Supplementary Information

Synergetic effects of lanthanide surface adhesion and photon-upconversion for enhanced near-infrared responsive photodegradation of organic contaminants in wastewater

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Experiment Sections:

Synthesis of $NaGdF_4$:Yb/Tm(49/1mol%)@$NaGdF_4$ Core-shell (NGFCS) Nanoparticles: In a typical procedure, 4 mL oleic acid was added into a 50-mL two-neck flask containing 2-mL water solution of $Gd(CH_3CO_2)_3$ (0.2 mmol), $Yb(CH_3CO_2)_3$ (0.196 mmol) and $Tm(CH_3CO_2)_3$ (0.004 mmol), followed by heating to and maintained at 150 ˚C with magnetic stirring. After removing water, 6 mL 1-octadecene was added and the mixture was heated at 150 ˚C for another 60 min before cooling down to 50 ˚C. Soon afterwards, 5.3 mL methanol solution containing NaOH (1 mmol) and NH_4F (1.32 mmol) was quickly injected to the flask, and the resultant solution was kept at 50 ˚C for 30 min while stirring. The reaction temperature was then slowly increased to 100 ˚C. After the methanol was evaporated, the solution was heated to 290 ˚C under a flow of argon and maintained at that temperature for 90 min. After cooling down to room temperature, the resulting $NaGdF_4$:49%Yb/1%Tm core nanoparticles were precipitated by centrifugation at 6000 rpm for 5 min, washed with the mixture of cyclohexane/ethanol/methanol several times, and redispersed in 4 mL of cyclohexane for succeeding shell growth.

The synthesis procedure of $NaGdF_4$:Yb/Tm (49/1mol%)@$NaGdF_4$ core-shell nanoparticles was identical to the synthesis of $NaGdF_4$:Yb/Tm core nanoparticles. 4 mL oleic acid and 6 mL 1-octadecene were added into a 50-mL two-neck flask containing 2-mL water solution of $Gd(CH_3CO_2)_3$ (0.2 mmol), followed by heating at 150 ˚C for 60 min. After cooling down to 50 ˚C, $NaGdF_4$:Yb/Tm core nanoparticles in 4 mL of cyclohexane were added along with a 5.3 mL methanol solution of NaOH (1 mmol) and NH_4F (1.32 mmol). The resulting mixture was stirring at 50 ˚C for 30 min and increased to 100 ˚C. Then the solution was heated at 290 ˚C under an argon flow for 90 min and cooled to room temperature. The resulting nanoparticles were precipitated by centrifugation at 6000 rpm for 5 min, washed with a mixture of cyclohexane/ethanol/methanol several times, and redispersed in 4 mL of cyclohexane.

Synthesis of $NaYF_4$:Yb/Tm(29/1mol%)@$NaYF_4$ Core-shell (NYFCS) Nanoparticles: In a typical procedure, 3 mL oleic acid was added into a 50-mL two-neck flask containing 2-mL

water solution of $Y(CH_3CO_2)_3$ (0.28 mmol), $Yb(CH_3CO_2)_3$ (0.116 mmol) and $Tm(CH_3CO_2)_3$ (0.004 mmol), followed by heating to 150 ˚C with magnetic stirring. After that, 7 mL 1-octadecene was added and the mixture was heated at 150 ˚C for 60 min before cooling down to 50 ˚C. Soon afterwards, 6 mL methanol solution containing NH_4F (1.6 mmol) and NaOH (1 mmol) was quickly injected to the reaction flask, and the resultant solution was kept at 50 ˚C for 30 min with stirring. The reaction temperature was then slowly increased to 100 ˚C. After the methanol was evaporated, the solution was heated at 290 ˚C under a flow of argon for 90 min. After cooling down to room temperature, the resulting $NaYF_4$:29%Yb/1%Tm core nanoparticles were precipitated by centrifugation at 6000 rpm for 5 min, washed with a mixture of cyclohexane/ethanol/methanol several times, and redispersed in 4 mL of cyclohexane.

For $NaYF_4$:Yb/Tm(29/1mol%)@$NaYF_4$ core-shell nanoparticles, the prepared $NaYF_4$:Yb/Tm core nanoparticles were isolated and used as seeds to induce a successive shell coating. 3 mL oleic acid and 7 mL 1-octadecene were added into a 50-mL two-neck flask containing 2-mL water solution of $Y(CH_3CO_2)_3$ (0.2 mmol), followed by heating at 150 ˚C for 60 min. After cooling down to 50 ˚C, $NaYF_4$:Yb/Tm core nanoparticles in 4 mL of cyclohexane were added along with a 6 mL methanol solution of NaOH (1 mmol) and NH_4F (1.6 mmol). The resulting mixture was stirring at 50 ˚C for 30 min and increased to 100 ˚C. Then the solution was heated at 290 ˚C under an argon flow for 90 min and cooled to room temperature. The resulting nanoparticles were precipitated by centrifugation at 6000 rpm for 5 min, washed with a mixture of cyclohexane/ethanol/methanol several times, and redispersed in 4 mL of cyclohexane.

Synthesis of $NaGdF_4$:Yb/Tm(49/1mol%)@$NaYF_4$ Core-shell (NGF/NYF) Nanoparticles: In a typical procedure, 4 mL oleic acid was added into a 50-mL two-neck flask containing 2-mL water solution of $Gd(CH_3CO_2)_3$ (0.2 mmol), $Yb(CH_3CO_2)_3$ (0.196 mmol) and $Tm(CH_3CO_2)_3$ (0.004 mmol), followed by heating to and maintained at 150 ˚C with magnetic stirring. After that, 6 mL 1-octadecene was added and the mixture was heated at 150 ˚C for another 60 min before cooling down to 50 ˚C. Soon afterwards, 5.3 mL methanol solution containing NaOH (1 mmol) and NH_4F (1.32 mmol) was quickly injected to the flask, and the resultant solution was kept at 50 ˚C for 30 min while stirring. The reaction temperature was then slowly increased to 100 ˚C. After the methanol was evaporated, the solution was heated to 290 ˚C under a flow of argon and maintained at that temperature for 90 min. After cooling down to room temperature, the resulting $NaGdF_4$:49%Yb/1%Tm core nanoparticles were precipitated by centrifugation at 6000 rpm for 5 min, washed with a mixture of cyclohexane/ethanol/methanol several times, and redispersed in 4 mL of cyclohexane. The as-synthesized $NaGdF_4$:Yb/Tm core nanoparticles were used as seeds to induce a successive shell coating and the synthesis procedure of $NaGdF_4$:Yb/Tm(49/1mol%)@$NaYF_4$ core-shell nanoparticles was identical to the synthesis of NYFCS nanoparticles.

Synthesis of $NaYF_4$:Yb/Tm(29/1mol%)@$NaGdF_4$ Core-shell (NYF/NGF) Nanoparticles: In a typical procedure, 3 mL oleic acid was added into a 50-mL two-neck flask containing 2-mL water solution of $Y(CH_3CO_2)_3$ (0.28 mmol), $Yb(CH_3CO_2)_3$ (0.116 mmol) and $Tm(CH_3CO_2)_3$ (0.004 mmol), followed by heating to 150 ˚C with magnetic stirring. After that, 7 mL 1-octadecene was added and the mixture was heated at 150 ˚C for 60 min before cooling down to 50 ˚C. Soon afterwards, 6 mL methanol solution containing NH_4F (1.6 mmol) and NaOH (1 mmol) was quickly injected to the reaction flask, and the resultant solution was kept at that temperature for 30 min while stirring. The reaction temperature was then slowly increased to 100 ˚C. After the methanol was evaporated, the solution was heated at 290 ˚C under a flow of argon for 90 min. After cooling down to room temperature, the resulting $NaYF_4$:29%Yb/1%Tm core nanoparticles were precipitated by centrifugation at 6000 rpm for 5 min, washed with a mixture of cyclohexane/ethanol/methanol several times, and redispersed

in 4 mL of cyclohexane. The as-synthesized $NaYF_4$:Yb/Tm core nanoparticles were used as seeds to induce a successive shell coating and the synthesis procedure of $NaYF_4$:Yb/Tm (29/1mol%)@$NaYF_4$ core-shell nanoparticles was identical to the synthesis of NGFCS nanoparticles.

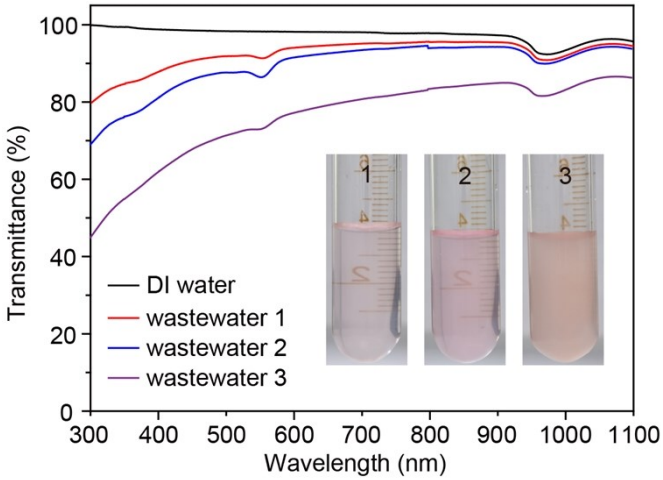

Fig. S1 Transmittance of light in deionized (DI) water and simulated wastewater. (Inset) photos of simulated wastewater 1-3. Wastewater 1: 0.6 g/L soil + 2 ppm RhB + 2 ppm TC + 2 ppm BPA, wastewater 2: 0.8 g/L soil + 5 ppm RhB + 5 ppm TC + 5 ppm BPA, wastewater 3: 1.5 g/L soil + 5 ppm RhB + 5 ppm TC + 10 ppm BPA.

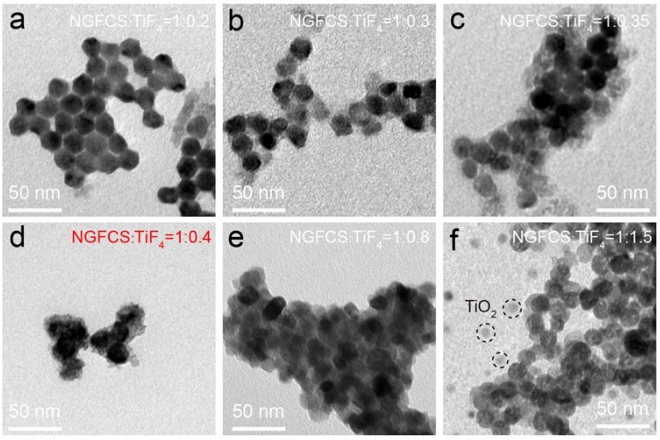

Fig. S2 TEM images of $NaGdF_4$:Yb/Tm@$NaGdF_4$@TiO_2 with different ratios of NGFCS to TiF_4. The molar ratio of NGFCS to TiF_4 is (a) 1:0.2, (b) 1:0.3, (c) 1:0.35, (d) 1:0.4, (e) 1:0.8, (f) 1:1.5.

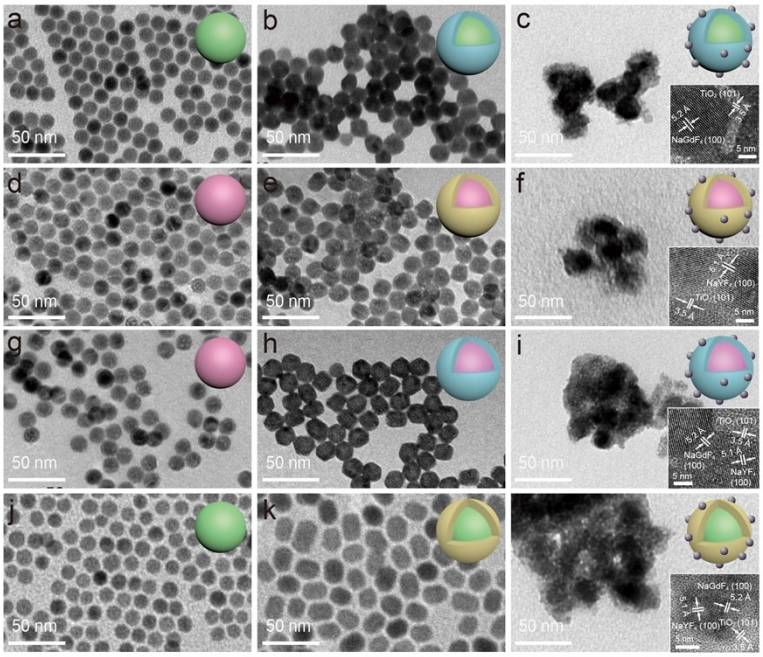

Fig. S3 Transmission electron microscopy (TEM) images of (a) $NaGdF_4$:Yb/Tm nanoparticles, (b) NGFCS nanoparticles, (c) NGFCS@TiO_2 nanocomposites, inset: high-resolution TEM of NGFCS@TiO_2 nanocomposites; (d) $NaYF_4$:Yb/Tm nanoparticles, (e) NYFCS nanoparticles, (f) NYFCS@TiO_2 nanocomposites, inset: high-resolution TEM of NYFCS@TiO_2 nanocomposites; (g) $NaYF_4$:Yb/Tm nanoparticles, (h) NYF/NGF nanoparticles, (i) NYF/NGF@TiO_2 nanocomposites, inset: high-resolution TEM of NYF/NGF@TiO_2 nanocomposites; (j) $NaGdF_4$:Yb/Tm nanoparticles, (k) NGF/NYF nanoparticles, (l) NGF/NYF@TiO_2 nanocomposites, inset: high-resolution TEM of NGF/NYF@TiO_2 nanocomposites.

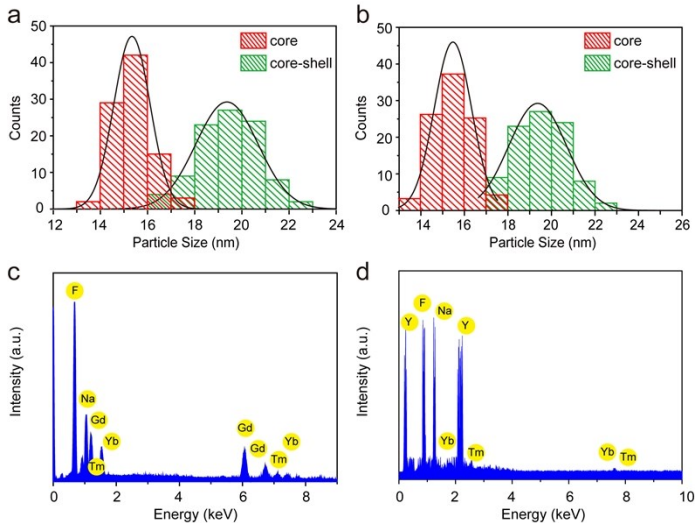

Fig. S4 Size distribution of (a) $NaGdF_4$:Yb/Tm and $NaGdF_4$:Yb/Tm@$NaGdF_4$ and (b) $NaYF_4$:Yb/Tm and $NaYF_4$:Yb/Tm@$NaYF_4$ upconversion nanoparticles. EDS spectra of (c) NGFCS and (d) NYFCS upconversion nanoparticles.

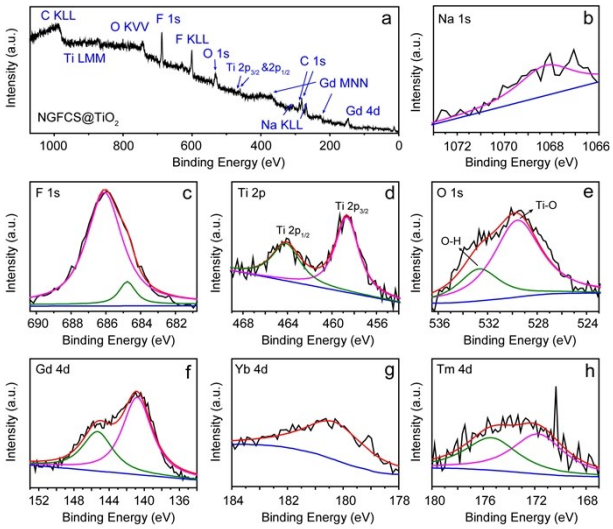

Fig. S5 (a) Wide XPS spectra for the NGFCS@TiO_2 nanocomposites, (b)-(g) High-resolution XPS spectra of Na 1s, F 1s, Ti 2p, O1s, Gd 4d, Yb 4d and Tm 4d, respectively.

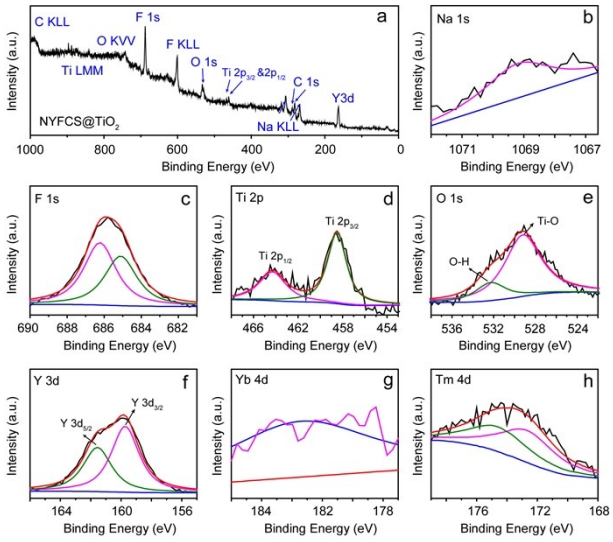

Fig.S6 (a) Wide XPS spectra for the NYFCS@TiO_2 nanocomposites, (b)-(g) High-resolution XPS spectra of Na 1s, F 1s, Ti 2p, O 1s, Y 3d, Yb 4d and Tm 4d, respectively.

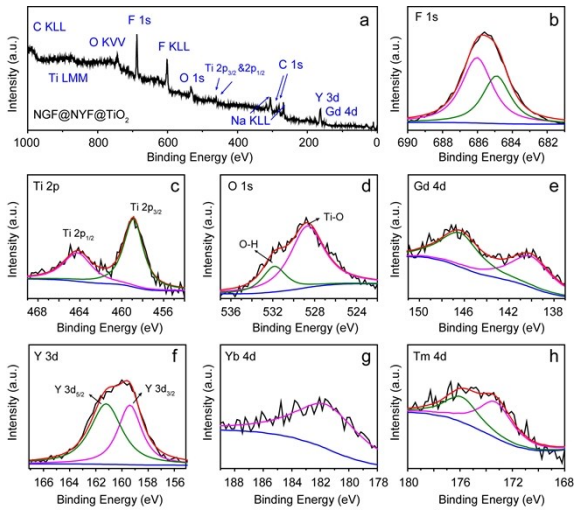

Fig. S7 (a) Wide XPS spectra for the NGF@NYF@TiO_2 nanocomposites, (b)-(g) High-resolution XPS spectra of F 1s, Ti 2p, O 1s, Gd 4d, Y 3d, Yb 4d and Tm 4d, respectively.

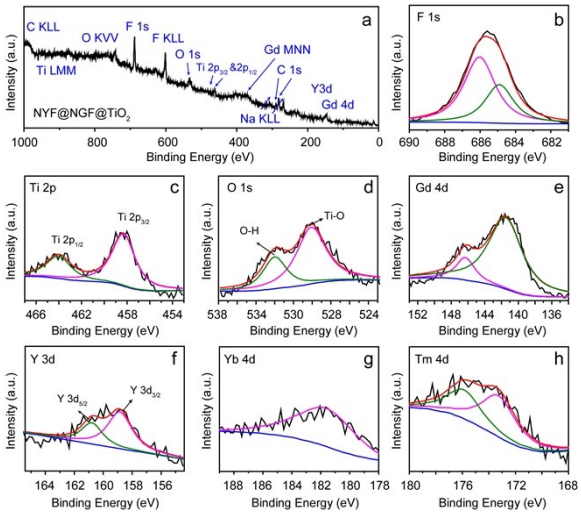

Fig. S8 (a) Wide XPS spectra for the NYF@NGF@TiO_2 nanocomposites, (b)-(g) High-resolution XPS spectra of F 1s, Ti 2p, O 1s, Gd 4d, Y 3d, Yb 4d and Tm 4d, respectively.

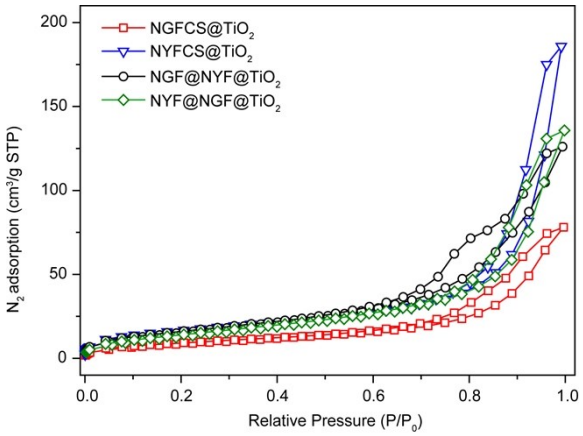

Fig. S9 N_2 adsorption−desorption isotherms of different samples.

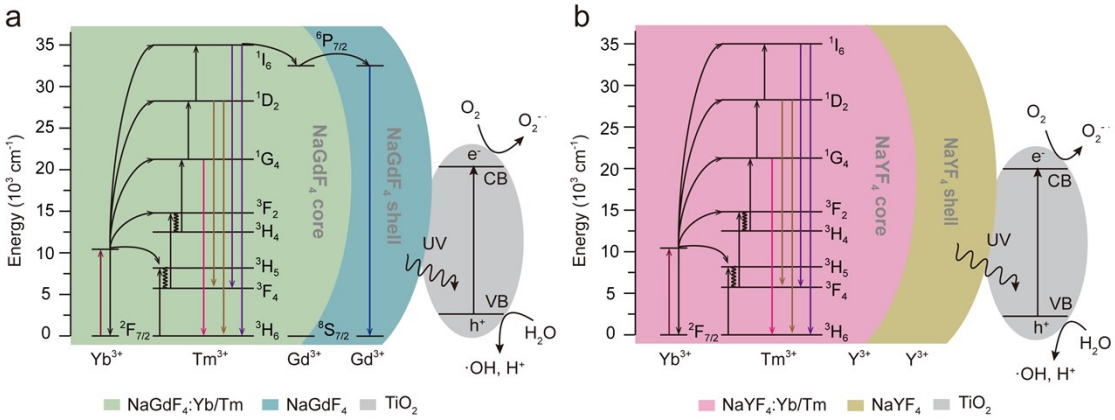

Fig. S10 Energy transfer processes involved in (a) NGFCS@TiO_2 and (b) NYFCS@TiO_2 nanocomposites.

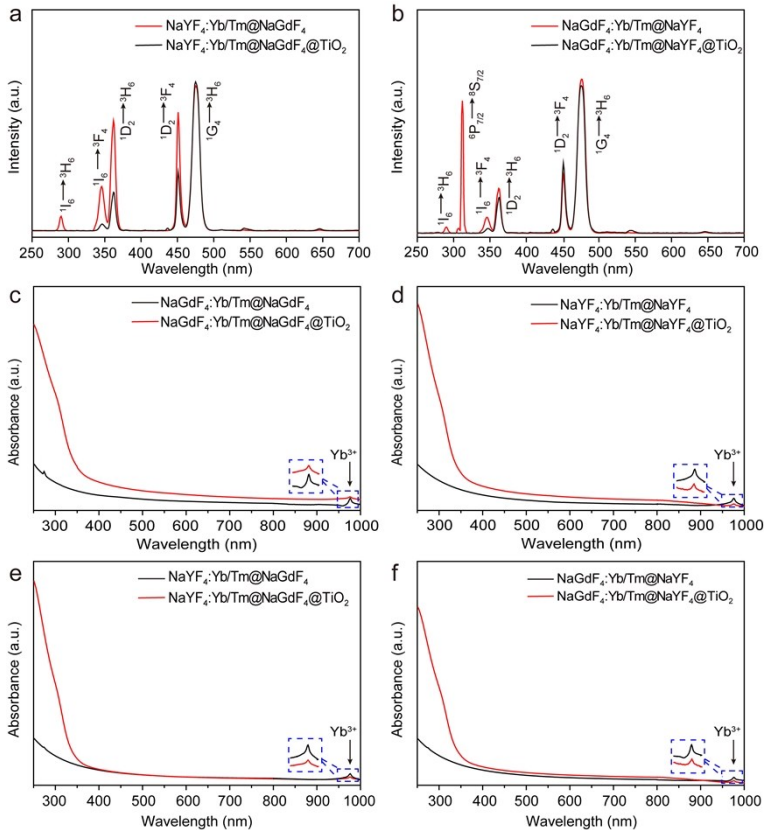

Fig. S11 (a) Upconversion luminescence spectra of (a) NYF/NGF and NYF/NGF@TiO_2 in aqueous solution, (b) NGF/NYF and NGF/NYF@TiO_2 in aqueous solution. UV-vis absorption spectra of (c) NGFCS and NGFCS@TiO_2, (d) NYFCS and NYFCS@TiO_2, (e) NYF/NGF and NYF/NGF@TiO_2, (f) NGF/NYF and NGF/NYF@TiO_2 in aqueous solution.

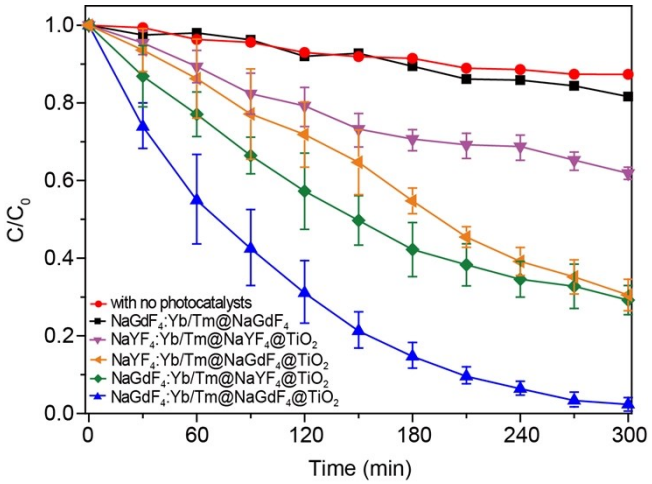

Fig. S12 Degradation of RhB in aqueous solution (20 ppm) with reaction time, in the absence and presence of NGFCS@TiO_2, NYFCS@TiO_2, NYF/NGF@TiO_2, NGF/NYF@TiO_2 and NGFCS under 980 nm excitation with a power density of 2.5 W/cm^2, respectively.

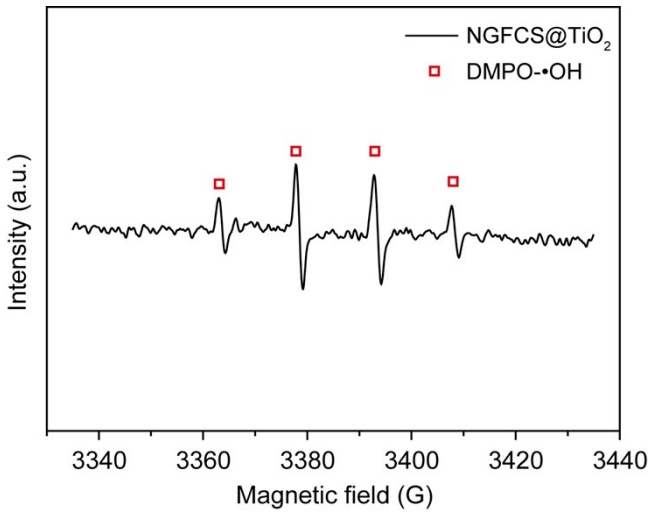

Fig.13 The DMPO spin-trapping ESR spectra recorded at ambient temperature in the water solution containing NGFCS@TiO_2 nanocomposites.

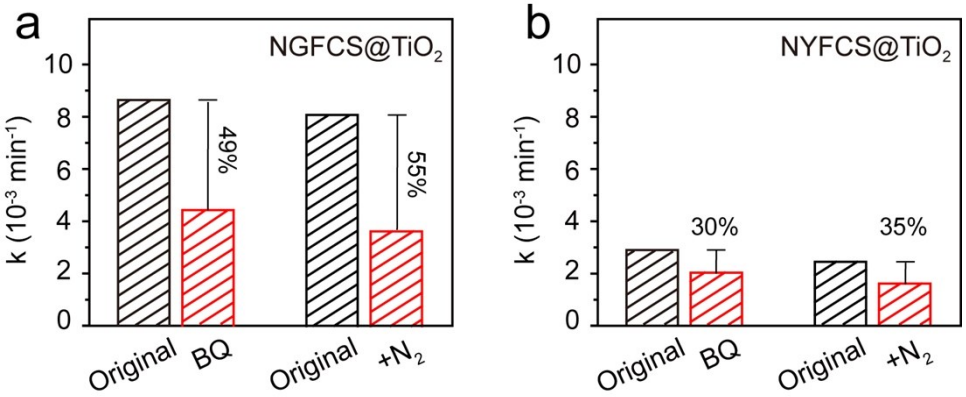

Fig. S14. RhB photodegradation efficiency comparison of differnt situations, with BQ trapping agent and purging of N_2 gas respectively, under 980 nm light excitation with (a) NGFCS@TiO_2 and (b) NYFCS@TiO_2 photocatalysts.

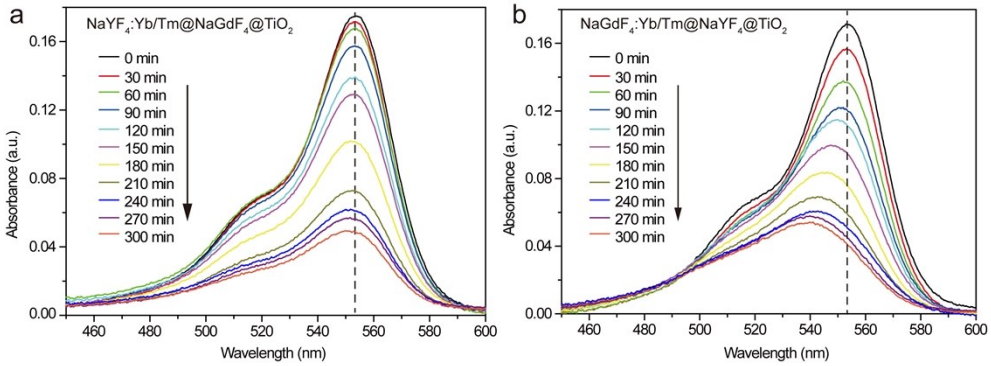

Fig. S15 Change of absorption spectra of RhB in aqueous solution (20 ppm) with reaction time, with the addition of (a) NYF/NGF@TiO_2, (b) NGF/NYF@TiO_2 under 980 nm excitation with a power density of 2.5 W/cm^2, respectively.

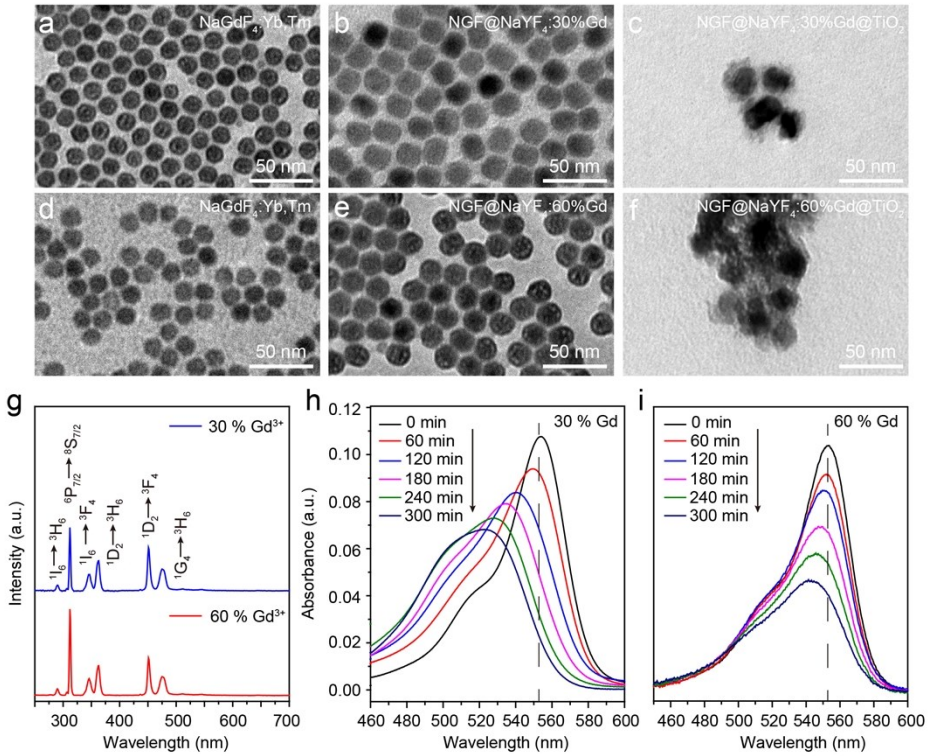

Fig. S16 TEM images of (a) $NaGdF_4$:Yb/Tm nanoparticles, (b) NGF@NYF:30%Gd nanoparticles, (c) NGF@NYF:30%Gd@TiO_2 composites, (d) $NaGdF_4$:Yb/Tm nanoparticles, (e) NGF@NYF:60%Gd nanoparticles, (f) NGF@NYF:60%Gd@TiO_2 composites. (g) Upconversion luminescence spectra of NGF@NYF:30%Gd and NGF@NYF:60%Gd nanoparticles in aqueous solution. Change of absorption spectra of RhB in aqueous solution (20 ppm) with reaction time, with the addition of (h) NGF@NYF:30%Gd@TiO_2 and (i) NGF@NYF:60%Gd@TiO_2 under 980 nm excitation.

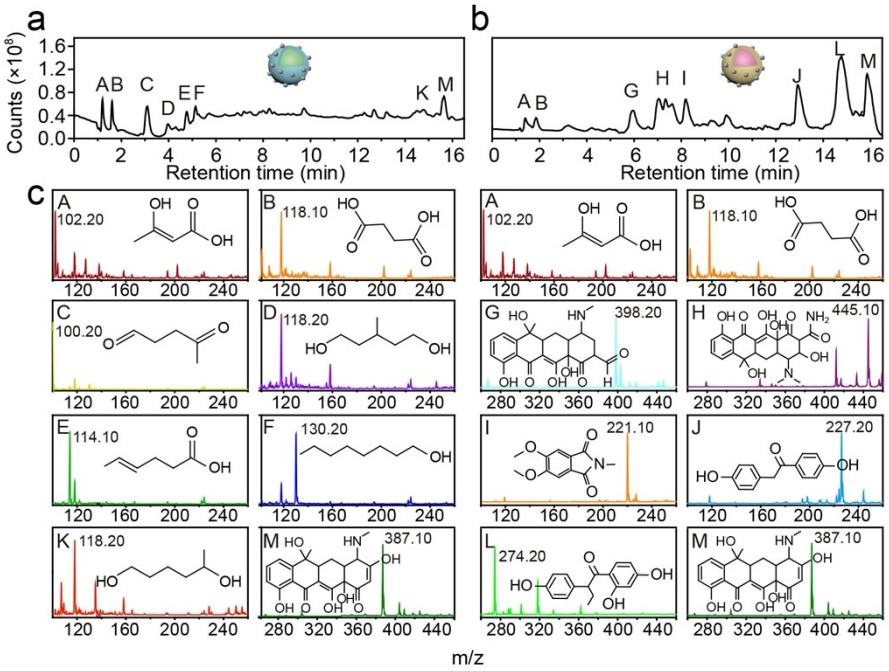

Fig. S17 (a), (b) The respective liquid chromatograms patterns for the intermediate products of TC catalyzed by NGFCS@TiO_2 and NYFCS@TiO_2, after 30 minutes under 980-nm light irradiation. (c) The corresponding ESI mass spectra of the intermediates detected in (a) and (b).

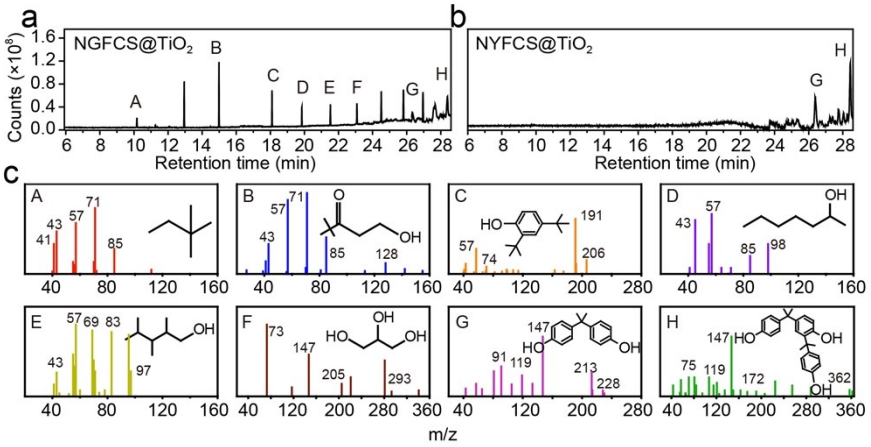

Fig. S18 (a), (b) The respective gas chromatograms patterns for the intermediate products of BPA catalyzed by NGFCS@TiO_2 and NYFCS@TiO_2, after 300 minutes under 980-nm light irradiation. (c) The corresponding ESI mass spectra of the intermediates detected in (a) and (b).

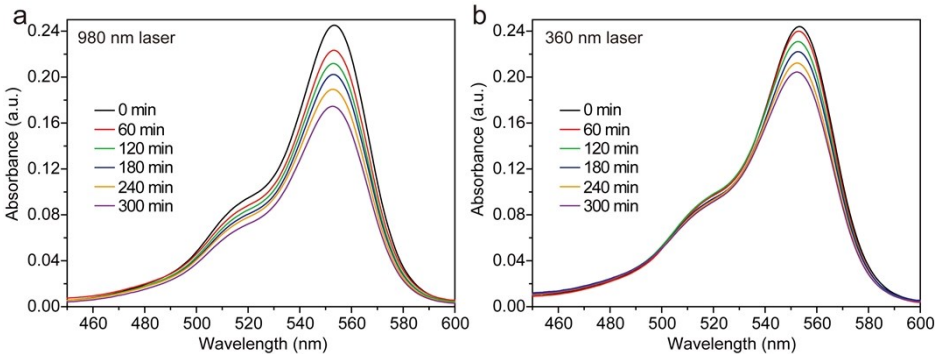

Fig. S19 Absorption spectra of RhB in aqueous solution (20 ppm) with reaction time, with the addition of NGFCS@TiO_2 under (a) 980 nm excitation (48 mW/cm^2) and (b) 360 nm excitation (44 mW/cm^2).The real wastewater was a barrier between the light source and RhB solution.

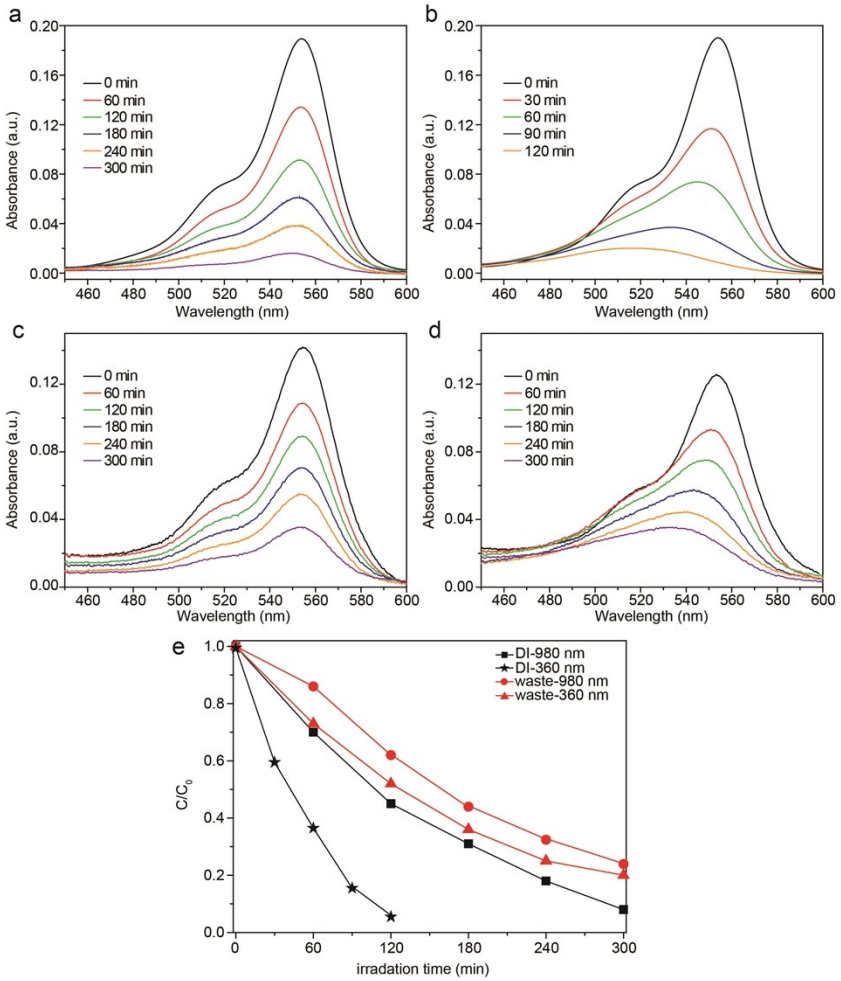

Fig. S20 Absorption spectra of RhB aqueous solution in DI water (20 ppm) against reaction time, with the addition of NGFCS@TiO_2 under (a) 980 nm excitation and (b) 360 nm excitation, with a power density of 2.5 W/cm^2. Absorption spectra of RhB in real wastewater (20 ppm) with reaction time, with the addition of NGFCS@TiO_2 under (c) 980 nm excitation and (d) 360 nm excitation, with a power density of 2.5 W/cm^2. (e) The photodegradation rates of RhB in the presence of NGFCS@TiO_2 activated by 980 nm and 360 nm light in DI water and real wastewater.

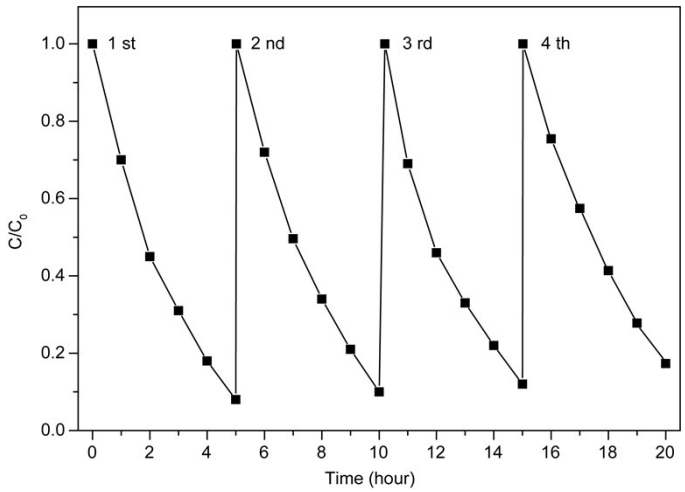

Fig. S21 The reusability of NGFCS@TiO_2 for photocatalytic degradation of RhB under NIR light irradiation.

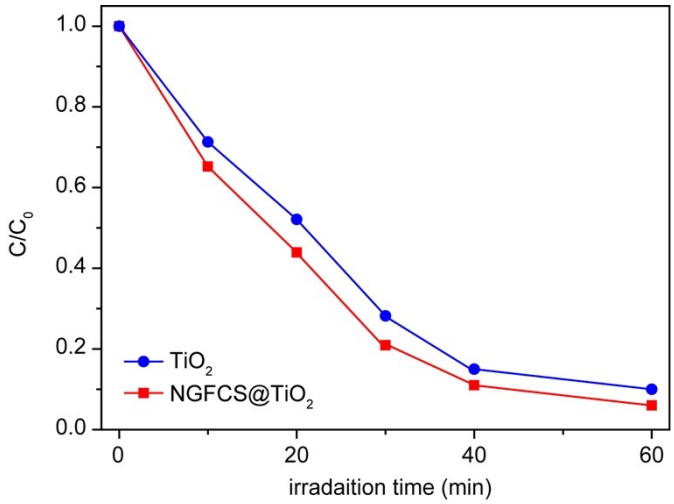

Fig. S22 RhB photodegradation efficiency with the presence of NGFCS@TiO_2 and pure TiO_2 under simulated sunlight irradiation (100 mW/cm^2).

Table S1 Surface porosity of different samples.

Photocatalysts	Surface area (m^2/g)	Pore volume (m^3/g)	Pore size (nm)
$NaGdF_4$:Yb/Tm@$NaGdF_4$@TiO_2	38.9	0.16	19.3
$NaYF_4$:Yb/Tm@$NaYF_4$@TiO_2	52.3	0.28	20.6
$NaYF_4$:Yb/Tm@$NaGdF_4$@TiO_2	47.8	0.20	17.9
$NaGdF_4$:Yb/Tm@$NaYF_4$@TiO_2	54.2	0.19	18.2

Table S2 The degradation rates and pseudo-first-order apparent rate constants (k) of RhB.

Photocatalysts	RhB degradation efficiency (%)	First-order rate constant (min^{-1})
$NaGdF_4$:Yb/Tm@$NaGdF_4$	17	$0.6*10^{-3}$
$NaGdF_4$:Yb/Tm@$NaGdF_4$@TiO_2	97	$11.7*10^{-3}$
$NaYF_4$:Yb/Tm@$NaYF_4$@TiO_2	38	$1.6*10^{-3}$
$NaYF_4$:Yb/Tm@$NaGdF_4$@TiO_2	68	$3.8*10^{-3}$
$NaGdF_4$:Yb/Tm@$NaYF_4$@TiO_2	70	$4.0*10^{-3}$