Supplementary Material (ESI) for Chemical Communications

Ytterbium Stabilized Ordered Mesoporous Titania for Near-infrared Photocatalysis

Zhen-Xing Li, Fu-Bo Shi, Tao Zhang, Hao-Shuai Wu, Ling-Dong Sun, Chun-Hua Yan*

Beijing National Laboratory for Molecular Sciences, State Key Laboratory of Rare Earth Materials Chemistry and Applications & PKU-HKU Joint Laboratory in Rare Earth Materials and Bioinorganic Chemistry, Peking University, Beijing 100871, China

Experimental Section

***Preparation of ordered mesoporous TiO_2:Yb^{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 $Yb(NO_3)_3{\cdot}5H_2O$ 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 ℃ drying oven to undergo the solvent evaporation process. After two days aging, the resultant material was calcined at 400 ℃ for 4 h in air by slowly increasing temperature from R.T. to 400 ℃ (1 ℃ min^{-1} ramping rate). High temperature treatment was carried out in air for 1h with a temperature ramp of 10 ℃ min^{-1}.

***Preparation of ordered mesoporous TiO_2:Yb^{3+},Tm^{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 $Yb(NO_3)_3{\cdot}5H_2O$ and 0.046 g (0.1 mmol) $Tm(NO_3)_3{\cdot}6H_2O$ 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 ℃ drying oven to undergo the solvent evaporation process. After two days aging, the resultant material was calcined at 400 ℃ for 4 h in air by slowly increasing temperature from R.T. to 400 ℃ (1 ℃ min^{-1} ramping rate). High temperature treatment was carried out in air for 1h with a temperature ramp of 10 ℃ min^{-1}.

***Preparation of worm-like mesoporous TiO_2:Yb^{3+},Tm^{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 $Yb(NO_3)_3{\cdot}5H_2O$ and 0.046 g (0.1 mmol) $Tm(NO_3)_3{\cdot}6H_2O$ 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 ℃ drying oven to undergo the solvent evaporation process. After two days aging, the resultant material was calcined at 400 ℃ for 4 h in air by slowly increasing temperature from R.T. to 400 ℃ (1 ℃ min^{-1} ramping rate). High temperature treatment was carried out in air for 1h with a temperature ramp of 10 ℃ min^{-1}.

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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 ℃ drying oven to undergo the solvent evaporation process. After two days aging, the resultant material was calcined at 400 ℃ for 4 h in air by slowly increasing temperature from R.T. to 400 ℃ (1 ℃ 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 ℃ drying oven to undergo the solvent evaporation process. After two days aging, the gel was heated at 60 ℃ for one day to remove ethanol completely. The resultant material was calcined at 550 ℃ for 4 h in air by slowly increasing temperature from R.T. to 550 ℃ (1 ℃ min^{-1} ramping rate).

Degradation of rhodamine B**:** The mesoporous TiO$_2$:Yb^{3+},Tm^{3+} (calcinated at 700 ℃) 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-Kα 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^{-3} Torr. With the Barrett-Joyner-Halenda (BJH) model, the pore volumes and pore size distributions were derived from the desorption branches of the isotherms.

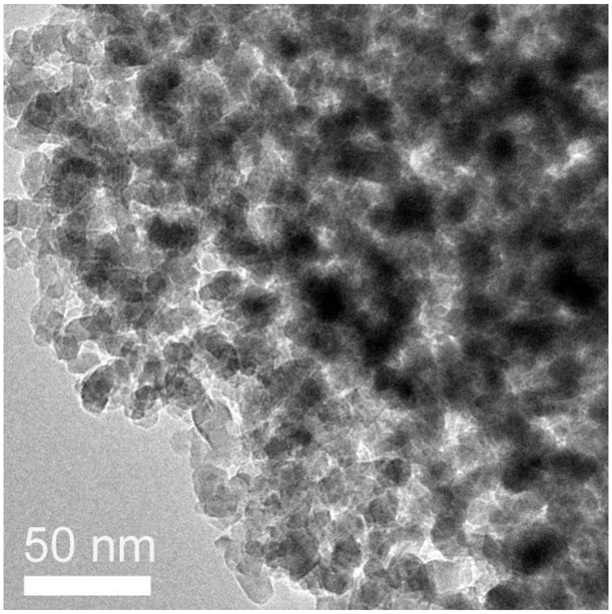

Fig. S1 TEM image of the mesoporous TiO_2 without doping Yb^{3+}.

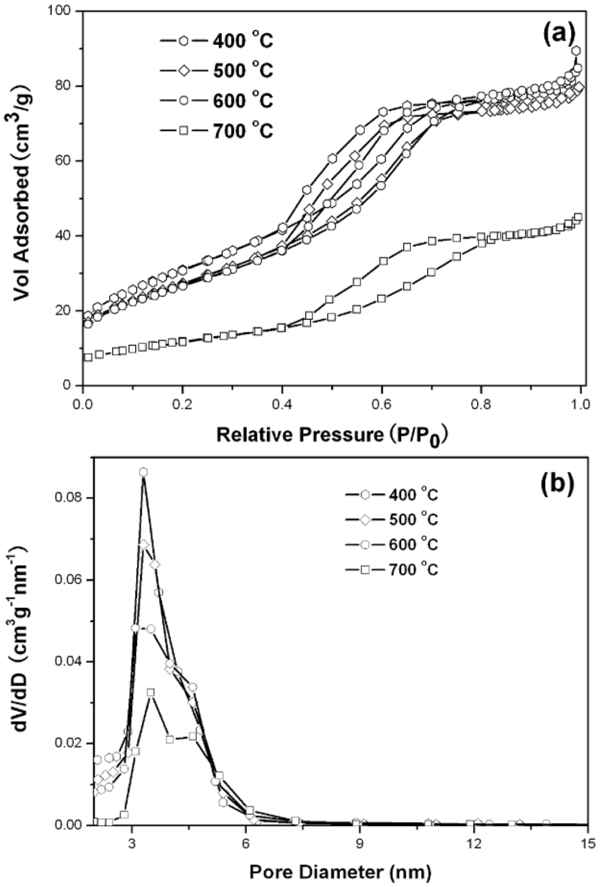

Fig. S2 (a) Nitrogen adsorption-desorption isotherms of the ordered mesoporous $TiO_2:Yb^{3+}$ calcined at different temperatures. (b) Pore size distribution curves of the ordered mesoporous $TiO_2:Yb^{3+}$ calcined at different temperatures.

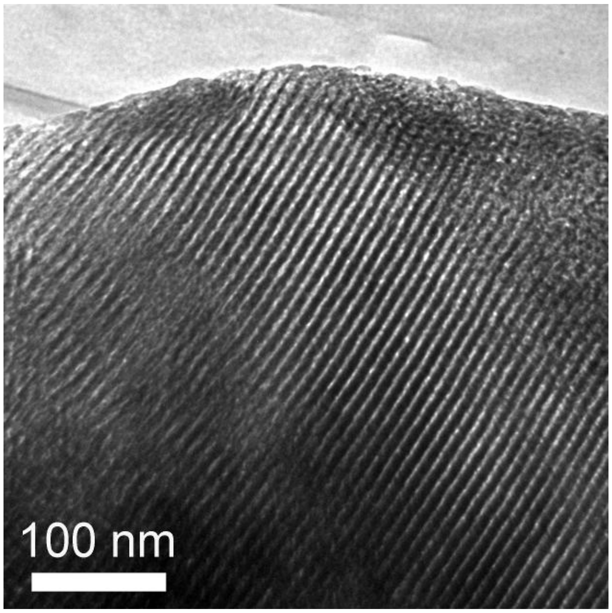

Fig. S3 TEM image of the ordered mesoporous TiO_2:Yb^{3+},Tm^{3+}.

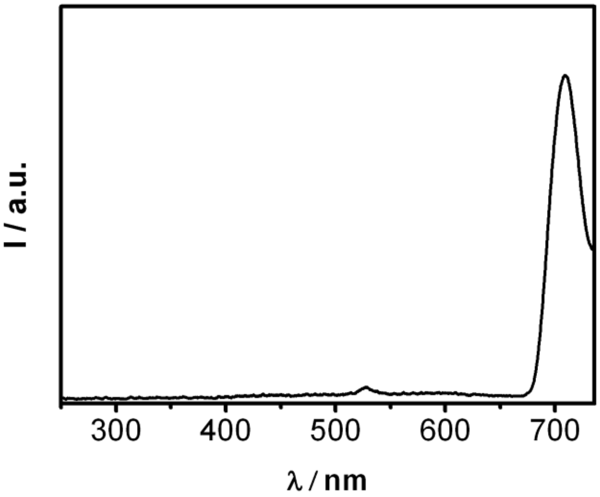

Fig. S4 Upconversion luminescence spectra of the ordered mesoporous TiO_2:Yb^{3+},Tm^{3+}.

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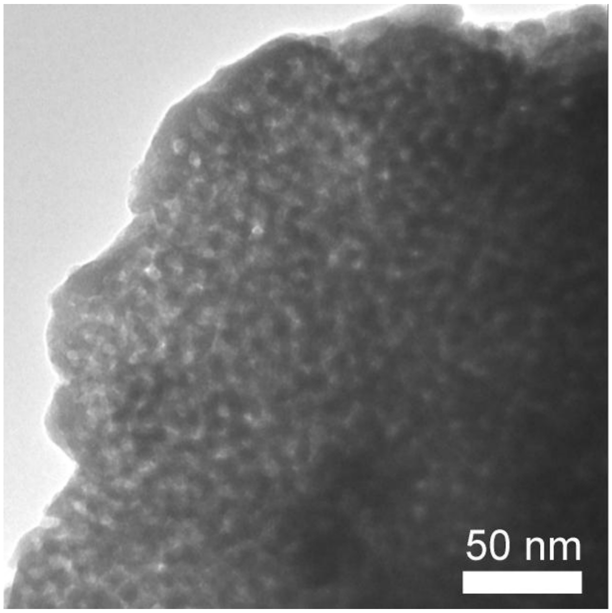

Fig. S5 TEM image of the worm-like mesoporous $TiO_2:Yb^{3+},Tm^{3+}$.

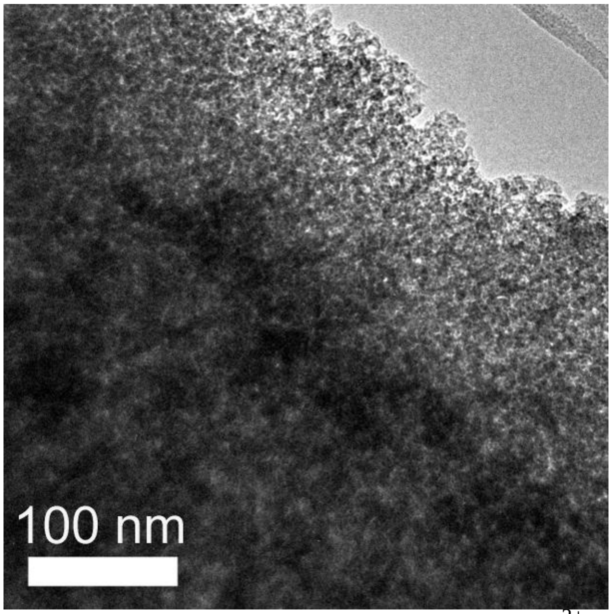

Fig. S6 TEM image of the mesoporous $SiO_2:Yb^{3+},Tm^{3+}$.

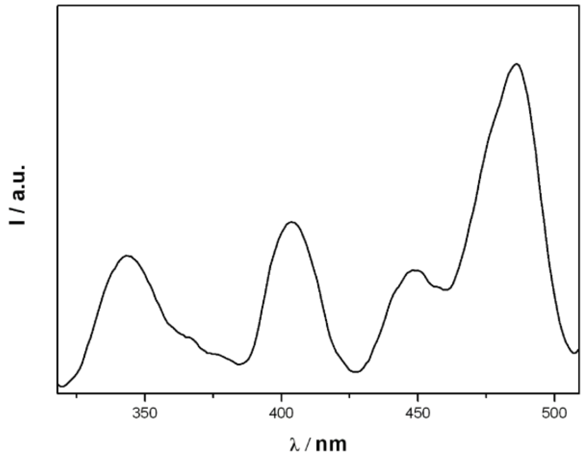

Fig. S7 Upconversion luminescence spectra of the the mesoporpus SiO_2:Yb^{3+},Tm^{3+}.

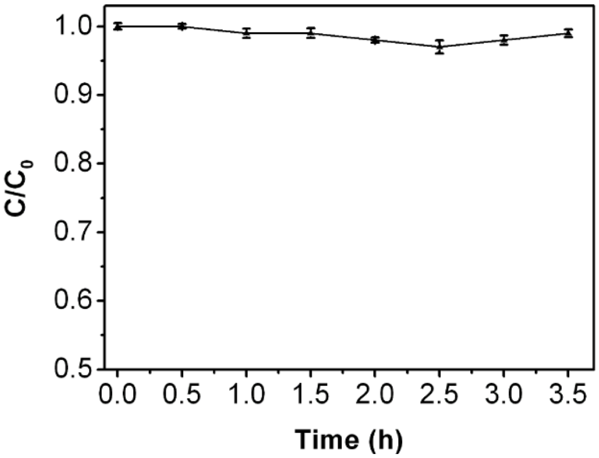

Fig. S8 Photocatalytic result of the mesoporpus SiO_2:Yb^{3+},Tm^{3+}.