Electronic Supplementary Information (ESI)

Near-infrared light responsive intensified multiphoton ultraviolet upconversion in nanostructure towards efficient reactive oxygen species production

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Calculation of loading concentration of ICG per nanoparticle

For $LiYbF_4$:Tm(1 mol%)@$LiYF_4$:Yb/Nd(10/50 mol%) core-shell nanoparticle, the radius of core-shell is Rcs=10.685 nm. And the volume of a single nanoparticle can be calculated by $V_{UCNP} = \frac{4}{3}\pi R_{cs}^3 =$ 5108.934 nm3

In addition, the volume of a $LiYF_4$ unit cell can be obtained from JCPDS database, which is V_{cell}=2.790 $\times 10^{-22}$ cm^3 (tetragonal phase, $LiYbF_4$, PDF#23-0371). So the number of cells in an upconversion particle can be obtained by:

$$N_0 = \frac{V_{UCNP}}{V_{cell}} = \frac{5108.934 \times 10^{-21}}{2.790 \times 10^{-22}} = 18311.591$$

The number of lanthanide ions in a UCNP particle, which is $N_{Ln^{3+}} = 1 \times 18311.591 = 18311.591$.

In the dye sensitization experiment, ligand-free UCNPs (200μL,0.1mmol/mL) and ICG (150μL, 0.1mg/mL, M=774,97g/mol) were added to the sample. And the number of UCNP particles in each sample can be calculated as:

$$N_{UCNPS} = \frac{200 \times 10^{-6} \times 0.1}{18311.591} = 1.092 \times 10^{-9} \text{ mol}$$

After the ICG was coated on the surface of the nanoparticles, the absorbance of the ICG-nanocrystal complex at 793 nm was measured. By comparing the measured absorbance with the calibration curve function (Figure S3), the accurate loading concentration of ICG on the upconversion nanoparticles was calculated by:

ICG loading molar concentration: 0.37134=0.02468X-0.10164

C_{ICG} =X=0.01916 μM =1.916×10^{-8} mol

Assuming that each ICG molecule can be completely attached to the surface of UCNPs, then the number of ICG molecules attached to each nanoparticle surface can be obtained by: $\frac{N_{\text{ICG}}}{\text{UCNPs}} = \frac{1.916 \times 10^{-8}}{1.092 \times 10^{-9}} = 17.5$

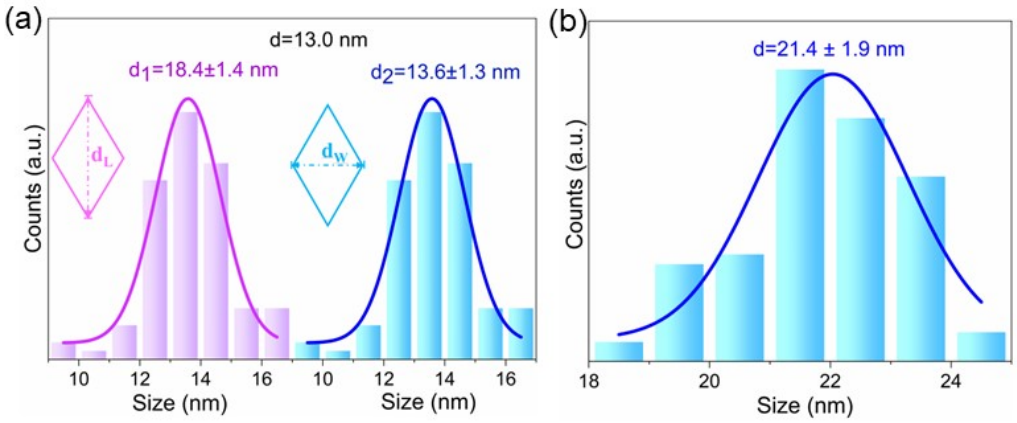

Fig. S1. The size distributions of as-synthesized $LiYbF_4$ core and $LiYbF_4$@$LiYF_4$:Yb/Nd core-shell nanoparticles in Fig.1 of the main text.

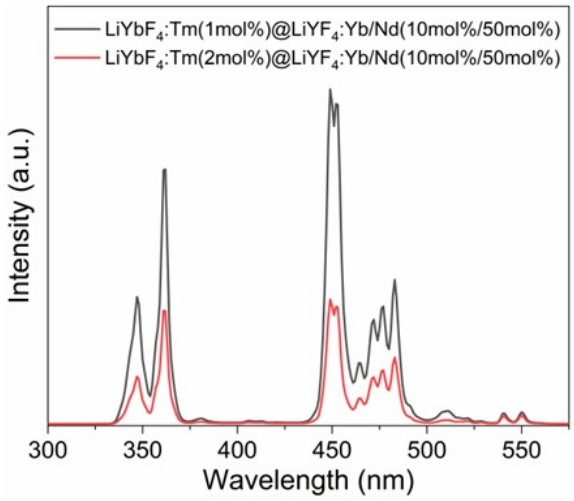

Fig. S2. A comparison of upconversion emission of $LiYbF_4$:Tm(1 mol%)@$LiYF_4$:Yb/Nd(10/50 mol%) and $LiYbF_4$:Tm(2 mol%)@$LiYF_4$:Yb/Nd(10/50 mol%) under 808 nm excitation.

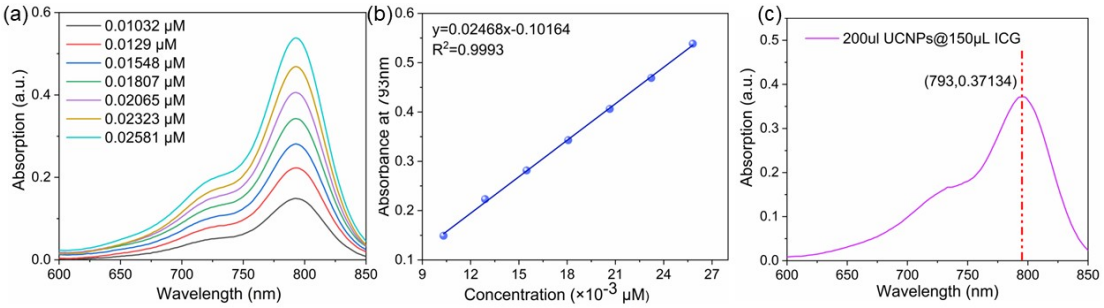

Fig. S3. (a)UV-vis absorption spectra of ICG DMF solution of different concentration. (b) Plot of the ICG calibration dataset showing the change in absorbance of ICG as a function of concentration. (c) Absorption spectrum of $LiYbF_4$:Tm@$LiYF_4$:Yb/Nd@ICG.

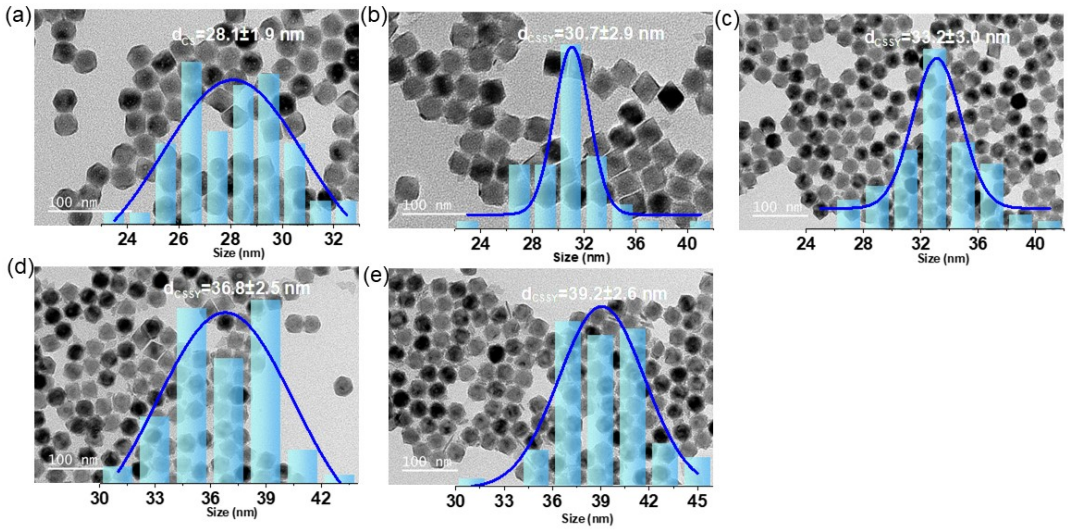

Fig. S4. TEM images and corresponding particle size distribution of $LiYbF_4$:Tm@$LiYF_4$:Yb/Nd coated with different thickness of $LiYF_4$ shell.

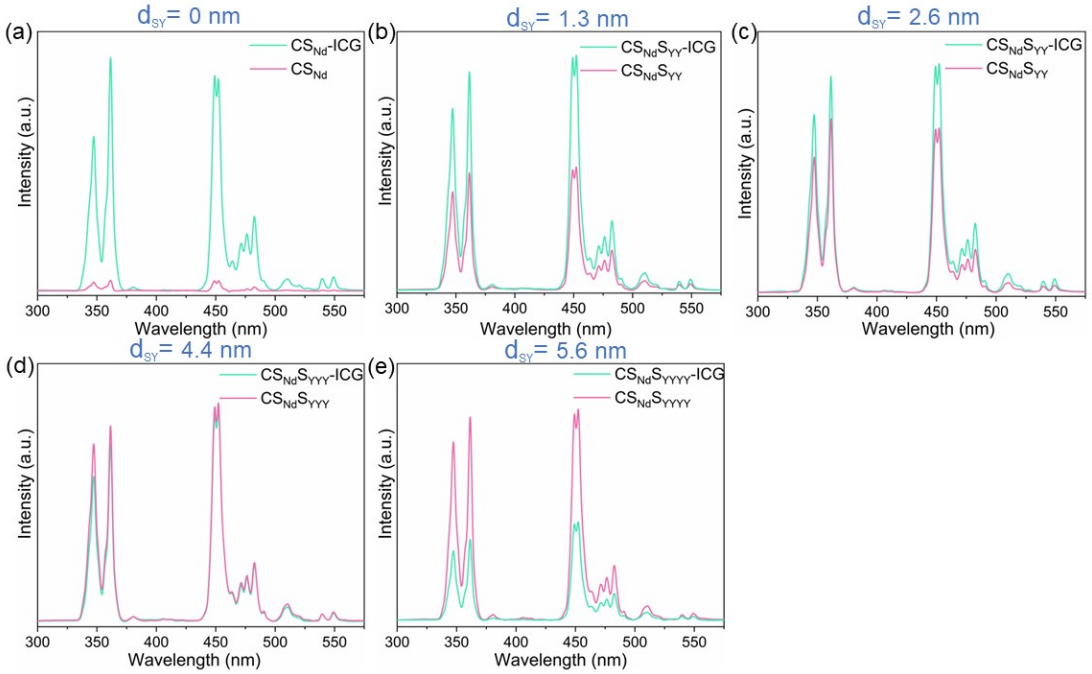

Fig. S5. The comparison of upconversion emission spectra of $LiYbF_4$:Tm@ $LiYF_4$:Yb/Nd with different thicknesses of $LiYF_4$ shells coated and uncoated ICG. Notably, $LiYbF_4$:Tm@$LiYF_4$:Yb/Nd@$LiYF_4$ was denoted by $CS_{Nd}S_Y$.

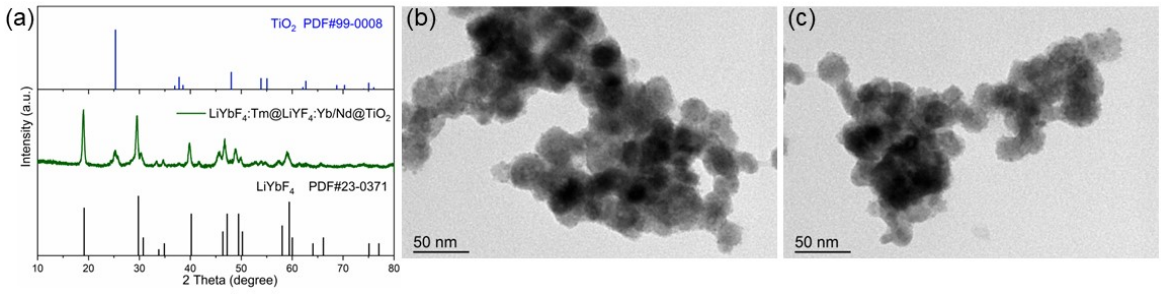

Fig. S6. (a) XRD pattern of the as-synthesized $LiYbF_4$:Tm@$LiYF_4$:Yb/Nd@TiO_2

nanocomposites. (b) and (c) TEM images of the as-synthesized $LiYbF_4$:Tm@$LiYF_4$:Yb/Nd @TiO_2 nanocomposites.