Supplementary Material

Facile synthesis of amino-functionalized indium metal-organic frameworks and their superior light photocatalytic activity for tetracycline degradation

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Experimental section

Materials

All reagents and solvents are of analytical grade and can be used without further purification. Indium nitrate ($In(NO_3)_3.xH_2O$, 99.9%) and 1,4-benzenedicarboxylic acid (H_2BDC, 99%) were purchased from Aladdin Co. Ltd. 2-aminoterephthalic acid ($H_2BDC\text{-}NH_2$, 98%), Ethanol (C_2H_5OH), N, N-dimethylformamide ($(CH_3)_2NCHO$, 99%), p-Benzoquinone, Tetracycline, EDTA disodium salt dihydrate were purchased from Macklin Biochemical Co. Ltd (Shanghai, China). Isopropyl alcohol (IPA, C_3H_8O) was purchased from GuoYao Group Chemical Reagent Co. Ltd.

Preparation of MIL-68(In) and In_2O_3

MIL-68(In) was prepared according to the literature [1]. $In(NO_3)_3 \cdot xH_2O$ (0.12g, 0.31 mmol) and terephthalic acid (H_2BDC) (0.12g, 0.72 mmol) were accurately weighed and put into a beaker containing 40 mL DMF and stirred on a magnetic stirrer at room temperature for 30 min until a stable and uniform solution was formed. Then the mixture was transferred to a 100-mL round-bottomed flask and heated for 30 min in an oil bath at 120 ^oC. After cooling to room temperature naturally, the product was collected and washed with distilled water and ethanol several times, and then dried at 60 ^oC overnight. In_2O_3 is prepared by annealing MIL-68(In) at 120 ^oC in the air for 2 h with a heating rate of 5 ^oC min^{-1}, and then further annealed at 500 ^oC for 2 h at the same heating rate.

Preparation of MIL-68(In)-NH_2

The solvothermal method was also adopted to prepare DMF as the solvent [2]. $In(NO_3)_3.xH_2O$ (2.31g, 7.68mmol) and 2-aminoterephthalic acid ($H_2BDC\text{-}NH_2$) (0.47g, 2.58mmol), put them into a beaker containing 20 mL DMF, place them In a magnetic stirrer at room temperature and stir for 30 min. The mixed solution was transferred into a 50 mL Teflon-lined autoclave and heated at 125 ^oC for 5 h. After the reaction, it was cooled to room temperature naturally. The products were collected by filtration and centrifugation, washed with DMF and ethanol for three times respectively, and then dried at 60 ^oC for 6 h.

Characterization methods

The crystal structure was detected by X-ray diffraction (XRD, SmartLab 9 KW) with Cu Kαradiation. The voltage and current were 40 kV and 100 mA. The Fourier

transform infrared (FT-IR, Vertex80+Hyperion200) spectrum was recorded in the range of 400-4000 cm^{-1}. The morphologies and structures were observed by scanning electron microscopy (SEM, S-4800) and Transmission electron microscopy (TEM, JEM-2100). The UV-Vis diffuse reflectance spectrum (UV-vis DRS, U-4100) was recorded in the wavelength range of 200-800 nm. A fluorescence spectrophotometer (F-4500) with an excitation wavelength of 290 nm was used to record the photoluminescence (PL) spectrum. X-ray photo electron spectroscopy (XPS) were acquired on ESCALAB250Xi spectrum, which was used to analyze the surface chemical composition. The specific surfaces were measured using the N_2 adsorption-desorption technique (Brunauer-Emmett-Teller, BET, ASAP2020 M + C). The intermediates of TC were analyzed by liquid chromatography–mass spectroscopy (LC-MS, LTQ Orbitrap XL). The photoelectrochemical measurements by using a normal three-electrode system in 0.5 M Na_2SO_4 solution were performed on an electrochemical workstation (CHI-660E, Chenhua)

Photocatalytic activity measurements

The photocatalytic activity of the as-prepared samples was detected at room temperature to investigate the degradation of tetracycline. First, the prepared samples were added to tetracycline solutions with different concentrations and stirred in the dark for 60 min to achieve the adsorption-desorption balance. And then, 2 mL of the solution was taken to measure the TC concentration. After that, the solution was placed under the lamp (xenon lamp, 280 nm < λ < 980 nm, 500 W) for photocatalytic reaction, a part of the solution (2 mL) was extracted at a certain time interval (10 min) to measure the TC concentration after filtered through a 0.2 μm filter. The concentrations of tetracycline in the solutions were analyzed by UV-vis spectrophotometer at the maximum absorption wavelength of 357 nm.

Photoelectrochemical measurement

The electrochemical experiment of the photocatalyst was performed on a CHI660E electrochemical workstation, and the measurement sample preparation steps are as follows: Disperse the sample (5 mg) in a mixture of Nafion solution (5 wt%) and ethanol solution (solution volume ratio 1:9). The mixed solution was evenly dropped on the surface of FTO conductive glass with an effective area of 1.0 cm×1.0 cm in 4 times, and 25 μL of the mixed solution was taken each time. In the electrochemical experiment, a three-electrode system was utilized, the Na_2SO_4 solution (0.5 M) was used as the electrolyte. And Pt foil electrode, Ag/AgCl electrode were regarded as the counter, reference electrode, respectively. Also, the photocurrent was measured at 1.0

V bias and a 300 W Xe lamp with illumination (λ > 420 nm) was treated as an analog visible light source. Conducted impedance test under the condition of bias voltage of -0.5 V, and its frequency range was set to 1-100,000 Hz.

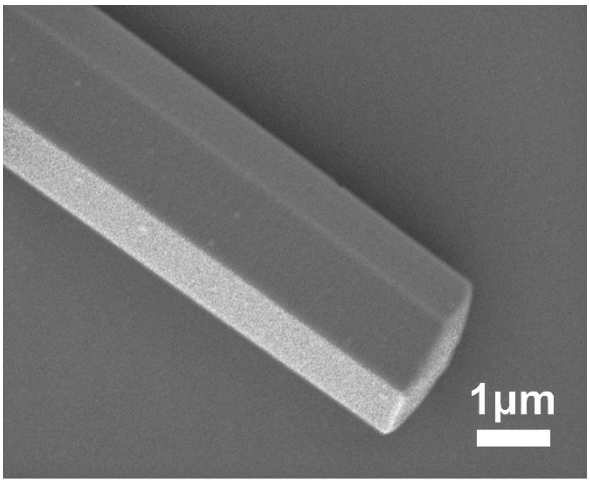

Fig. S1. SEM enlarged image of MIL-68 (In).

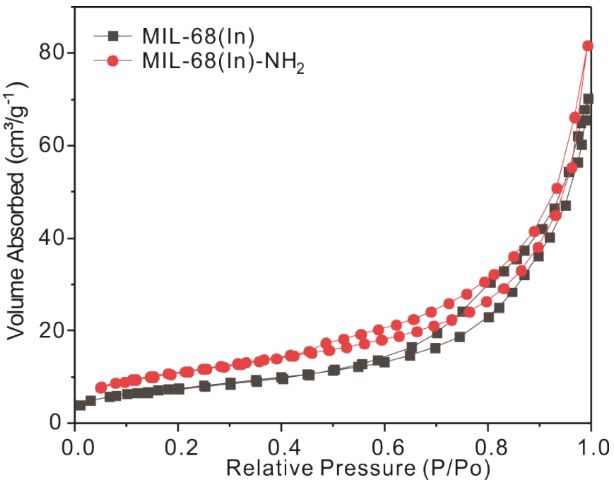

Fig. S2. N_2 adsorption–desorption isotherms of MIL-68(In) and MIL-68(In)-NH_2.

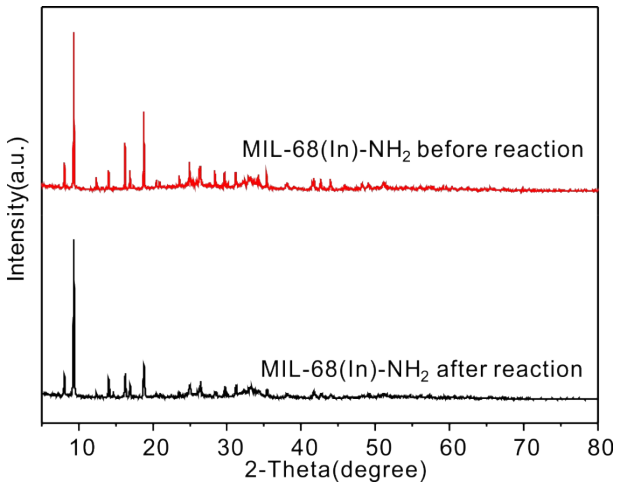

Fig. S3. XRD pattern of MIL-68(In)-NH_2 before and after reaction.

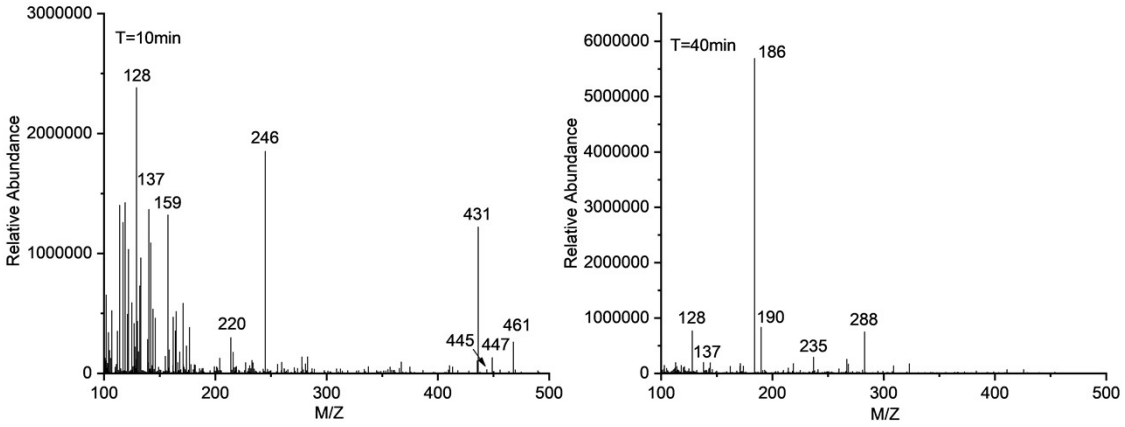

Fig. S4. Mass spectra of the TC and intermediates eluted at different reaction time.

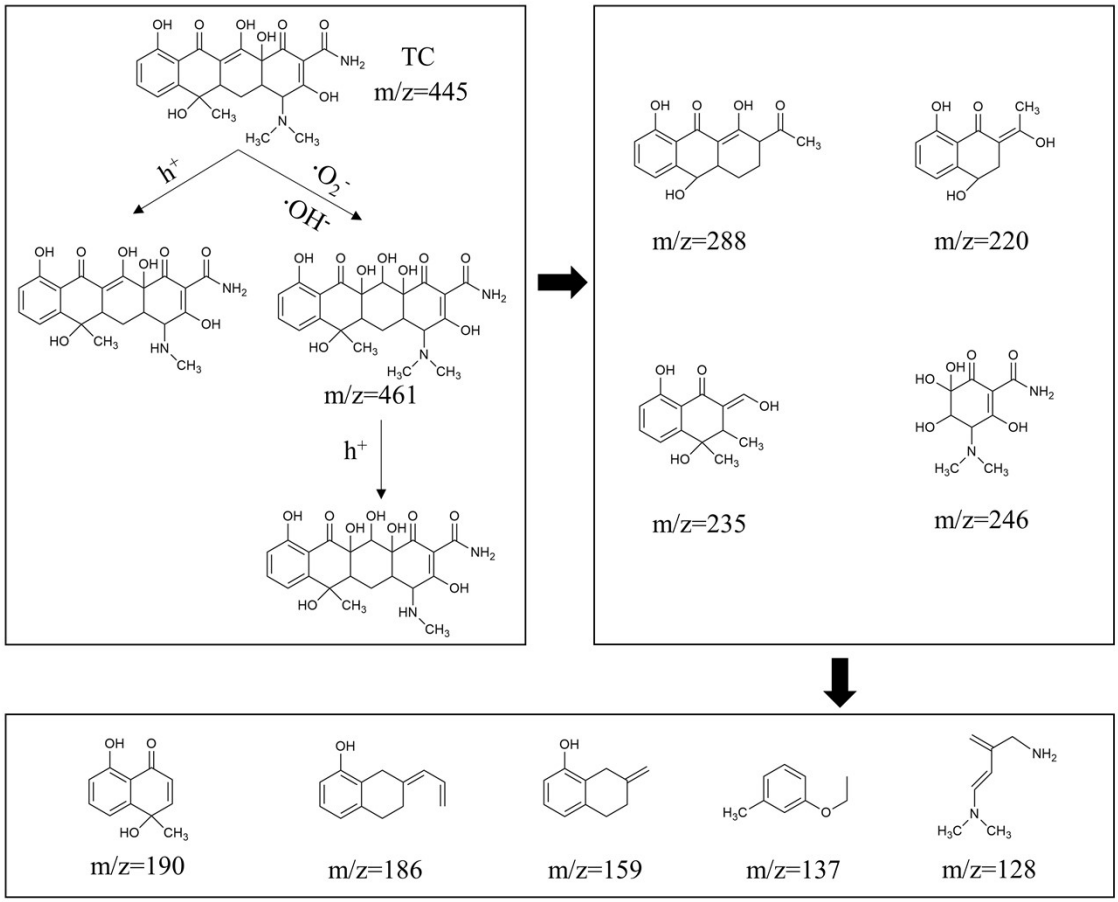

Fig. S5. Schematic diagram of the proposed intermediates and degradation routes of TC.

Table 1.
Parameters on the kinetic of tetracycline degradation process of MIL-68(In) and MIL-68(In)-NH_2.

Photocatalyst	Equation	$K_0(min^{-1})$	R^2
MIL-68(In)	y=0.01164x+0.15081	1.16×10^{-2}	0.97055
MIL-68(In)-NH_2	y=0.02629x+0.46801	2.63×10^{-2}	0.94675

Supplementary references

1. S. Wang, B. Y. Guan and X. W. D. J. J. o. t. A. C. S. Lou, 2018, **140**, 5037-5040.
2. L. Wu, M. Xue, S.-L. Qiu, G. Chaplais, A. Simon-Masseron, J. J. M. Patarin and m. materials, 2012, **157**, 75-81.