Electronic Supplementary Information (ESI)

Amorphous TiO$_2$@NH$_2$-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(OC\textsubscript{4}H\textsubscript{9})\textsubscript{4}, 99.99%), tetracycline (98%), monopotassium phosphate (KH\textsubscript{2}PO\textsubscript{4}, 98%), 2-aminoterephthalic acid (H\textsubscript{2}ATA, 99%), orthophosphoric acid (H\textsubscript{3}PO\textsubscript{4}, 85% p.a.) are supplied by Alfa Aesar. Benzyl alcohol (C\textsubscript{7}H\textsubscript{8}O, > 98%), benzaldehyde (C\textsubscript{7}H\textsubscript{6}O, > 98%), benzotrifluoride (BTF, 99%) are purchased from Aladdin. Ethanol (EtOH) and N, N-dimethylformamide (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\textalpha\textsubscript{1} radiation (\lambda=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 BaSO\textsubscript{4} 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 NH\textsubscript{2}-MIL-125(Ti)

According to a typical solvothermal method\textsuperscript{1}, H\textsubscript{2}ATA (2.7g, 15 mmol) and Ti(OC\textsubscript{4}H\textsubscript{9})\textsubscript{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 TiO\textsubscript{2}@NH\textsubscript{2}-MIL-125(Ti) (denoted as LP-3)

Amorphous TiO\textsubscript{2}@NH\textsubscript{2}-MIL-125(Ti) composite was synthesized through a facile method. Typically, the as-synthesized NH\textsubscript{2}-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 NH\textsubscript{2}-MIL-125(Ti) was dispersed at 40 mL MeOH in a flask under ultrasound for 20min, subsequently, 500 µL 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 TiO\textsubscript{2} 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 µL) was chosen based on our experimental experience by investigating different amount of Ti: 200 µL, 400 µL, 500 µL, 600 µL, 1000 µL (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 TiO\textsubscript{2}/NH\textsubscript{2}-MIL-125(Ti)

Amorphous TiO\textsubscript{2}@NH\textsubscript{2}-MIL-125(Ti) composite was synthesized through a similar method for LP-3.
Typically, 500 µL 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 NH$_2$-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 TiO$_2$@NH$_2$-MIL-68(In) and TiO$_2$@NH$_2$-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/cm$^2$ 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 KH$_2$PO$_4$ 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 chosen 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 O$_2$, 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 Na$_2$SO$_4$ 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, and an atom-based
representation for the summation of the van der Waals 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 NH$_2$-MIL-125(Ti)$^2$, which
indicated that the Tetra-n-butyl titanate could diffuse into the framework of NH$_2$-MIL-125(Ti).
Table S1. Photocatalytic oxidation of benzyl alcohol in the presence of different catalysts.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NH$_2$-MIL-125(Ti)</td>
<td>21.9</td>
<td>98.5</td>
</tr>
<tr>
<td>2</td>
<td>LP-1</td>
<td>25</td>
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<tr>
<td>3</td>
<td>LP-2</td>
<td>30</td>
<td>99</td>
</tr>
<tr>
<td>4</td>
<td>LP-3</td>
<td>37</td>
<td>99</td>
</tr>
<tr>
<td>5</td>
<td>LP-4</td>
<td>15</td>
<td>98</td>
</tr>
<tr>
<td>6</td>
<td>LP-5</td>
<td>5</td>
<td>94.3</td>
</tr>
</tbody>
</table>

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 NH$_2$-MIL-125(Ti) (a) and LP-3 (b); TEM image of TiO$_2$/NH$_2$-MIL-125(Ti) (c); XRD image of TiO$_2$/NH$_2$-MIL-125(Ti) and NH$_2$-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 \( \text{NH}_2\text{-MIL-125(Ti)} \) and LP-3 at 77 K; (b) Pore size distribution of \( \text{NH}_2\text{-MIL-125(Ti)} \) and LP-3.
Fig. S7. Degradation of tetracycline over different photocatalysts.
<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
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<tr>
<td>1</td>
<td>NH₂-MIL-125(Ti)</td>
<td>21.9</td>
<td>98.5</td>
</tr>
<tr>
<td>2</td>
<td>LP-3</td>
<td>37</td>
<td>99.5</td>
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<tr>
<td>a³</td>
<td>P25</td>
<td>93</td>
<td>8.9</td>
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<td>b⁴</td>
<td>LP-3</td>
<td>0.42</td>
<td>99</td>
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<tr>
<td>c⁵</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>d⁶</td>
<td>Pt/NH₂-MIL-125(Ti)</td>
<td>10</td>
<td>98</td>
</tr>
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<td>e⁷</td>
<td>Pt/NH₂-MIL-125(Ti)</td>
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<td>98</td>
</tr>
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<td>8</td>
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<td>9</td>
<td>TiO₂/NH₂-MIL-68(In)</td>
<td>10</td>
<td>97.5</td>
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<tr>
<td>10</td>
<td>TiO₂/NH₂-MIL-101(Cr)</td>
<td>3</td>
<td>72</td>
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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.

Table S3. The content of Ti in the reaction solution

<table>
<thead>
<tr>
<th>Element</th>
<th>Content (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>-</td>
</tr>
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</table>
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$_2$-MIL-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)).
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