

Supplementary Information

Constructing 2D MOF/In₂S₃ heterojunctions for efficient solar-driven H₂O₂ synthesis in pure water

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1.1. Materials

Aluminum chloride hexahydrate ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, 99.99%), hexadecyl trimethyl ammonium bromide (CTAB, 99%) and thioacetamide (AR, 99%) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. Pyrrole (AR), propionic acid (PA, AR $\geq 99.5\%$), potassium hydroxide (KOH, 95%), Methyl 4-formylbenzoate (98%), EDTA disodium salt dihydrate (EDTA-2Na, 98%), Isopropyl alcohol (IPA, AR $\geq 99.5\%$), 4-Hydroxy-TEMPO (TEMPO, 98%), Thioacetamide (AR, 99%), Potassium hydrogen phthalate (HPLC, $\geq 99.5\%$), potassium iodide (KI, 99%) and Sodium Sulfate (Na_2SO_4) were purchased from Shanghai Macklin Biochemical Co., Ltd. N,N-Dimethylformamide (DMF, $\geq 99.5\%$), ethyl acetate (EA, $\geq 99.5\%$), ethanol ($\geq 99.5\%$), methanol (MeOH, $\geq 99.5\%$) and tetrahydrofuran (THF, $\geq 99.5\%$) were purchased from Hangzhou Gaojing Fine Chemical Co., Ltd. Nafion perfluorinated resin solution (5wt.%), Hydrochloric Acid (HCl, 37%) and Indium (III) Nitrate ($\text{In}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$, 99.9%) were purchased from Adamas. All of these materials are directly used.

1.2. Instrumentation

The X-ray diffraction (XRD) patterns of the samples were acquired using an X-ray diffractometer (Rigaku SmartLab SE, Japan) for Cu-K α radiation. FT-IR spectra were obtained by measuring with a spectrometer (Nicolet iS50, Thermo Scientific, USA). The microstructure was investigated using scanning electron microscopy (SEM) (ZEISS GeminiSEM 300, Germany) and transmission electron microscopy (TEM) (JEOL JEM-F200, Japan). The surface properties were studied by X-ray photoelectron spectroscopy (XPS) (Thermo Scientific K-Alpha, USA). The ultraviolet-visible spectra (UV-vis) were determined using a UV-visible spectrophotometer (UV3600) with BaSO_4 as the substrate. The Steady-state photoluminescence (PL) spectra were carried out by a fluorescence spectrophotometer (F-7000, Hitachi, Japan) with 420 nm wavelength light irradiation. The electrochemical properties were investigated using an electrochemical workstation (CHI660E, China).

2. Preparation of materials

2.1. Synthesis of tetrakis (4-carboxyphenyl) porphyrin (TCPP) ligand

1) Synthesis of 5,10,15,20-Tetrakis (4-methoxycarbonylphenyl) porphyrin (TPPCOOMe)

TCPP was prepared according to the literature ¹. Pyrrole (3.1 mL, 0.045 mol) and methyl 4-formylbenzoate (6.9 g, 0.042 mol) and 100 mL of propionic acid were added to a 250 mL flask and refluxed at 140 °C for 12 h. The reaction solution was cooled to room temperature and then placed in the refrigerator for 12 h. Then the reaction solution was filtrated and washed with ethyl acetate and ethanol until the filtrate was clarified and collected to give purple powder of TPPCOOMe (1.9 g, 2.24 mmol, 21.3% yield). Subsequently, the sample was dried in a vacuum oven at 80 °C for 12 h.

2) Synthesis of tetrakis (4-carboxyphenyl) porphyrin (TCPP)

2.468 g of TPPCOOMe and 8.4 g of KOH, along with 80 mL H_2O , 80 mL MeOH, and 80 mL THF was added into a 500 mL flask and refluxed at 90 °C for 24 h. After cool to room temperature, the solution was acidified by the addition of 1 M hydrochloric acid, and a large amount of precipitate was obtained. The purple solid was collected by filtration, washed with water and dried in vacuum.

3. Characterization of materials

3.1 XRD pattern

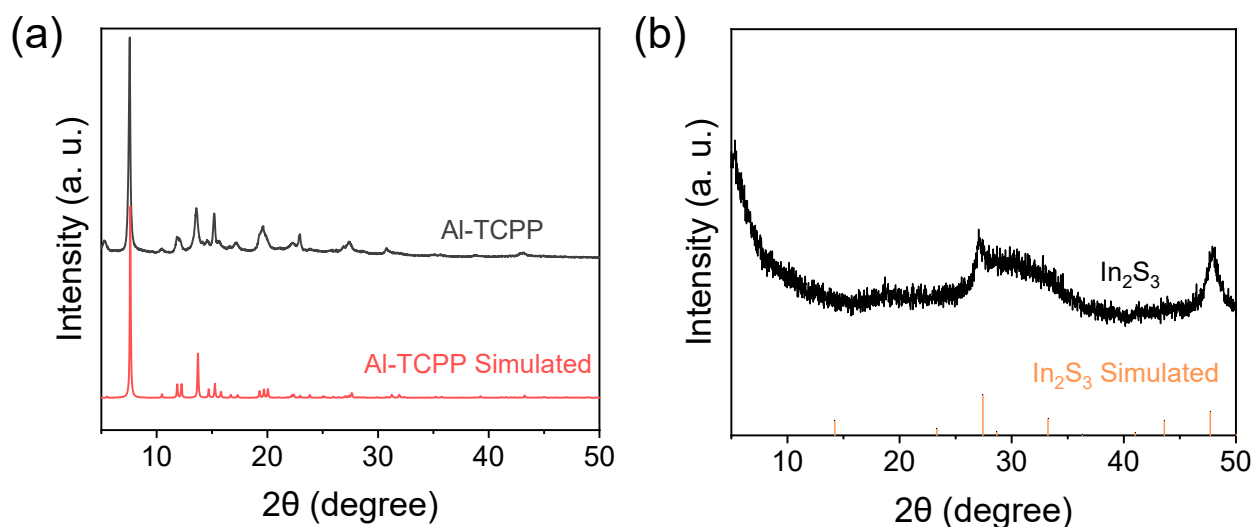


Figure S1. XRD patterns of Al-TCPP (a) and In_2S_3 (b).

4. Photocatalytic experiment

4.1 Photocatalytic production of H_2O_2

Photocatalytic H_2O_2 production experiments were conducted in 100 mL of homemade glass equipment at 25 °C. The sample film was prepared as follows procedure, 5 mg of photocatalyst and 20 μL of nafion perfluorinated resin were dispersed ultrasonically into 10 mL of anhydrous ethanol. Subsequently, 5 mg of the sample was loaded onto a hydrophobic PTFE filter film by a filtration device and the sample film was dried in a vacuum oven overnight at 70 °C. The dried sample film was placed into photocatalytic equipment containing 30 mL of pure water. The mixture was stirred in the dark with O_2 bubbling (20mL/min) for 20 min to reach O_2 adsorption-desorption equilibrium. Then it was irradiated with a 300 W xenon lamp (CEL-PH300-T6) with a cutoff filter ($\lambda > 420$ nm). During irradiation, 1 mL of reaction solution was taken every 30 min for 4 times.

4.2 Determination of H_2O_2 concentration

The H_2O_2 concentration was detected by iodometric method ². 1 mL of the reaction solution was mixed with 0.5 mL of 0.4 M KI solution and 0.5 mL of 0.1 M potassium hydrogen phthalate solution and hold for 15 min. The H_2O_2 molecules react with iodide anions under acidic conditions to give triiodide anions which show a strong adsorption at around 350 nm. The concentration of triiodide anion was detected by UV-vis spectroscopy, from which the quantity of produced H_2O_2 was estimated. The H_2O_2 concentration was calculated from equation (1), where A is the absorbance value at 350 nm.

$$[\text{H}_2\text{O}_2] (\mu\text{M}) = 144.66319A - 2.92727 \quad (1)$$

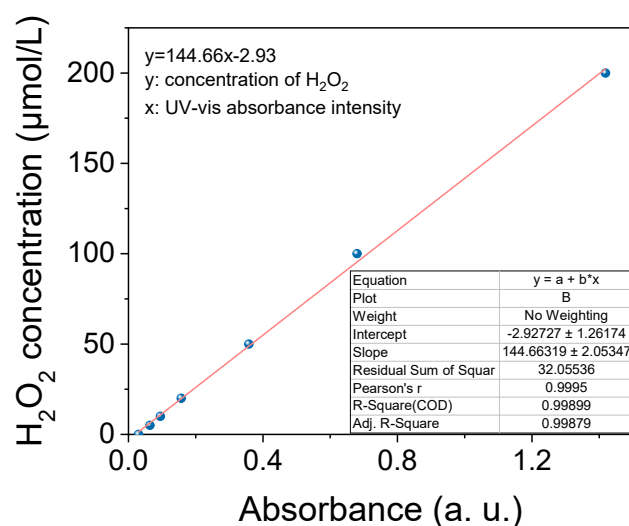


Figure S2. The linear fitting curve of concentration of H₂O₂ vs UV-vis absorbance intensity in a pure water environment.

4.3. Comparison of photocatalytic activities

Table S1. Comparison of photocatalytic activities on H₂O₂ production from O₂ and water over MOF photocatalysts³⁻⁸.

Sample	H ₂ O ₂ production rate/ $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$	Reaction condition	Ref.
Al/In15%	422.88	5.0 mg, distilled water 30.0 mL, Xe lamp ($\lambda > 420$ nm, 300 $\text{mW}\cdot\text{cm}^{-1}$)	This work
Al-TCPP4-TBAPy6	127.00	5.0 mg, distilled water 5.0 mL, Xe lamp ($\lambda > 420$ nm, 100 $\text{mW}\cdot\text{cm}^{-1}$)	3
MIL-125-PDI	24.00	5.0 mg, distilled water/acetonitrile (1:4) 5.0 mL, Xe lamp ($\lambda > 420$ nm, 800 $\text{mW}\cdot\text{cm}^{-1}$)	4
MIL-001	7.00	5.0 mg, distilled water 5.0 mL, Xe lamp ($\lambda > 420$ nm, 100 $\text{mW}\cdot\text{cm}^{-1}$)	3, 5
Ni/Hf-0.5	10.70	5.0 mg, distilled water 5.0 mL, Xe lamp ($\lambda > 420$ nm, 100 $\text{mW}\cdot\text{cm}^{-1}$)	6
NM/n-WO _{3-x}	8.41	20mg, distilled water 50.0 mL, Xe lamp ($\lambda > 420$ nm, 300 $\text{mW}\cdot\text{cm}^{-1}$)	7

B/BF-750	280.50	20mg, distilled water/CH ₃ OH (9:1) 50.0 mL, Xe lamp ($\lambda >$ 420 nm, 300 mW·cm ⁻¹)	8
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4.4 AQY

The determination of the apparent quantum yield (AQY) for photocatalysis H₂O₂: production was obtained under xenon lamp (300 W) equipped with single wavelength filter (400, 450, 500, 600 nm). The AQY is obtained as follow:

$$AQY(H_2O_2) = \frac{2N(H_2O_2)}{N(Photos)} \times 100\% = \frac{2 \times n(H_2O_2) \times N_A \times h \times c}{P \times S \times T \times \lambda} \times 100\%$$

Where N(H₂O₂) is the number of H₂O₂ molecules, N(Photos) is the numbers of incident photos, the n(H₂O₂) refers to H₂O₂ evolution (mol), N_A is the Avogadro constant (6.023 X 10²³ mol⁻¹), h is the Planck constant (6.626X10⁻³⁴ J·s), c is the light speed (3X10⁸ m·s⁻¹), P is the average spectral irradiance (W/cm⁻¹), S is the irradiation area (12.56 cm²), T is the irradiation times (3600 s), λ is the wavelength of monochromatic light (m).

Table S2. AQY of Al/In15% at selected wavelengths (400, 450, 500, and 600 nm).

Wavelength (nm)	400	450	500	600
AQY (%)	1.2	1.37	1.21	1.44

4.5. Cycling stability test

The H₂O₂ evolution cycling tests were conducted under the same procedure of photocatalytic reactions. The sample film was placed into photocatalytic equipment containing 30 mL of pure water. The mixture was stirred in the dark with O₂ bubbling for 20 min to reach O₂ adsorption-desorption equilibrium. Then it was irradiated with a 300 W xenon lamp (CEL-PH300-T6) with a cutoff filter ($\lambda >$ 420 nm). During irradiation, 1 mL of reaction solution was taken every 30 min for 4 times. Then, the reacted photocatalyst film in the cycling experiment was rinsed with deionized water for the next cycle.

4.6. H₂O₂ degradation test

The H₂O₂ degradation experiments over the as-synthesized photocatalysts was investigated by degrading 500 μ mol L⁻¹ H₂O₂ under visible light irradiation. The dried sample film was placed into photocatalytic equipment containing 30 mL of 500 μ mol L⁻¹ H₂O₂. The mixture was stirred in the dark with Ar bubbling for 1 h to remove O₂ from the system. Then it was irradiated with a 300 W xenon lamp (CEL-PH300-T6) with a cutoff filter ($\lambda >$ 420 nm). During irradiation, 1 mL of the reaction solution was taken every 20 min for 4 times.

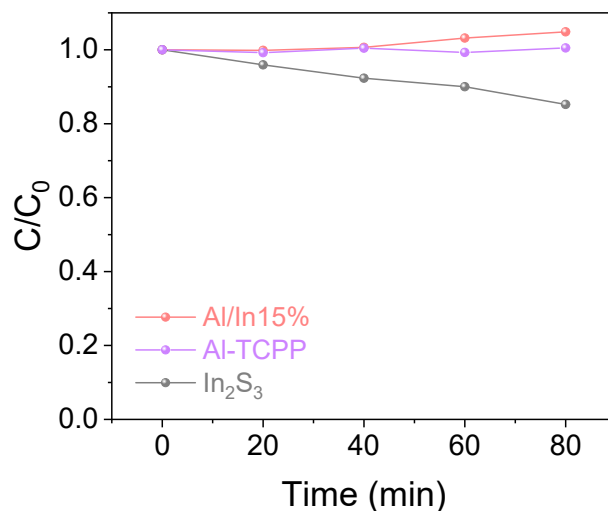


Figure S3. The photocatalytic degradation of H₂O₂ of In₂S₃, Al-TCPP and Al/In15% under irradiation and oxygen-free condition.

4.7 Tests on the catalytic H₂O₂ evolution in different atmospheres.

The H₂O₂ evolution in different atmospheres tests were conducted under the same procedure of photocatalytic reactions. The sample film was immersed in 30 mL pure water and stirred in the dark for 20 min with O₂ bubbling (20 mL/min) to achieve adsorption-desorption equilibrium. Then the reaction system was irradiated with a 300 W xenon lamp (CEL-PH300-T6) with a cutoff filter ($\lambda > 420$ nm). During irradiation, 1 mL of reaction solution was taken every 30 min and the concentrations of H₂O₂ were determined via UV-vis spectroscopy by an iodometry method. Ar was bubbled with rate of 20 mL/min for 1 h to create an Ar atmosphere, following the same procedure as for the O₂ atmosphere. For air atmosphere, the lid of the reactor was opened and use the air directly. The other operational procedures were the same as those under the O₂ atmosphere.

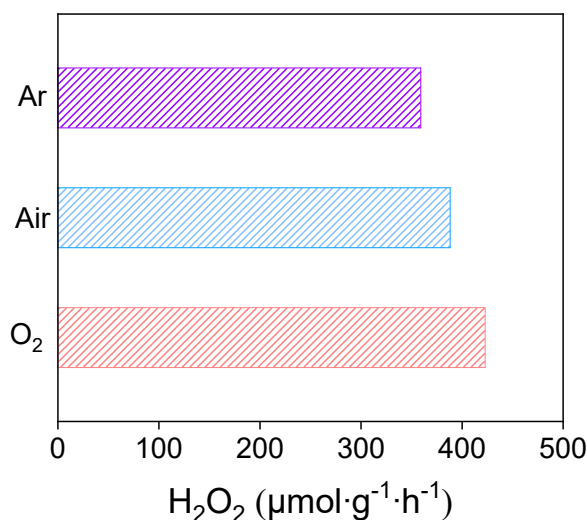


Figure S4. H₂O₂ evolution catalyzed by Al/In15% under different atmospheric conditions.

4.8. Detection of reactive species

The active trapping experiments were conducted by adding different types of excess scavengers (0.1 mmol) into the test solution before the photocatalytic reaction. 4-Hydroxy-TEMPO (TEMPO) was employed for the trapping of $\cdot\text{O}_2^-$, and Ethylenediaminetetraacetic acid disodium salt (EDTA-2Na) for holes. In addition, the addition of 5 mL of isopropyl alcohol (IPA) was used to trap hydroxyl radicals ($\cdot\text{OH}$).

4.9. Electrochemical measurements

Electrochemical measurements were performed on an electrochemical workstation (CHI660E) with a three-electrode system. In a typical process, 2 mg catalyst was ultrasonically dispersed in 1 mL EtOH containing nafion perfluorinated resin (5 wt%, 50 μ L). Subsequently, the mixed solution (100 μ L) was dropped onto a fluorine-doped tin oxide (FTO, 1 cm \times 1 cm window) glass electrode, dried at room temperature, then it was used as the working electrode. Hg/HgCl₂ and Platinum plate electrodes were used as reference and counter electrodes, respectively. The supporting electrolyte was 0.1 mol·L⁻¹ Na₂SO₄ solution. Transient photocurrents were measured with a switching photoperiod of 20 s, where the visible light source was a 300 W xenon lamp (UV filter $\lambda > 420$ nm). Measurement of electrochemical impedance in the range of 0.005 HZ-1000 HZ at an open circuit voltage of -0.4 V.

Rotating disk electrode (AFMSRCE) measurements were performed on a VSP multichannel electrochemical workstation system with a three-electrode cell using a saturated Ag/AgCl electrode and a C rod electrode as the reference and counter electrode, respectively. The working electrode was prepared as follows: catalyst (3 mg) was dispersed by ultrasound in a solution of 0.5 ml isopropanol, 0.48 ml H₂O, 20 μ L Nafion (5 wt%). The slurry (3 μ L) was put onto a disk electrode and dried at room temperature. The linear sweep voltammogram (LSV) was obtained in an O₂-saturated 0.1 M phosphate buffer solution (pH 7.0) with a scan rate 10 mV s⁻¹. 1h after ultrasound, the electron transfer number (n) involved in the overall O₂ reduction was determined by the slopes of the Koutecky–Levich plots with the following equations:

$$j^{-1} = j_k^{-1} + B^{-1}\omega^{-1/2}$$

$$k(\text{slope}) = B^{-1}$$
$$B = 0.2nFv^{-1/6}CD^{2/3}$$

Where j is the current density, j_k is the kinetic current density, ω is the rotating speed (rpm), F is the Faraday constant (96485 C mol⁻¹), ν is the kinetic viscosity of water (0.01 cm² s⁻¹), C is the bulk concentration of O₂ in water (1.2 \times 10⁻⁶ mol cm⁻³), and D is the diffusion coefficient of O₂ (1.9 \times 10⁻⁵ cm² s⁻¹), respectively.

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