

Electronic Supplementary Information for

The “Molecule Pump” Prototype for Exceptionally High

Efficiency Adsorption and Decomposition of Rhodamine B

Based on TiO₂@MIL-100 Composite

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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). Reduced iron powder, trimesic acid (1, 3, 5-BTC) and HF were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Titanium butoxide (TBOT) and concentrated HNO₃ were purchased from Tianjin Kermel Chemical Reagent Co. Ltd. (Tianjin, China). Ethanol was 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. An 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 mesopore distribution. UV-vis adsorption spectrum was measured using a UV-visible spectrophotometer (Thermo Fisher, Evolution 201, USA).

Synthesis of MIL-100

MIL-100 was synthesized under hydrothermal conditions according to Férey et al.^[S1] Typically, 277.5 mg reduced iron powder, 687.5 mg 1, 3, 5-BTC, 200 μ L HF, 190 μ L concentrated nitric acid were mixed with 20mL ultrapure water in a Teflon-lined bomb. The bomb was then sealed, placed in an oven and heated at 150 °C for 12 h. The light orange solid product was isolated and washing with ultrapure water and hot ethanol. The obtained MIL-100 was evacuated in vacuum at 50 °C for 24 h to form activated MIL-100.

Synthesis of Pure TiO₂ Crystals

To fabricate pure TiO₂ crystals, TBOT (2 mL) and anhydrous ethanol (10 mL) were mixed homogeneously under magnetic stirring in a 50 mL flask for 30 min. The solution of anhydrous ethanol (10 mL), ultrapure water (2 mL) and acetate (1 mL) which was adjusted to pH = 2 with nitric acid (1 mol L⁻¹) was dropped slowly into the

50 mL flask at a speed of 1 drop per second. Then, the mixture was stirred for another 2 h before dried in an oven of 50 °C. The resulted TiO₂ particles were further grinded into powder and calcined in oven for 3 h at 300 °C.

Fabrication of TiO₂@MIL-100 Composite

To prepare the TiO₂@MIL-100 composite, MIL-100 (100 mg) was added into the mixed solution of TBOT (2 mL) and anhydrous ethanol (10 mL). The suspension was mixed homogeneously under magnetic stirring for 1 h (Suspension A). The solution of anhydrous ethanol (10 mL), ultrapure water (2 mL) and acetate (1 mL) was adjusted to pH = 2 with nitric acid (1 mol L⁻¹) (Solution B). Solution B was slowly dropped into suspension A (1 drop per second) under continued stirring to form suspension C. After stirring for another 2 h, the resulted TiO₂@MIL-100 composite was isolated, and activated in oven for 3 h at 300 °C. The as-synthesized TiO₂@MIL-100 composite was about 600 mg.

Determination of Equilibrium Time for Adsorption of RhB

The batch adsorption experiment method was applied to examine adsorption of RhB. Adsorption kinetic curve and adsorption isotherm were made to characterize the adsorption of RhB on the MIL-100 and TiO₂@MIL-100. MIL-100 and TiO₂@MIL-100 were dried at 50 °C under vacuum for more than 72 h before use.

To determine the equilibrium time for the adsorption of RhB on TiO₂@MIL-100, 60 mg TiO₂@MIL-100 was mixed with 10 mL of RhB solution (50 mg L⁻¹) in a 20

mL vial. The mixtures were maintained at 30 °C for various pre-determined periods (10 min to 4 h). After adsorption for a pre-determined time, the mixture was centrifuged at 8000 rpm for 3 min, and the concentration of RhB in the supernatant was determined by a UV-vis spectrometer at 553 nm, which is the maximum absorption wavelength of RhB. The amounts of adsorbed RhB were calculated based on the difference between the initial and subsequent concentrations of RhB. The adsorption capacity (q_t , mg g⁻¹) at time t was then calculated for the kinetics study. The adsorption of RhB by pure MIL-100 followed the same procedure for comparison, except for the amount of MIL-100 changed to 10 mg for each vial.

Determination of the Maximum Adsorption Capacity of RhB

Eight initial concentrations of RhB (10 mg L⁻¹, 20 mg L⁻¹, 30 mg L⁻¹, 40 mg L⁻¹, 50 mg L⁻¹, 60 mg L⁻¹, 70 mg L⁻¹ and 80 mg L⁻¹) were used to investigate the maximum adsorption capacity of RhB on TiO₂@MIL-100 and MIL-100. Typically, 60 mg TiO₂@MIL-100 was mixed with 10 mL RhB solution in a 20 mL vial at the temperature of 30 °C for 4 h. The mixture was then centrifuged at 8000 rpm for 3 min, and the supernatant was sampled for UV-vis analysis. The adsorbed RhB amounts were calculated and expressed as q_e (mg g⁻¹). The adsorption of RhB by MIL-100 followed the same procedure for comparison, except for the amount of MIL-100 changed to 10 mg for each vial.

Photocatalytic Activity of Pure TiO₂ Crystals for Degradation of RhB

Pure TiO₂ crystals activated at 300 °C were used to investigate the photocatalytic activity. The photocatalytic experiments for degradation of RhB in water were performed in a UV-light reactor. Typically, 100 mg of TiO₂ was added to 100 mL solution of RhB under vigorous stirring with initial concentration of 20 mg L⁻¹, 40 mg L⁻¹, 60 mg L⁻¹ and 80 mg L⁻¹, respectively. 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 RhB was measured using a UV-vis spectrometer.

Photocatalytic Activity of Pure MIL-100 Crystals for Degradation of RhB

Pure MIL-100 crystals were used to investigate the photocatalytic activity. The photocatalytic experiments for degradation of RhB in water were performed in a UV-light reactor. Typically, 20 mg of MIL-100 was added to 100 mL solution of RhB under vigorous stirring with initial concentration of 20 mg L⁻¹, 40 mg L⁻¹, 60 mg L⁻¹ and 80 mg L⁻¹, respectively. 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 RhB was measured using a UV-vis spectrometer.

Evaluation of Adsorptive and Catalytic Activity of TiO₂@MIL-100

Adsorptive and photocatalytic activity experiments of TiO₂@MIL-100

composites for adsorption and degradation of RhB in water was performed in a UV-light reactor. Typically, 120 mg TiO₂@MIL-100 was dispersed in 100 mL RhB solution (at four initial concentrations, 20 mg L⁻¹, 40 mg L⁻¹, 60 mg L⁻¹ and 80 mg L⁻¹, respectively) 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 RhB 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-100 was measured for degradation of RhB under UV irradiation by monitoring the residual amount of RhB 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 RhB in the supernatant was determined by a UV-vis spectrometer.

Determination of the Adsorption Isotherms and Langmuir Equation

To evaluate the difference in maximum adsorption capacities of RhB on MIL-100 and TiO₂@MIL-100, the adsorption isotherms were fitted with the Langmuir equation in the concentration range of 10-80 mg L⁻¹ at 30 °C (eq 1).^[S2]

$$\frac{C_e}{q_e} = \frac{C_e}{Q_0} + \frac{1}{Q_0 b} \quad (1)$$

Where C_e (mg L⁻¹) is the equilibrium concentration of RhB, q_e (mg g⁻¹) is the equilibrium adsorption capacity of RhB, Q_0 is the maximum adsorption capacity (mg g⁻¹), and b is the Langmuir constant (L mol⁻¹).

Regeneration of TiO₂@MIL-100 Composite

To investigate the reusability of TiO₂@MIL-100 composite for the adsorption and decomposition of RhB, TiO₂@MIL-100 composite used for one or more times was immersed into fresh ethanol. After stirring for 2 h, the resulted TiO₂@MIL-100 composite was isolated and collected. The above procedure was repeated for 2 times. Then, the refreshed TiO₂@MIL-100 composite was evacuated in vacuum at 50 °C for 24 h before use.

Table S1. Elemental distributions in the fabricated TiO₂@MIL-100 composite from EDAX

Element	W_t (%)	A_t (%)
Fe content from EDAX	4.66	1.95
C content from EDAX	13.33	25.92
O content from EDAX	33.03	48.24
Ti content from EDAX	48.98	23.89

Reference:

[S1] Yoon, J. W.; Seo, Y.-K.; Hwang, Y. K.; Chang, J.-S.; Leclerc, H.; Wuttke, S.; Bazin, P.; Vimont, A.; Daturi, M.; Bloch, E.; Llewellyn, P. L.; Serre, C.; Horcajada, P.; Grenèche, J.-M.; Rodrigues, A. E.; Férey, G. Controlled Reducibility of a Metal–Organic Framework with Coordinatively Unsaturated Sites for Preferential Gas Sorption. *Angew. Chem. Int. Ed.* **2010**, *49*, 5949-5952.

[S2] Jiang, J.-Q.; Yang, C.-X.; Yan, X.-P. Zeolitic Imidazolate Framework-8 for Fast Adsorption and Removal of Benzotriazoles from Aqueous Solution. *ACS Appl. Mater. Interfaces* **2013**, *5*, 9837-9842.

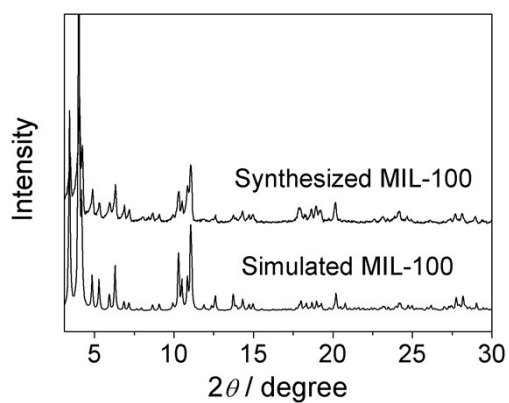


Fig. S1 XRD pattern of the synthesized MIL-100 and simulated MIL-100.

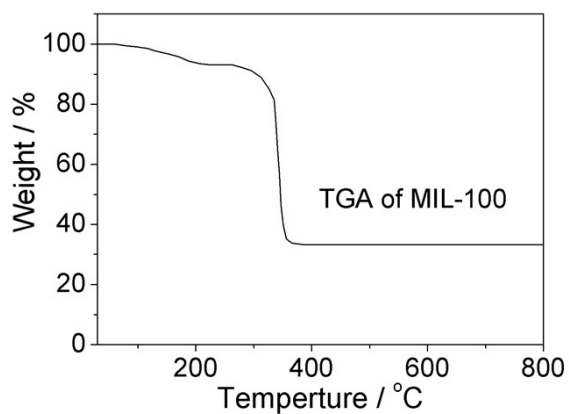


Fig. S2 TGA curve of the synthesized MIL-100.

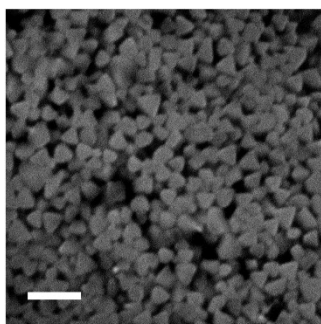


Fig.S3 SEM image of the synthesized MIL-100. The scale bar in the image was 10 μm .

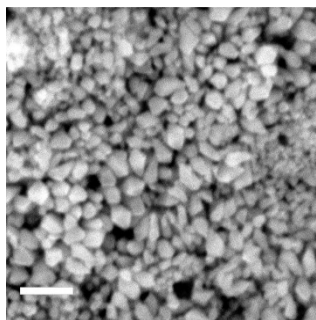


Fig. S4 SEM image of synthesized $\text{TiO}_2@\text{MIL-100}$ composite. The scale bar in the image was 10 μm .

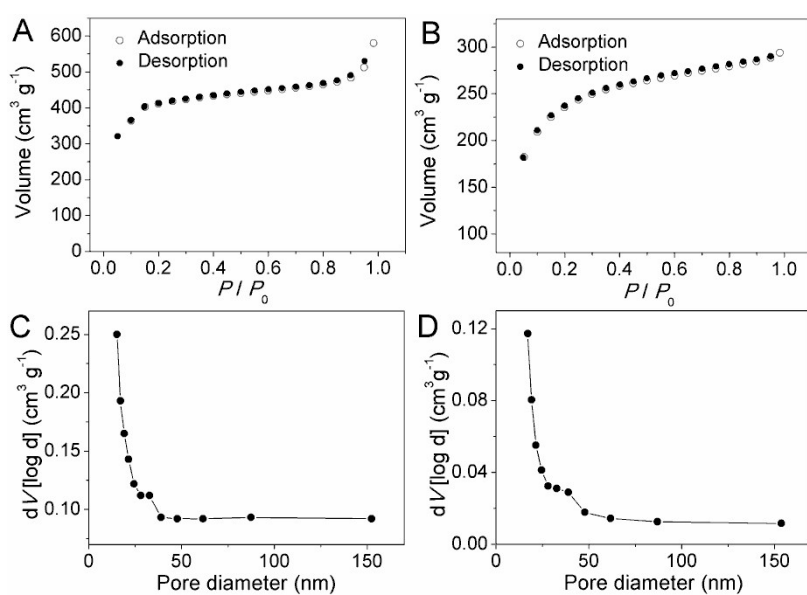


Fig. S5 N_2 adsorption-desorption isotherms of MIL-100 (A), and $\text{TiO}_2@\text{MIL-100}$ (B); pore size distribution curves of MIL-100 (C) and $\text{TiO}_2@\text{MIL-100}$ (D).

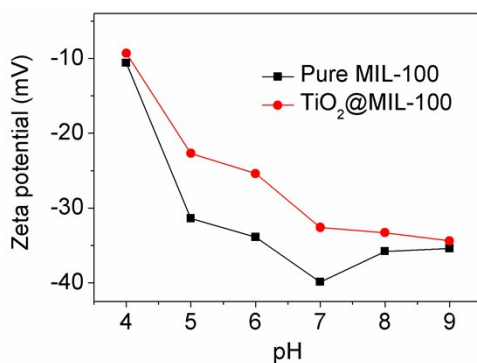


Fig. S6 Zeta potential of pure MIL-100 (black) and the fabricated $\text{TiO}_2@\text{MIL-100}$ (red).

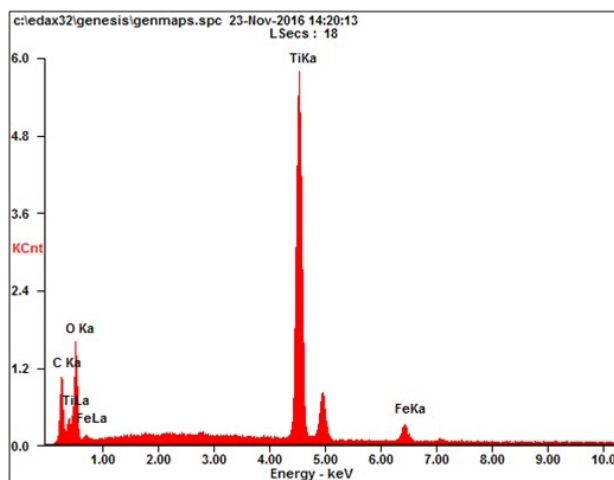


Fig. S7 EDAX patterns of the fabricated TiO₂@MIL-100 composite.

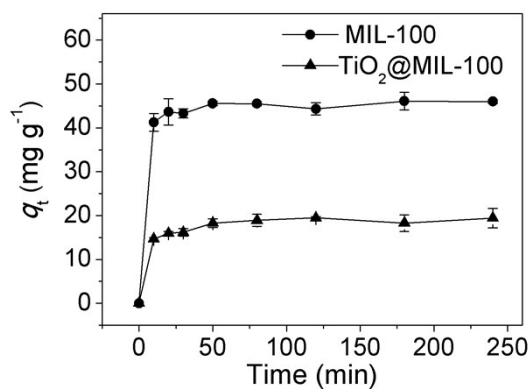


Fig. S8 Time-dependent adsorption of RhB on pure MIL-100 and TiO₂@MIL-100 at 30 °C.

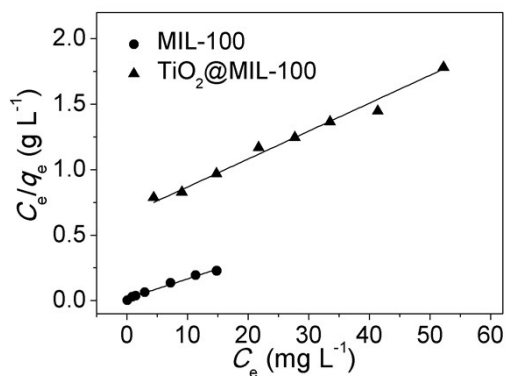


Fig. S9 Corresponding Langmuir plots for RhB on pure MIL-100 and TiO₂@MIL-100 at different initial concentrations at 30 °C

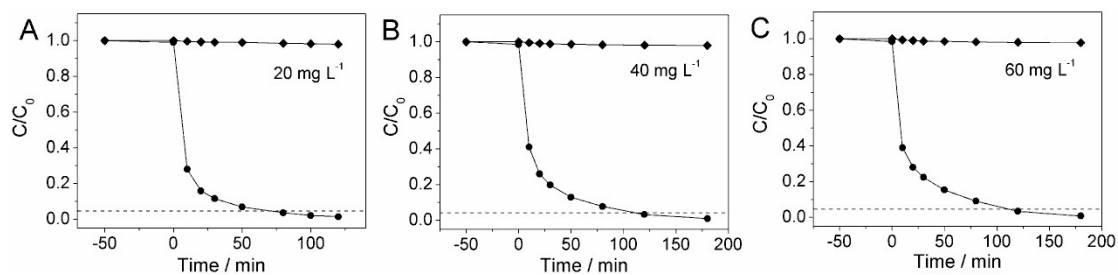


Fig. S10 UV irradiation of RhB after adsorption for 50 min in dark based on pure TiO₂ at different initial concentrations (•) and degradation of RhB under UV irradiation without catalyst (◆).

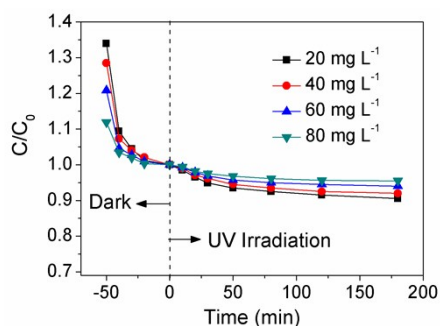


Fig. S11 UV irradiation of RhB after adsorption for 50 min in dark based on pure MIL-100 at different initial concentrations.

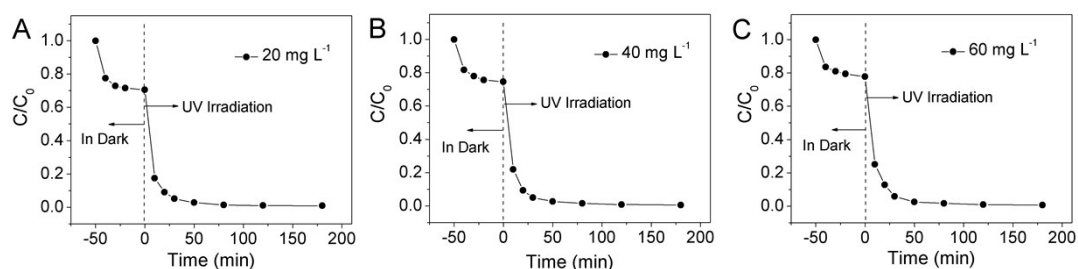


Fig. S12 Evaluation of adsorptive and photocatalytic activity of TiO₂@MIL-100 at different initial RhB concentrations after adsorbed for 50 min.

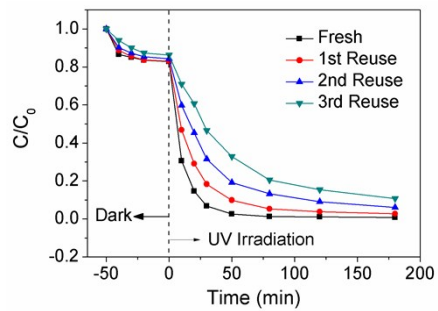


Fig. S13 Time-dependent adsorption and decomposition of RhB based on fresh and regenerated $\text{TiO}_2@\text{MIL-100}$ composite.

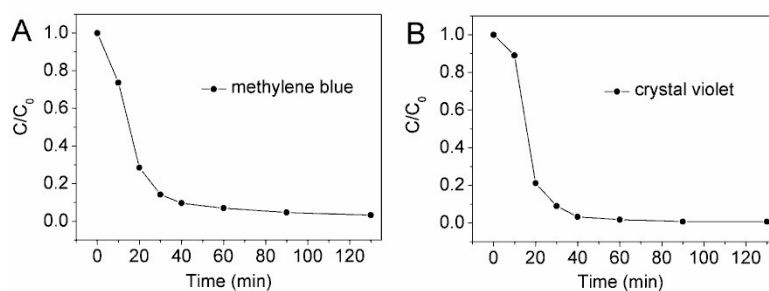


Fig. S14 Degradation efficiency (C/C_0) for methylene blue (A) and crystal violet (B) after adsorbed for 10 min in dark based on $\text{TiO}_2@\text{MIL-100}$ composite.