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Electronic Supplementary Information (ESI) Amorphous TiO₂@NH₂-MIL-125(Ti) Homologous MOF-encapsulated Heterostructures with Enhanced Photocatalytic Activity

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Experimental section

Materials and characterization methods

Tetra-n-butyl titanate (Ti(OC₄H₉)₄, 99.99%), tetracycline (98%), monopotassium phosphate (KH₂PO₄, 98%), 2-aminoterephthalic acid (H₂ATA, 99%), orthophosphoric acid (H₃PO₄, 85% p.a.) are supplied by Alfa Aesar. Benzyl alcohol (C₇H₈O, > 98%), benzaldehyde (C₇H₆O, > 98%), benzotrifluoride (BTF, 99%) are purchased from Aladdin. Ethanol (EtOH) and N, N-dimethyl-formamide (DMF) are purchased from Guanghua Chemicals. HPLC-grade methanol (MeOH) and acetonitrile are obtained from Merck used for HPLC analyses.

Powder X-ray diffraction (XRD) analyses are conducted using a Bruker D8 Advance diffractometer with monochromatized Cu K α radiation (λ = 0.15418 nm) source at 40 kV and 40 mA. The morphologies of the prepared samples are obtained through Scanning electron microscope (SEM) and transmission electron microscopy (TEM). The chemical compositions of the samples are investigated by X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi). UV–vis diffused reflectance spectra (DRS) are carried out on a UV–vis spectrophotometer (UV-3600, Shimadzu, Japan), with BaSO₄ as a reflectance standard. The electrochemical measures are conducted on the electrochemical work station (CHI660D Instruments) using three-electrode system. ASAP 2460 V2.01 apparatus (Micromeritics Instrument Corp., USA) is used to record the Brunauer– Emmett–Teller (BET) surface area and porous structure, with nitrogen adsorption and desorption isotherms of samples analysed at 77 K. Electron spin resonance (ESR) signals are measured on a JES FA200, (JEOL) electron paramagnetic resonance spectrometer under visible light.

Synthesis of NH₂-MIL-125(Ti)

According to a typical solvothermal method¹, H_2ATA (2.7g, 15 mmol) and $Ti(OC_4H_9)_4$ (1.3 mL, 3.75 mmol) were added into a solution mixed with MeOH (5 mL) and DMF (45 mL), and then stirred for 30 min. The prepared solution was poured into the Teflon-lined stainless steel autoclave (100 mL) and maintained at 150 °C for 3 days. Afterward, the resultant suspension was centrifuged, washed with MeOH and DMF respectively for several times, and lastly dried in an oven at 60 °C.

Synthesis of amorphous TiO₂@NH₂-MIL-125(Ti) (denoted as LP-3)

Amorphous TiO₂@NH₂-MIL-125(Ti) composite was synthesized through a facile method. Typically, the as-synthesized NH₂-MIL-125(Ti) was treated at 150 °C under vacuum for 12 h to remove the guest species in its pore structures. 0.4 g NH₂-MIL-125(Ti) was dispersed at 40 mL MeOH in a flask under ultrasound for 20min, subsequently, 500 μ L tetrabutyl titanate was slowly dropped to the above flask under vigorous stirring for 1h under room temperature and diffused to the pores of MOF. Then, the temperature rose rapidly to 85 °C and the mixture was refluxed for 12h to hydrolyze the tetrabutyl titanate completely to form amorphous TiO₂ within the framework. Afterwards, the obtained yellow product is collected by centrifugation and washes with MeOH several times, then dried at 60 °C. This amount (500 μ L) was chosen based on our experimental experience by investigating different amount of Ti: 200 μ L, 400 μ L, 500 μ L, 600 μ L, 1000 μ L (denoted as LP-X, X=1,2,3..). Due to the excellent performance of LP-3, as shown in Table S1, we choose it as the representative for further investigation.

Synthesis of amorphous TiO₂/NH₂-MIL-125(Ti)

Amorphous TiO₂@NH₂-MIL-125(Ti) composite was synthesized through a similar method for LP-3.

Typically, 500 μ L tetrabutyl titanate was slowly dropped to a flask containing MeOH 40 mL under stirring. Then, the temperature rose rapidly to 85 °C and the mixture was refluxed for 12h to hydrolyze the tetrabutyl titanate. Afterward, 0.4 g NH₂-MIL-125(Ti) was added into the flask and the mixture was allowed to stir for 6 h. Finally, the obtained yellow product is collected by centrifugation and washes with MeOH several times, then dried at 60 °C.

Synthesis of amorphous TiO₂@ NH₂-MIL-68(In) and TiO₂@NH₂-MIL-101(Cr).

The synthesis of amorphous $TiO_2@NH_2-MIL-68(In)$ and amorphous $TiO_2@NH_2-MIL-101(Cr)$ are similar to the above procedures except the adding of $NH_2-MIL-68(In)$ and $NH_2-MIL-101(Cr)$.

Photocatalytic degradation of tetracycline

The photocatalytic degradation of tetracycline over photocatalysts is conducted using a 500 W Xe lamp. The distance is fixed at 15 cm from the light source to the reactor (25 mg photocatalyst and 50 ml of 30 ppm tetracycline aqueous solution), and the light intensity is about 25 mW/cm² under visible irradiation. Before photocatalytic degradation reaction, the suspensions are stirred in dark for 1 h to get absorption–desorption equilibrium. Under illumination, about 2 mL of suspension is withdrawn at given time intervals, centrifuged, and filtered with 0.45 µm membrane for HPLC (Waters LC system) analysis, which contains an Zorbax SB-C18 reverse-phase column (25 cm × 5.0 µm × 4.6 mm). 0.05 M KH₂PO₄ buffer solution acidified at pH=3 and methanol are used as mobile phases A and B ($v_A/v_B = 75/25$), respectively, with a rate of 1 mL min⁻¹. The oven temperature is set as 25 °C. The injection volume is 20 µL and the detector wavelength is choen at 250 nm.

Photocatalytic oxidation of benzyl alcohol

The oxidation of benzyl alcohol over the photocatalyst is carried out under a 300 W Xe lamp irradiation (PLS-SXE 300, Beijing Perfectlight Co., Ltd) using a 420 nm cut-off filter. The distance is fixed at 10 cm from the light source to the reactor. The as-prepared photocatalyst (50 mg) was suspended into 6 mL of the solvent of benzotrifluoride (BTF) containing 0.3 mmol of benzyl alcohol. The reaction suspension is degassed and saturated with 0.1 atm O₂, and then stirred for 1 h in dark in order to get absorption–desorption equilibrium. The reaction products after irradiated for 10.5 h are quantified with a GC-FID (Agilent 7890B) using a column (HP-5 capillary). After photocatalytic reaction, the catalyst was recycled for cycle tests.

Active Radicals Measurement

For the ESR measurements, 10 mg of the photocatalyst powder is placed in a quartz sample tube. To test the reactivity of the photo-generated charges and O_2 , 1atm of N_2 and air are introduced into each sample tube, respectively. The measurement of photo-generated e⁻/h⁺ are carried out at 133K upon visible light, while the measurement of O_2 , was performed at ambient temperature with a spot UV-vis light source (420 nm UV-cutoff filter). The signals were taken every 4 min.

Photoelectrochemical measurement

An electrochemical work station (CHI660D Instruments) is employed for the electrochemical experiments. 5 mg samples are dispersed in 1 mL of ethanol and ultrasonicated for 1 h, 0.3 mL of

mixture solution is dropped to the pretreated ITO surface and dried in air, and then transfers to the oven at 120 °C for 5 h. A standard three electrode system is employed to record the photocurrents and electrochemical impedance spectra (EIS), which is composed of the reference electrode (a saturated calomel electrode, SCE), working electrodes and counter electrode (a Pt foil). The 0.1 M Na₂SO₄ aqueous solution is used as the electrolyte.

Molecular simulation section

In order to illustrate the problem seriously and thoroughly, we conducted the simulation using the material studio, as shown in Figure S1.

The molecular simulations were done using the Materials Studio 2017 R2 software package of Accelrys, Inc. (San Diego, CA). Atomistic packing models were generated using the Amorphous Cell module and were subsequently equilibration using molecular dynamics (MD) simulations with the Forcite module. The Universal force field was used during each stage of the simulations. In all cases, the non-bond interactions were calculated up to a cut-off distance of 18.5 Å, which was truncated using a cubic spline function with a width of 1 Å. For this, a group-based representation for the summation of the electrostatic interactions were used during packing model generation, equilibrium and subsequent production runs. The respective Andersen thermostat temperatures, and Berendsen pressure control algorithms were used throughout. The molecular dynamics simulation was performed by using NPT ensemble for 100 ps in order to get a reliable average state. Based on the data of molecular simulation, the radius of gyration can be calculated.

The radius of gyration is a parameter commonly used to describe the size of the molecular. The probability distribution about the radius of gyration for Tetra-n-butyl titanate in the MeOH solution was shown in Figure S2. It was noted that the radius of gyration (fluctuation at 3.5 Å) of the Tetra-n-butyl titanate was smaller than the window size (5-7 Å) of NH₂-MIL-125(Ti)², which indicated that the Tetra-n-butyl titanate could diffuse into the framework of NH₂-MIL-125(Ti).

	OH Cataly Visible lig	yst,O ₂ ght, 10.5h	o
Entry	Catalyst	Conversion (%)	Selectivity (%)
1	NH ₂ -MIL-125(Ti)	21.9	98.5
2	LP-1	25	99
3	LP-2	30	99
4	LP-3	37	99
5	LP-4	15	98
6	LP-5	5	94.3





Figure S1. The equilibrium geometry of Tetra-n-butyl titanate in the MeOH solution.



Figure S2. The probability distribution about the radius of gyration for Tetra-n-butyl titanate in the MeOH solution.





Fig. S3. SEM images of NH₂-MIL-125(Ti) (a) and LP-3 (b); TEM image of TiO₂/NH₂-MIL-125(Ti) (c); XRD image of TiO₂/NH₂-MIL-125(Ti) and NH₂-MIL-125(Ti) (d).



Figure S4. The molecular structure of $TiO_2@NH_2-MIL-125(Ti)$. (The TiO_2 (green ball) was encapsulated into the framework of $NH_2-MIL-125(Ti)$)



Fig. S5. XPS images of NH_2 -MIL-125(Ti) and LP-3, (a) O 1s and (b) Ti 2p.(The inset table corresponding to the Ti content)



Fig. S6. (a)Nitrogen adsorption-desorption isotherms of NH₂-MIL-125(Ti) and LP-3 at 77 K; (b) Pore size distribution of NH₂-MIL-125(Ti) and LP-3.



Fig. S7. Degradation of tetracycline over different photocatalysts.

	OH Cataly Visible light	st,O ₂)
Entry	Catalyst	Conversion (%)	Selectivity (%)
1	NH ₂ -MIL-125(Ti)	21.9	98.5
2	LP-3	37	99.5
a3	P25	93	8.9
^b 4	LP-3	0.42	99
^c 5	-	-	-
^d 6	Pt/NH ₂ -MIL-125(Ti)	10	98
^e 7	Pt/NH ₂ -MIL-125(Ti)	13.8	98
8	CdS	25	99
9	TiO ₂ /NH ₂ -MIL-68(In)	10	97.5
10	TiO ₂ /NH ₂ -MIL-101(Cr)	3	72

Table S2. Photocatalytic oxidation of benzyl alcohol in the presence of different catalysts.

a. Under UV light irradiation

b. In dark.

c. Without photocatalyst but under visible light irradiation.

d. Pt/NH₂-MIL-125(Ti) synthesized following reference³.

e. Pt/NH₂-MIL-125(Ti) synthesized following reference⁴.



Fig. S8. Reusability of LP-3 in the photocatalytic oxidation of methyl benzyl alcohol under visible light irradiation.

Content (ppm)
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Fig. S9. The XRD patterns of LP-3 before and after photocatalytic oxidation.



Fig. S10. The SEM images of LP-3 (a) before and (b) after photocatalytic oxidation.



Figure S11. EDS element mappings of $TiO_2@NH_2-MIL-68(In)$ (a) and $TiO_2@NH_2-MII-101(Cr)$ (e). (In (b), N (c), Ti (d) in $TiO_2@NH_2-MIL-68(In)$; Cr (f), N (g), Ti (h) in $TiO_2@NH_2-MIL-101(Cr)$).







a.

Figure S12. The original GC graphs. (a) the sample after photocatalytic reaction over LP-3, the peak inside the red circle corresponds to benzyl benzoate; (b) standard sample.

Reference

- 1. D. Sun, L. Ye and Z. Li, *Applied Catalysis B: Environmental*, 2015, **164**, 428-432.
- M. D.-Hardi, C. Serre, T. Frot, L. Rozes, G. Maurin, C. Sanchez and G. Ferey, J. Am. Chem. Soc. 2009, 131, 10857-10859
- 3. L. Shen, M. Luo, L. Huang, P. Feng and L. Wu, *Inorg Chem*, 2015, 54, 1191-1193.
- 4. Y. Horiuchi, T. Toyao, M. Saito, K. Mochizuki, M. Iwata, H. Higashimura, M. Anpo and M. Matsuoka, *The Journal of Physical Chemistry C*, 2012, **116**, 20848-20853.