Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary Information

Metal-organic frameworks (MOFs) as precursors towards TiO_x/C composites for photodegradation of organic dye

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Materials and equipments

All of the reagents used were obtained from commercial suppliers and were used without further purification. Powder X-ray diffraction (PXRD) patterns were obtained on a Bruker D8 Advance X-ray Powder Diffractometer equipped with a Cu sealed tube (λ = 1.54178 Å) at a scan rate of 0.02 deg s^{-1}. The simulated PXRD patterns were obtained from single-crystal structures using the program Mercury. Field-emission scanning electron microscopy (FE-SEM) was conducted on an FEI Quanta 600 SEM (20 kV) equipped with an energy dispersive spectrometer (EDS, Oxford Instruments, 80 mm^2 detector). Field-emission transmission electron microscopy (FE-TEM) was conducted on a JEOL-JEM 2010F and JEOL-JEM 3010. Thermogravimetric analyses (TGA) were performed using a Shimadzu DTG-60AH in the temperature range of 35 to 1000 ˚C under flowing air (50 ml/min) at a heating rate of 10 °C min^{-1}.

Synthesis of samples

MIL-125 was synthesized according to a previous report (Y. H. Fu, D. R. Sun, Y. J. Chen, R. K. Huang, Z. X. Ding, X. Z. Fu and Z. H. Li, *Angew. Chem. Int. Ed.*, 2012, **51**, 3364-3367). In brief, benzene-1,4-dicarboxylic acid (498.4 mg) and titanium (IV) butoxide (255.2 mg) were dissolved in a mixed solvent of anhydrous *N,N*- dimethylformamide (DMF) (9 ml) and anhydrous methanol (1 ml). The solution was transferred into a 20 ml autoclave with Teflon liner and heated to 160 °C within 1 hour, held at 160 °C for 20 hours, and then cooled to room temperature. The product was collected through centrifuge, washed with DMF followed by methanol and then dried under vacuum to afford off-white powder.

T4 was prepared by weighing MIL-125 (~100 mg) in a ceramic boat and placing it in a quartz tube (1 inch diameter). The tube was sealed airtight, held at 80 °C for 45 minutes, and then heated under Ar gas flow from room temperature to 400 °C within 2 hours. The sample was maintained at 400 °C under a constant Ar gas flow for 5 hours before it was cooled down to room temperature to afford T4 as black powder. T6, T8, and T10 were synthesized similarly while being heated and maintained at 600 °C, 800 °C, and 1000 °C, respectively (yield: 30-40%).

Porous carbon was prepared by washing T10 with HF (5% aqueous solution) and dried under vacuum, which was used as a blank comparison in the photodegradation experiments.

X-ray photoelectron spectroscopy experiments

X-ray photoelectron spectroscopy (XPS) experiments were done with a Kratos AXIS Ultra DLD surface analysis instrument using a monochromatic Al K_α radiation (1486.71 eV) at 15 kV as the excitation source. The takeoff angle of the emitted photoelectrons was 90° (the angle between the plane of sample surface and the entrance lens of the detector). Peak position was corrected by referencing the C 1s peak position of adventitious carbon for a sample (284.8 eV), and shifting all other peaks in the spectrum accordingly. Fitting was done using the program CasaXPS. Each relevant spectrum was fit to a Shirley/Linear type background to correct for the rising edge of backscattered electrons that shifts the baseline higher at high binding energies. Peaks were fit as asymmetric Gaussian/Lorentzians, with 0-30 % Lorentzian character. The FWHM of all sub-peaks was constrained to 0.7-2 eV, as dictated by instrumental parameters, lifetime broadening factors, and broadening due to sample charging. With this native resolution set, peaks were added, and the best fit, using a least-squares fitting routine, was obtained while adhering to the constraints mentioned above.

N_2 sorption measurements

N_2 sorption isotherms were measured up to 1 bar using a Micromeritics ASAP 2020 surface area and pore size analyzer. Before the measurements, the samples (~100 mg) was degassed under reduced pressure ($< 10^{-2}$ Pa) at 150 °C for 12 h. UHP grade N_2 and He were used for all the measurements. Oil-free vacuum pumps and oil-free pressure regulators were used to prevent contamination of the samples during the degassing process and isotherm measurement. The temperature of 77 K was maintained with a liquid nitrogen bath. Pore size distribution data were calculated from the N_2 sorption isotherms based on non-local density functional theory (NLDFT) model in the Micromeritics ASAP2020 software package (assuming slit pore geometry).

Photodegradation of methylene blue

Photocatalytic performance of TiO_x/C composites was assessed by the photodegradation of methylene blue (MB). A certain amount of sample (20mg) was dispersed into 100 ml of MB aqueous solution (20 ppm, pH was maintained at 7.0) and left under stirring in dark for 1 hour to reach physisorption equilibrium of MB. The solution was then irradiated with a mercury UV light in a photoreactor (SGY-II Type B Photoreactor). A mercury light source (UV, 500W) was placed approximately 10 cm away from the solution as the source of solar energy. Small amounts of solution (5 ml each) were taken at different time intervals, centrifuged to remove solid suspensions, and then subjected to UV-Vis absorption spectroscopy (Shimadzu UV-1601 PC) to determine the MB content based on the absorption peak at 664 nm (M. Boehme and W. Ensinger, *Nano-Micro Lett.*, 2011, **3**, 236-241). The photodegradation data at irradiation time equal or less than 20 minutes were used to fit the kinetics as first order model based on Equation S1:

$$kt = \ln(C_0 / C) \qquad \text{Equation S1}$$

Where k is apparent first-order rate constant (min^{-1}), t is time (min), C_o and C are concentrations of MB at time of 0 and t, respectively.

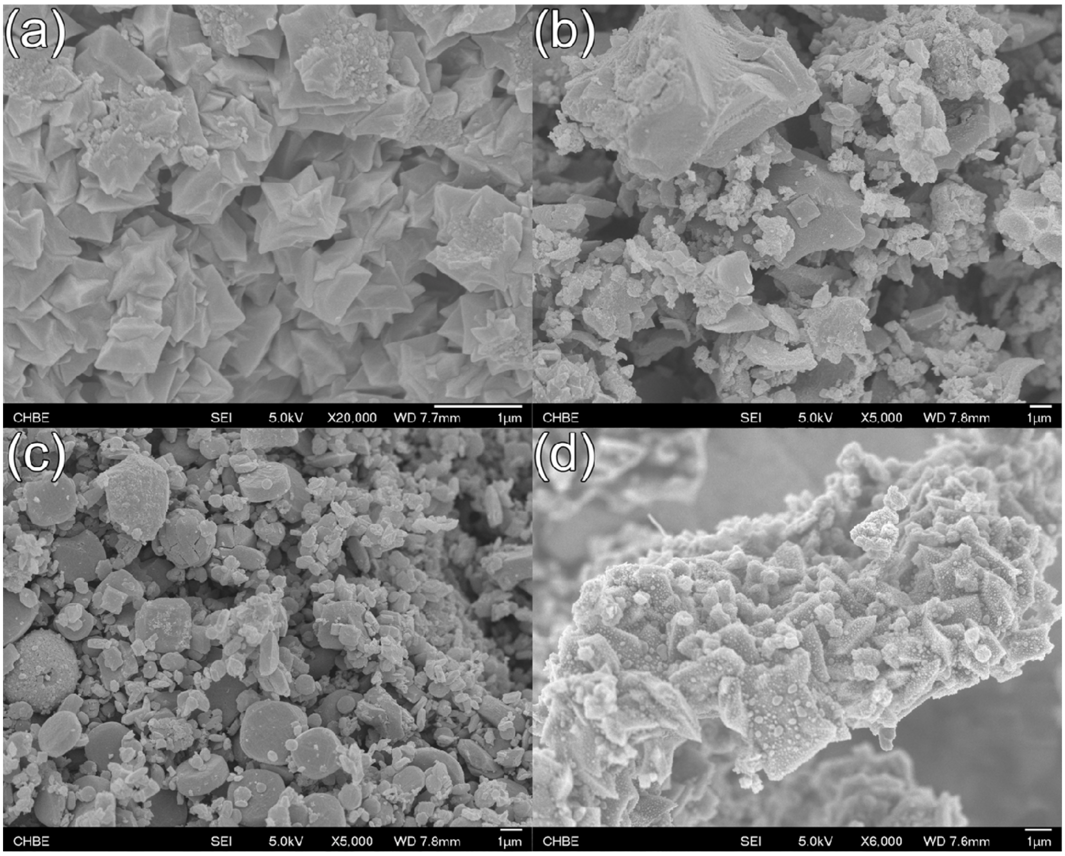

Figure S1. SEM images of (a) T4, (b) T6, (c) T8, and (d) T10 (scale bar, 1 μm).

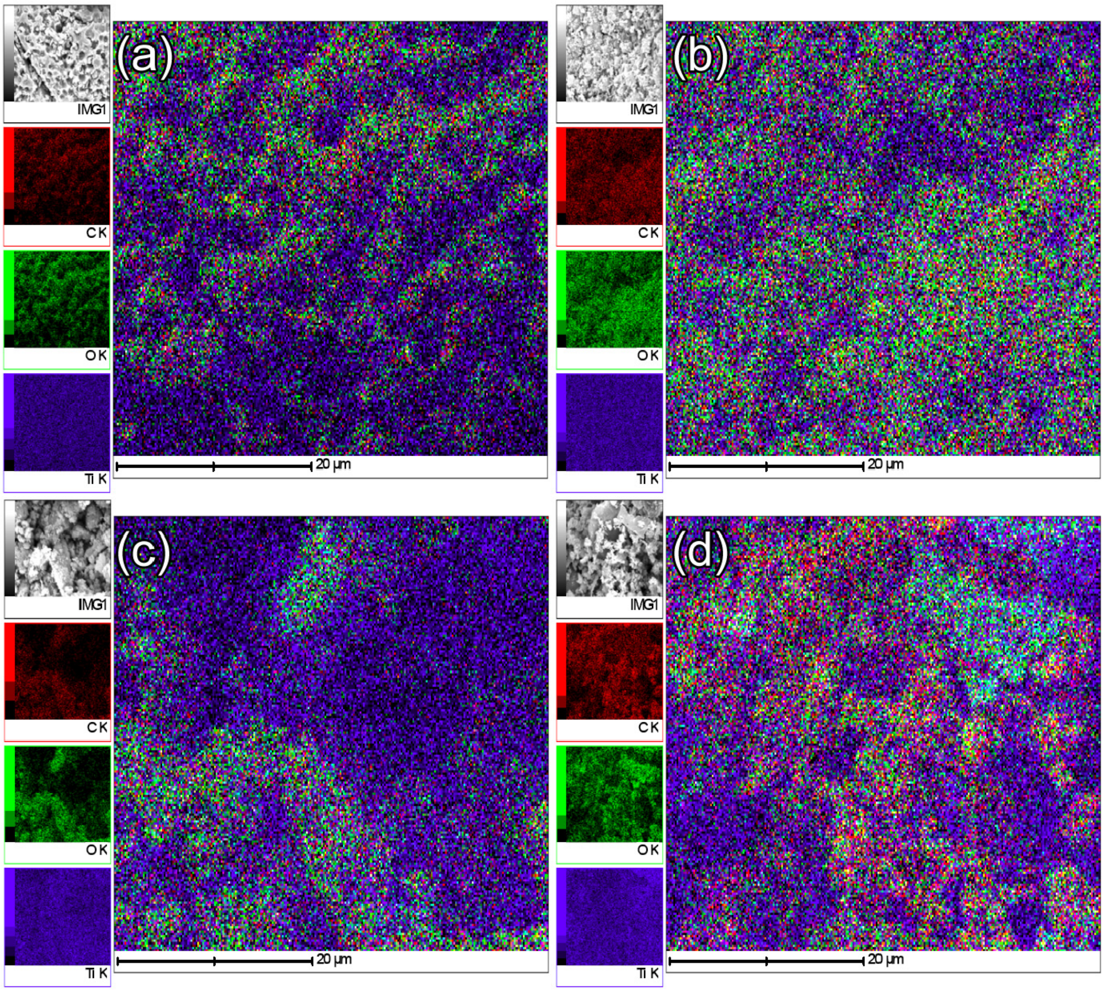

Figure S2. EDS elemental mapping of (a) T4, (b) T6, (c) T8, (d) T10 (red, C K; green, O K; blue, Ti K; scale bar, 20 µm).

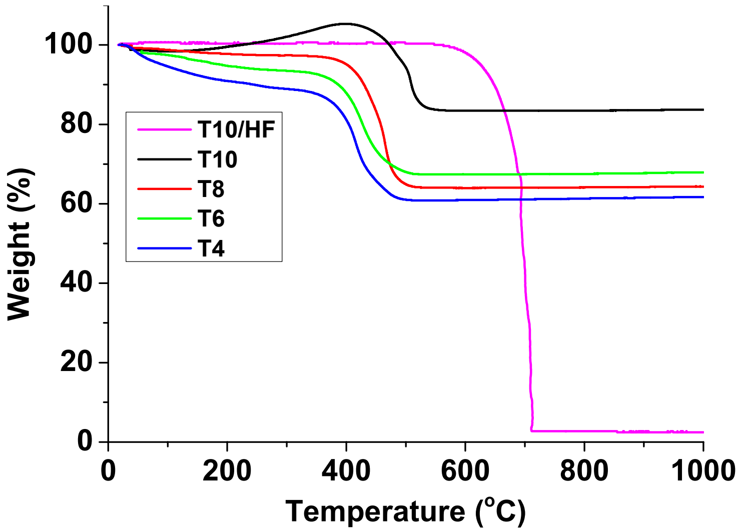

Figure S3. TGA curves of pyrolyzed samples.

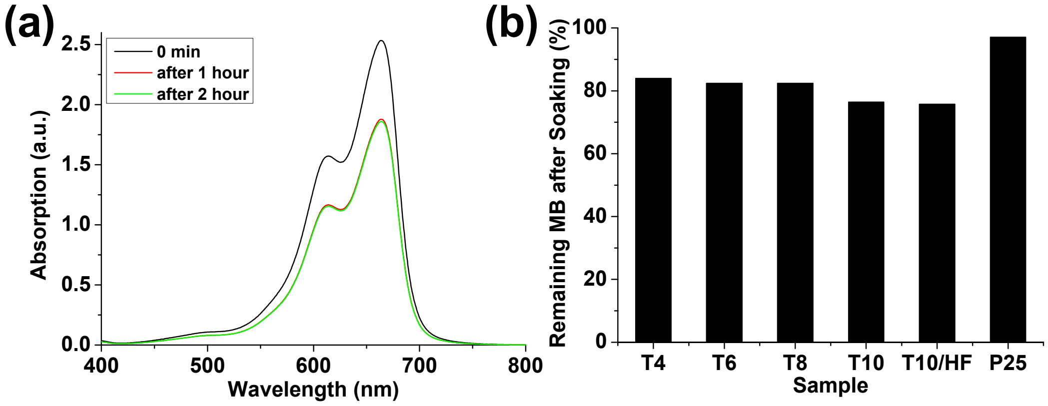

Figure S4. (a) UV-Vis absorption spectra of MB solution soaked with T10 for different durations. (b) Remaining fractions of MB after being soaked with various samples.

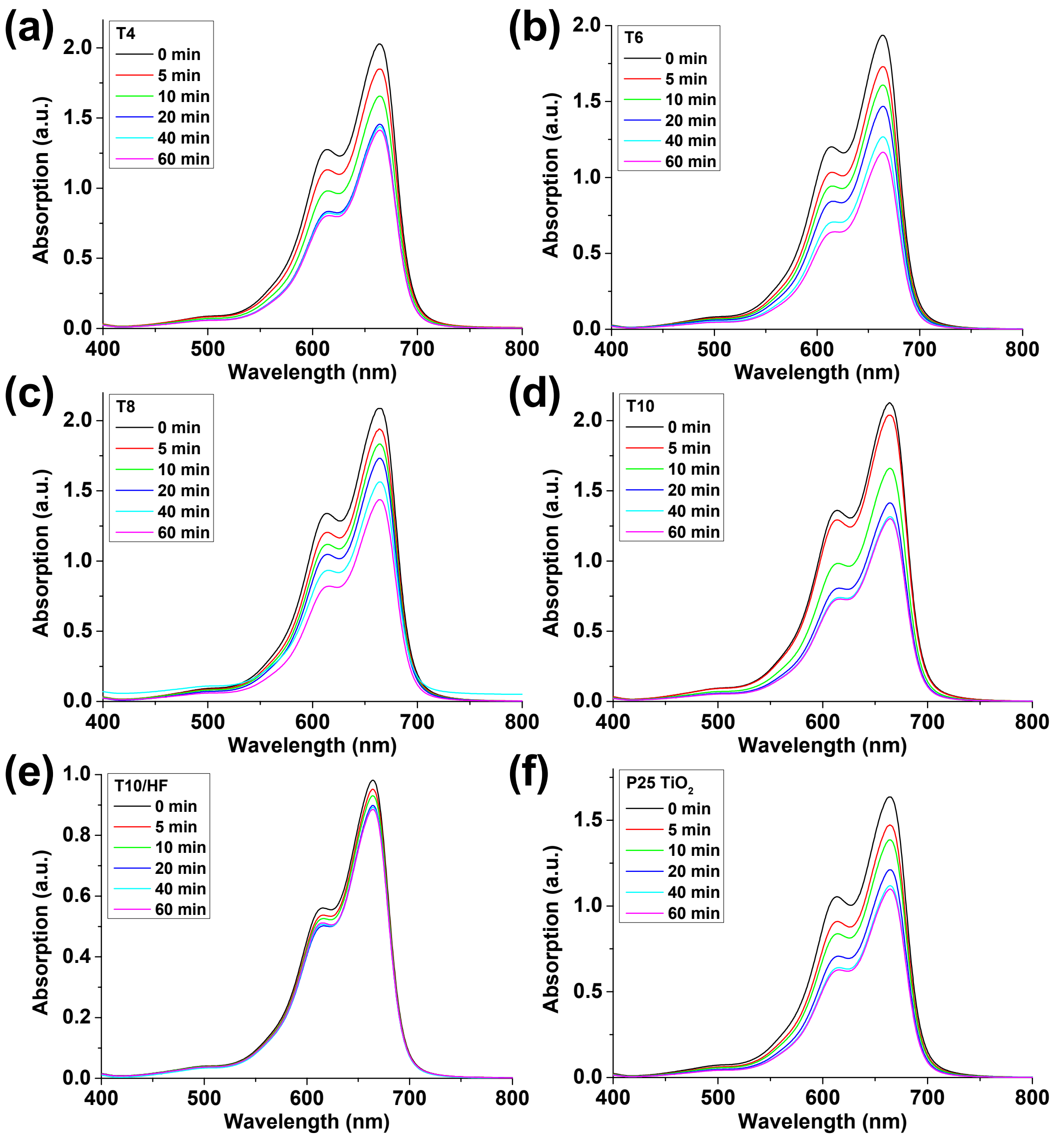

Figure S5. UV-Vis absorption spectra of MB solution during photodegradation experiments under different time intervals for (a) T4, (b) T6, (c) T8, (d) T10, (e) T10/HF, and (f) P25 TiO_2.