Supplementary Information (SI) for CrystEngComm.

Supporting Information

Defect engineering of MIL-125-NH_2 nanocrystalline enables piezoelectric–photocatalytic overall water splitting

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1. Chemicals:

Tetrabutyl titanate ($C_{16}H_{36}O_4Ti$, Shanghai Macklin Biochemical Co., Ltd.), Cobalt chloride hexahydrate ($CoCl_2 \cdot 6H_2O$), Sodium borohydride ($NaBH_4$), terephthalic acid ($C_8H_6O_4$), 2-Amino benzoic acid ($C_8H_7NO_4$) were obtained from Shanghai Aladdin Biochemical Technology Co., Ltd. N, N-Dimethylformamide (C_3H_7NO) and methyl alcohol (CH_4O) were supplied by Tianjin Fuyu Fine Chemical Co., Ltd.

2. Sample preparation.

MIL-125-NH_2 was prepared by a simple solvothermal method. 0.52 ml of tetraisobutyl titanate and 1.08 g of PTA were added to a beaker. 24.3 ml of DMF and 2.7 ml of methanol were thoroughly mixed and labeled as solution A. Solution A was slowly added to the aforementioned beaker. The mixture was dispersed uniformly using an ultrasonic cleaner and stirred at room temperature for 30 minutes before being transferred to a reaction vessel. The reaction was carried out at 150°C for 24 hours in a drying oven and then cooled. Finally, the sample was washed twice with DMF and methanol, dried in a 60 ℃ drying oven, and collected. The resulting product was MIL-125-NH_2.

$MIL-125-NH_2$ was dispersed in 10 mL of deionized water, and then transferred to an ultrasonic cleaning machine for ultrasonic treatment for 30 minutes. Subsequently, NaBH4 was rapidly added to the $MIL-125-NH_2$ solution and vigorously stirred. Finally, D-MIL-125-NH_2 was obtained. The samples were named DTX, where X represents the amount of borohydride sodium added, with X = 0.5, 1, 2, 5, and 10.

3. Characterization.

The powder X-ray diffraction (XRD) patterns were recorded on a D/max 2500 VL/PC diffractometer (Japan) equipped with graphite monochromatized Cu Kα radiation (λ = 1.54060 Å). The scanning electron microscope (SEM) uses a scanning electron microanalytical instrument of model QUANTA FEG 250 produced by the American company FEI. Corresponding work voltage and current is 40 kV and 100 mA, respectively. The atomic force microscope (AFM) used in this paper is the Dimension Icon model produced by the American company Bruker. The Fourier Transform Infrared Spectroscopy (FTIR) is a Fourier Transform Infrared Spectroscopy analyzer of the Nicolet iS10 model produced by the American company The Brunauer-Emmett-Teller (BET) method was employed. The micro-porous physical and chemical adsorption instrument of model ASAP2020M+C produced by the American company Micromeritics was used. The specific surface area of the samples was calculated by the BET method, and the pore size distribution of the samples was determined by the BJH method. Before the test, all samples were degassed for more than 8 hours under a nitrogen atmosphere at $150^{o}C$. Thermo. Photoluminescence Spectroscopy (PL) uses a fluorescence analyzer of the model Horiba Fluorumax-4 produced by the American company HORIBA. The UV−Vis absorption and diffused reflectance spectra were recorded using a Cary 5000 UV-Vis spectrometer (Viarian, USA) with $BaSO_4$ as a reflectance standard. The transient photocurrent responses experiments were carried out at room temperature using a conventional three-electrode system with a glassy carbon electrode (3mm in diameter), (sheet resistance 20−25 Ω/square) with a geometrical area of 1.0 ± 0.1 cm^2 as the working electrode, a platinum wire as the auxiliary electrode, and a Ag/AgCl electrode as the reference electrode. All the samples were dispersed in deionized water with a concentration of 1.5

mg/mL and deposited on the glassy carbon electrode and dried infrared light irradiation. Na_2SO_4 (0.5 M) mixture solution was used as the supporting electrolyte. The transient photocurrent responses measurements were performed with a CHI 660E electrochemical station (Shanghai Chenhua Co. Ltd, China) under 365 nm of irradiation in 0.5 M Na_2SO_3 mixed solutions.

4. Photocatalytic Hydrogen Production.

This paper uses the photocatalytic integrated system produced by Beijing Zhongjiao Jin Yuan Technology Co., Ltd. to conduct the performance test of piezoelectric-photo catalytic water splitting. Under room temperature and atmospheric pressure, the generation rates of hydrogen and oxygen under ultrasonic (28 kHz, 70 W), visible light ($\lambda \geqslant 420$ nm), and combined ultrasonic and visible light irradiation were evaluated. Generally, 10 mg of the prepared photocatalyst was suspended in 15 ml of pure water and ultrasonically dispersed. The reactor was coated with vacuum grease and connected to the photocatalytic system. The bottom of the reactor was stirred by a continuous magnetic stirrer (600 r/min). A 300 W xenon arc lamp was used as the light source to trigger the photocatalytic reaction. Before irradiation, the system was evacuated with a vacuum pump for 5 minutes to ensure the reactor was in an anaerobic state. The content of H_2 and O_2 was analyzed using gas chromatography (GC7920, CEAULIGHT, China) and TCD detector. During the ultrasonic test, the continuous magnetic stirrer was replaced with an ultrasonic cleaning machine, and the reaction temperature was maintained at 25^{o}C by using cooling circulating water, while the other operation methods were the same as those in the photocatalytic test.The focused intensity on the flask was about 200 $mW \cdot cm^{-2}$, which was measured by a FZ-A visible-light radiometer (CEAU-Light, China). In a typical photocatalytic H_2-production experiment, 10 mg of the as-prepared photocatalyst was suspended in 15 mL of mixe. Before irradiation, the system was vacuumed for 5 min via the vacuum pump to completely remove the dissolved oxygen and ensure the reactor was in an anaerobic condition. H_2 content was analyzed by gas chromatography (GC-7900, CEAU-Light, China). All glass wares were carefully rinsed with DI water prior to usage. The photocatalytic stability was performed in the same processing parameters.

5. Electrochemical measurements

All the electrochemical measurements were conducted by Bio-Logic SP150 electrochemical station using three-electrode system at room temperature with a glassy carbon electrode (3 mm in diameter), (sheet resistance 20-25 Ω^{-2}) as the working electrode, a platinum wire as the auxiliary electrode, and an Ag/AgCl electrode as the reference electrode. For the electrochemical measurements, 4 mg of the catalysts were dispersed in 2 mL of 9:1 v/v water/Nafion by sonication to form a homogeneous ink. Typically, 5 μL well-dispersed catalysts were covered on the glassy carbon electrode and then dried in an ambient environment for measurements. The electrocatalyst was prepared with a catalyst loading of 0.14 mg cm^{-2}. The electrolyte of transient photocurrent responses experiments, electrochemical impedance spectroscopy (EIS), and Mott-Schottky (M-S) was in 0.5 M Na_2SO_4 aqueous solution, and the electrolyte of linear sweep voltammetry (LSV) was in 1 M KOH solution for the HER and OER results, respectively. EIS was performed at an impressed voltage of -0.3 eV, for voltage ranging from -2.5 V to 2.5 V. M-S was measured for a scan voltage ranging from -1 V to 0.5 V at 500-2000 Hz. The transient photocurrent responses measurement was performed under full light irradiation, and the LSV obtained at a scan rate of 1 mV/s.

6. Supporting Figures.

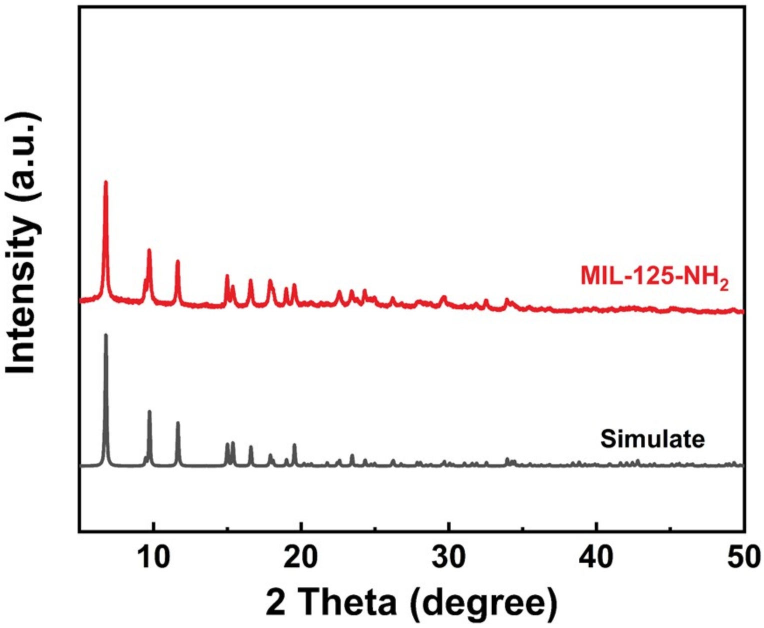

Fig. S1. The PXRD pattens of the MIL-125-NH_2 obtained from the experiment (Red) and the simulated XRD of MIL-125 (Black).

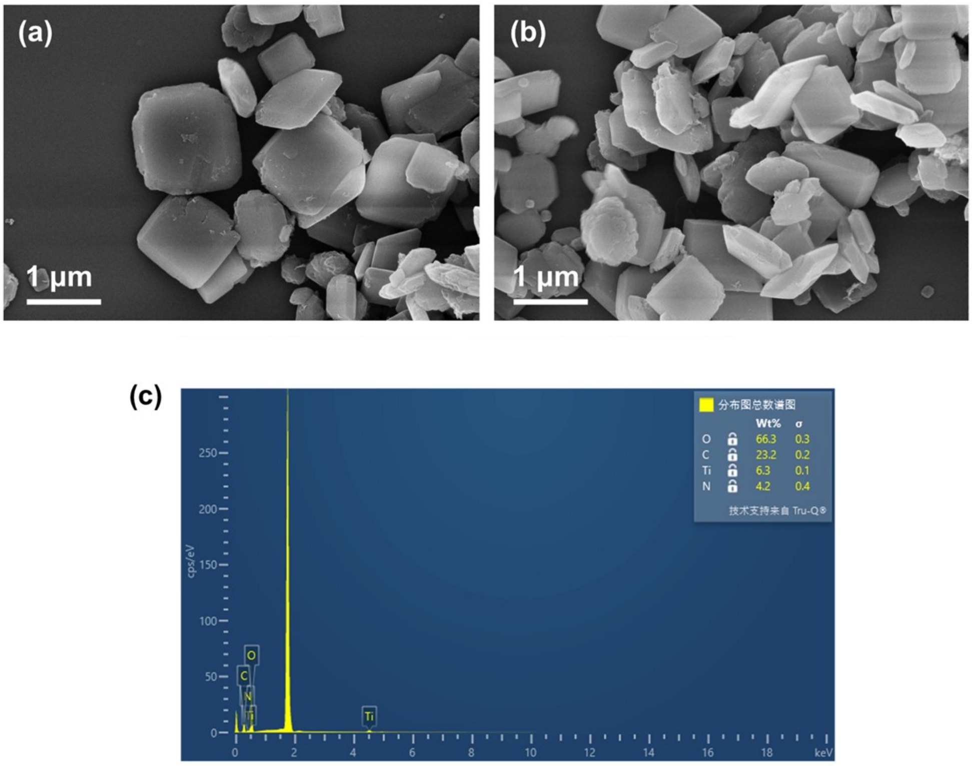

Fig. S2. The SEM image of (a, b) MIL-125-NH_2. (c) EDS percentage of MIL-125-NH_2

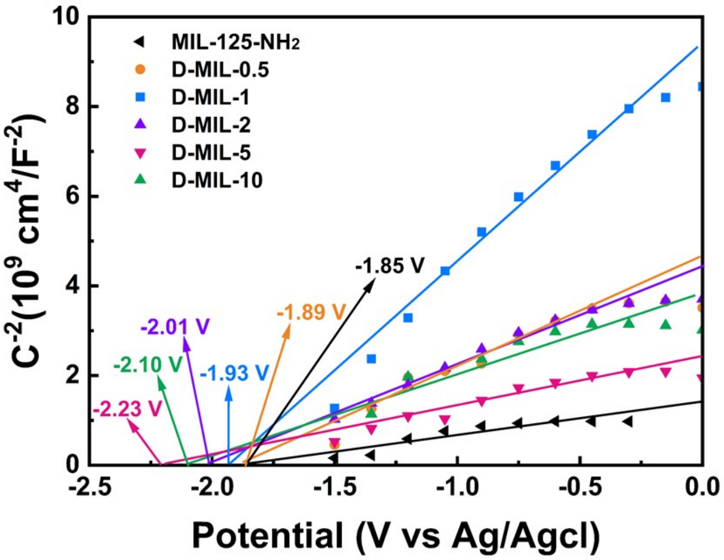

Fig. S3. The Mott-Schottky curves of the MIL-125-NH_2 and D-MIL-X samples.

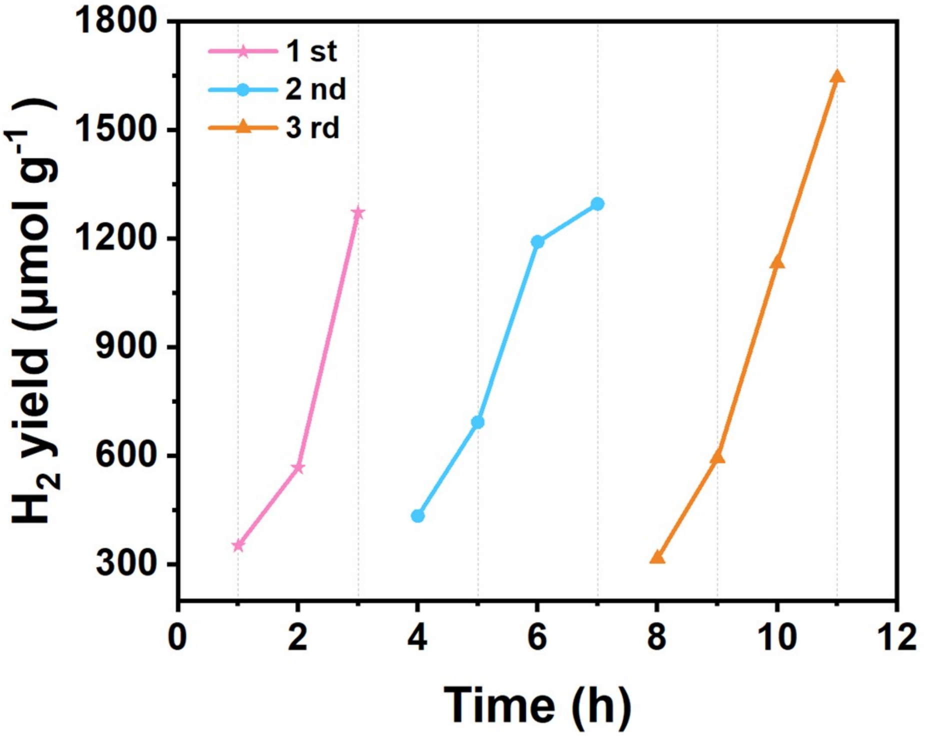

Fig. S4 The time-yield plots H_2 under light conditions of D-MIL-5 sample after 12h stability testing.

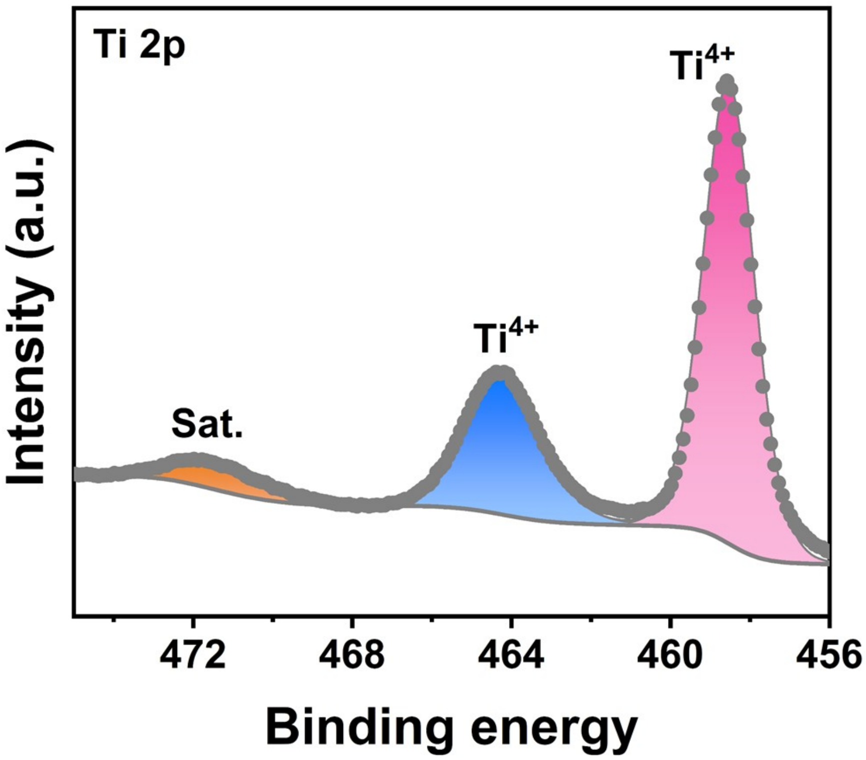

Fig. S5 The XPS spectrum of Ti 2p after stability testing.

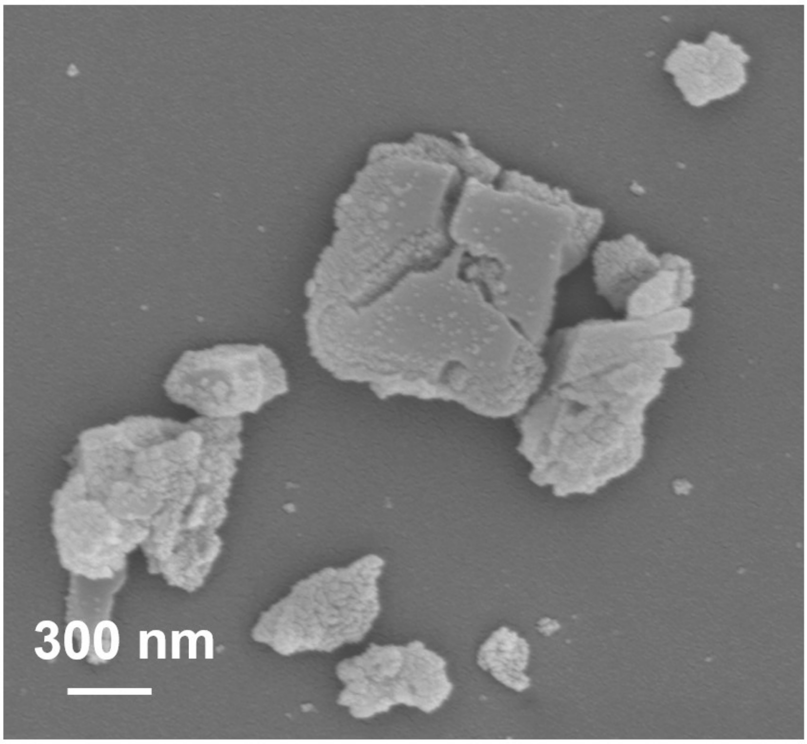

Fig. S6 The SEM image of D-MIL-5 after stability testing.

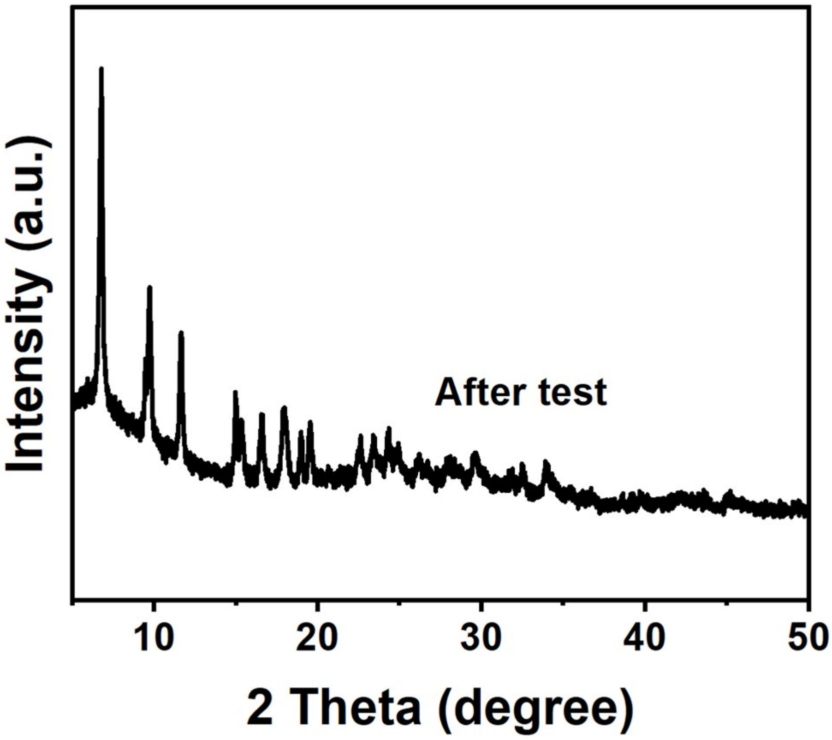

Fig. S7 The XRD of D-MIL-5 after stability testing.

Table.1 The (BET) specific area of different samples.

Sample	MIL-125-NH_2	D-MIL-0.5	D-MIL-1	D-MIL-2	D-MIL-5	D-MIL-10
nm	6.14	4.13	5.09	15.01	18.75	19.74

Table.2 The relative fraction Ti^{3+}/ (Ti^{3+} + Ti^{4+}) for MIL-125-NH_2 and D-MIL-X

	Ti^{3+}	Ti^{4+}
MIL-125-NH_2	0	73.53%
D-MIL-5	12.79%	70.70%

Table.3 The relative fraction defect-related O for MIL-125-NH_2 and D-MIL-X

	defect-related O
MIL-125-NH_2	28.85%
D-MIL-5	52.37%