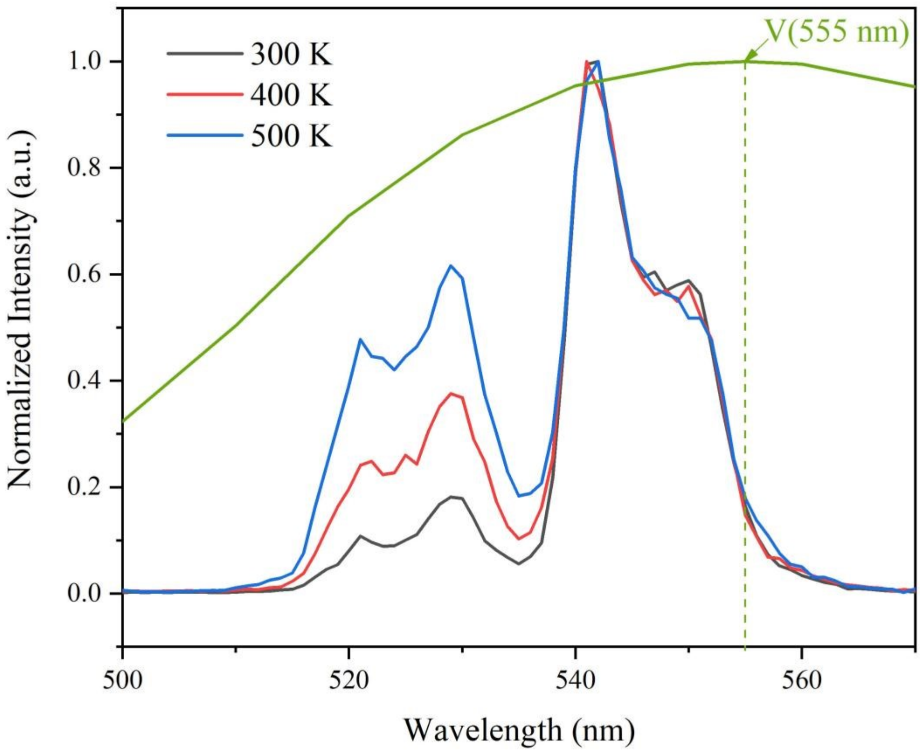

Figure S6 Normalized upconversion spectra of $NaGdF_4:Nd^{3+}/Yb^{3+}/Er^{3+}$ under 808 nm excitation and various temperatures as well as part of the visibility function V(λ) in the 500-570 nm range.