Supporting Information

Ultra-stable Two Dimensional Metal-organic Frameworks for Photocatalysis of H_2 production

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Experimental Section

Materials: Indium (III) nitrate ($In(NO_3)_3$) were supplied by Shanghai Macklin Biochemical Co., Ltd. The tetrakis (4-carboxyphenyl) porphyrin (TCPP) were supplied by Jilin Zhongkeyanshen science and Technology Co., Ltd. Cetyltrimethylammonium bromide (CTAB) were purchased from Meryer Chemical Technology Co., Ltd. N, N-dimethylformamide (DMF), acetonitrile, nitric acid (HNO_3, 68%) , ethanol and acetone were purchased from Beijing Tongguang Fine Chemical Co., Ltd. Hydrogen hexachloroplatinate(IV) hexahydrate ($H_2PtCl_6 \bullet 6H_2O$) and TEOA were supplied by Aladdin Industrial Corporation (Shang-hai). All chemical reagents were used as received without further purification.

Synthesis of 2D In-TCPP NS: The 2D In-TCPP NS was prepared by a surfactant-assisted synthetic method. Typically, TCPP (50 mg, 0.07 mmol), indium (III) nitrate (46.5 mg, 0.149 mmol) and CTAB (200 mg) were introduced into deionized water (3.15 mL). The suspension was sonicated for 10 min at room temperature, then transferred into a 25 mL of Teflon lined autoclave, and heated at 120 °C for 16 h. After cooling down to room temperature, the product was collected by centrifugation at 10000 rpm for 5 min, washed twice with DMF (2 × 20 mL) and twice with acetone (2 × 20 mL) in order to remove the unreacted precursors and the excess CTAB molecules. Finally, the solids were dried under vacuum at 80 °C.

Synthesis of 3D In-TCPP bulk: The 3D In-TCPP bulk was obtained by a surfactant-free synthetic method. Typically, TCPP (50 mg, 0.07 mmol) and indium (III) nitrate (46.5 mg, 0.149 mmol) were introduced into deionized water (3.15 mL). The suspension was sonicated for 10 min at room temperature, then transferred into a 25 mL of Teflon lined autoclave, and heated at 180 °C for 16 h. The product was collected by centrifugation at 10000 rpm for 5 min, washed twice with DMF (2 × 20 mL) and twice with acetone (2 × 20 mL) in order to remove the unreacted precursors. Finally, the solids were dried under vacuum at 80 °C.

Synthesis of 3D In-TCPP bulk (DMF): The 3D In-TCPP bulk (DMF) were synthesized according to the previous report [25] with some modifications. TCPP (50 mg, 0.07 mmol) and indium (III) nitrate (46.5 mg, 0.149 mmol) were introduced into DMF (5.85 mL) and HNO_3 (0.4 ml, pH = 2.5) mixed solution. The suspension was sonicated for 10 min at room temperature, then transferred into a 25 mL of Teflon lined autoclave, and heated at 180 °C for 16 h. The product was collected by centrifugation at 10000 rpm for 5 min, washed twice with DMF (2 × 20 mL) and twice with acetone (2 × 20 mL) in order to remove the unreacted precursors. Finally, the solids were dried under vacuum at 80 °C.

Mott−Schottky Plot Measurements: 1 mg of the sample was added into a mixed solution contains 5 μL Nafion and 1 mL of ethanol, then dispersed by sonication. After that, 10 μL of the suspension solution was dropped on a glassy-carbon electrode to prepare the working electrode. Mott−Schottky plots were measured on an electro-chemical workstation (AUTOLAB) in a standard three electrode system with Pt plate as the counter electrode and Ag/AgCl as the reference electrode. The test frequencies were selected at 500, 800, and 1000 Hz, respectively. 0.5 M Na_2SO_4 solution was used as the electrolyte.

Electrochemical Impedance Spectroscopy Measurements: 1 mg of the sample was added to a mixed solution contains 5 μL Nafion and 1 mL of ethanol, then dispersed by sonication. After that, 10 μL of the suspension solution was dropped on a glassy-carbon electrode to prepare the working electrode. Electrochemical Impedance Spectroscopy were measured on an electro-chemical workstation (AUTOLAB) in a standard three electrode system with Pt plate as the counter electrode and Ag/AgCl as the reference electrode. 0.5 M Na_2SO_4 solution was used as the electrolyte.

Photocurrent Tests: Photoelectrochemical measurements were performed on a CHI 660D electrochemical workstation using a standard three-electrode system. Pt plate as the counter electrode, Ag/AgCl as the reference electrode, a 300 W Xenon lamp as the light source, and 0.5 M Na_2SO_4 solution was used as the electrolyte. The sample (1 mg) was added into a mixed solution contains Nafion (5 μL) and ethanol (1 mL), then dispersed by sonicating. The working electrodes

were prepared by dropping the suspension (10 μL) onto the surface of ITO plate (1 cm×1 cm), then dried at room temperature.

Photocatalytic H_2 Production: Photocatalytic H_2 production reactions were carried out in a 200 mL of closed quartz flask reactor. 5 mg of the photocatalyst was dispersed in 103 mL of a mixed solution comprised of CH_3CN, H_2O, and TEOA with a volume ratio of 100 : 1 : 2. Before irradiation, 10 μL of H_2PtCl_6 (40 μg/μL) was added into the solution, after that, the reactor was degassed for 1 h to drive away the residual air. Photocatalytic hydrogen production was then triggered by irradiating the suspension using a 300 W of xenon lamp (PLS-SXE300D). The gas products were analyzed periodically using a gas chromatograph (GC-2014 SHIMADZU) equipped with a TCD detector.

Characterization: TEM images were obtained on a HT-7700Exalens transmission electron microscope. SEM images were obtained on a SU8010 transmission electron microscope. Powder XRD (Bruker XRD D8 Advance) was used to characterize the crystal structures of the materials. AFM images were taken by using a NTEGR Prima equipment. Fourier transform infrared (FTIR) spectra were measured by Frontier Mid/Far FT-IR. N_2 adsorption−desorption isotherms were measured by Micromeritics ASAP 2020-HD88. UV–vis diffuse reflectance spectroscopy (Cary 5000) was used to measure the light absorption of the samples. PL spectroscopy (FLS1000) was used to get the time-resolved PL decay spectra .

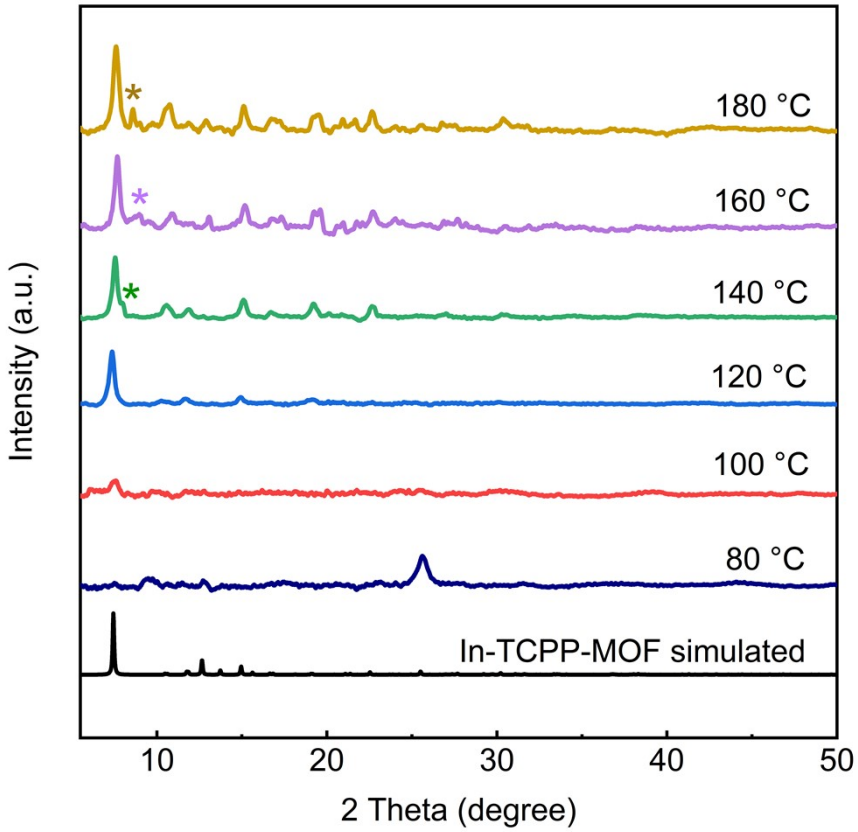

Figure S1 PXRD patterns of the 2D In-TCPP NS prepared at different temperatures.

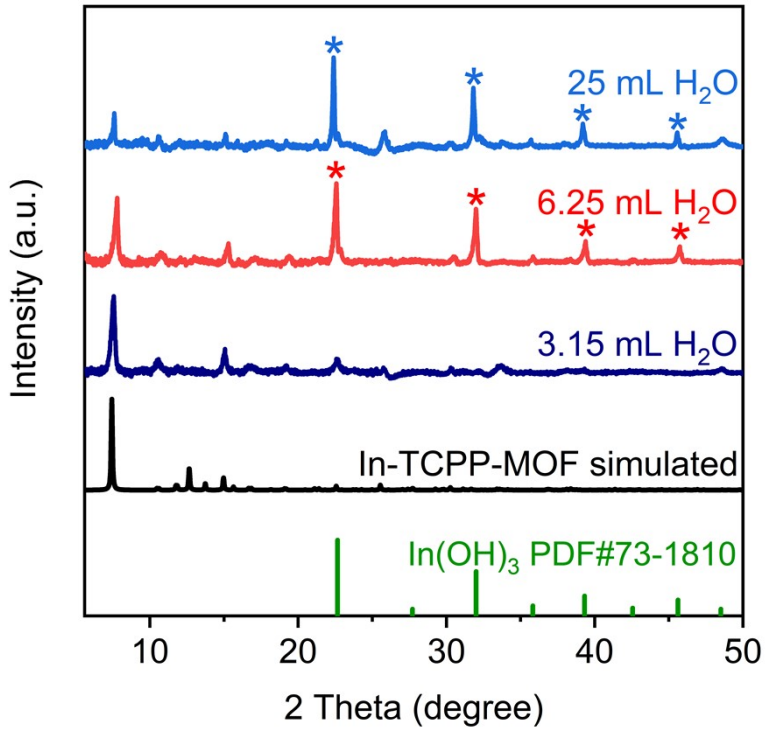

Figure S2 PXRD patterns of the 2D In-TCPP NS prepared with different dosage of H_2O.

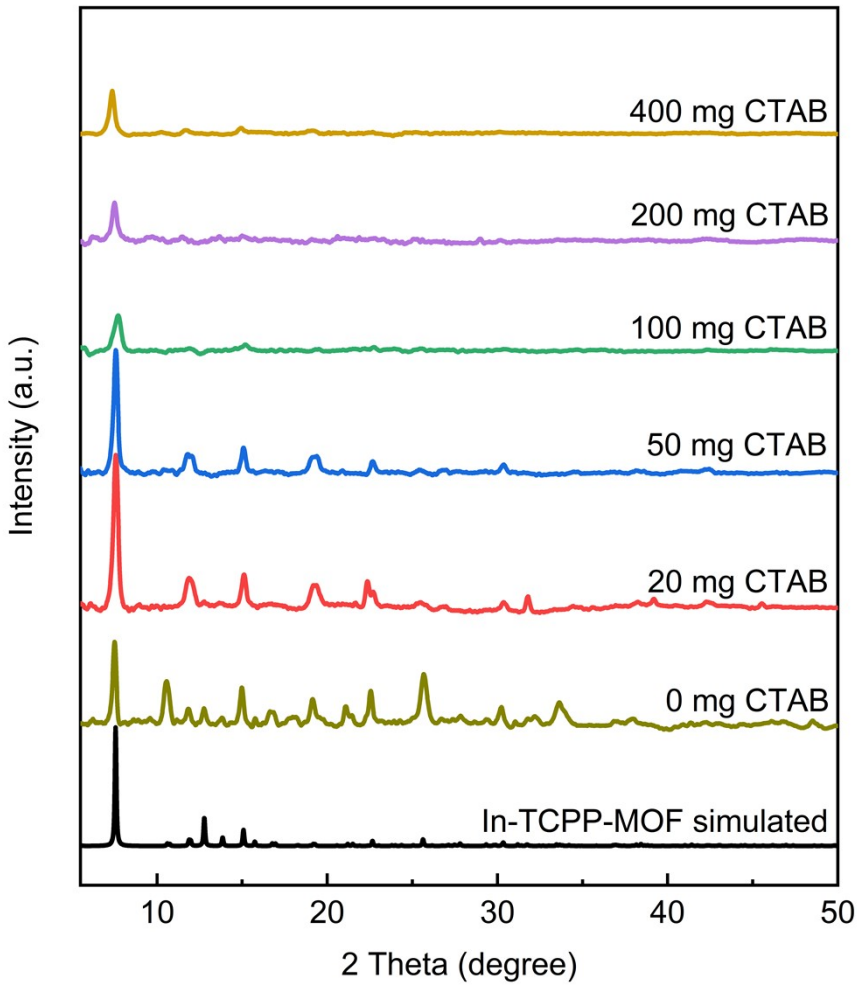

Figure S3 PXRD patterns of the In-TCPP MOF with different amounts of CTAB in the reaction solution.

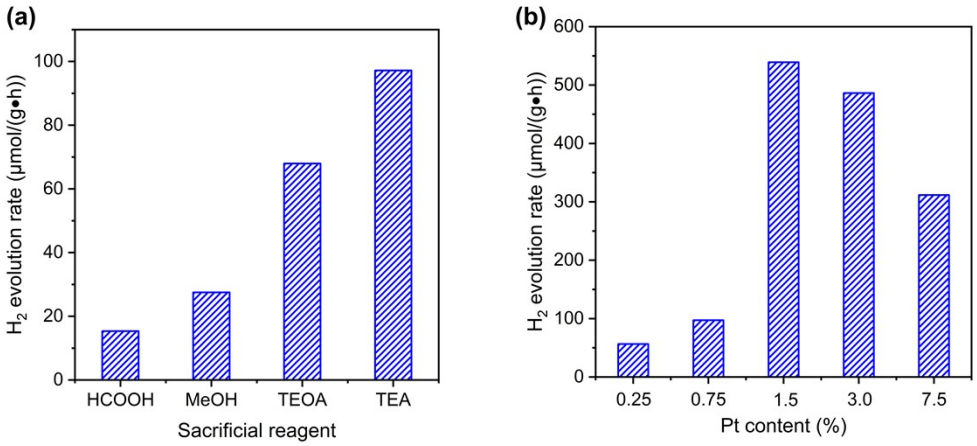

Figure S4 Sacrificial reagents (a) and co-catalyst amounts optimization (b) experimental results.

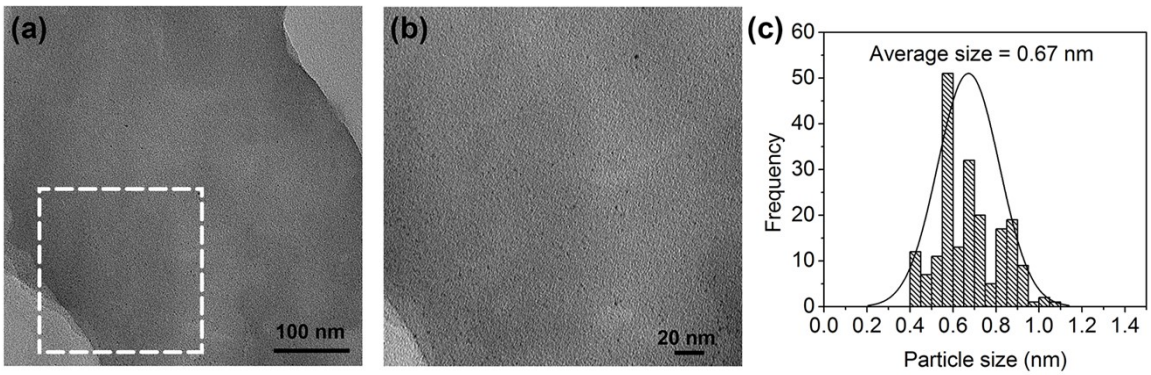

Figure S5 TEM images of the 2D In-TCPP NS (a) and (b) after loading with Pt. The particle size distribution of Pt on the 2D In-TCPP NS (c).

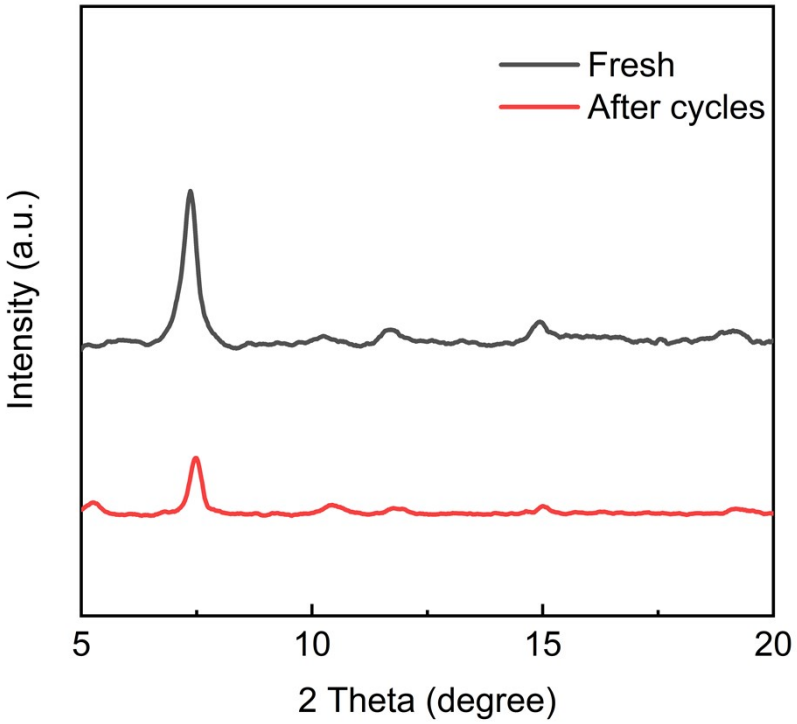

Figure S6 PXRD patterns of the 2D In-TCPP NS before and after photocatalytic reaction.

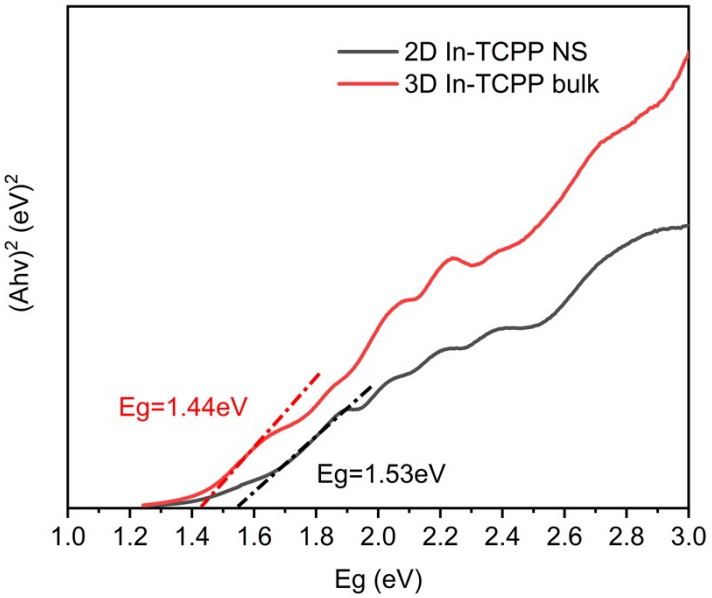

Figure S7 Tauc plots of the 2D In-TCPP NS and 3D In-TCPP bulk.

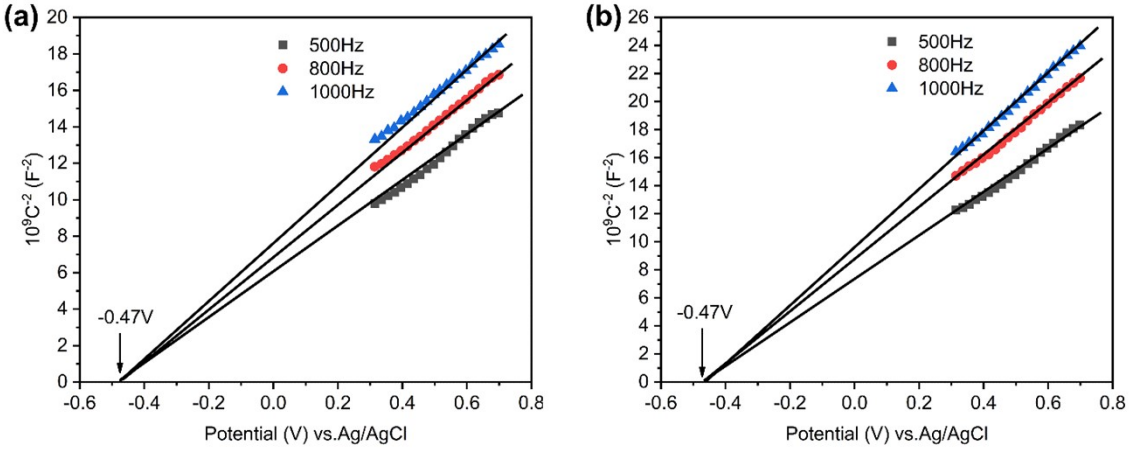

Figure S8 Mott-Schottky plots of the 2D In-TCPP NS (a) and 3D In-TCPP bulk (b).

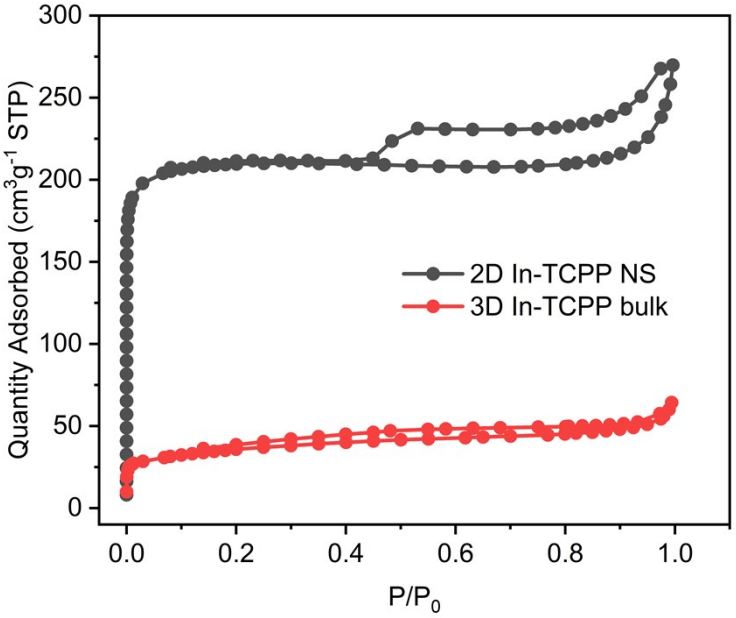

Figure S9 N_2 adsorption-desorption isotherms of the 2D In-TCPP NS and 3D In-TCPP bulk.

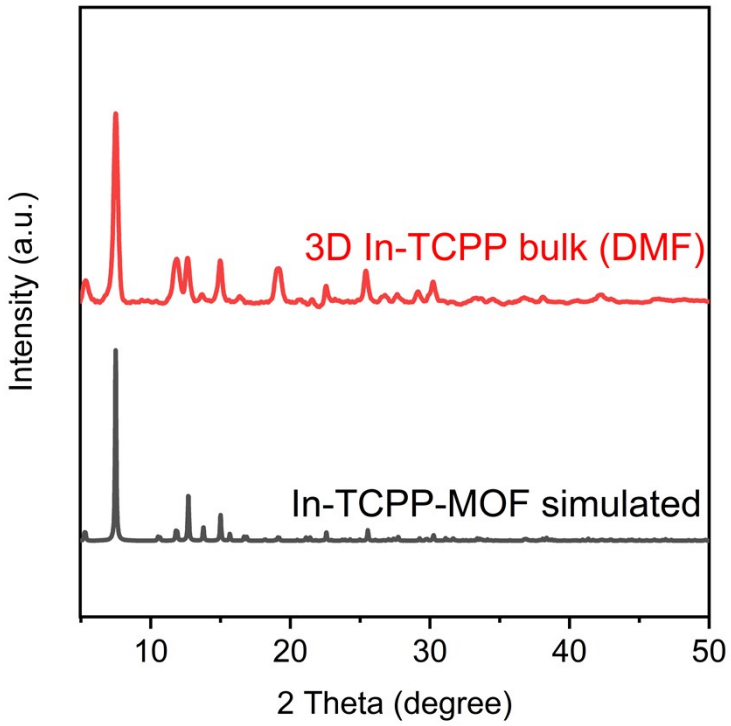

Figure S10 PXRD pattern of the 3D In-TCPP bulk (DMF).

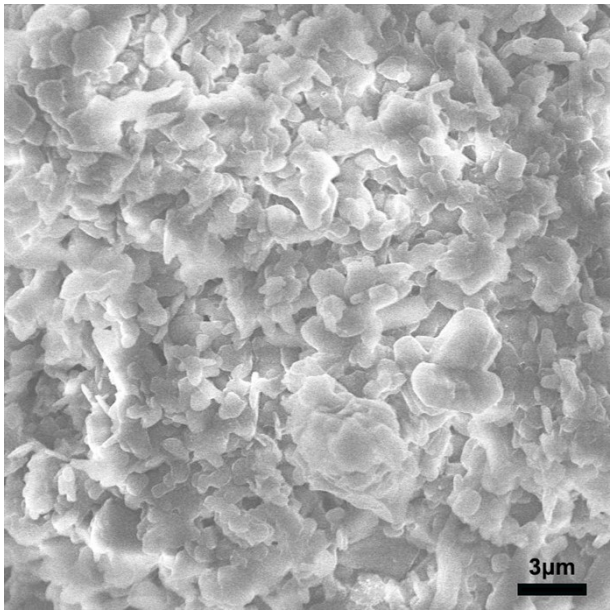

Figure S11 SEM image of the 3D In-TCPP bulk (DMF).

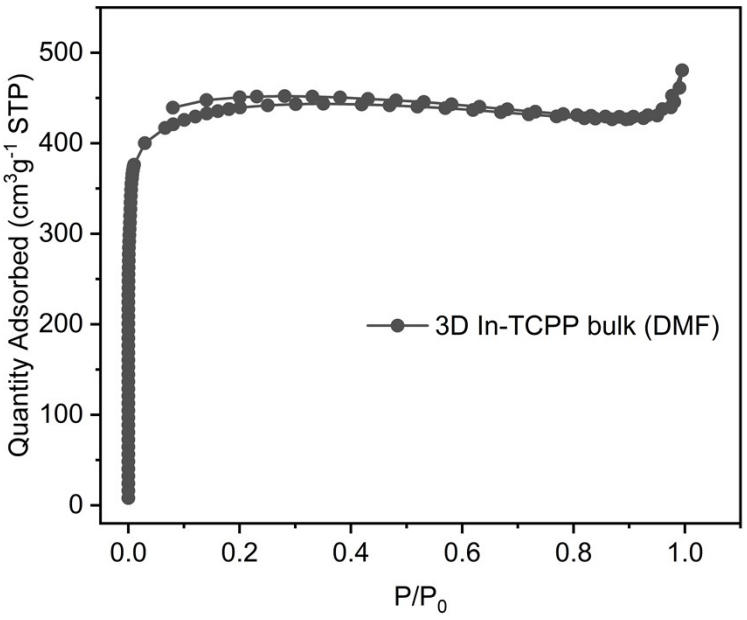

Figure S12 N_2 adsorption-desorption isotherm of the 3D In-TCPP bulk (DMF).

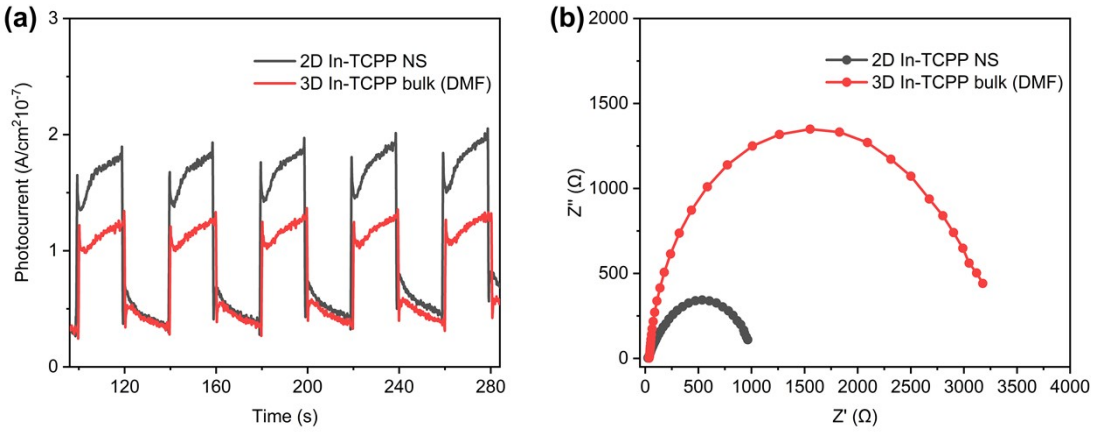

Figure S13 Photocurrent responses (a) and EIS Nyquist plots (b) of the 2D In-TCPP NS and 3D In-TCPP bulk (DMF).

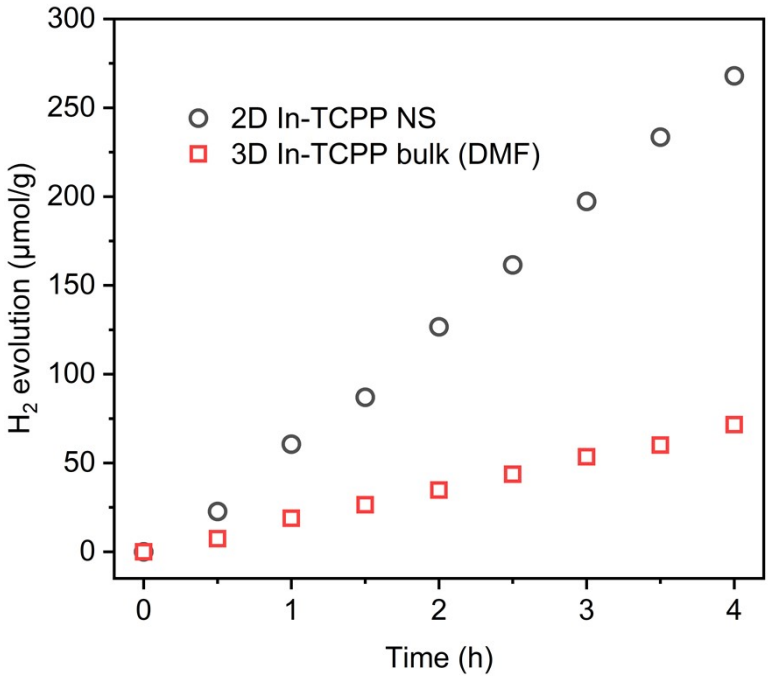

Figure S14 Photocatalytic H_2 production performances of the 2D In-TCPP NS and 3D In-TCPP bulk (DMF).

Table S1 The comparison of the photocatalytic H_2 production rate of 2D In-TCPP NS with those of other reported MOF-based photocatalysts.

Photocatalyst	Dimension	Cocatalyst	Light source	Activity ($\mu mol \cdot g^{-1} \cdot h^{-1}$)	Refs.
2D In-TCPP NS	**2D**	**Pt**	**UV-vis light**	**539.07**	**This work**
2D NMF	2D	Pt	> 420 nm	0	Adv. Energ. Mater., 2019, 9, 1803402.
Cu-TCPP MOF	2D	Pt	> 420 nm	2.0	Angew. Chem. Int. Ed., 2019, 58, 10198.
2D Co-MOF	2D	EY	UV-vis light	25	J. Colloid Interface Sci., 2021, 583, 435.
UiO-67-NS	2D	Pt	300 W Xe lamp	31	ACS Appl. Energy Mater., 2019, 2, 298.
UiO-66-NH_2	3D	Pt	UV-vis light	20.74	J. Phys. Chem. C, 2012, 116, 20848.
MUV-11	3D	Pt	Solar simulator	0.3	J. Am. Chem. Soc., 2019, 141, 13124.
Cd-TBAPy	3D	Pt	> 420 nm	4.3	Adv. Mater., 2018, 30, 1803401.
[Dy_2 (abtc) $(H_2O)_2(OH)_2$]·$2H_2O$	3D	Pt	> 320 nm	21.53	CrystEngComm, 2018, 20, 3228.
[Cu(DSPTP) $(H_2O)_2$]·$2H_2O$	3D	Pt	> 420 nm	18.94	Int. J. Hydrog. Energy, 2017, 42, 26605.
MOF-808	3D	Pt	Xenon lamp	1.7	Angew. Chem. Int. Ed., 2018, 130, 5477.
ACM-1	3D	Pt	> 380 nm	67	Angew. Chem. Int. Ed., 2020, 132, 13570.
ZSTU-2	3D	Pt	> 420 nm	350	J. Mater. Chem. A, 2019, 7, 11928.
MIL-125-NH_2	3D	Pt	> 420 nm	367	J. Phys. Chem. C, 2012, 116, 20848.
Ti-MOF-Ru$(tpy)_2$	3D	Pt	> 420 nm	182	Chem. Commun., 2014, 50, 6779.
USTC-8(In)	3D	Pt	> 380 nm	341.3	ACS Catal., 2018, 8, 4583.