## **Electronic Supplementary Information**

# Facet-dependent photocatalytic hydrogen production of metal-organic

### framework NH<sub>2</sub>-MIL-125(Ti)

Fan Guo, Jin-Han Guo, Peng Wang, Yan-Shang Kang, Yi Liu, Jing Zhao\* and Wei-Yin Sun\* Coordination Chemistry Institute, State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing National Laboratory of Microstructures, Collaborative Innovation Center of Advanced Microstructures, Nanjing University, Nanjing 210023, China

#### **Experimental section**

**Materials and syntheses.** All commercial available chemicals were purchased and used without further purification. In a typical experiment, 2-amino-1,4-benzenedicarboxylic acid (H<sub>2</sub>bdc-NH<sub>2</sub>) (0.21 g, 1.16 mmol) and cetyltrimethylammonium bromide (CTAB) were dissolved in 10 mL of 7:3 (v/v) mixture of methanol (CH<sub>3</sub>OH) and N,N-dimethylformamide (DMF). Then tetra-*n*-butyl titanate [Ti(OC<sub>4</sub>H<sub>9</sub>)<sub>4</sub>] (0.225 mL, 0.75 mmol) was added and the reaction mixture was sonicated for an additional 5 min at room temperature. The above solution was then transferred to a 30 mL Teflonlined bomb reactor and kept in an oven at 150 °C for 8 h. The resulted yellow powder was isolated by centrifugation, washed with DMF and methanol for 3 times, respectively, and dried under vacuum for 5 h at 80 °C. During the syntheses, the employed CTAB aqueous solution was at concentrations of 0, 1 mM, 2 mM, 3 mM and 4 mM, respectively, while other conditions remain unchanged.

Structural characterization. Powder X-ray diffraction (PXRD) data were collected on a Bruker D8 Advance X-ray diffractometer with Cu-K $\alpha$  ( $\lambda$  = 1.5418 Å) radiation. Scanning electron microscopy (SEM) measurements were performed on a Hitachi S-4800 field emission scanning electron microscope at an accelerating voltage of 5 kV. SEM-EDS elemental mapping images were measured on JEOL JSM-7800F. Transmission electron microscopy (TEM) images were obtained on JEOL-2100F TEM instrument with an operating voltage of 100 kV. Thermogravimetric analyses (TGA) were performed by means of TGA-DSC1 thermal analyzer (Mettler-Toledo Instrumentation) in the temperature range of 30 – 800 °C under a nitrogen atmosphere with a heating rate of 10 °C min<sup>-1</sup>. Fourier transform Infrared (FT-IR) spectra were recorded using KBr discs in the range of 400 - 4000 cm<sup>-1</sup> on a Bruker Vector 22 FT-IR spectrophotometer. UV-visible diffuse reflectance spectra of the powder samples were measured on a UV3600 Scan Spectrophotometer at room temperature using white standard of BaSO<sub>4</sub> as a reference to exclude the background. Photoluminescence spectra were measured on an Aminco Bowman Series 2 spectrofluorometer with a xenon arc lamp as light source. Nitrogen (N<sub>2</sub>) and carbon dioxide (CO<sub>2</sub>) sorption experiments were carried out on a Belsorp-max volumetric gas sorption instrument. Prior to the measurement of N<sub>2</sub> and CO<sub>2</sub> sorption, the samples were activated under vacuum at 180  $\,^{\circ}$ C for about 5 h. X-ray photoelectron spectroscopy (XPS) was performed on UIVAC-PHI 5000 VersaProbe using monochromatized Al Ka at hv = 1486.6 eV. The C 1s peak was used as the reference peak.

**Photoelectrochemical measurements.** To prepare the photoelectrodes, the as-synthesized sample (1 mg) was dispersed into 1 mL MeOH and 10  $\mu$ L Nafion under ultrasound. Then above solution was added to the surface of indium-tin oxide (ITO) substrate with an exposed area of 1.0 x 1.0 cm<sup>2</sup> drop by drop and dried at 50 °C. The characterizations were performed in a standard three-electrode setup with the photocatalyst-cotaed ITO as the working electrode, Ag/AgCl as the reference electrode and platinum plate as the counter electrode. A 0.1 M Na<sub>2</sub>SO<sub>4</sub> was used as the electrolyte. The electrochemical impedance spectroscopy was performed on the Zahner Zennium electrochemical workstation in a standard three-electrode system with a bias potential of -0.3 V and a frequency range from 10<sup>-2</sup> to 10<sup>5</sup> Hz in nitrogen atmosphere. Photocurrent measurements were performed on a CHI 730E electrochemical work station (Chenhua Instrument, Shanghai) under a 300 W xenon lamp (Zolix) equipped with a 400 nm UV cutoff filter. The reference electrode was an aqueous SCE electrode and the photo-responsive signals of the samples were measured under chopped light at 0.5 V.

**Photocatalytic hydrogen production reaction.** Photocatalyst (20.0 mg) was added to a Pyrex reaction vessel (Aulight) containing a mixture of triethanolamine (TEOA, 1.5 mL), deionized water (1 mL) and acetonitrile (CH<sub>3</sub>CN, 27.5 mL). After that, the obtained solution was thoroughly degassed by a vacuum pump for approximately 20 min during stirring to ensure the system was under anoxic environment. The sample was in visible light illumination with a 300 W xenon lamp (Zolix) equipped with a 400 nm UV cutoff filter. The total

irradiation time for the photocatalytic  $H_2$  production experiment was 30 h and every 10 h the reaction system was evacuated by the vacuum pump. The procreant gas samples were analyzed by a gas chromatography (Lu Chuang GC-9860, N<sub>2</sub> carrier, TCD detector) equipped with a 1m TDX-01 column and were quantified by a calibration plot to the internal hydrogen standard.

**Apparent quantum yield test.** The apparent quantum yield (AQY) for  $H_2$  evolution was determined under 420 nm LED (Merry Change LED 100C) monochromatic irradiation, while other procedure was consistent with the photocatalytic hydrogen production reaction. The irradiation area was controlled with a radius of 2.5 cm. The total intensity of incident light irradiation was measured as 16.00 mW/cm<sup>2</sup> for 420 nm (the irradiation intensity was determined by CEAULIGHT CEL-NP200 spectroradiometer). The AQY was calculated as follow:

$$AQY = \frac{N_e}{N_p} \times 100\% = \frac{2 \times M \times N_A \times h \times c}{S \times P \times t \times \lambda} \times 100\%$$

Where,  $N_p$  is the total incident photons,  $N_e$  is the total reactive electrons, M is the amount of H<sub>2</sub> molecules,  $N_A$  is Avogadro constant, h is the Planck constant, c is the speed of light, S is the irradiation area, P is the intensity of irradiation light, t is the photoreaction time,  $\lambda$  is the wavelength of the monochromatic light.

**EPR measurements.**  $NH_2$ -MIL-125(Ti) added to mixture containing deionized water, TEOA and  $CH_3CN$ , then transferred above suspension 50-60 µL to the EPR resonator, and degassed by several freeze-pump-thaw procedures and sealed. The same Xe lamp was used in this measurement at room temperature. The solution EPR spectra were obtained using a Bruker EMX plus-6/1 variable temperature X-band apparatus at 110 K and simulated with the software of WINEPR SimFonia.

**Computational methods.** The calculations of the  $NH_2$ -MIL-125(Ti) surface structure were based on DFT, as implemented in the Vienna ab initio simulation (VASP) code. The

exchange-correlation energy was represented by the generalized-gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE). The Ti 3p<sup>6</sup>3d<sup>2</sup>4s<sup>2</sup>, O 2s<sup>2</sup>2p<sup>4</sup>, N 2s<sup>2</sup>sp<sup>4</sup>, C 2s<sup>2</sup>2p<sup>2</sup> and H 1s<sup>1</sup> are treated as valence electrons. The energy cutoff for the plane-wave basis set was 500 eV. The fully optimized crystal parameters for bulk MOF NH<sub>2</sub>-MIL-125(Ti) were 19.09Å, 19.07Å, 18.14Å, 90°, 90.06° and 90.08°, which were in good agreement with the experimental values. A  $2 \times 2 \times 2$  Monkhorst k-point mesh was used for the Brillouin-zone integrations of the unit cell. For each surface, the supercells, which were constructed from the relaxed unit cell of MOF, were periodically repeated along the surface normal and separated by vacuum layers. The constructed slabs with a vacuum thickness of  $\sim 15$  Å can sufficiently suppress the interaction between adjacent slabs. All atoms in the slabs were relaxed until the residual force was less than 0.01 eV/Å. The geometries of the reduced surfaces were fully relaxed. To minimize the effect of size, all the microcrystals were prepared with a similar size in the range of 1 µm for edge lengths or diameters. Their corresponding activities were then measured by using the same setup and under essentially identical conditions to minimize any possible variations. The schematic view of creating as-cut surfaces are shown in Fig. S2. It should be noted that the ligand exchange energies ( $\Delta E_{exchange}$ ) could be obtained by the model reaction replacing H<sub>2</sub>bdc-NH<sub>2</sub> by HOAc.

$$\text{Ti}_8\text{O}_8(\text{OH})_4(\text{H}_2\text{bdc-NH}_2)_{12} + \text{HOAc} \longrightarrow \text{Ti}_8\text{O}_8(\text{OH})_4(\text{H}_2\text{bdc-NH}_2)_{11}(\text{OAc}) + \text{H}_2\text{bdc-NH}_2$$

For all the surfaces, the general principle is that the least number of bonds have to be broken, therefore, the number of terminal acetate groups other than  $bdc^{2}-NH_2$  needed to saturate the surface is the smallest.

$$E_{mol} = E_{OAc-} + \Delta E_{exchange}$$

**Judgement of crystal facets for NH2-MIL-125(Ti).** The exposed surface of the nanoplates shown in Fig. 2a and 2b is attributed to the {001} facet,<sup>[1]</sup> and the outside surface of the octahedron exhibited in Fig. 2e is assigned to the {111} facets as reported previously.<sup>[2,3]</sup> The

two corners along with the *c* axis of the octahedron were cut away to generate tetragon-like plate with eight {111} and two {001} facets, in which the four corners of the tetragon were further cut away to give the truncated tetragon-like plate morphology with appearance of eight {110} facets as illustrated in Fig. 2c. The angle between the {001} and {111} facets observed in the SEM image (Fig. 2c) is 123 °, which is in agreement with the calculated angle of 126 °. The truncated octahedron morphology shown in Fig. 2d was achieved by cutting off the six corners of the octahedron to produce two {001}, four {100} and eight {111} facets.<sup>[4,5]</sup> The observed angles in the SEM image (Fig. 2d) are 120 ° (between the {100} and {111} facets) and 126 ° (between the {001} and {111} facets), which are in agreement with the corresponding calculated angles of 124 ° and 126 °.



Fig. S1 Surface structures of the  $\{001\}$ ,  $\{110\}$ ,  $\{110\}$  and  $\{111\}$  facets for NH<sub>2</sub>-MIL-125(Ti).



Fig. S2 Schematic view of the creating as-cut surfaces for {001}, {110}, {100} and {111} facets.



Fig. S3 SEM-EDS elemental mapping images of the samples, showing the distribution of Ti (red). The deepest red color in T110 illustrates that the surface contains the most Ti.



Fig. S4 PXRD patterns of  $NH_2$ -MIL-125(Ti) obtained under different concentrations of CTAB: (a) 0, (b) 1 mM, (c) 2 mM, (d) 3 mM and (e) 4 mM, respectively.



Fig. S5 FT-IR spectra of NH<sub>2</sub>-MIL-125(Ti) obtained under different concentrations of CTAB: (a) 0, (b) 1 mM, (c) 2 mM, (d) 3 mM and (e) 4 mM.



Fig. S6 XPS spectra of as-synthesized NH<sub>2</sub>-MIL-125 obtained under different concentrations of CTAB: (a) 0, (b) 1 mM, (c) 2 mM, (d) 3 mM and (e) 4 mM.



Fig. S7 TG curves of (a) disk-like plates, (b) rounded rectangle-like plates, (c) truncated tetragonal-like plates, (d) truncated octahedrons and (e) octahedrons structures under a nitrogen atmosphere.



Fig. S8 Nitrogen adsorption and desorption isotherms (at 77 K) of NH<sub>2</sub>-MIL-125(Ti) prepared with different concentrations of CTAB: (a) 0, (b) 1 mM, (c) 2 mM, (d) 3 mM and (e) 4 mM. BET surface areas calculated from the N<sub>2</sub> adsorption isotherms display these samples have approximate specific surface areas of 1398.1 m<sup>2</sup>/g, 1274.5 m<sup>2</sup>/g, 1256.3 m<sup>2</sup>/g, 946.5 m<sup>2</sup>/g, and 880.1 m<sup>2</sup>/g, respectively.



Fig. S9 CO<sub>2</sub> adsorption of (a) T001-1, (b) T001-2, (c) T110, (d) T100 and (e) T111 at 273 K.



Fig. S10 SEM image of T110 after 30 h recycling experiments.



Fig. S11 PXRD patterns of T110 before (a) and after (b) 30 h recycling experiments.



Fig. S12 EPR spectra of NH<sub>2</sub>-MIL-125(Ti) T110 in the dark and upon irradiation. No EPR signal was detected in the dark, after illumination under visible light for 10 minutes, an obvious signal centered at 1.926 was observed, which is attributed to the paramagnetic  $Ti^{3+}$  generated by LMCT, and the diminutive downfield feature at g = 2.003 (inset) was associated with the TEOA free radicals.<sup>[6]</sup>



Fig. S13 Mass spectrum of the finally formed gases composed of  $H_2$ , HD, and  $D_2$ . The air was removed by bubbling with pure  $N_2$  before measurements.



Fig. S14 Hydrogen production rate of (a) T001-1, (b) T001-2, (c) T110, (d) T100 and (e) T111.

Table S1. Average percentages of  $\{001\}$ ,  $\{110\}$ ,  $\{100\}$  and  $\{111\}$  facets (%) in T110, T100, and T111

Sample	{001}	{110}	{100}	{111}
T110	52.85	4.69		42.46
T100	11.92		10.26	77.82
T111				100

Table S2. Atomic concentrations (%) of C 1s, N 1s, O 1s, and Ti 2p in T001-1, T001-2,

T110, T100 and T111	determined by XPS
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Sample	C 1s	N 1s	O 1s	Ti 2p
T001-1	67.93	4.51	24.25	3.31
T001-2	67.56	4.63	24.33	3.48
T110	66.17	4.47	25.47	3.90
T100	67.17	4.71	24.57	3.56
T111	69.11	4.68	23.07	3.15

Adsobent	Amine Type	CO <sub>2</sub> Adsorption	References
		Capacity (mg/g)	
MIL-125	/	98	[7]
NH <sub>2</sub> -MIL-125(Ti)(T	H <sub>2</sub> bdc-NH <sub>2</sub>	241	This work
001-1)			
NH <sub>2</sub> -MIL-101(Fe)	H <sub>2</sub> bdc-NH <sub>2</sub>	67	[8]
DETA-MIL-101(Cr)	Diethylenetriamine	79	[9]
NH <sub>2</sub> -Zr-MOF	H <sub>2</sub> bdc-NH <sub>2</sub>	196	[10]
$Zn_2(Atz)_2(ox)$	3-Amino-1,2,4-triazole	189	[11]
ZIF-1	5-Aminotetrazole	246	[12]

Table S3. Comparison of  $CO_2$  adsorption by amine-functionalized MOFs at 273 K

Catalyst	Light source	Sacrificial agent	Hydrogen evolution	References
	(nm)		rate (µmol/g•h)	
NH <sub>2</sub> -MIL-125(Ti)	>380	TEOA	17	[13]
NH <sub>2</sub> -MIL-125(Ti)	>420	TEOA	0	[14]
RuN <sub>3</sub> /ZIF-67	>405	TEOA	4.85	[15]
CdS/MCM-41	>420	TEOA	55.5	[16]
NH <sub>2</sub> -UiO-66(Zr)	>420	Na <sub>2</sub> S	0	[17]
Pt/NH <sub>2</sub> -UiO-66(Zr)	>380	TEOA	50.26	[18]
NH <sub>2</sub> -MIL-125(Ti)(T110)	>400	TEOA	60.8	This work

 Table S4. Summary of recent reports on MOF-based photocatalysts

Semiconductor	Co-catalyst	Light source (nm)	AQY (%)	References
BiYWO <sub>6</sub>	0.5 wt% RuO <sub>2</sub>	420	0.17	[19]
$C_3N_4$	3 wt% Pt-1 wt% $CoO_x$	405	0.3	[20]
BiVO <sub>4</sub> :In,Mo	3 wt% RuO <sub>2</sub>	420-800	3.2	[21]
0.4 wt%Pt/SrTiO <sub>3</sub> :Cr,Ta	1 wt% PtO <sub>x</sub> /WO <sub>3</sub>	420	0.1	[22]
1 wt% Ru/SrTiO <sub>3</sub> :Rh	BiVO <sub>4</sub>	420	4.2	[23]
$0.5 \text{ wt\% Pt/H}_4\text{Nb}_6\text{O}_{17}$	$0.5 \text{ wt\% IrO}_2\text{-}0.5 \text{ wt\%}$	480	0.05	[24]
	PtO <sub>x</sub> /WO <sub>3</sub>			
NH <sub>2</sub> -MIL-125(Ti)(T110)	_	420	3.60	This work

Table S5. Summary of AQY on semiconductor-based photocatalysts

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