

## Supporting Information:

# Enhanced Photo-induced Surface Reactivity of Mesoporous Titania Modified with Benzene Siloxane

*Xiaonao Liu, Junfang Guo, Liping Xiao, Jie Fan\**

## Experimental

**Synthesis of BS-mTiO<sub>2</sub> materials:** BS-mTiO<sub>2</sub> is synthesized by AcHE process<sup>13</sup>. In a typical synthesis of a mesostructured membrane, 10mmol of Ti(OBu)<sub>4</sub>, 0.1 mmol of BTEB, 40mmol of acetic acid, 12 mmol of HCl (or HNO<sub>3</sub>) and 1.6 g of F127 (EO<sub>96</sub>PO<sub>70</sub>EO<sub>96</sub>, MW = 12000 g/mol) were dissolved in 30mL ethanol. The mixture was stirred vigorously for 1 hour and transferred into a Petri dish (diameter 125 mm). The ethanol was evaporated at 40 °C with a relative humidity of ~ 40%. After 12 hours, a transparent membrane formed, and was transferred into a 65 °C oven and aged for an additional 24 hours. As-synthesized mesostructured hybrids were calcined at 350 °C in air for 6 hours (ramp rate 2 °C/min) in order to obtain mesoporous membranes. The membrane materials are ground into fine powders before use for the photocatalytic reaction.

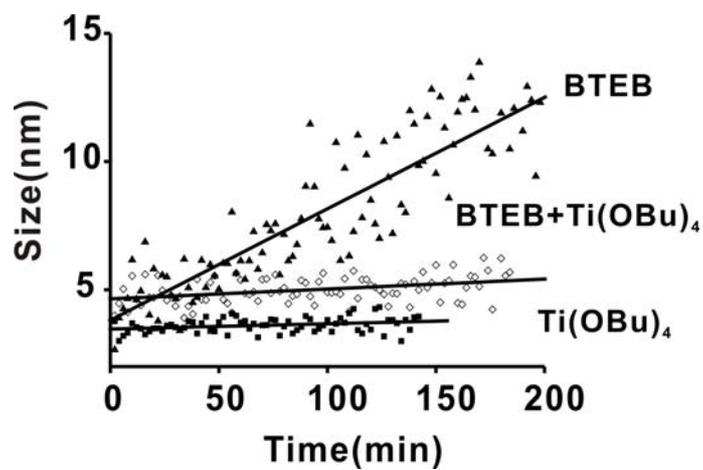
**Characterization:** The particle size of the titania and organosilica precursors in the AcHE solution and the isoelectric point of catalysts were assessed by Nano-ZS ZEN3600 (MALVERN Instrument) at 25 °C. For the isoelectric point measurements, the suspension fluid was a 1g/L aqueous solution of potassium chloride. The concentration of catalyst in the suspension was 0.5 mg mL<sup>-1</sup>. The pH value of the suspension was adjusted using solution of 0.05μmol hydrochloric acid and 0.05μmol potassium hydroxide. FT-IR spectra of the samples were recorded on a Nicolet NEXUS 470 FT-IR spectrometer. The concentrations of the samples in KBr were kept around 0.5-0.6%. SAXRD and WXR patterns were recorded on a Bruker D8 diffractometer using Cu<sub>Kα</sub> radiation. TEM images were taken using a JEOL 2010 electron microscope operating at 200 keV. Nitrogen sorption analysis was carried out at 77 K using a Micrometrics TriStar 3000 system. Solid-state <sup>13</sup>C and <sup>29</sup>Si NMR analyses were performed at room temperature on a Bruker DMX 500 MHz NMR spectrometer using a 4mm magic-angle spinning (MAS) probe. The photocatalyst powders were spun at a rate of 10 kHz for <sup>13</sup>C MAS NMR and at a rate of 4kHz

for  $^{29}\text{Si}$  MAS NMR spectra. TGA was carried out on a TG/DTA 320 system (ramp rate: 10 °C/min). The photoluminescence emission spectra were carried out on a fluorospectrophotometer (RF 5301 PC) by using a 280 nm excitation wavelength of a Xe lamp with 150 W powders at room temperature. A Shimadzu UV-2401 UV-visible spectrophotometer was used to obtain the reflectance spectra of the catalysts over a range of 200-700 nm.

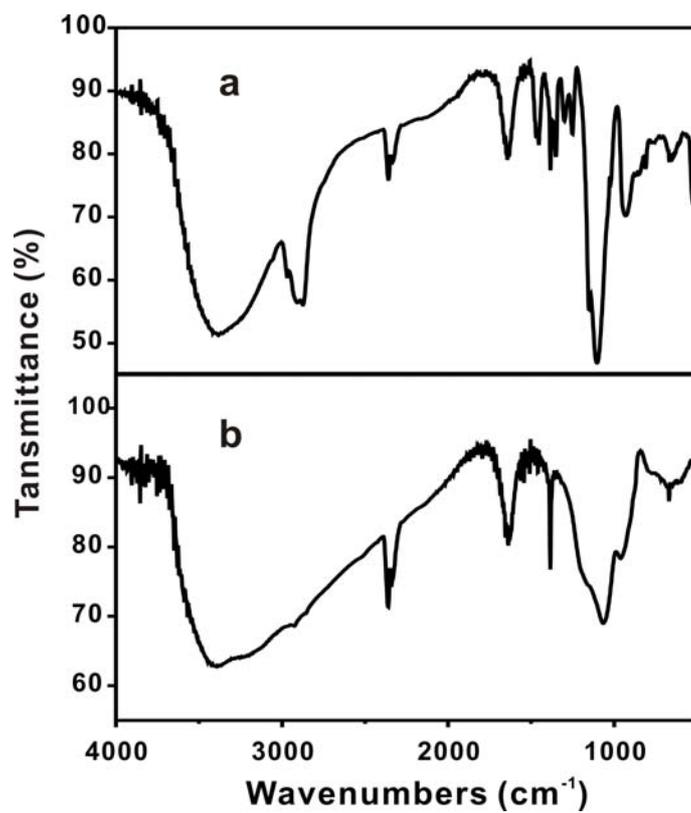
**Photocatalytic reaction:** The MB photo-degradation was carried out under top-irradiation by a 100 W high-pressure Hg lamp. The solution was continuously stirring in a 100 mL water-jacketed Pyrex-glass bottle to maintain a reaction temperature at 25 °C. A typical reaction system contained 50 mg of catalyst powders and 100mL of the MB solution (15 mg/L). Prior to the irradiation, the MB solution with the photocatalyst powders was kept in the dark for 2 hours to ensure the sorption equilibrium. The concentration change of MB is monitored by UV-vis spectroscopy.

**EPR and Spinning Trapping Experiment:** X-band EPR signals were recorded at ambient temperature on a Bruker EPR A-300 spectrometer. The settings for the EPR spectrometer were as follows: center field, 3511.39 G; sweep width, 100 G; microwave frequency, 9.86 G; modulation frequency, 100 kHz; power, 101 mW; conversion time, 10msec. The spin trapping experiments were performed as follows: 5,5-Dimethyl-pyrroline-N-oxide (DMPO) spin-trapping reagent and other chemicals were purchased from Sigma-Aldrich Chemical Co. and used without further purification. Stock solutions of DMPO (0.8 M) in deaerated water were prepared under argon and stored in the dark at -20 °C. The stock DMPO solution was first diluted to 0.08M with phosphate buffer solution (pH = 7.6) prior to the reaction with any solid substrate. The solid catalyst (~ 2.0 mg) was mixed with calculated amount of ice-cooled DMPO solution (0.08 M). The mixture was quickly transferred into a glass capillary tube and tested by EPR spectroscopy at room temperature upon photo-irradiation. A 100 W Hg lamp (LOT Oriel) was used as the light source.

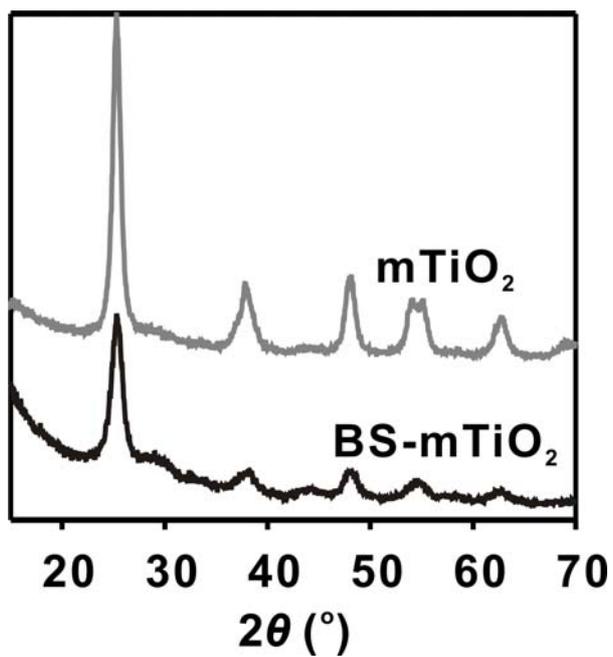
**Fig. S1** Size evolution of individual titania and benzene siloxane precursors and their mixture in AcHE solution at room temperature as monitored by time-resolved dynamic light scattering (DLS).



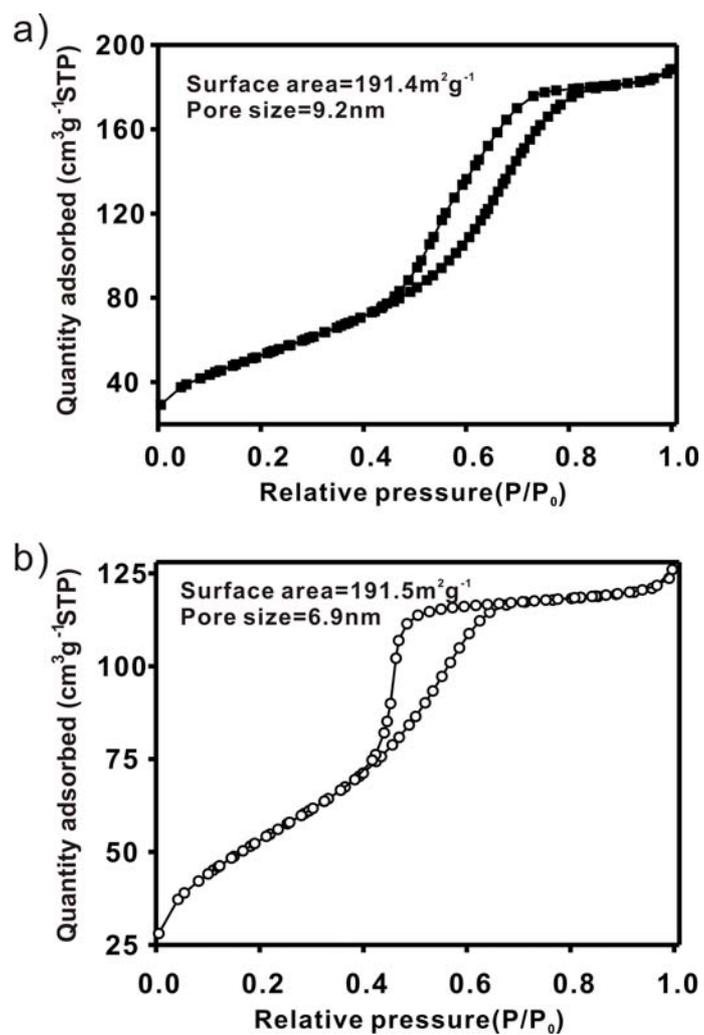
**Fig. S2** FT-IR spectra of (a), as-made BS-  $m\text{TiO}_2$  prepared by using amphiphilic triblock copolymer F127 as a template, and (b), calcined BS-  $m\text{TiO}_2$  at 350 °C.



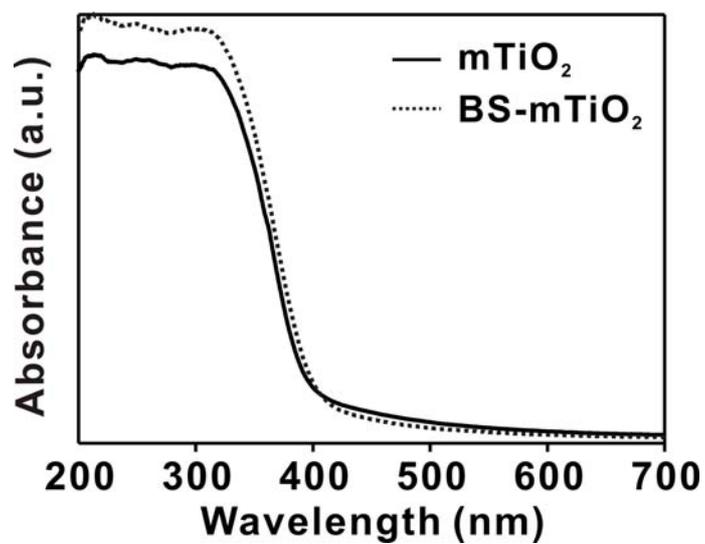
**Fig. S3** Wide-angle X-ray diffraction patterns of  $m\text{TiO}_2$  and BS-  $m\text{TiO}_2$  calcined at 350 °C in air.



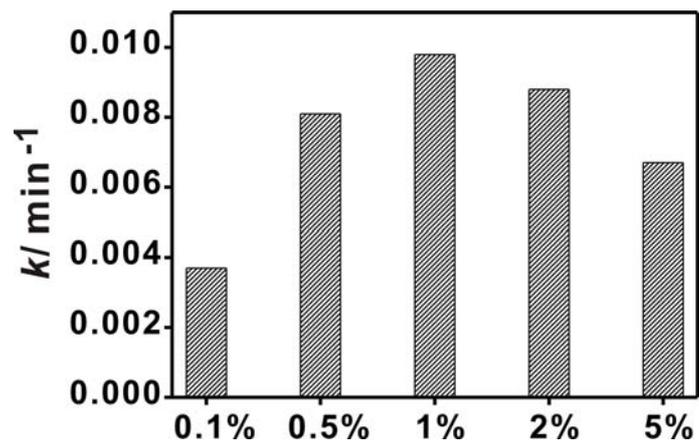
**Fig. S4** Nitrogen sorption isotherms of a) mTiO<sub>2</sub> and b) BS- mTiO<sub>2</sub> calcined at 350 °C.



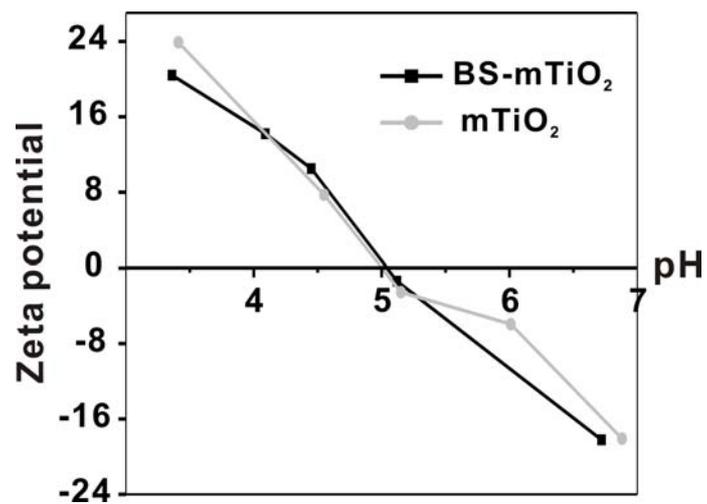
**Fig. S5** UV-vis absorbance spectra of  $\text{mTiO}_2$  and BS-  $\text{mTiO}_2$  calcined at  $350\text{ }^\circ\text{C}$ .



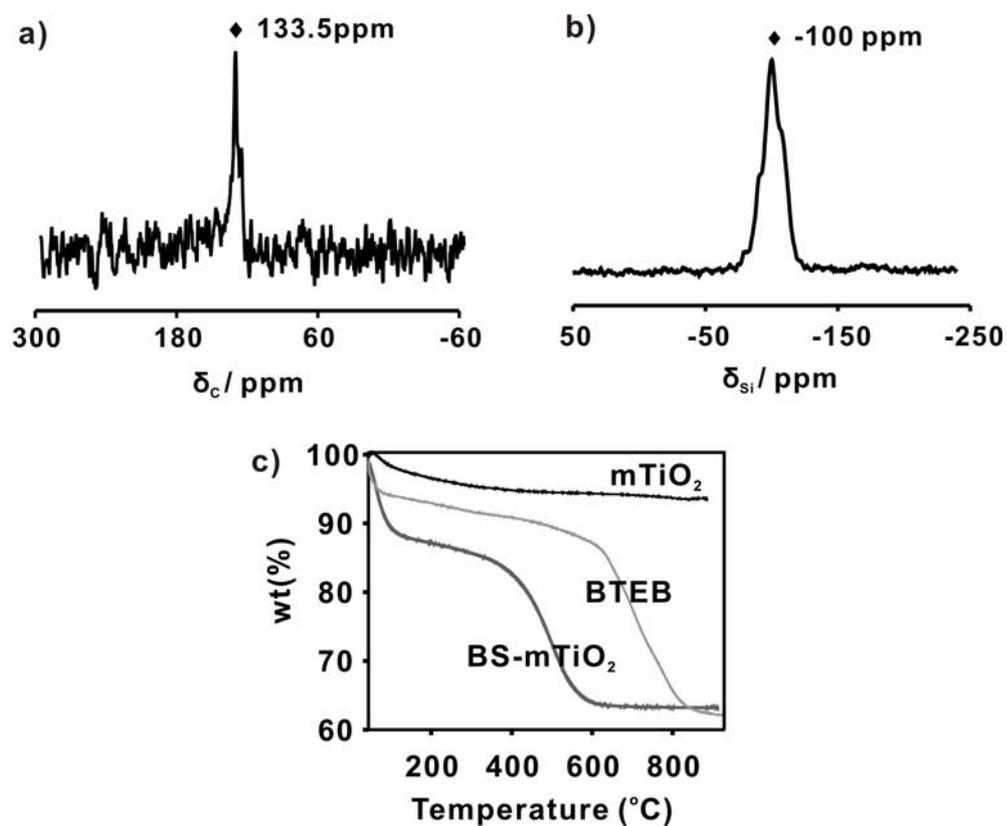
**Fig. S6** Reaction rate constants of BS- mTiO<sub>2</sub> photocatalysts with different B/T ratios (calcined at 350 °C).



**Fig. S7** Zeta potential-pH value plots of  $m\text{TiO}_2$  and BS-  $m\text{TiO}_2$  calcined at  $350\text{ }^\circ\text{C}$ .



**Fig. S8** a) Solid-state  $^{13}\text{C}$  CP and b)  $^{29}\text{Si}$  MAS NMR spectra of BS-  $\text{mTiO}_2$  (B/T = 0.5) calcined at 350  $^\circ\text{C}$ . c) TGA curves of BTEB xerogel,  $\text{mTiO}_2$  and BS- $\text{mTiO}_2$  (B/T = 0.5) calcined at 350  $^\circ\text{C}$  in air.



- [1] J. Fan, S. W. Boettcher, G. D. Stucky, *Chemistry of Materials* **2006**, *18*, 6391.  
[2] E. P. Barrett, L. G. Joyner, P. P. Halenda, *Journal of the American Chemical Society* **1951**, *73*, 373.