Electronic Supplementary Information

Intense multiphoton upconversion of Yb^{3+}-Tm^{3+} doped β-$NaYF_4$ individual nanocrystals by saturation excitation

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Experimental Section

Chemicals.

Yttrium (III) acetate hydrate (99.9%), ytterbium(III) acetate hydrate (99%), thulium acetate hydrate (99.9%), holmium (III) acetate hydrate (99.99%), 1-octadecene (90%), oleic acid (90%) were purchased from Sigma-Aldrich. Sodium hydroxide (NaOH, >98%), Ammonium fluoride (NH_4F, >98%), cyclohexane, methanol, acetone , and ethanol were purchased from Sinopharm Chemical Reagent Co., Ltd. All of the chemicals were used without any further purification process.

Synthesis of β-$NaYF_4$: 20 mol %Yb^{3+}-2 mol %Ho^{3+} /Tm^{3+} nanocapsules: 2 mL water solution of $Ln(CH_3CO_2)_3$ (0.2 M, Ln = Y, Yb, and Ho/Tm) was added to a

50-mL flask containing 7 mL of oleic acid and 7 mL of 1-octadecene. The mixture was heated at 150 ℃ for 30 min to remove the water from the solution. Shortly thereafter, 6 mL of methanol solution containing NH_4F (1.6 mmol) and NaOH (1 mmol) was added and the resultant solution was stirred for 30 min at 50 ℃. After the methanol was evaporated, the solution was heated to 290 ℃ under argon for 1.5 h and then cooled down to room temperature. The resulting nanocapsules were precipitated by addition of acetone, collected by centrifugation at 6000 rpm for 5 min, washed with ethanol several times, and re-dispersed in cyclohexane.

Synthesis of β-$NaYF_4$: 20 mol %Yb^{3+}-2 mol %Ho^{3+} nanospheres: 2 mL water solution of $Ln(CH_3CO_2)_3$ (0.2 M, Ln = Y, Yb, and Ho) was added to a 50-mL flask containing 3 mL of oleic acid and 7 mL of 1-octadecene. The mixture was heated at 150 ℃ for 30 min to remove the water from the solution. Shortly thereafter, 6 mL of methanol solution containing NH_4F (1.6 mmol) and NaOH (1 mmol) was added and the resultant solution was stirred for 30 min at 50 ℃. After the methanol was evaporated, the solution was heated to 290 ℃ under argon for 1.5 h and then cooled down to room temperature. The resulting nanospheres were precipitated by addition of acetone, collected by centrifugation at 6000 rpm for 5 min, washed with ethanol several times, and re-dispersed in cyclohexane.

General materials characterization: Transmission electron microscopy (TEM) measurements were carried out on a CM200 transmission electron microscope (Philips) operating at an acceleration voltage of 160 kV. Scanning electron microscopy (SEM) was performed on a SU-8010 field emission scanning electron microscope (HITACHI) operated at 2 kV. Powder X-ray diffraction (XRD) data were recorded on a RIGAKU D/MAX 2550/PC diffractometer (Japan) with a slit of 0.02 ° at a scanning speed of 5 °min-1 using Cu Kα radiation (λ=1.5406 Å).

Individual optical characterization:

1) The sample preparation is as follow: one drop of the diluted nanocrystals solution is spin coated on a glass slide. The concentration of the diluted solution is considered to be appropriate when several bright spots could be scanned in an area of 10×10 μm^2.

2) In the home-made confocal setup, the excitation laser is focused by a 1.4 NA, ×100 oil objective, and the emitted light is collected with the same objective and filtered by a 900 nm short-pass filters to remove residual laser light. For the detection of upconversion fluorescence we use a spectrometer (ACTON, SpectraPro-300i). The schematic diagram is shown in Figure S1.

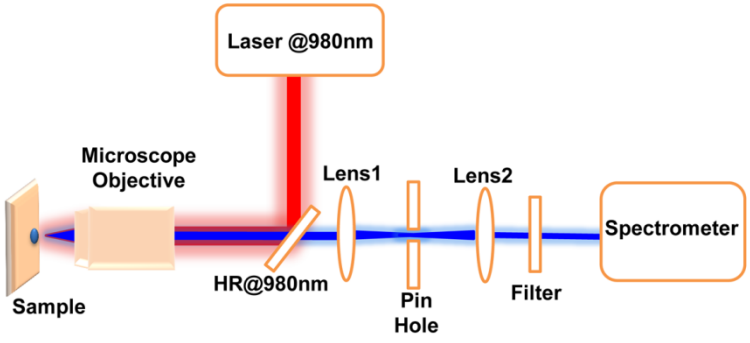

Figure S1. Schematic diagram of the home-made confocal setup**.**

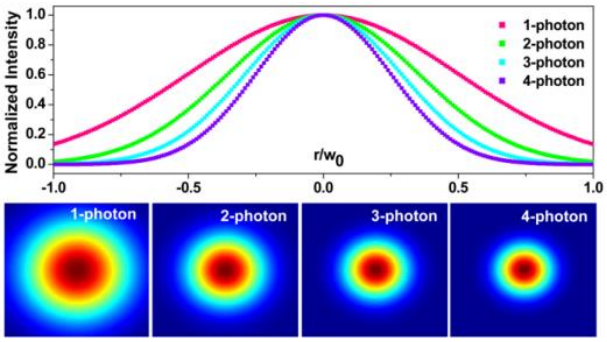

Fig. S2. Simulation of the imaging resolution differences between 1, 2, 3, 4-photon upconversion processes.