Electronic Supplementary Material (ESI) for Nanoscale

Supporting Information

Synthesis of lanthanide-doped $NaYF_4$@TiO_2 core-shell composites with highly crystalline and tunable TiO_2 shells under mild conditions and their upconversion-based photocatalysis

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1. Experimental

Materials

$YCl_3 \cdot 6H_2O$ (99.99%), $YbCl_3 \cdot 6H_2O$ (99.99%), $TmCl_3 \cdot 6H_2O$ (99.99%), NaOH (98+%), NH_4F(98+%) and oleic acid (90%), PVP-40 (99%) were all purchased from Sigma-Aldrich. TiF_4 (99%) was purchased from Acros. All raw materials were used as starting materials without further purification.

Synthesis of the microrods

A 1.5 mL deionized water solution of 0.3 g NaOH was mixed with 5 mL ethanol and 5 mL oleic acid under stirring. 2 mL 0.2 M $RECl_3$ mixture solution (Y:Yb:Tm = 70:30:0.5) and 1 mL 2 M NH_4F was selectively added into the above solution. Then the solution was transferred into a 20 mL of Teflon-lined autoclave and heat at 220 ^oC for 12 h. The obtained rods were collected by centrifugation, washed with deionized water and ethanol several times.

Synthesis of the nanorods

A 1.5 mL deionized water solution of 0.3 g NaOH was mixed with 5 mL ethanol and 5 mL oleic acid under stirring. 2 mL 0.2 M $RECl_3$ mixture solution (Y:Yb:Gd:Tm = 40:30:30:0.5) and 1 mL 2 M NH_4F was selectively added into the above solution. Then the solution was transferred into a 20 mL of Teflon-lined autoclave and heat at 200 ^oC for 3 h. The obtained rods were collected by centrifugation, washed with deionized water and ethanol several times.

Remove the ligand on rods

The as-prepared oleic acid-capped rods were dispersed in a 0.1 M HCl solution, followed by ultrasonication to remove the surface ligands. After the reaction, the nanoparticles were collected via centrifugation. The resulting products were washed with deionized water and ethanol several times, and kept in deionized water.

Hydrothermal coating of TiO_2.

Microcomposites: Typically, 0.2 mmol as-prepared ligand-free $NaYF_4$:Yb,Tm microrods were transferred into 4 mL 0.2 g/mL PVP-40 solution with the aid of stirring and ultrasonication. Then 20 mL ethanol was added under stirring for more than 30 min. 4 mL 0.04 M TiF_4 was dropwise added into the solution under stirring. Then the whole solution was transferred into a 40 mL Teflon-lined autoclave and heat at 180 ^oC for 4 h. Finally the as-prepared products were collected by centrifugation, washed with deionized water and ethanol several times and dried at 90 ^oC.

Nanocomposites: Similar to the procedures for microrods, except for varying the amount of $NaYF_4$:Yb,Tm,Gd nanorods and fixing the amount of TiF_4. The concentration of TiF_4 is 0.04 M and the molar ratio of ($NaYF_4$:Yb,Tm,Gd):(TiF_4) is varied from 1:2 to 1:10.

TiO_2 nanoflowers: Similar to the procedures for microrods, except for adding no fluorides rods into the solution.

2. Characterization

Low-resolution transmission electron microscopy (**TEM**) measurements were carried out on a JEL-1400 transmission electron microscope (JEOL) operating at an acceleration voltage of 120 kV. High-resolution transmission electron microscopy (**HRTEM**) measurements were carried out on a Tecnai G2 F20 S-TWIN transmission electron microscope (FEI) operating at an acceleration voltage of 200 kV. Scanning electron microscopy (**SEM**) was performed on a FEI NOVA NanoSEM 230 scanning electron microscope operated at 5 kV. Powder X-ray diffraction (**XRD**) data were recorded on a Siemens D5005 X-ray diffractometer with CuK α radiation (1.5406 Å). UV-vis transmission spectrum was recorded on a Shimadzu UV-2450 spectrophotometer. Photoluminescence (**PL**) spectra were recorded at room temperature with a DM150i monochromator equipped with a R928 photon counting photomultiplier tube (PMT), in conjunction with a 980 nm diode laser. Time-resolved fluorescence decay curves were measured by a fluorescence spectrometer (FLS920, Edinburgh) equipped with a 980 nm pulsed laser.

3. Photocatalytic measurements

In a typical photocatalytic test, 1 mL 5 mg/L methylene blue (MB) solution was added into a small glass bottle kept with 10 mg as-prepared products. The mixture of catalysts, solution and dyes was kept in dark for 12 h. Then a 1.5 W 980 nm diode laser (Sintec Optronics) was used as the irradiation source. After irradiation for a designated time, 0.05 mL of the MB aqueous solution was taken out, diluted with 0.95 mL DI water and followed by centrifugation. The supernatant was taken out for UV-Vis absorption spectrum measurement. The relative concentration of residual MB solution (C/C_0) at each time interval was determined by the ratio of intensity of the characteristic absorption peak of MB (663 nm) to the initial one.

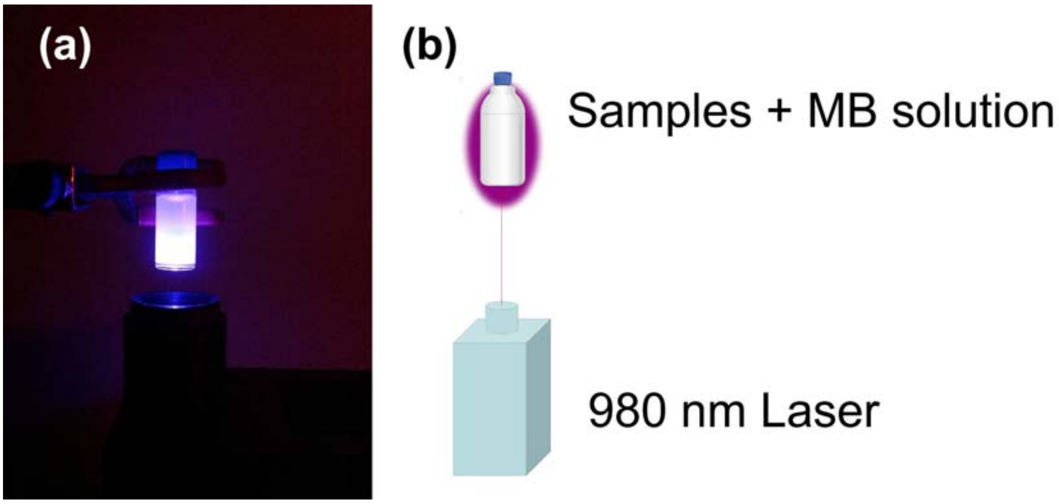


Fig. S1 (a) The optical image of the MB solution with $NaYF_4$:Yb,Tm@TiO_2 under 980 nm laser irradiation and (b) Scheme of the near-infrared photocatalytic experiment.

4. Size distribution

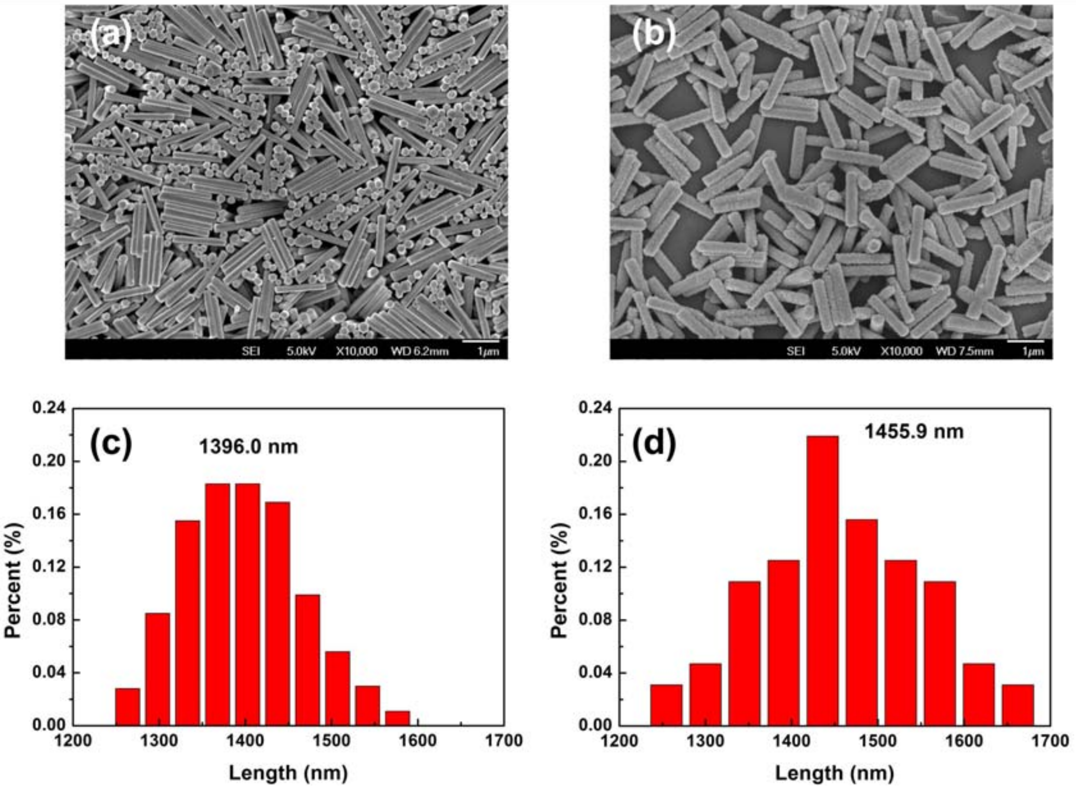


Fig. S2 (a) SEM image and (c) Corresponding length distribution of $NaYF_4$:Yb,Tm microrods; (b) SEM image and (d) Corresponding length distribution of $NaYF_4$:Yb,Tm@TiO_2 composites (0.04 M TiF_4).

*After coating of TiO_2 shell, the size of rods is increased while the size distribution is slightly broadened.

5. Influence of PVP

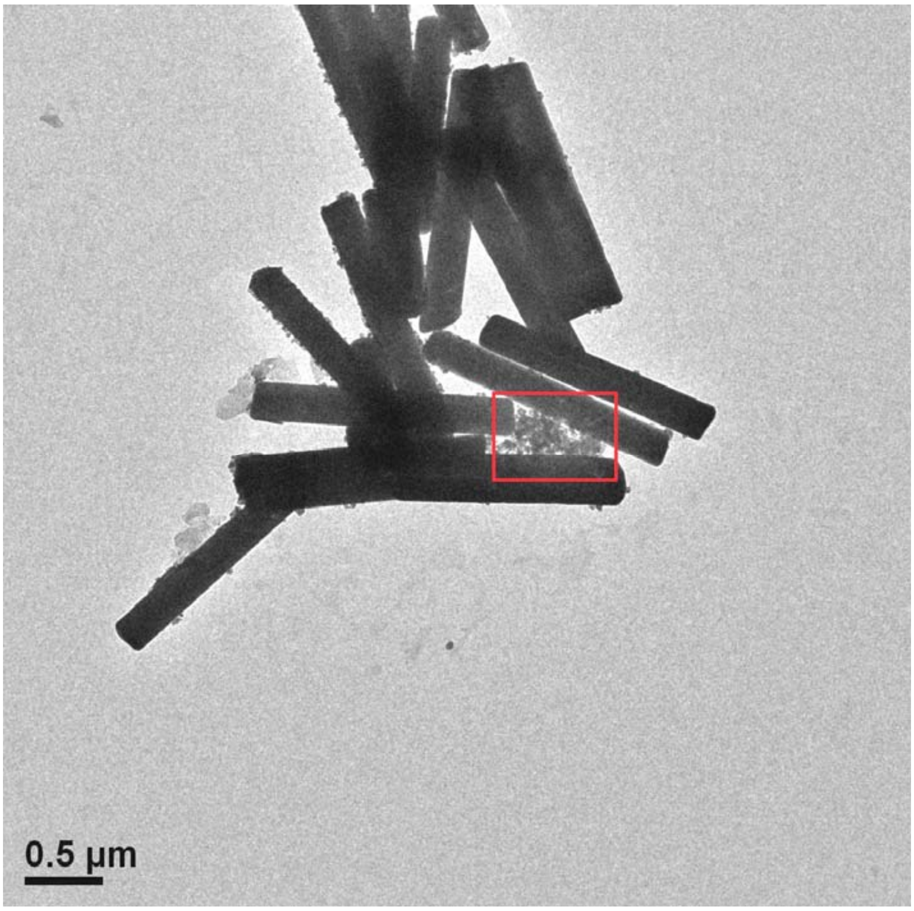


Fig. S3 TEM image of the $NaYF_4$:Yb,Tm/TiO_2 samples synthesized without PVP (Highlight: agglomerated TiO_2).

*The concentration of TiF_4 was fixed at 0.04 M. Without the presence of PVP, no continuous shell was formed and the self-aggregation of TiO_2 was observed. It indicates that, without PVP, the rods easily precipitated to the bottom of the solution hence very little amount of TiF_4 was coated on the TiF_4. More TiO_2 particles were self-nucleated and agglomerated. Consequently, PVP is of great importance to the successful coating. [X. W. Lou and L. A. Archer, *Adv. Mat.*, 2008, **20**, 1853]

6. Treatment with Titanium alkoxide

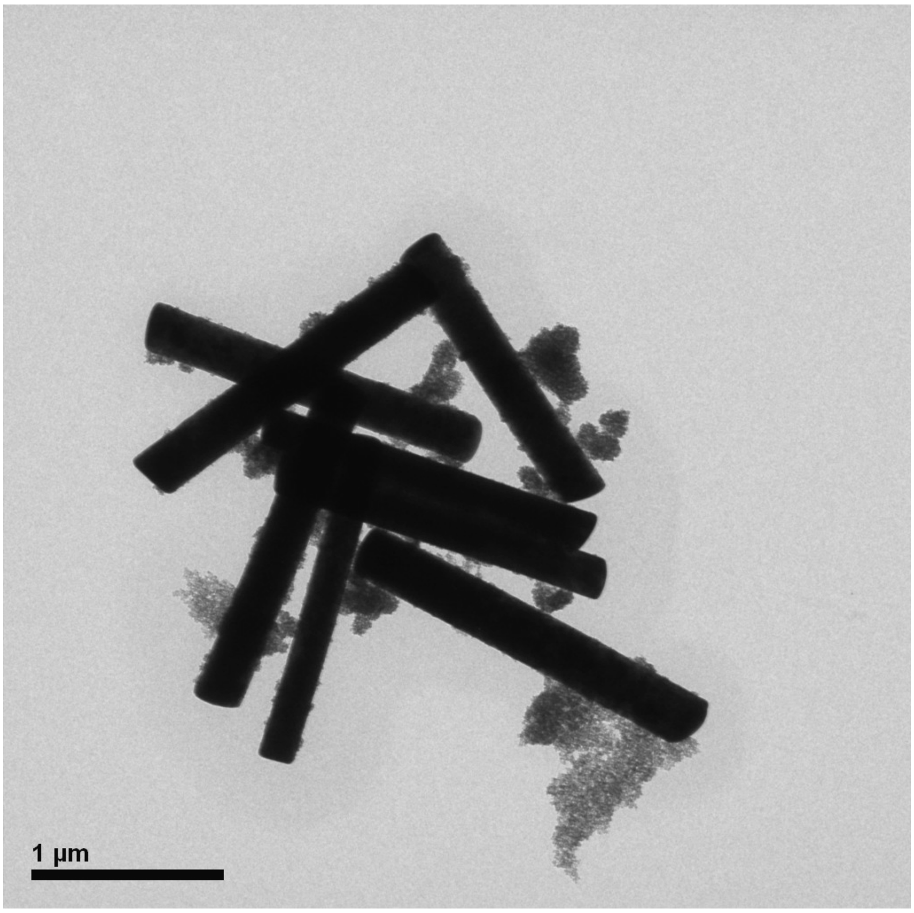


Fig. S4 TEM image of the $NaYF_4$:Yb,Tm/TiO_2 samples synthesized with Titanium butoxide.

*The hydrothermal process is similar to the typical coating, except to replace the TiF_4 to Titanium butoxide with same Titanium amount (0.16 mmol). No continuous shell was formed and the self-aggregation of TiO_2 was observed.

7. Treatment with nanoplates

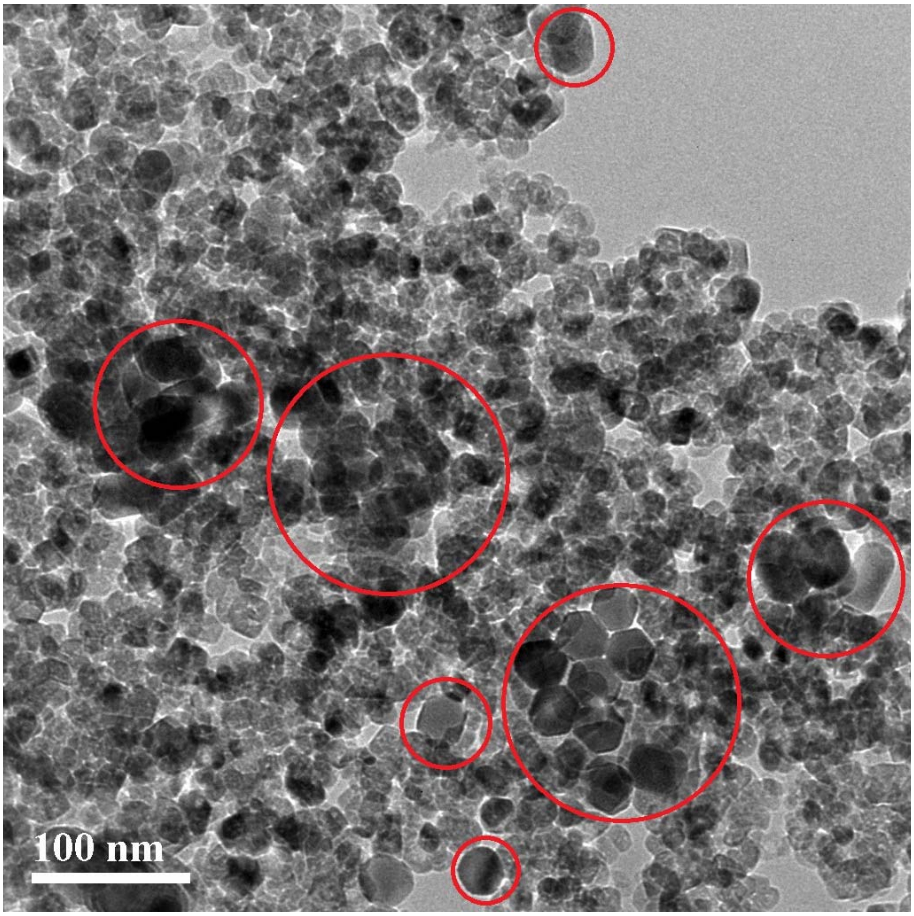


Fig. S5 TEM image of the $NaYF_4$:Yb,Tm/TiO_2 samples synthesized with $NaYF_4$:Yb,Tm nanoplates (Highlight: fluoride nanoplates).

*The hydrothermal process is similar to the typical coating, except to replace $NaYF_4$:Yb,Tm rods to nanoplates. No core/shell structure is achieved.

8. Energy-dispersive X-ray spectroscopy (EDX)

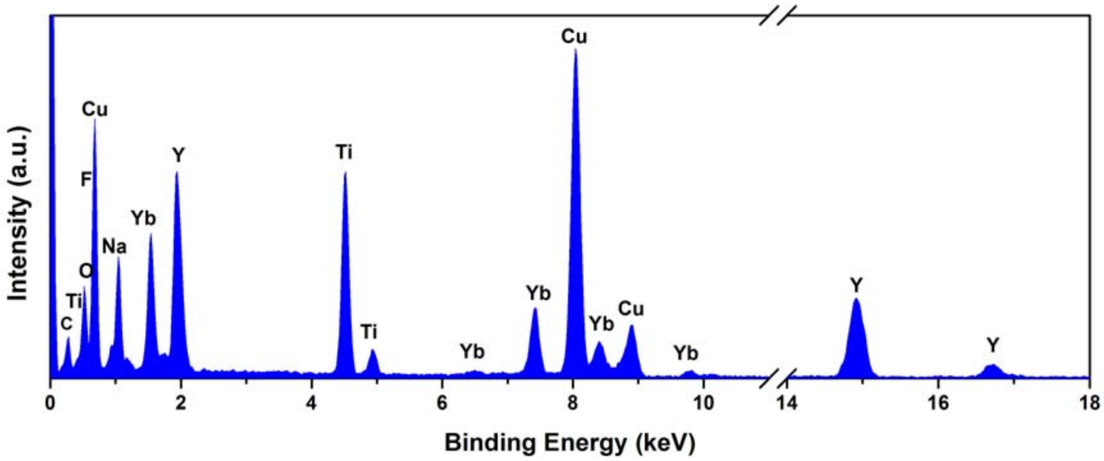


Fig. S6 EDX analysis of $NaYF_4$:Yb,Tm@TiO_2 (0.04 M TiF_4).

Table S1. Relative elements amount in $NaYF_4$:Yb,Tm@TiO_2 (0.04 M TiF_4)

Element	Weight (%)	Atomic (%)
C	2.2	8.01
O	4.44	12.12
F	11.77	27.09
Na	4.39	8.34
Ti	11.29	10.31
Cu	29.37	20.2
Y	19.67	9.67
Yb	16.86	4.26
Totals	**100**	**100**

* The C and Cu elements were derived from the carbon-supported copper grid for TEM.

9. PL ratio

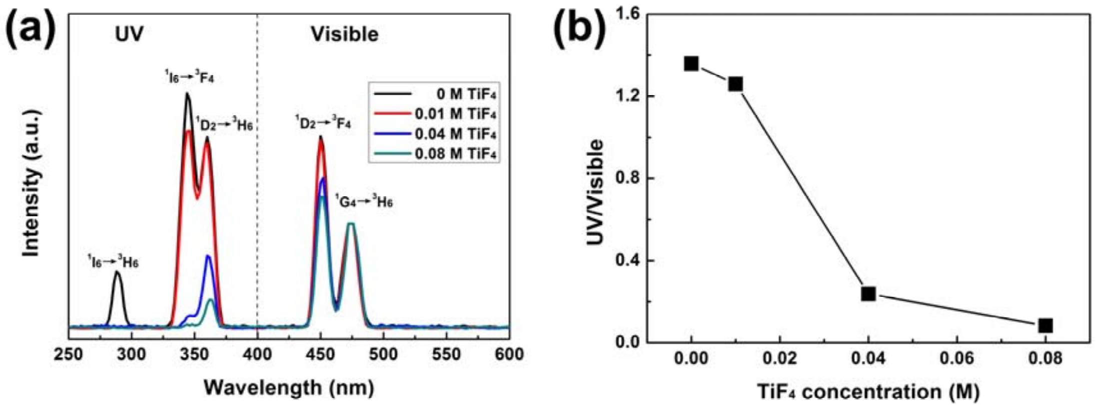


Fig. S7 (a) Upconversion PL spectra of NaYF$_4$:Yb,Tm and NaYF$_4$:Yb,Tm@TiO$_2$ with different TiF$_4$ concentration (Normalized at 476 nm), (b) Relative ratio of integrated intensity of UV peaks *vs.* visible light peaks.

10. Photoluminescence dynamic curves

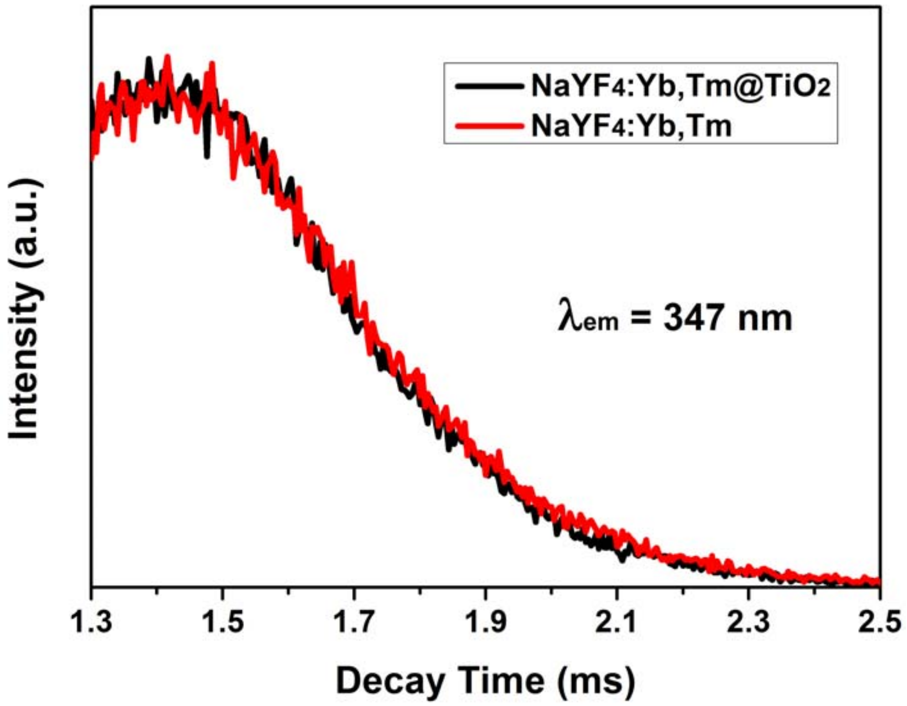


Fig. S8 Time-resolved fluorescence decay curves of Tm^{3+} (λ_{em} = 347 nm) of as-prepared samples recorded upon 980 nm NIR excitation.

* No significant decrease of average decay time is observed after TiO_2 coating. The result indicats that the mechanism of energy transfer in this core/shell structure is the classical radiation-reabsorption process, rather than Förster resonance energy transfer (FRET) [Y. Tang, W. Di, X. Zhai, R. Yang and W. Qin, *Acs Catal.*, 2013, **3**, 405].

11. Detection of free radicals

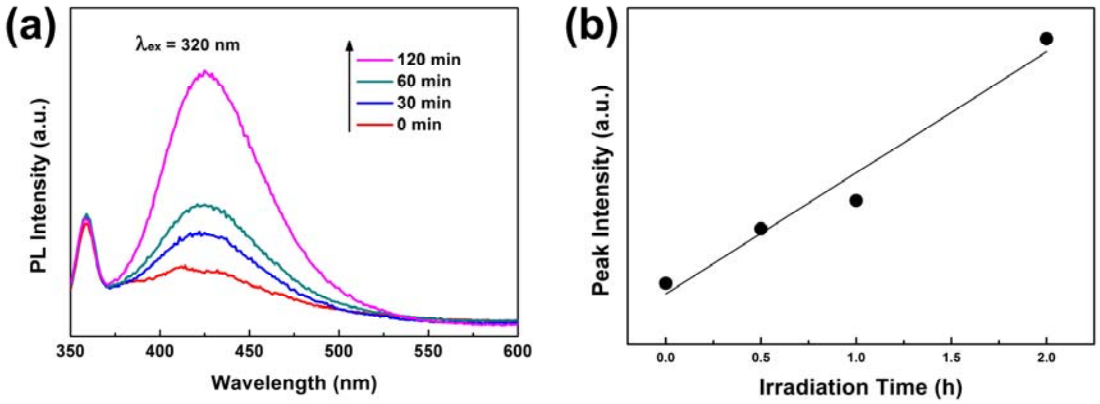
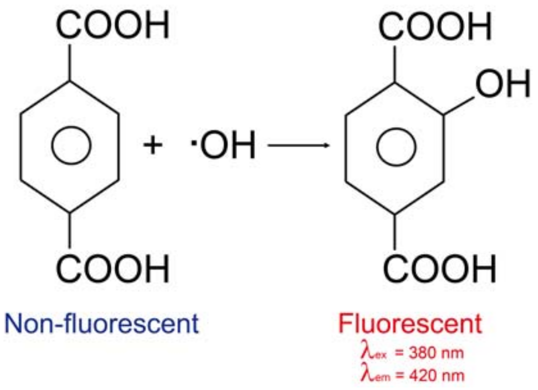


Fig. S9 (a) Time-dependent fluorescence spectra of the terephthalic acid solution containing 10 mg of $NaYF_4$:Yb,Tm@TiO_2 core/shell composite under near-infrared irradiation and (b) the integration of the emission of hydroxyterephthalic acid as a function of NIR irradiation time in the presence of $NaYF_4$:Yb,Tm@TiO_2



*The generation of radicals in solution was detected by the photoluminescence measurement with terephthalic acid as a probe molecule. The procedure was similar to that of the photocatalytic activity test except that the dye aqueous solution was replaced by the terephthalic acid and NaOH mixture aqueous solution. [C. Li, F. Wang, J. Zhu, and J. C. Yu, *Appl. Catal. B-Environ.*, 2010, **100**, 433; N. Zhang, S. Liu, X. Fu and Y. J. Xu, *J. Phys. Chem. C*, 2011, **115**, 9136.]

11. Optical images

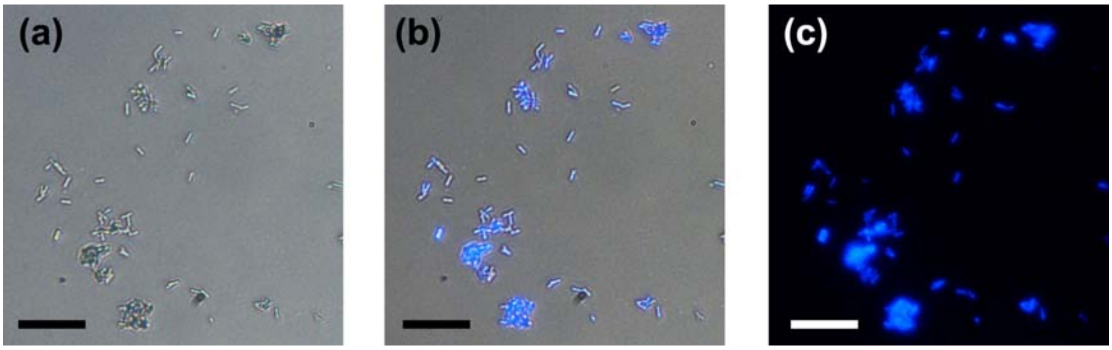


Fig. S10 Optical images of $NaYF_4$:Yb,Tm@TiO_2: (a) Bright-field optical image, (b) Merged bright-field optical image under 980 nm laser irradiation and (c) Dark-field optical image under 980 nm laser irradiation (scale bar: 10 μm).