Electronic Supplementary Material (ESI) for Chemical Communications

Supplementary information for:

Facile synthesis of spiny mesoporous titania tubes with enhanced photocatalytic activity

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Experimental section

Preparation of spiny TiO_2 tube

In brief, 1 g of Titanium oxysulfate-sulfuric acid complex hydrate ($TiOSO_4 \cdot xH_2SO_4 \cdot xH_2O$, Sigma-Aldrich Corp (No. 333980)) was dispersed in a mixture solution of 26 ml absolute ethanol, 13 ml ethyl ether and 13 ml ethylene glycol. After 1 hour of agitation under ultrasonic irradiation, a homogenous suspension was formed and transferred into a 100 ml Teflon pot and sealed tightly in a stainless steel bomb. Then, the reactor was heated to 110 °C and maintained for a certain period of time. The white precipitate was then centrifuged and washed with absolute ethanol for several times, vacuum dried at 60 °C overnight and calcined at 500 °C for 5 h.

Characterization of the product

Transmission electron microscopy (TEM) images were recorded with a JEM-2100 electron microscope (JEOL, Japan) at an accelerating voltage of 200 kV. Scanning electron microscopy (SEM) and Energy dispersive X-ray spectrum (EDX) were taken with a Quanta 200F field emission scanning electron microscope (FEI, USA) equipped with an energy dispersive X-ray spectroscope. X-ray photoelectron spectroscopy (XPS) were recorded with a MICROLAB MK II (VG, UK). The X-ray diffraction (XRD) pattern was recorded with a PANalytical X'Pert Pro

X-ray diffractometer (PANalytical, Netherland) equipped with Cu-Ka radiation (40Kv, 200mA). Fourier transform infrared spectroscopy (FT-IR) was performed on Equinox55 (Bruker, Germany). Nitrogen adsorption-desorption isotherms were measured with a Micromeritics ASAP2000 V3.01 analyser. The Brunauer-Emmett-Teller (BET) specific areas were calculated using the BET equation. The pore size distribution was obtained using the Barret-Joyner-Halenda (BJH) equation. UV-Vis diffuse reflectance spectra (DSR) was performed on Hitachi U4100 spectrometer.

Photocatalytic activity

The photocatalytic activity of the calcined materials were examined by degradation of azo dye Rhodamine B (Rh.B) at 25 °C in a custom made 100 ml reactor containing 0.01 g TiO_2 samples and 50 ml Rh.B solution (2 mg/L). An 8 W mercury lamp with characteristic wavelength of 365 nm was used as UV light source. The lamp was mounted 15 cm over the solution. Before the irradiation of the UV light, the suspension was magnetically stirred in the dark at the speed of 1000 rpm for 1 h to ensure the adsorption equilibrium and eliminate the diffusion effects. The equilibrium concentration of Rh.B was used as initial concentration. The photocatalysis was started by irradiating the mixture with UV light. After reaction for 1.5 h, catalyst was separated and the concentrations of Rh.B left in the samples were detected by UV-Vis spectroscope (Hitachi U4100, Japan). The photocatalytic activity of the close-grained tubes (prepared for 24 hours), the mechanically crushed spiny TiO_2 tubes and the commercial Degussa P25 were also determined using the same procedure for comparison.

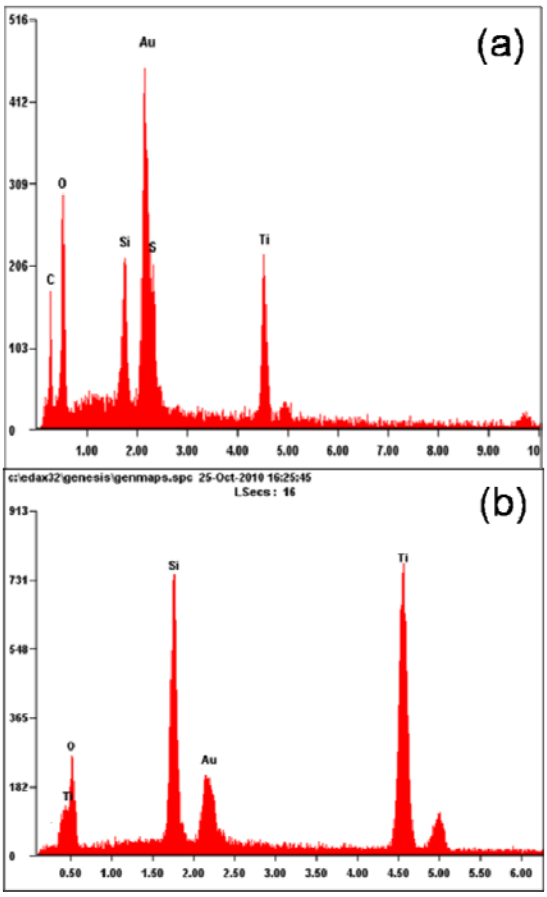

Figure S1. EDX spectrum of the spiny titania tube before (a) and aftrer (b) calcination at 500 °C for 5 h. (Si is from the monocrystalline silicon supporter, Au is from the golden vaccum sputtered as conductive coating).

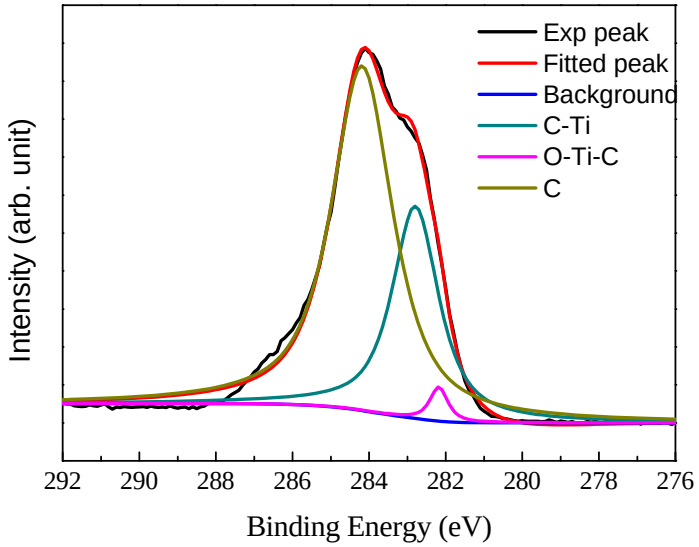

Figure S2. Deconvolution of C 1s XPS peak of the spiny titania tubes synthesized for 60 hours before calcination.

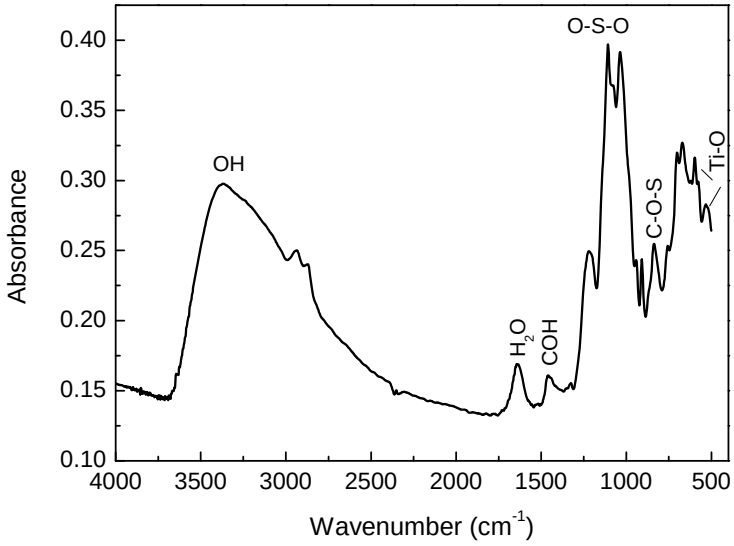

Figure S3. FI-IR spectra of the spiny titania tube synthesized for 60 hours before calcinations.

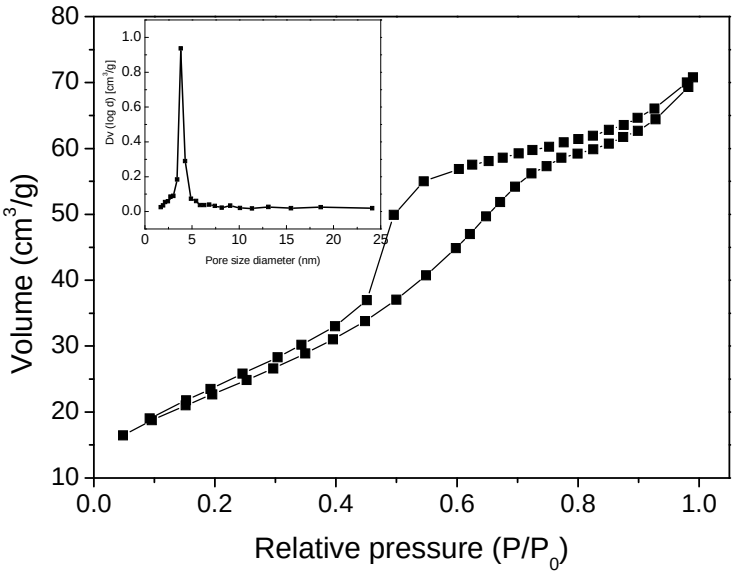

Figure S4. Nitrogen adsorption desorption isotherm of the calcined spiny titania tube synthesized for 60 hours and the corresponding pore size distribution plot (insetted).

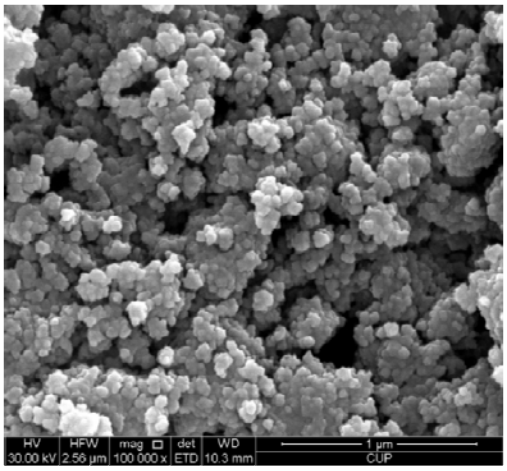

Fig. S5 SEM image of the mechanically crushed spiny mesoporous TiO_2 tubes (synthesized for 60 h).

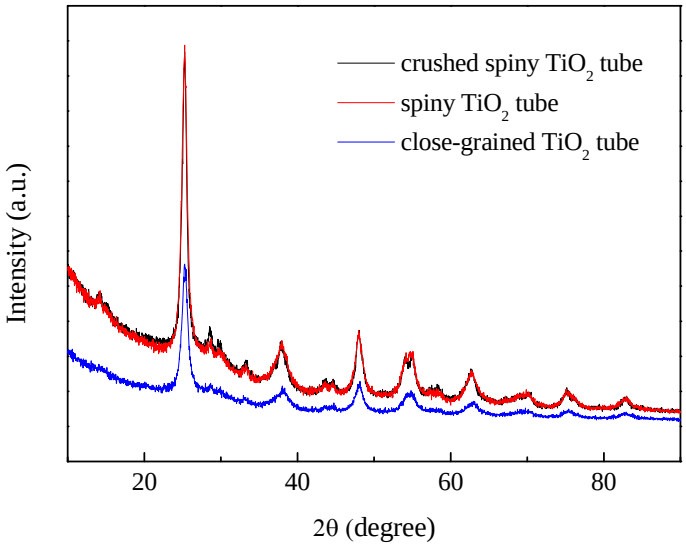

Fig. S6 X-ray diffraction pattern of the calcined close-grained surface titania tube (synthesized for 24 h), calcined spiny mesoporous titania tube (synthesized for 60 h) and its mechanically crushed sample.

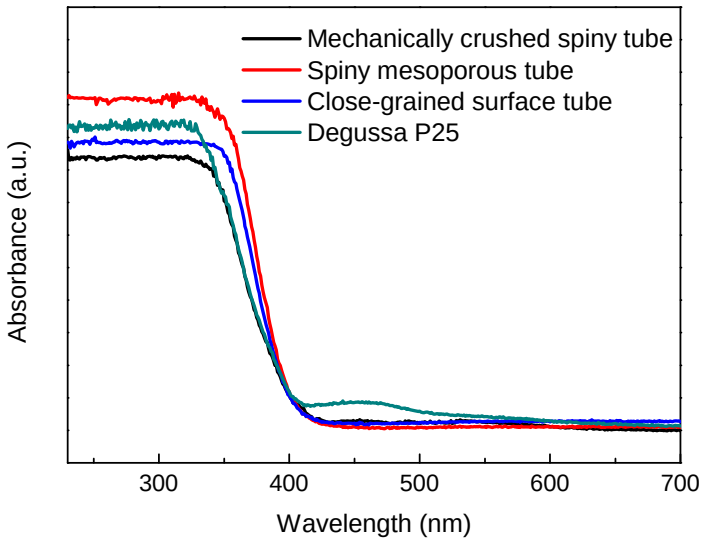

Fig. S7 UV-Vis diffuse reflectance spectra (UV-Vis DRS) of calcined spiny TiO_2 tubes (synthesized for 60 h) and its crushed samples, close-grained surface TiO_2 tubes (synthesized for 24 h), and the Degussa P25.

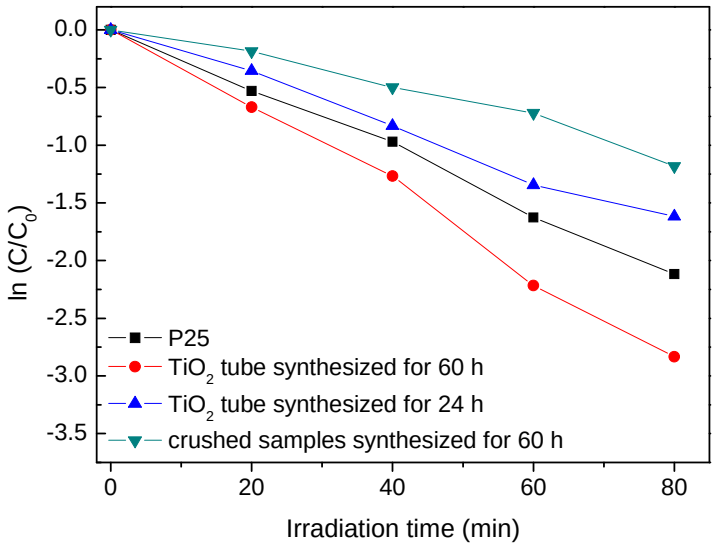

Fig. S8 Relations between $\ln(C/C_0)$ and reaction time under UV light irradiation. C: concentration of Rh.B, C_0: equilibrium concentration of Rh.B after adsorption.

Table S1. Weight and atom ratio of the prepared spiny titania tube before calcination.

Element	Wt%	At%
Ti	26.72	10.34
C	24.68	38.10
S	8.21	4.75
O	40.39	46.81
Total	100	100

Table S2. BET surface area (S_{BET}) and pore volume (V_P) of the calcined titania tube synthesized for different period of time.

Samples	1h	12h	24h	36h	60h	60h (crushed)
S_{BET} (m^2/g)	8.36	38.2	63.8	84.5	111.2	122.8
V_P ($cm^{3/}g$)	0.0128	0.0527	0.111	0.130	0.242	0.238