

Electronic Supplementary Information

Fabrication of TiO₂@MIL-53 Core-Shell Composite for Exceptionally Enhanced Adsorption and Degradation of Nonionic Organics

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EXPERIMENTAL SECTION

Chemicals and Reagents

All reagents and chemicals used were at least of analytical grade. Ultrapure water (18.2 M Ω cm) was obtained from a WaterPro water purification system (Labconco Corp., Kansas City, MO). Al(NO₃)₃·9H₂O and terephthalic acid were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Titanium butoxide (TBOT) was purchased from Tianjin Kermel Chemical Reagent Co. Ltd. (Tianjin, China). Ethanol and acetonitrile were purchased from Tianjin Concord Technology Corporation (Tianjin, China).

Ethanol was pre-treated before use to remove trace water. Typically, appropriate amount of sodium ethoxide and 500 mL ethanol were poured into a flask, and the suspension was refluxed under magnetic stirring in a solvent distillation device for 5 h. The distilled ethanol was then evaporated and collected in a solvent distillation head. The resulted anhydrous ethanol was sealed and kept in a vacuum dryer.

Instrumentation

The X-ray diffraction (XRD) patterns were recorded with a D/max-2500 diffractometer (Rigaku, Japan) using Cu K α radiation ($\lambda=1.5418$ Å). The thermogravimetric analysis (TGA) experiments were performed on a DTG-60 thermal gravimetric analyzer (Shimadzu, Japan) from room temperature to 800 °C at a ramp rate of 10 °C min⁻¹. The scanning electron microscopy (SEM) micrographs were recorded on a Phenom G2 scanning electron microscope at 15.0 kV. Transmission electron microscopy (TEM) images were obtained by using a Hitachi H-7650 transmission electronic microscope (Hitachi, Japan). A Autosorb-IQ surface area and pore size analyzer (Quantachrome, Florida, FL, USA) was used to measure the Brunauer-Emmett-Teller (BET) surface area, pore volume and pore size distribution of the synthesized materials at 77K in the range $0.02 \leq P/P_0 \leq 0.20$. The Barrett-Joyner-Halenda (BJH) method was used to calculate the micropore distribution. UV-vis adsorption spectrum was measured using a UV-visible spectrophotometer (Thermo Fisher, Evolution 201, USA).

Synthesis of MIL-53

MIL-53 was synthesized under hydrothermal conditions according to Loiseau et al.^[S1]

Typically, 1300 mg $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and 288 mg terephthalic acid were mixed with 5 mL of ultrapure water in a Teflon-lined stainless steel autoclave, which was heated at 220 °C for 3 days. After cooling down, the white power obtained was washed with ultrapure water and hot ethanol. Then, the solid was dried and activated upon heating in air at 330 °C for 3 days to remove the unreacted terephthalic acid from the pores. Pure MIL-53 samples for SEM and TEM characterizations were re-dissolved by anhydrous ethanol, and the suspension was dropped onto the sample table before SEM and TEM characterizations.

Synthesis of Pure TiO_2 Crystals

To fabricate pure TiO_2 crystals, TBOT (2 mL) and anhydrous ethanol (16 mL) were mixed homogeneously under magnetic stirring in sealed vial. Then, the mixture was transferred into a Teflon-lined stainless steel autoclave and heated at 220 °C for 3 h. After cooling down, the white power was isolated and washed with hot ethanol. Then, the solid was dried in oven at 50 °C. The resulted TiO_2 was further activated in oven for 3 h at 100 °C, 200 °C and 300 °C, respectively.

Fabrication of TiO_2 @MIL-53 Core-Shell Composite

To prepare the TiO_2 @MIL-53 core-shell composites, MIL-53 (100 mg) was added into the mixed solution of TBOT (2 mL) and anhydrous ethanol (16 mL). The suspension was mixed homogeneously under magnetic stirring for 0.5 h in a sealed vial. Then the suspension was transferred into a Teflon-lined stainless steel autoclave and heated at 220 °C for 3 h. After cooling down, the white power was isolated and washed with hot ethanol. Then, the solid was dried in oven at 50 °C. The composite of TiO_2 @MIL-53 was further activated in oven for 3 h at 100 °C, 200 °C and 300 °C, respectively. TiO_2 @MIL-53 samples for SEM and TEM characterizations were re-dissolved by anhydrous ethanol, and the suspension was dropped onto the sample table before SEM and TEM characterizations.

Determination of Equilibrium Time for Adsorption of Sudan Red III (SR_{III})

The batch adsorption experiment method was applied to examine adsorption of SR_{III}. Adsorption kinetic curve and adsorption isotherm were made to characterize the adsorption of SR_{III} on the MIL-53 and TiO_2 @MIL-53. MIL-53 and TiO_2 @MIL-53 were dried at 50 °C under vacuum for more than 72 h before use.

To determine the equilibrium time for the adsorption of SR_{III} on TiO₂@MIL-53, 60 mg TiO₂@MIL-53 was mixed with 10 mL of SR_{III} solution (30 mg L⁻¹) in a 20 mL vial. The mixtures were maintained at 30 °C for various pre-determined periods (10 min to 6 h). After adsorption for a pre-determined time, the mixture was centrifuged at 8000 rpm for 3 min, and the concentration of Sudan III in the supernatant was determined by a UV-vis spectrometer at 502 nm, which is the maximum absorption wavelength of SR_{III}. The amounts of adsorbed SR_{III} were calculated based on the difference between the initial and subsequent concentrations of SR_{III}. The adsorption capacity (q_t , mg g⁻¹) at time t was then calculated for the kinetics study.

Determination of the Maximum Adsorption Capacity of SR_{III}

Nine initial concentrations of SR_{III} (10 mg L⁻¹, 15 mg L⁻¹, 20 mg L⁻¹, 25 mg L⁻¹, 30 mg L⁻¹, 35 mg L⁻¹, 40 mg L⁻¹, 45 mg L⁻¹ and 50 mg L⁻¹) were used to investigate the maximum adsorption capacity of SR_{III} on TiO₂@MIL-53 and MIL-53. Typically, 70 mg TiO₂@MIL-53 was mixed with 10 mL SR_{III} solution in a 20 mL vial at the temperature of 30 °C for 6 h. The mixture was then centrifuged at 8000 rpm for 3 min, and the supernatant was sampled for UV-vis analysis. The adsorbed SR_{III} amounts were calculated and expressed as q_e (mg g⁻¹).

Photocatalytic Activity of Pure TiO₂ Crystals for Degradation of SR_{III}

Pure TiO₂ crystals activated at 100 °C, 200 °C and 300 °C was used to investigate the photocatalytic activity. The photocatalytic experiments for degradation of SR_{III} were performed in a UV-light reactor. Typically, 100 mg of TiO₂ was added to 100 mL solution of SR_{III} with concentration of 50 mg L⁻¹ under vigorous stirring. The reactor is illuminated with a 175 W high-pressure mercury lamp. At regular time intervals of illumination, a sample of mixture is collected and centrifuged, and the concentration of SR_{III} was measured using a UV-vis spectrometer. The results were corrected for decomposition of SR_{III} in the absence of catalysts.

Evaluation of Adsorptive and Catalytic Activity of TiO₂@MIL-53

Adsorptive and photocatalytic activity experiments of TiO₂@MIL-53 composites for adsorption and degradation of SR_{III} was performed in a UV-light reactor. Typically, 150 mg TiO₂@MIL-53 was dispersed in 100 mL SR_{III} solution at 30 mg L⁻¹ under stirring in the dark. After adsorption for a pre-determined time, the mixture was collected and centrifuged at 8000 rpm for 3 min, and the concentration of SR_{III} in the supernatant was determined by a UV-vis

spectrometer. Then the 175 W high-pressure mercury lamp with 365 nm wavelength situated above the solution was turned on for photocatalysis. The photocatalytic activity of TiO₂@MIL-53 was measured for degradation of SR_{III} under UV irradiation by monitoring the residual amount of SR_{III} in the solution. After degradation for a pre-determined time, the mixture was collected and centrifuged at 8000 rpm for 3 min, and the concentration of SR_{III} in the supernatant was determined by a UV-vis spectrometer.

References

[S1] T. Loiseau, C. Serre, C. Huguenard, G. Fink, F. Taulelle, M. Henry, T. Bataille and G. Férey, *Chem. Eur. J.*, 2004, **10**, 1373-1382.

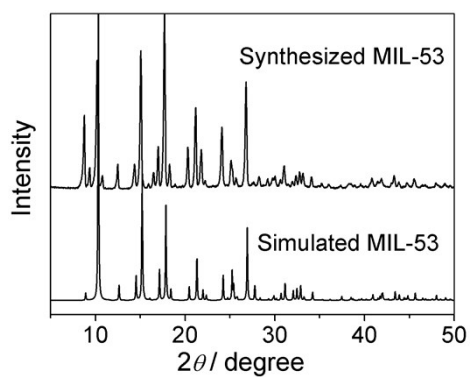


Fig. S1 XRD patterns of simulated and synthesized MIL-53.

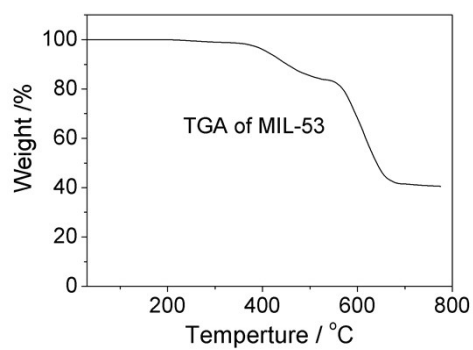


Fig. S2 TGA curve of the synthesized MIL-53.

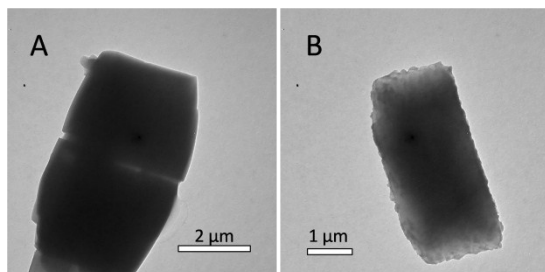


Fig. S3 TEM images of (A) the synthesized MIL-53 crystal; (B) the prepared TiO₂@MIL-53 core-shell composite.

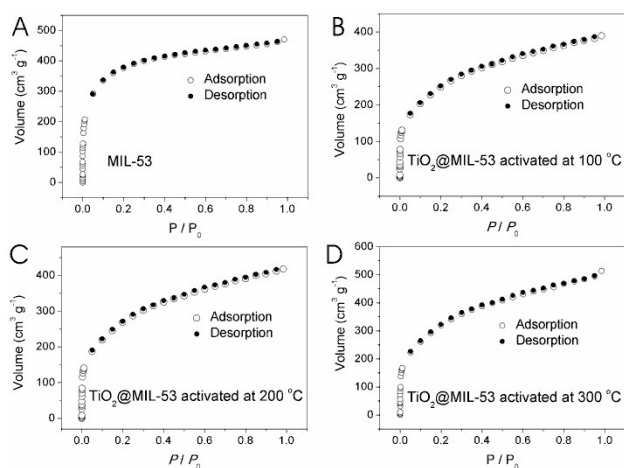


Fig. S4 BET adsorption isotherms of (A) MIL-53; (B) TiO₂@MIL-53 activated at 100 °C; (C) TiO₂@MIL-53 activated at 200 °C and (D) TiO₂@MIL-53 activated at 300 °C.

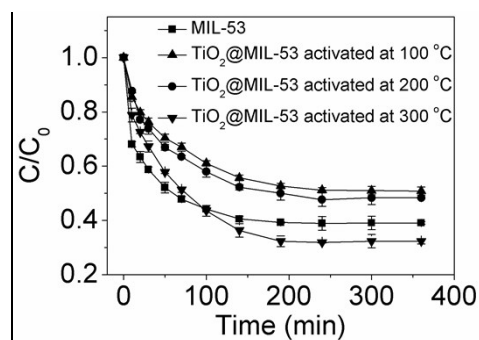


Fig. S5 Time-dependent adsorption of Sudan Red III on MIL-53, 100 °C-activated TiO₂@MIL-53, 200 °C-activated TiO₂@MIL-53 and 300 °C-activated TiO₂@MIL-53.

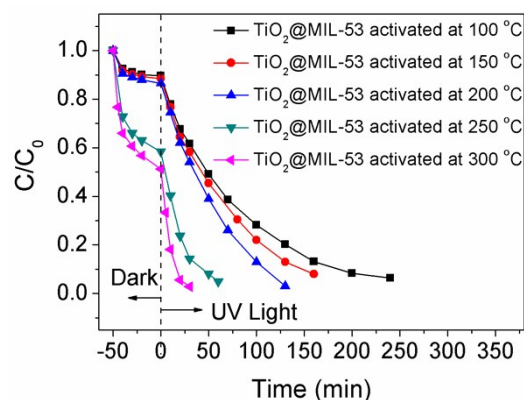


Fig. S6 Comparison of TiO₂@MIL-53 core-shell composites activated at different temperatures for the adsorption and decomposition of Sudan Red III.