

## Supporting Information

for

### **Structure Determines Performance: Isomeric Ti-MOFs for Photocatalytic Synthesis of Hydrogen Peroxide**

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## 1. Experimental

**Materials** 2-aminoterephthalic acid (H<sub>2</sub>ATA) and Tetra-n-butyltitanate Ti(OC<sub>4</sub>H<sub>9</sub>)<sub>4</sub> were purchased from Macklin. ZrCl<sub>4</sub> and TiCl<sub>4</sub> were purchased from Aladdin Co. Anhydrous N,N-dimethylformamide (DMF), methanol (MeOH), hexane, Anhydrous tetrahydrofuran (THF) and anhydrous dichloroethane purchased from Shanghai Chemical Reagent Co. All the reagents were used as received without further purification.

### 1.1 Synthesis of NH<sub>2</sub>-UiO-66(Zr)

NH<sub>2</sub>-UiO-66(Zr) was prepared following a previous reported procedure with slight modifications. ZrCl<sub>4</sub> (0.052 g, 0.22 mmol) and 2-aminoterephthalic acid (H<sub>2</sub>ATA) (0.04 g, 0.22 mmol) were dissolved in anhydrous N,N-dimethylformamide (DMF) (10 ml) at room temperature. The thus-obtained mixture was stirred at room temperature for 10 minutes and was transferred to a 25 ml Teflon lined stainless steel autoclave flask at 120°C for 24 hours. After hydrothermal treatment, the resultant suspension was washed with DMF and methanol respectively, extracted by Soxhlet extractor with methanol and vacuum dried to obtain the product.

### 1.2 Synthesis of NH<sub>2</sub>-MIL-125(Ti)

NH<sub>2</sub>-MIL-125(Ti) was synthesized according to a reported method. First, H<sub>2</sub>ATA acid (0.54 g, 3 mmol) and Ti(OC<sub>4</sub>H<sub>9</sub>)<sub>4</sub> (0.26 mL, 0.75 mmol) were added to a solution of N,N-dimethylformamide (9 ml) and methanol (1 ml). The mixture was stirred at ambient temperature for 30 min, transferred to 25 ml Teflon lined stainless steel autoclave, and heated for 24 h at 150 °C. After the reaction, the product of the synthesis was collected by centrifugation and washed with DMF followed by methanol to remove unreacted organic linkers. The obtained yellow solid was dried under vacuum overnight.

### 1.3 Synthesis of NH<sub>2</sub>-MIL-125-D

H<sub>2</sub>ATA (0.145 g, 0.8 mmol) and Ti(OC<sub>4</sub>H<sub>9</sub>)<sub>4</sub> (0.136 g, 0.4 mmol) were added into a solution containing DMF (9 mL) and dry MeOH (1 mL) and stirred for 30 min

at room temperature. The prepared solution was then transferred to a 20 ml high-temperature-resistant glass flask at 153 °C for 24 hours. Once the synthesis was completed, the resultant suspension was filtered, washed with DMF and MeOH separately, extracted by Soxhlet extractor with MeOH, and finally dried to obtain a bright-yellow solid product.

#### **1.4 Synthesis of NH<sub>2</sub>-UiO-66(Ti)**

The post-synthetic exchange of NH<sub>2</sub>-UiO-66(Ti) was carried out according to the previous reported procedure with some modifications. NH<sub>2</sub>-UiO-66(Zr) (0.28 g) was dispersed in anhydrous DMF (7 ml). TiCl<sub>4</sub>(THF)<sub>2</sub> (0.34 g) was added to the above suspension under inner condition. The mixture was incubated at 120 °C for 16 days. The solids were separated from the solvent via centrifugation, and washed with fresh DMF and methanol. The solids were dried at 40 °C in a vacuum for 24 hours to get NH<sub>2</sub>-UiO-66(Ti).

#### **1.5 Synthesis of TiCl<sub>4</sub>(THF)<sub>2</sub>**

TiCl<sub>4</sub>(THF)<sub>2</sub> was synthesized according to the previous reported procedure with slight modifications. TiCl<sub>4</sub> (2.9 ml, 26.4 mmol) was dissolved in anhydrous dichloroethane (50 ml) in a 250 mL round-bottomed flask under inert conditions. Anhydrous tetrahydrofuran (THF) (8.6 ml, 105.8 mmol) was added to the above solution at 0 °C to form a yellow solution. Anhydrous n-hexane (100 ml) was used to precipitate yellow powder. The resultant powder was washed twice with n-hexane (50 mL) and dried for 3 hours over a Schlenk line. The resulted yellow TiCl<sub>4</sub>(THF)<sub>2</sub> was used immediately for post-synthetic exchange.

#### **1.5 Characterization**

The morphology and microstructure were studied by field emission scanning electron microscopy (FE-SEM, JEOL JSM-7001F). The UV-visible absorption spectrum (UV-vis) was measured using a Shimadzu UV-2600 spectrometer, and BaSO<sub>4</sub> was selected as the reference sample. The phase and chemical composition were investigated by X-ray photoelectron spectroscopy (XPS, Perkin-Elmer PHI 5000C), X-ray diffraction (XRD, D/MAX2500PC) with Cu K $\alpha$  ( $\lambda=1.5406$  Å) at 40

kV and 150 mA, and Fourier transform infrared spectroscopy (FT-IR, Nicolet iS50). Nitrogen sorption/desorption curves were obtained using Quantachrome NOVA 3000e. Furthermore, to evaluate the optical and electrochemical performance, we used photoluminescence (PL, FLS 980), an electrochemical workstation (CHI-760E) with a three-electrode system.

## 1.6 Photocatalytic Preparation of Hydrogen Peroxide

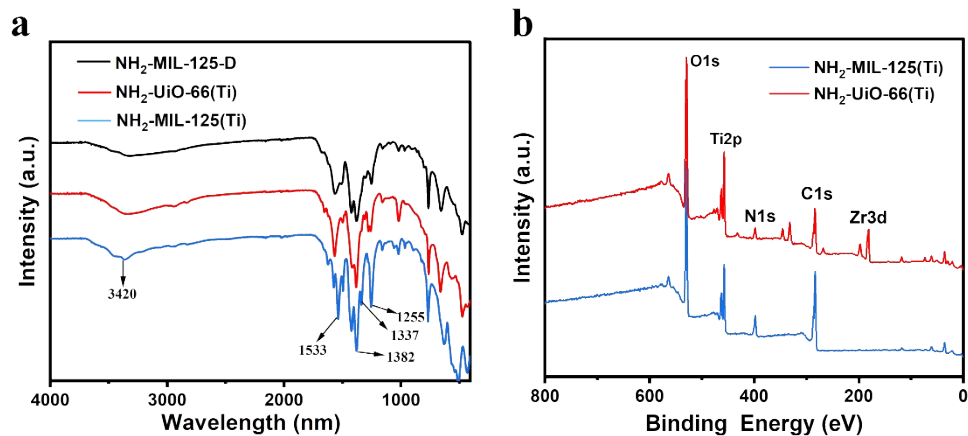
To measure the photocatalytic activity, 50 mL of pure water in the presence of 15 mg of catalyst was placed in a typical photocatalytic quartz reactor. Oxygen was passed in the dark and stirred for 15 min to ensure dissolved oxygen equilibrium. A 300 W Xe lamp ( $\lambda \geq 420$  nm) was used as a visible light source. Magnetic stirring at ambient pressure and temperature and aliquots of the reaction solution were collected and analysed.

## 1.7 Detection of Hydrogen Peroxide

$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  (0.278 g, 1 mmol) was added into 20 ml water to form Ferrous sulphate solution. DPD (N,N-diethyl-phenylenediamine sulfate) (0.5247 g, 2 mmol) was added to 50 ml of 0.05 mol/L sulphuric acid solution to be used as a colour developer. Remove 0.8 ml of reaction solution from the reactor, drop into a solution containing 6 ml of water, 0.6 ml of DPD and 0.6 ml of ferrous sulphate, develop the colour for 5 min and then measure the absorbance at 551 nm (Fig. S4) to determine the concentration of  $\text{H}_2\text{O}_2$  against the standard curve (Fig. S5).

## 2. Author Contributions

Prof. H.T. and H.B.H. designed the project and wrote the manuscript; Y.Z.Z. carried out most of the synthesis and characterization experiments in this work; Y.Z.Z. assisted the synthesis of materials; T.Q.Z and Z.L. conducted the electron microscope studies.



**Fig. S1** (a). FT-IR spectra of NH<sub>2</sub>-MIL-125-D, NH<sub>2</sub>-UiO-66(Ti) and NH<sub>2</sub>-MIL-125(Ti). (b). XPS survey spectra.

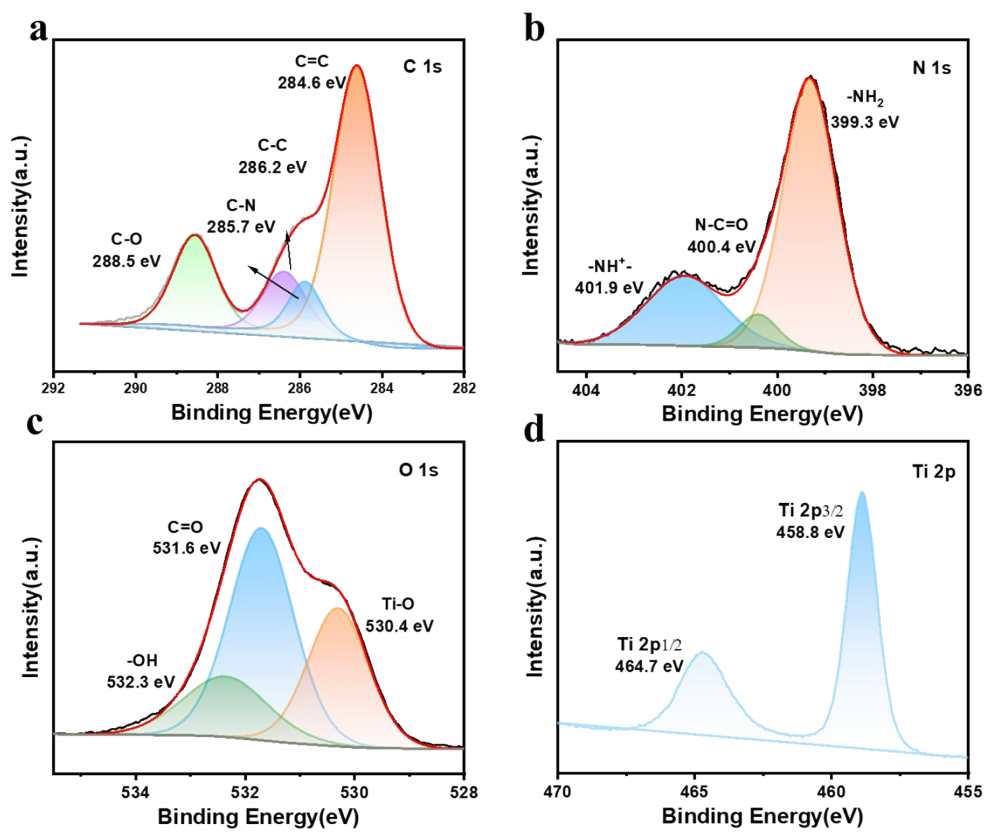
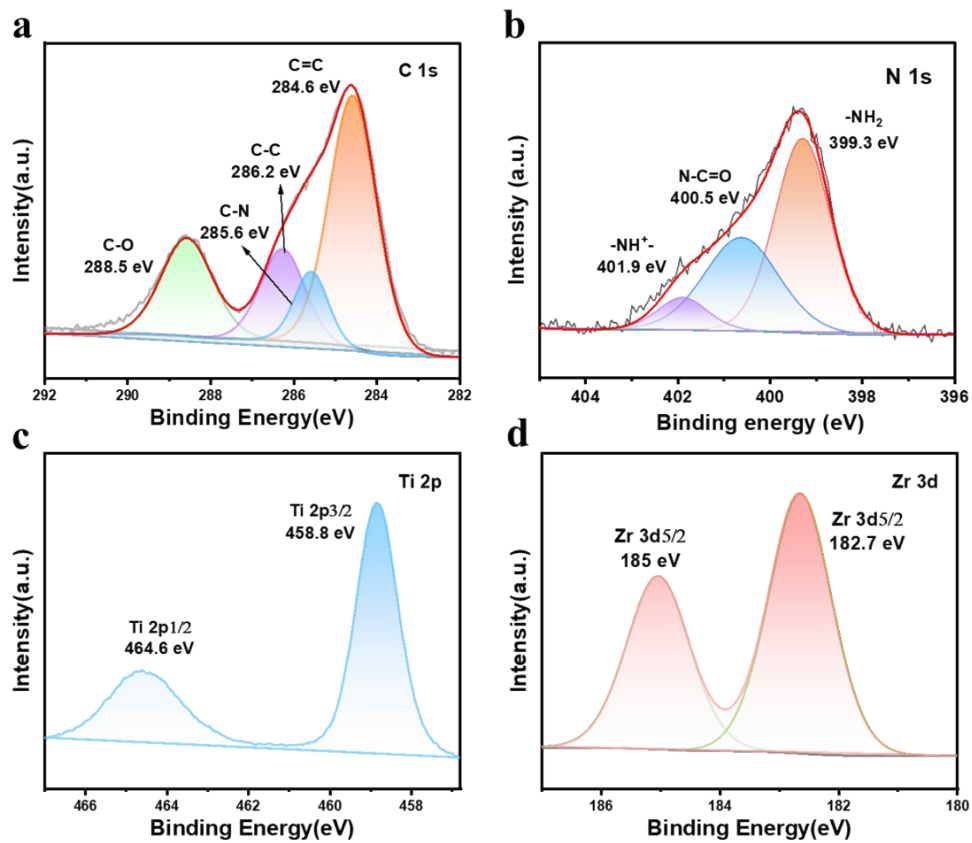
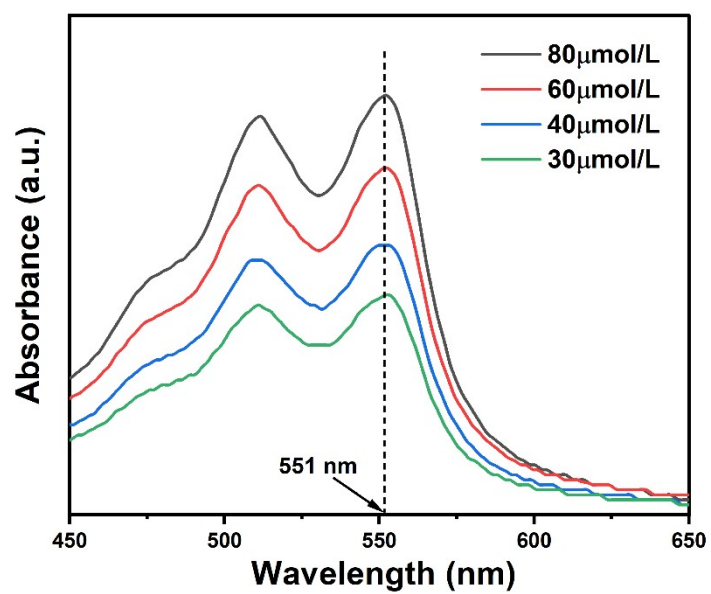


Fig. S2 XPS spectra of the NH<sub>2</sub>-MIL-125(Ti).

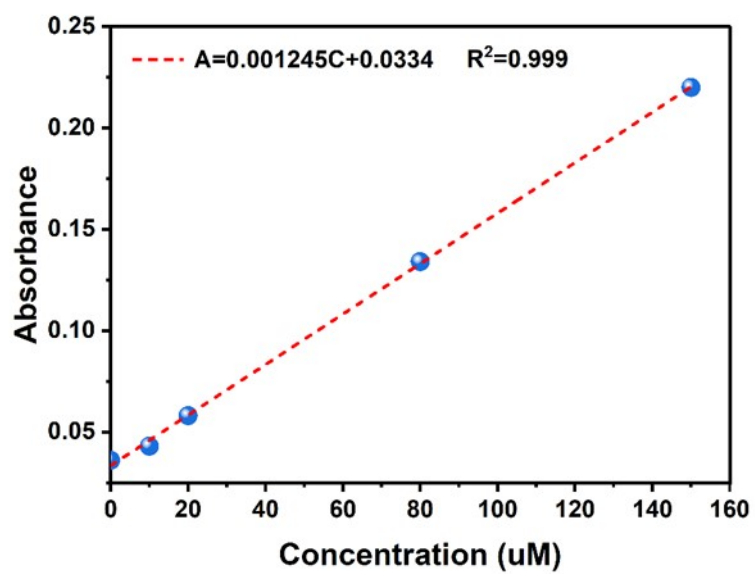


**Fig. S3** XPS spectra of the NH<sub>2</sub>-UiO-66(Ti).

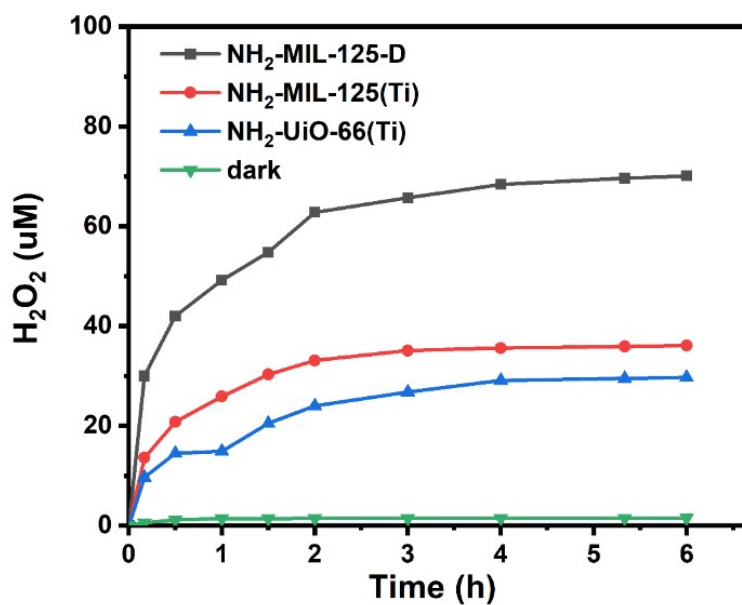


**Fig. S4** The UV absorption diagrams of photocatalytic production of  $\text{H}_2\text{O}_2$  for four selected samples.

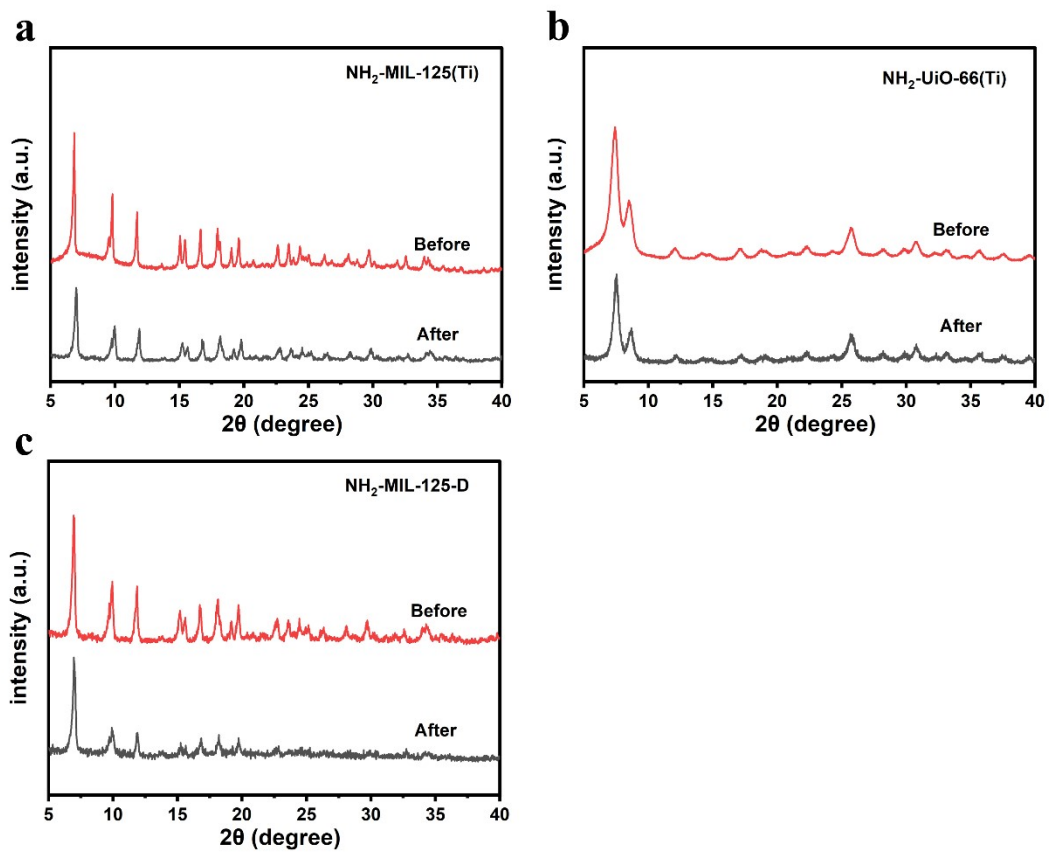




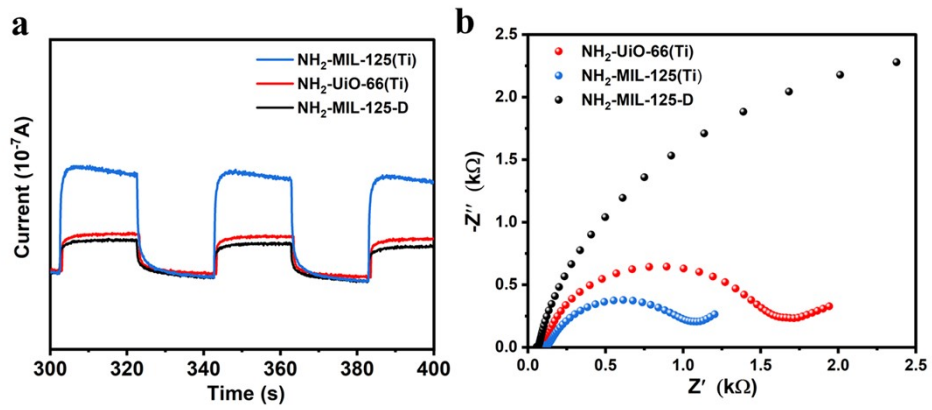
**Fig. S5** Standard calibration curves for quantitation of H<sub>2</sub>O<sub>2</sub> at 551 nm.



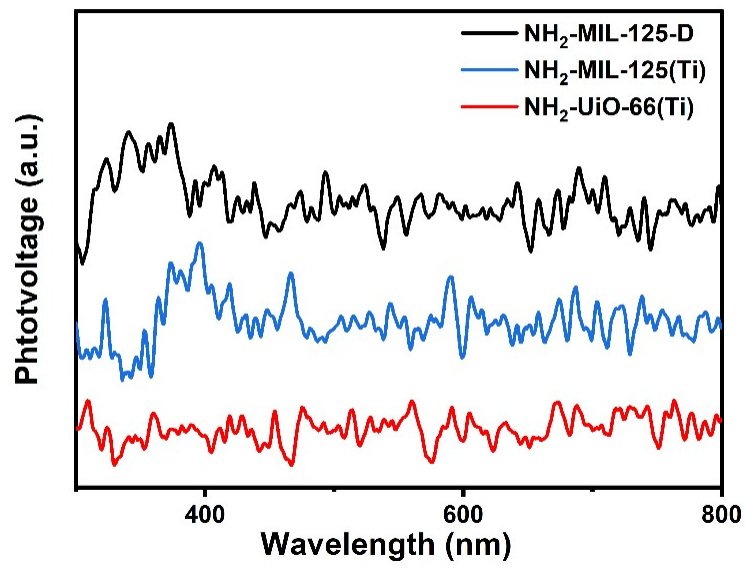
**Fig. S6** Time courses of H<sub>2</sub>O<sub>2</sub> production under photoirradiation ( $\lambda \geq 420$  nm) of a pure water system composed by 15.0 mg catalysts.



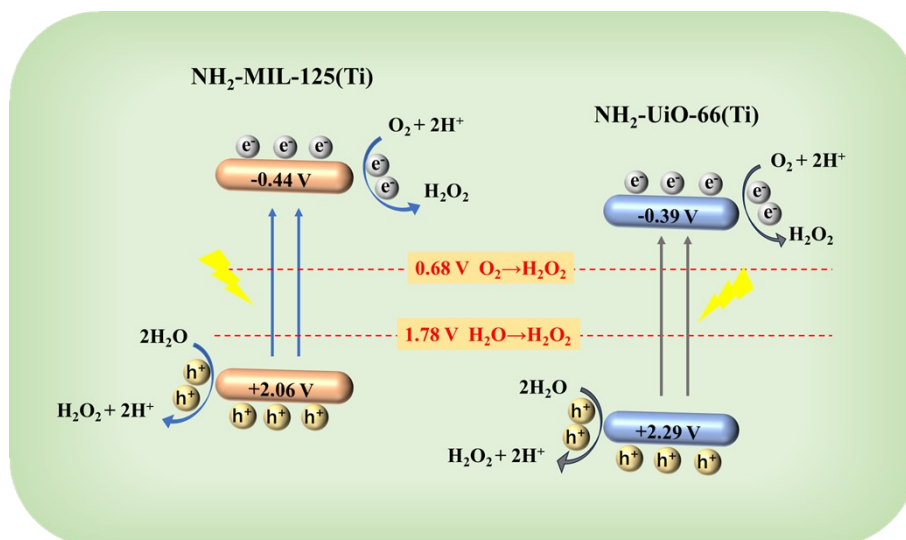
**Fig. S7** The XRD pattern of (a) NH<sub>2</sub>-MIL-125(Ti), (b) NH<sub>2</sub>-UiO-66(Ti), (c) NH<sub>2</sub>-MIL-125-D after the reaction.



**Fig. S8** (a) Photocurrent response curves (i-t). (b) EIS Nyquist plots.



**Fig. S9** The SPV spectra of the NH<sub>2</sub>-UiO-66(Ti), NH<sub>2</sub>-MIL-125(Ti) and NH<sub>2</sub>-MIL-125-D.



**Scheme 1.** The mechanisms of photocatalytic  $\text{H}_2\text{O}_2$  production.

Table 1. Comparison with published works

Entry	Photocatalyst	H <sub>2</sub> O <sub>2</sub> production ( $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ )	Irradiation condition	Solvent system	Ref.
1	Pd/A/BiVO <sub>4</sub>	805.9	>420	water	1
2	RF523	50	>420	water	2
3	CdS@ZnInS	604.8	>420	water	3
4	g-C <sub>3</sub> N <sub>4</sub> /PDI	24.1	>420	water	4
5	CTF-BDDBN	4.9	>420	water	5
6	ZIF-8/C <sub>3</sub> N <sub>4</sub>	2641	>420	water	6
7	MIL-111/001	917	>420	water	7
8	Cd <sub>0.5</sub> Zn <sub>0.5</sub> S	151.6	>420	water	8
9	NH <sub>2</sub> -MIL-125-D	101	>420	water	This work

## References

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