Experimental Section

**Preparation of ordered mesoporous TiO\textsubscript{2}:Yb\textsuperscript{3+}:** 0.9 g of Pluronic F127 was dissolved in 20 mL of ethanol at room temperature (R.T.). Then 1.048 g (4 mmol) of titanyl acetylacetonate and 0.449 g (1 mmol) of Yb(NO\textsubscript{3})\textsubscript{3}·5H\textsubscript{2}O were added into the above solution with vigorous stirring. The mixture are covered with polyethylene (PE) film, stirred at R.T. for about 5 h, and then put into a 100 °C drying oven to undergo the solvent evaporation process. After two days aging, the resultant material was calcined at 400 °C for 4 h in air by slowly increasing temperature from R.T. to 400 °C (1 °C min\textsuperscript{-1} ramping rate). High temperature treatment was carried out in air for 1 h with a temperature ramp of 10 °C min\textsuperscript{-1}.

**Preparation of ordered mesoporous TiO\textsubscript{2}:Yb\textsuperscript{3+},Tm\textsuperscript{3+}:** 0.9 g of Pluronic F127 was dissolved in 20 mL of ethanol at room temperature (R.T.). Then 1.048 g (4 mmol) of titanyl acetylacetonate, 0.449 g (1 mmol) of Yb(NO\textsubscript{3})\textsubscript{3}·5H\textsubscript{2}O and 0.046 g (0.1 mmol) Tm(NO\textsubscript{3})\textsubscript{3}·6H\textsubscript{2}O were added into the above solution with vigorous stirring. The mixture are covered with PE film, stirred at R.T. for about 5 h, and then put into a 100 °C drying oven to undergo the solvent evaporation process. After two days aging, the resultant material was calcined at 400 °C for 4 h in air by slowly increasing temperature from R.T. to 400 °C (1 °C min\textsuperscript{-1} ramping rate). High temperature treatment was carried out in air for 1 h with a temperature ramp of 10 °C min\textsuperscript{-1}.

**Preparation of worm-like mesoporous TiO\textsubscript{2}:Yb\textsuperscript{3+},Tm\textsuperscript{3+}:** 0.9 g of Pluronic F127 was dissolved in 20 mL of ethanol at room temperature (R.T.). Then 1.048 g (4 mmol) of titanyl acetylacetonate, 0.449 g (1 mmol) of Yb(NO\textsubscript{3})\textsubscript{3}·5H\textsubscript{2}O and 0.046 g (0.1 mmol) Tm(NO\textsubscript{3})\textsubscript{3}·6H\textsubscript{2}O were added into the above solution with vigorous stirring. The mixture are covered with PE film, stirred at R.T. for about 5 h, and then put into a 60 °C drying oven to undergo the solvent evaporation process. After two days aging, the resultant material was calcined at 400 °C for 4 h in air by slowly increasing temperature from R.T. to 400 °C (1 °C min\textsuperscript{-1} ramping rate). High temperature treatment was carried out in air for 1 h with a temperature ramp of 10 °C min\textsuperscript{-1}.
Preparation of mesoporous TiO$_2$: 0.9 g of Pluronic F127 was dissolved in 20 mL of ethanol at room temperature (R.T.). Then 1.310 g (5 mmol) of titanyl acetylacetonate was added into the above solution with vigorous stirring. The mixture are covered with PE film, stirred at R.T. for about 5 h, and then put into a 100 °C drying oven to undergo the solvent evaporation process. After two days aging, the resultant material was calcined at 400 °C for 4 h in air by slowly increasing temperature from R.T. to 400 °C (1 °C min$^{-1}$ ramping rate).

Preparation of mesoporous SiO$_2$:Yb$^{3+}$,Tm$^{3+}$: 1 g of Pluronic 123 was dissolved in 6 mL of ethanol at room temperature (R.T.). Then 2.08 g of TEOS, 0.2 g of aqueous HCl (1 mol/L), 1.122 g (2.5 mmol) of Yb(NO$_3$)$_3$·5H$_2$O and 0.115 g (0.25 mmol) Tm(NO$_3$)$_3$·6H$_2$O were added into the above solution with vigorous stirring. The mixture are covered with PE film, stirred at R.T. for about 5 h, and then put into a 30 °C drying oven to undergo the solvent evaporation process. After two days aging, the gel was heated at 60 °C for one day to remove ethanol completely. The resultant material was calcined at 550 °C for 4 h in air by slowly increasing temperature from R.T. to 550 °C (1 °C min$^{-1}$ ramping rate).

Degradation of rhodamine B: The mesoporous TiO$_2$:Yb$^{3+}$,Tm$^{3+}$ (calcinated at 700 °C) and mesoporous pure TiO$_2$ were dispersed into 1 mL rhodamine B (RhB) aqueous solution (10 mg L$^{-1}$) and the resulting solution was stirred in dark for 2 h to equilibrate the adsorption-desorption of RhB on the sample surface. The 2 W 980 nm laser was used as an irradiation source. At given time intervals, the supernate was analyzed by recording the variations of the absorption band maximum (554 nm) on a Shimadzu UV-3100 spectrometer. For comparison, all the samples tested for the activity were weighted exactly same (50 mg).

Characterization: The small and wide angle X-ray diffraction (XRD) patterns were recorded on a Rigaku D/MAX-2000 diffractometer (Japan) using Cu-K$\alpha$ radiation. Transmission electronic microscopy (TEM), and selected area electron diffraction (SAED) were performed with a JEOL-2100 transmission electron microscope (Japan) operated at 200 kV. Energy-dispersive X-ray spectroscopy (EDS) were taken on a JEOL-2100F transmission electron microscope (Japan) equipped with an EDS detector. The UC luminescence spectra were recorded on a Hitachi F-4500 fluorescence spectrophotometer equipped with an external tunable 2 W 980 nm laser diode. The UV-vis spectra was recorded on a Hitachi U-3010 spectrometer. The nitrogen adsorption and desorption isotherms at 78.3 K were measured on an ASAP 2010 analyzer (Micromeritics Co. Ltd.). Measurements were performed after outgassing the sample at 573 K under a vacuum, down to a residual pressure less than 10$^{-8}$ Torr. With the Barrett-Joyner-Halenda (BJH) model, the pore volumes and pore size distributions were derived from the desorption branches of the isotherms.
Fig. S1 TEM image of the mesoporous TiO$_2$ without doping Yb$^{3+}$.

Fig. S2 (a) Nitrogen adsorption-desorption isotherms of the ordered mesoporous TiO$_2$:Yb$^{3+}$ calcined at different temperatures. (b) Pore size distribution curves of the ordered mesoporous TiO$_2$:Yb$^{3+}$ calcined at different temperatures.
**Fig. S3** TEM image of the ordered mesoporous TiO$_2$:Yb$^{3+}$,Tm$^{3+}$.

**Fig. S4** Upconversion luminescence spectra of the ordered mesoporous TiO$_2$:Yb$^{3+}$,Tm$^{3+}$. 
Fig. S5 TEM image of the worm-like mesoporous TiO$_2$:Yb$^{3+}$,Tm$^{3+}$.

Fig. S6 TEM image of the mesoporous SiO$_2$:Yb$^{3+}$,Tm$^{3+}$. 
Fig. S7 Upconversion luminescence spectra of the mesoporous SiO$_2$:Yb$^{3+}$,Tm$^{3+}$.

Fig. S8 Photocatalytic result of the mesoporous SiO$_2$:Yb$^{3+}$,Tm$^{3+}$. 