Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Video-rate upconverting display by optimizing lanthanide ions dopedupconversion nanoparticles

Laixu Gao,[a,b] Xuchen Shan,[b] Xiaoxue Xu,*[b] Yongtao Liu,[b] Baolei Liu,[b] Songquan Li,[a]

Shihui Wen,[b] Chenshuo Ma,[b] Dayong Jin[b] and Fan Wang*[b,c]

[a]*School of Physical Science and Technology, Lingnan Normal University, Zhanjiang, 524048, China.*

[b]*Institute for Biomedical Materials and Devices (IBMD), Faculty of Science, University of Technology Sydney, NSW 2007, Australia*

[c]*School of Electrical and Data Engineering, Faculty of Engineering and Information Technology, University of Technology Sydney, Ultimo 2007, Australia*

1. Experiments: synthesis and characterization

Synthesis of $NaYF_4$: Yb^{3+}, Tm^{3+}.

Upconversion nanocrystals were synthesized according to the previously reported method[1, 2]. In a typical experiment, 1 mmol $RECl_3 \cdot 6H_2O$ (RE = Y, Yb, Tm) with the desired molar ratio were added to a flask containing 6 mL OA and 15 mL ODE. The mixture was heated to 160 °C under argon flow for 30 min to obtain a clear solution and then cooled down to about 40 °C, followed by the addition of 5 mL methanol solution of NH_4F (4 mmol) and NaOH (2.5 mmol). After stirring for 30 min, the solution was heated to 80 °C under argon flow for 20 min to expel methanol, and then the solution was further heated to 310 °C for another 90 min. Finally, the reaction solution was cooled down to room temperature. The products were precipitated by ethanol and centrifuged, then washed for three times with cyclohexane, ethanol, and methanol to get the nanoparticles.

Characterization

A series of UCNPs, $NaYF_4$: 20%Yb^{3+}, x%Tm^{3+} (x=0.5, 1, 2, 4 and 6), were synthesized and characterized. The morphology characterization was conducted using Transmission Electron Microscopy (TEM) and the TEM images are shown in Fig. S1. The average size of the UCNPs with different Tm^{3+} doping concentrations is all about 40 nm. The size distributions are shown in Fig. S2.

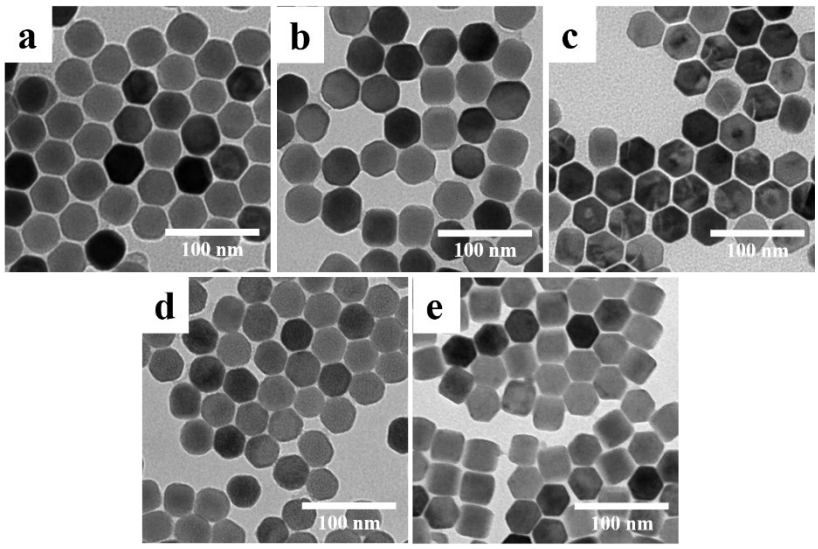

Fig. S1 TEM images of the UCNPs with different Tm^{3+} doping concentration: (a) 0.5%, (b) 1%, (c) 2%, (d) 4% and (e) 6%.

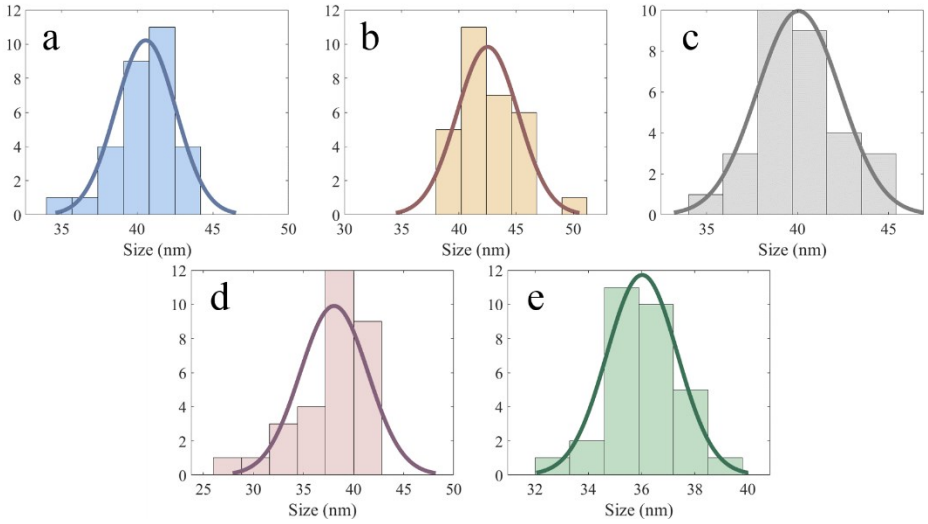

Fig. S2 The size distributions of the UCNPs with different Tm^{3+} doping concentration: (a) 0.5%, (b) 1%, (c) 2%, (d) 4% and (e) 6%.

2. Up-conversion Energy transfer Process

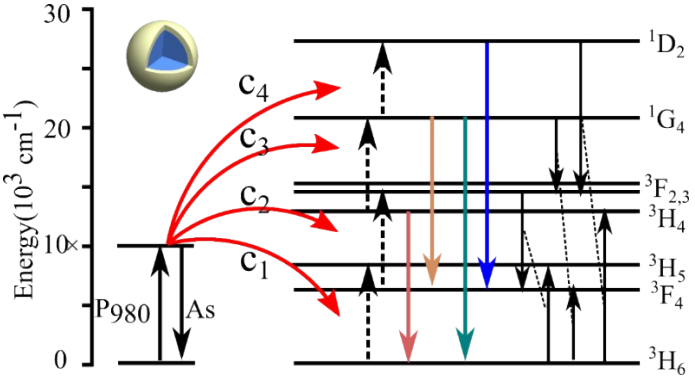

Fig. S3 Schematic diagram of the up-conversion energy transfer process

$$\frac{dn_1}{dt} = -c_1 n_1 n_{S2} + a_{21} w_2 n_2 + a_{31} w_3 n_3 + a_{41} w_4 n_4 + a_{51} w_5 n_5 - k_{41} n_1 n_4 - k_{31} n_1 n_3$$

$$\frac{dn_2}{dt} = c_1 n_1 n_{S2} - c_2 n_2 n_{S2} - a_{21} w_2 n_2 + a_{32} w_3 n_3 + a_{42} w_4 n_4 + a_{52} w_5 n_5 + k_{41} n_1 n_4 + 2k_{31} n_1 n_3$$

$$\frac{dn_3}{dt} = c_2 n_2 n_{S2} - c_3 n_3 n_{S2} - (a_{31} + a_{32}) w_3 n_3 + a_{43} w_4 n_4 + a_{53} w_5 n_5 + 2k_{51} n_5 n_1 + k_{41} n_4 n_1 - k_{31} n_3 n_1$$

$$\frac{dn_4}{dt} = c_3 n_3 n_{S2} - c_4 n_4 n_{S2} - (a_{43} + a_{42} + a_{41}) w_4 n_4 - b_4 n_4 + a_{54} w_5 n_5 - k_{41} n_1 n_4$$

$$\frac{dn_5}{dt} = c_4 n_4 n_{S2} - (a_{54} + a_{53} + a_{52} + a_{51}) w_5 n_5 - b_5 n_5 - k_{51} n_1 n_5$$

$$\frac{dn_{S2}}{dt} = P_{980}n_{S1} - a_S n_{S2} - (c_1 n_1 + c_2 n_2 + c_3 n_3 + c_4 n_4)n_{S2}$$

To investigate the underlying cause of the rising and decay time in the Tm^{3+} doped UCNPs system, we simplified the energy level diagram as shown in Fig. S3. It involves two energy levels associated with the sensitizer Yb^{3+} and five associated levels with the activator Tm^{3+}. $^2F_{7/2}$ and $^2F_{5/2}$, $^3H_6$, $^3H_5/^3F_4$ and $^3F_{2,3}/^3H_4$, represented as S1, S2, 1, 2, 3, 4, 5 respectively. Five energy level rate equations were built up for understanding the long rising time. During the excitation process, the excitation photons are absorbed by Yb^{3+} only and then transferred to Tm^{3+} because of the higher obsecration cross-section of Yb^{3+} at 980 nm. C*i* (*i*=1,2,3,4) is the energy transfer ratio between Yb^{3+} on the excited level and Tm^{3+} both on the ground and the intermediate levels. From the rate equations, at the beginning of excitation, there is no population of ions on the excited levels, and all ions distributed on the ground state. When Yb^{3+} only transfer the pumping energy to Tm^{3+} ground state, the new distribution will be built from ground state to excited state in Tm^{3+} level by level. The emission would be achieved by the spontaneous radiation from the excited state. So the rising and decay time is determined by the energy transfer rate c*i* and the spontaneous radiation probability respectively. The c*i* has a similar scale with *w* as shown in the previous papers [2] (c =N1*10^4, w=N2*10^4). So they should have the same scale rising and decay time.

The pumping and decay curve of UCNPs is shown in Fig. S4. The lifetime time just includes the decay part which is fitted to an exponential function as the lifetime of the nanoparticles.

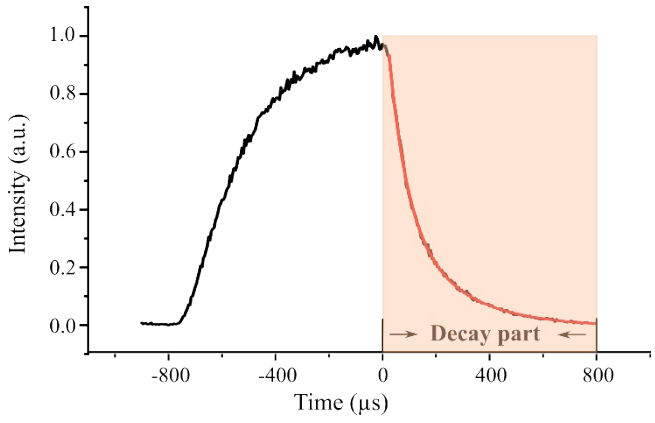

Fig. S4 The rising and decay curve of upconversion nanoparticles.

3. Power density of focusing spot

We calculated the power density using the equation below according to Zhou's work[3].

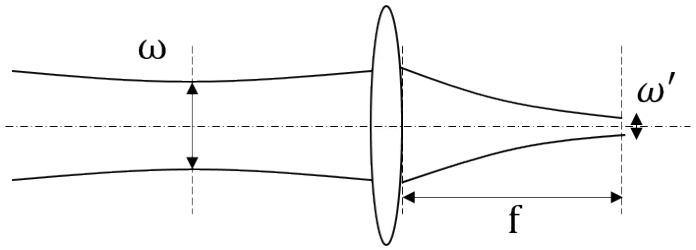

Fig. S5 The focus of a gaussian beam.

The focused light path of the gaussian beam is shown in Fig. S5. The display screen is located in the focal plane of the lens. The incident light power is 582 mW, the wavelength $\lambda = 980\ nm$, the focal length $f = 50\ mm$, the beam waist diameter $\omega = 5\ mm$, the focusing spot diameter can be calculated as follow:

$$\omega' = \frac{\lambda f}{\pi \omega} = 12.4\ \mu m$$

The power density $\rho =$ Power/focused spot area, so

$$\rho = \frac{582}{\pi(\frac{\omega'}{2})^2} = 0.48\ MW/cm^2$$

4. References

1. Liu, D.; Xu, X.; Du, Y.; Qin, X.; Zhang, Y.; Ma, C.; Wen, S.; Ren, W.; Goldys, E. M.; Piper, J. A.; Dou, S.; Liu, X.; Jin, D., Three-dimensional controlled growth of monodisperse sub-50 nm heterogeneous nanocrystals. *Nat. Commun.* **2016**, *7*, 10254.
2. Liu, Y.; Lu, Y.; Yang, X.; Zheng, X.; Wen, S.; Wang, F.; Vidal, X.; Zhao, J.; Liu, D.; Zhou, Z.; Ma, C.; Zhou, J.; Piper, J. A.; Xi, P.; Jin, D., Amplified stimulated emission in upconversion nanoparticles for super-resolution nanoscopy. *Nature.* **2017**, *543* (7644), 229-233.
3. Zhou B.et al. The Principle of Laser, The sixth edition. *National Defence Industry Press.* **2009**, 79-80.