Electronic Supplementary Information (ESI) for:

Balancing power density based quantum yield characterization of upconverting nanoparticles for arbitrary excitation intensities

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Content:

S1. Rate equation analysis for the NIR UC emission of Yb^{3+}/Tm^{3+} codoped system

The mechanism of the NIR UC emission in Yb^{3+}/Tm^{3+} codoped nanoparticles is depicted in Fig. S1. First, the Tm^{3+} ion at state $^3H_6$ is excited to state $^3H_5$ through a phonon-assisted energy transfer from an excited Yb^{3+} ion. Subsequently, the Tm^{3+} ion relaxes non-radiatively to the lower state $^3F_4$ and is further excited to state $^3F_{2,3}$ through a second energy transfer process from excited Yb^{3+} to the Tm^{3+} ion. Finally, the Tm^{3+} ion at state $^3F_{2,3}$ decays to state through an efficient non-radiative relaxation, and the NIR UC emission at 800 nm is generated by the transition of $^3H_4 \rightarrow {}^3H_6$.

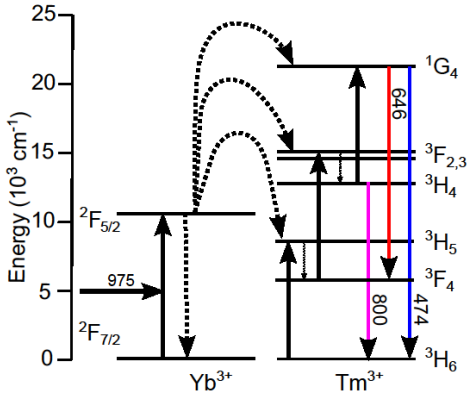

Fig. S1 Schematic energy level diagrams of the Yb^{3+} and Tm^{3+} ions and the proposed UC mechanism following the excitation of 975-nm light.

The contribution of radiative rates to the depletion of states $^3H_5$ and $^3F_{2,3}$ are much less than their non-radiative decay rates, thus are omitted in the following discussion. Then the power-density dependent behavior of the NIR UC emission intensity under CW excitation can be described by the following steady rate equations:

$$\frac{\mathrm{d}N_{\mathrm{Yb1}}}{\mathrm{d}t} = \sigma\rho N_{\mathrm{Yb0}} - \frac{N_{\mathrm{Yb1}}}{\tau_{\mathrm{Yb1}}} = 0\,, \tag{S1.1a}$$

$$\frac{\mathrm{d}N_1'}{\mathrm{d}t} = C_0 N_0 N_{\mathrm{Yb1}} - \beta_1' N_1' = 0\,, \tag{S1.1b}$$

$$\frac{\mathrm{d}N_1}{\mathrm{d}t} = \beta_1' N_1' - C_1 N_1 N_{\mathrm{Yb1}} - \frac{N_1}{\tau_1^{\mathrm{rad}}} = 0\,, \tag{S1.1c}$$

$$\frac{\mathrm{d}N_2'}{\mathrm{d}t} = C_1 N_1 N_{\mathrm{Yb1}} - \beta_2' N_2' = 0\,, \tag{S1.1d}$$

$$\frac{\mathrm{d}N_2}{\mathrm{d}t} = \beta_2' N_2' - \frac{N_2}{\tau_2^{\mathrm{rad}}} = 0\,, \tag{S1.1e}$$

where N_0, N_1, N_1', N_2 and N_2' denote the population densities of the states $^3H_6$, $^3F_4$, $^3H_5$, $^3H_4$ and $^3F_{2,3}$ of Tm^{3+} ions, respectively, while N_{Yb0} and N_{Yb1} are the population densities of the states $^2F_{7/2}$ and $^2F_{5/2}$ of Yb^{3+} ions, respectively; σ denotes the absorption cross-section of Yb^{3+} ion; ρ is the excitation photon flux, which is linearly related with power-density; τ_1^{rad} and τ_2^{rad} are the radiative lifetimes of Tm^{3+} ions at states $^3F_4$ and $^3H_4$; τ_{Yb1} is the lifetime of Yb^{3+} ions at $^2F_{5/2}$ state; C_0, and C_1 are ETU rates from excited Yb^{3+} ions to the Tm^{3+} ions at states $^3H_6$ and $^3F_4$, respectively; β_1' and β_2' represent the non-radiative decay rates for $^3H_5 \rightarrow {}^3F_4$ and $^3F_{2,3} \rightarrow {}^3H_4$, respectively. In this model, the depletion of the population density of the $^2F_{5/2}$ (Yb^{3+}) state due to ETU process is omitted, because the ETU rates at the $^2F_{5/2}$ (Yb^{3+}) state are much lower than its linear decay rate. For the same reason, the contribution to the depletion of state $^3H_4$ due to ETU to even higher states is not considered either. Under these assumptions, the population densities of different levels at steady state can be obtained from eqns (S1.1a) - (S1.1e)

$$N_{\mathrm{Yb1}} = \tau_{\mathrm{Yb1}} \sigma N_{\mathrm{Yb0}} \rho\,, \tag{S1.2a}$$

$$N_1' = \frac{C_0 N_0 N_{\mathrm{Yb1}}}{\beta_1'} = \frac{C_0 N_0 \tau_{\mathrm{Yb1}} \sigma N_{\mathrm{Yb0}} \rho}{\beta_1'}\,, \tag{S1.2b}$$

$$N_1 = \frac{C_0 N_0 N_{\mathrm{Yb1}}}{\frac{1}{\tau_1^{\mathrm{rad}}} + C_1 N_{\mathrm{Yb1}}} = \frac{C_0 N_0 \tau_{\mathrm{Yb1}} \sigma N_{\mathrm{Yb0}} \rho}{\frac{1}{\tau_1^{\mathrm{rad}}} + C_1 \tau_{\mathrm{Yb1}} \sigma N_{\mathrm{Yb0}} \rho} \ , \tag{S1.2c}$$

$$N_2' = \frac{C_1 N_1 N_{\mathrm{Yb1}}}{\beta_2'} = \frac{C_0 C_1 N_0 (\tau_{\mathrm{Yb1}} \sigma N_{\mathrm{Yb0}} \rho)^2}{\beta_2' (\frac{1}{\tau_1^{\mathrm{rad}}} + C_1 \tau_{\mathrm{Yb1}} \sigma N_{\mathrm{Yb0}} \rho)} , \tag{S1.2d}$$

$$N_2 = \tau_2^{\mathrm{rad}} \beta_2' N_2' = \frac{\tau_2^{\mathrm{rad}} C_0 C_1 N_0 (\tau_{\mathrm{Yb1}} \sigma N_{\mathrm{Yb0}} \rho)^2}{\frac{1}{\tau_1^{\mathrm{rad}}} + C_1 \tau_{\mathrm{Yb1}} \sigma N_{\mathrm{Yb0}} \rho} . \tag{S1.2e}$$

Thus, the power-density dependence of the UC steady-state emission from state $^3H_4$ has the form of

$$I = \frac{N_2}{\tau_2^{\mathrm{rad}}} h\nu = \frac{C_0 C_1 \tau_{\mathrm{Yb1}}^2 N_0 h\nu \sigma^2 N_{\mathrm{Yb0}}^2 \rho^2}{\frac{1}{\tau_1^{\mathrm{rad}}} + C_1 \tau_{\mathrm{Yb1}} \sigma N_{\mathrm{Yb0}} \rho} \ . \tag{S1.3}$$

S2. Rate equation analysis for the green UC emission of Yb^{3+}/Er^{3+} codoped system

The mechanism of the NIR UC emission in Yb^{3+}/Er^{3+} codoped nanoparticles is depicted in Fig. S2. As seen, the Er^{3+} is promoted from the ground state $^4I_{15/2}$ to the $^4F_{7/2}$ state through two ETU processes from excited Yb^{3+} ions. Then the Er^{3+} ion relaxes non-radiatively to the lower states $^2H_{11/2}/^4S_{3/2}$, and generates green UC emissions through the transition of $^2H_{11/2}/^4S_{3/2} \rightarrow {}^4I_{15/2}$.

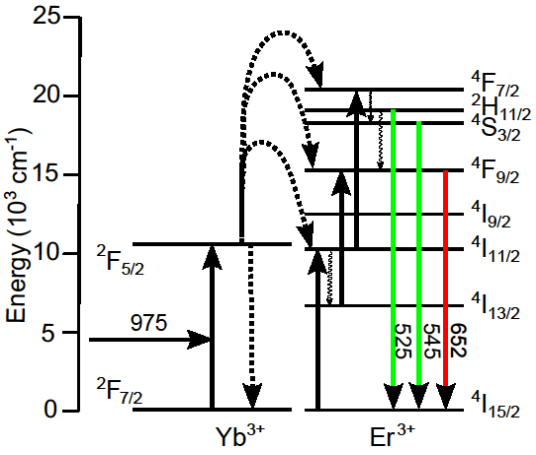

Fig. S2 Schematic energy level diagrams of the Yb^{3+} and Er^{3+} ions and the proposed UC mechanism following the excitation of 975-nm light.

The power-density dependent behavior of the green UC emission intensity under CW excitation can be described by the following rate equation model:

$$\frac{\mathrm{d}N_{\mathrm{Yb1}}}{\mathrm{d}t} = \sigma \rho N_{\mathrm{Yb0}} - \frac{N_{\mathrm{Yb1}}}{\tau_{\mathrm{Yb1}}} = 0 \ , \tag{S2.1a}$$

$$\frac{\mathrm{d}N_1}{\mathrm{d}t} = C_0 N_0 N_{\mathrm{Yb1}} - C_1 N_1 N_{\mathrm{Yb1}} - \beta_1 N_1 - \frac{N_1}{\tau_1^{\mathrm{rad}}} = 0 \ , \tag{S2.1b}$$

$$\frac{\mathrm{d}N_2'}{\mathrm{d}t} = C_1 N_1 N_{\mathrm{Yb1}} - \beta_2' N_2' = 0 \ , \tag{S2.1c}$$

$$\frac{dN_2}{dt} = \beta_2' N_2' - \beta_2 N_2 - \frac{N_2}{\tau_2^{rad}} = 0 \,, \tag{S1.1d}$$

where N_0, N_1, N_2 and N_2' denote the population densities of the states $^4I_{15/2}$, $^4I_{11/2}$, $^2H_{11/2}/^4S_{3/2}$ and $^4F_{7/2}$ of Er^{3+} ions, respectively, while N_{Yb0} and N_{Yb1} are the population densities of the states $^2F_{7/2}$ and $^2F_{5/2}$ of Yb^{3+} ions, respectively; σ denotes the absorption cross-section of Yb^{3+} ion; ρ is the excitation photon flux, which is linearly related with power-density; τ_1^{rad} and τ_2^{rad} are the radiative lifetimes of Er^{3+} ions at states $^4I_{11/2}$ and $^2H_{11/2}/^4S_{3/2}$; τ_{Yb1} is the lifetime of Yb^{3+} ions at $^2F_{5/2}$ state; C_0, and C_1 are ETU rates from excited Yb^{3+} ions to the Er^{3+} ions at states $^4I_{15/2}$ and $^4I_{11/2}$, respectively; β_1, β_2 and β_2' represent the non-radiative decay rate for $^4I_{11/2} \rightarrow {}^4I_{13/2}$, $^4F_{7/2} \rightarrow {}^2H_{11/2}/{}^4S_{3/2}$, and $^2H_{11/2}/^4S_{3/2} \rightarrow {}^4F_{9/2}$, respectively. In this model, the depletion of the population density of $^2F_{5/2}$ (Yb^{3+}) state due to ETU process is omitted, because the ETU rates at $^2F_{5/2}$ (Yb^{3+}) state are much lower than its linear decay rate. For the same reason, the contribution to the depletion of state $^2H_{11/2}/^4S_{3/2}$ due to ETU to even higher states is not considered either. Under these assumptions, the population densities of different levels at steady state can be obtained from eqns (S2.1a) - (S2.1d)

$$N_{Yb1} = \tau_{Yb1} \sigma N_{Yb0} \rho \,, \tag{S2.2a}$$

$$N_1 = \frac{C_0 N_0 N_{Yb1}}{\frac{1}{\tau_1^{rad}} + \beta_1 + C_1 N_{Yb1}} = \frac{C_0 N_0 \tau_{Yb1} \sigma N_{Yb0} \rho}{\frac{1}{\tau_1^{rad}} + \beta_1 + C_1 \tau_{Yb1} \sigma N_{Yb0} \rho} \,, \tag{S2.2b}$$

$$N_2' = \frac{C_1 N_1 N_{Yb1}}{\beta_2'} = \frac{C_0 C_1 N_0 (\tau_{Yb1} \sigma N_{Yb0} \rho)^2}{\beta_2' (\frac{1}{\tau_1^{rad}} + \beta_1 + C_1 \tau_{Yb1} \sigma N_{Yb0} \rho)}, \tag{S2.2c}$$

$$N_2 = \frac{\beta_2' N_2'}{\frac{1}{\tau_2^{rad}} + \beta_2} = \frac{C_0 C_1 N_0 (\tau_{Yb1} \sigma N_{Yb0} \rho)^2}{\left(\frac{1}{\tau_2^{rad}} + \beta_2\right)(\frac{1}{\tau_1^{rad}} + \beta_1 + C_1 \tau_{Yb1} \sigma N_{Yb0} \rho)}. \tag{S2.2d}$$

Let

$$\frac{1}{\tau_1^{rad}} + \beta_1 = \frac{1}{\tau_1} \,, \tag{S2.3}$$

and

$$\frac{1}{\tau_2^{rad}} + \beta_2 = \frac{1}{\tau_2} \,, \tag{S2.4}$$

where τ_1 and τ_2 are the lifetimes of the state $^4I_{11/2}$ and $^2H_{11/2}/^4S_{3/2}$ of Er^{3+}, respectively, including the contribution of non-radiative decays, then we can obtain the power-density dependence of the green UC steady-state emission from the state $^2H_{11/2}/^4S_{3/2}$

$$I = \frac{N_2}{\tau_2^{rad}} h\nu = \frac{C_0 C_1 \tau_{Yb1}^2 (\tau_2/\tau_2^{rad}) N_0 h\nu \sigma^2 N_{Yb0}^2 \rho^2}{\frac{1}{\tau_1} + C_1 \tau_{Yb1} \sigma N_{Yb0} \rho} \,. \tag{S2.5}$$

S3. Rate equation analysis for the green UC emission of Yb^{3+}/Ho^{3+} codoped system

The mechanism of the NIR UC emission in Yb^{3+}/Ho^{3+} codoped nanoparticles is depicted in Fig. S3. As seen, the Ho^{3+} at the ground state $^5I_8$ is promoted to the $^5I_6$ state through one energy transfer from excited Yb^{3+}, and is further promoted to the $^5S_2/^5F_4$ state through another energy transfer from the excited Yb^{3+} ions. The strong green UC emission can then be generated through the transition of $^5S_2/^5F_4 \rightarrow {}^5I_8$.

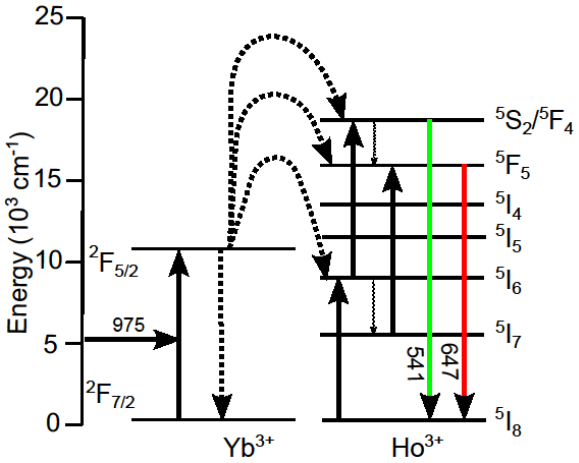

Fig. S3 Schematic energy level diagrams of the Yb^{3+} and Ho^{3+} ions and the proposed UC mechanism following the excitation of 975-nm light.

The power-density dependent behavior of the green UC emission intensity under CW excitation can be described by the following rate equation model:

$$\frac{dN_{Yb1}}{dt} = \sigma\rho N_{Yb0} - \frac{N_{Yb1}}{\tau_{Yb1}} = 0\,, \tag{S3.1a}$$

$$\frac{dN_1}{dt} = C_0 N_0 N_{Yb1} - C_1 N_1 N_{Yb1} - \beta_1 N_1 - \frac{N_1}{\tau_1^{rad}} = 0\,, \tag{S3.1b}$$

$$\frac{dN_2}{dt} = C_1 N_1 N_{Yb1} - \beta_2 N_2 - \frac{N_2}{\tau_2^{rad}} = 0\,, \tag{S3.1c}$$

where N_0, N_1, and N_2 denote the population densities of the states $^5I_8$, $^5I_6$, and $^5S_2/^5F_4$ of Ho^{3+} ions, respectively, while N_{Yb0} and N_{Yb1} are the population densities of the states $^2F_{7/2}$ and $^2F_{5/2}$ of Yb^{3+} ions, respectively; σ denotes the absorption cross-section of Yb^{3+} ion; ρ is the excitation photon flux, which is linearly related with power-density; τ_1^{rad} and τ_2^{rad} are the radiative lifetimes of Ho^{3+} ions at states $^5I_6$ and $^5S_2/^5F_4$; τ_{Yb1} is the lifetime of Yb^{3+} ions at $^2F_{5/2}$ state; C_0, and C_1 are ETU rates from excited Yb^{3+} ions to the Ho^{3+} ions at states $^5I_8$ and $^5I_6$, respectively; β_1 and β_2 represents the non-radiative decay rate for $^5I_6 \rightarrow {}^5I_7$ and $^5S_2/^5F_4 \rightarrow {}^5F_5$, respectively. In this model, the depletion of the population density of $^2F_{5/2}$ (Yb^{3+}) state due to ETU process is omitted, because the ETU rates at $^2F_{5/2}$ (Yb^{3+}) state are much lower than its linear decay rate. For the same reason, the contribution to the depletion of state $^5S_2/^5F_4$ due to ETU to even higher states is not considered either. Under these assumptions, the population densities of different levels at steady state can be obtained from eqns (S3.1a) - (S3.1c)

$$N_{Yb1} = \tau_{Yb1}\sigma N_{Yb0}\rho\,, \tag{S3.2a}$$

$$N_1 = \frac{C_0 N_0 N_{Yb1}}{\frac{1}{\tau_1^{rad}} + \beta_1 + C_1 N_{Yb1}} = \frac{C_0 N_0 \tau_{Yb1}\sigma N_{Yb0}\rho}{\frac{1}{\tau_1^{rad}} + \beta_1 + C_1 \tau_{Yb1}\sigma N_{Yb0}\rho}\,, \tag{S3.2b}$$

$$N_2 = \frac{C_1 N_1 N_{Yb1}}{\frac{1}{\tau_2^{rad}} + \beta_2} = \frac{C_0 C_1 N_0 (\tau_{Yb1}\sigma N_{Yb0}\rho)^2}{\left(\frac{1}{\tau_2^{rad}} + \beta_2\right)\left(\frac{1}{\tau_1^{rad}} + \beta_1 + C_1 \tau_{Yb1}\sigma N_{Yb0}\rho\right)}\,. \tag{S3.2c}$$

Let

$$\frac{1}{\tau_1^{\mathrm{rad}}} + \beta_1 = \frac{1}{\tau_1} \ , \tag{S3.3}$$

and

$$\frac{1}{\tau_2^{\mathrm{rad}}} + \beta_2 = \frac{1}{\tau_2} , \tag{S3.4}$$

where τ_1 and τ_2 are the lifetimes of the state $^5I_6$ and $^5S_2/^5F_4$ of Ho^{3+}, respectively, including the contribution of non-radiative decays, then we can obtain the power-density dependence of the green UC steady-state emission from the state $^5S_2/^5F_4$

$$I = \frac{N_2}{\tau_2^{\mathrm{rad}}} h\nu = \frac{C_0 C_1 \tau_{\mathrm{Yb1}}^2 (\tau_2/\tau_2^{\mathrm{rad}}) N_0 h\nu \sigma^2 N_{\mathrm{Yb0}}^2 \rho^2}{\frac{1}{\tau_1} + C_1 \tau_{\mathrm{Yb1}} \sigma N_{\mathrm{Yb0}} \rho} . \tag{S3.5}$$

The NIR UC emission originating from Tm^{3+}, the green UC emission from Er^{3+} and the green UC emission from Ho^{3+} have unified form of eqn (3). For the NIR UC emission of Tm^{3+},

$$\tau_1 = \tau_1^{\mathrm{rad}} . \tag{S3.6}$$

and

$$\tau_2 = \tau_2^{\mathrm{rad}} . \tag{S3.7}$$

S4. The derivation of the analytical expression for the slope efficiency the power-density dependence curve

The UC emission has a power-density dependence of

$$I = \frac{\mathrm{a}\rho^2}{\mathrm{b}+\mathrm{c}\rho} \ , \tag{S4.1}$$

where

$$\mathrm{a} = C_0 C_1 \tau_{\mathrm{Yb1}}^2 (\tau_2/\tau_2^{\mathrm{rad}}) N_0 h\nu \sigma^2 N_{\mathrm{Yb0}}^2 , \tag{S4.2}$$

$$\mathrm{b} = \frac{1}{\tau_1} \ , \tag{S4.3}$$

and

$$\mathrm{c} = C_1 \tau_{\mathrm{Yb1}} \sigma N_{\mathrm{Yb0}} . \tag{S4.4}$$

Mathematically, the slope efficiency of the UC emission in a double-logarithmic scale is given by the derivative of log$I$ over logρ, *i.e.*,

$$k \equiv \frac{\mathrm{d}\log I}{\mathrm{d}\log\rho} = \frac{\mathrm{d}\log I}{\mathrm{d}\rho} \cdot \frac{\mathrm{d}\rho}{\mathrm{d}\log\rho} = \frac{\mathrm{d}\log\left(\frac{\mathrm{a}\rho^2}{\mathrm{b}+\mathrm{c}\rho}\right)}{\mathrm{d}\rho} \cdot \rho$$

$$= \frac{\left(\frac{a\rho^2}{b+c\rho}\right)'}{\frac{a\rho^2}{b+c\rho}} \cdot \rho = \frac{\frac{2a\rho(b+c\rho)-ca\rho^2}{(b+c\rho)^2}}{\frac{a\rho^2}{b+c\rho}} \cdot \rho$$

$$= 1 + \frac{1}{1+\frac{c\rho}{b}} = 1 + \frac{1}{1+\tau_1 \cdot C_1 \tau_{Yb1} \sigma N_{Yb0} \rho} \quad \text{(S4.5)}$$