Supplementary Information

The Cu ions anchored in the porphyrin center acts as transient metal centers of 2D-MOFs for enhancing photocatalytic hydrogen production

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Materials and experimental Section

Materials

Titanium (IV) Butoxide (Ti(OBu)$_4$, 99%), Benzoic Acid (C$_7$H$_6$O$_2$, RG), *N, N*-Diethylformamide (DEF) (C$_5$H$_{11}$NO, 99%), Pyrrole (C$_4$H$_5$N, 99%), Methyl 4-Formylbenzoate (C$_9$H$_8$O$_3$, 98%), Copper (II) Chloride Dihydrate (CuCl$_2$·2H$_2$O, 99%), Cobalt (II) Chloride Hexahydrate (CoCl$_2$·6H$_2$O, 99%), Nickel (II) Chloride Hexahydrate (NiCl$_2$·6H$_2$O, 99.9%), Solvent Red 43 (C$_{20}$H$_8$Br$_4$O$_5$) were purchased from Adamas. Tetrahydrofuran (C$_4$H$_8$O, 99%), Methyl Alcohol (CH$_3$OH, 99.9%), Propionic Acid (C$_3$H$_6$O$_2$, 99.5%), *N, N*-Dimethylformamide (DMF) (C$_3$H$_7$NO, 98%), KOH (90%) were purchased from Chron Chemicals. All chemicals could be used without further purification.

Experimental Section

5,10,15,20-tetrakis(4-methoxycarbonylphenyl) porphyrin (TMCPP).

In a 500 ml round bottom flask, methyl *p*-formyl benzoate (0.086 mol, 14.41 g) was added to propionic acid (250 mL) to make it completely dissolved, and then the pyrrole (0.086 mol, 6.09 mL) dissolved in propionic acid (20 mL) was added dropwise. Subsequently, the mixture was heated to 150 °C under reflux for 12 h in a high-temperature oil bath. After the reaction, the mixture was cooled to room temperature and filtered, washed with a large amount of MeOH, ethyl acetate and a small amount of THF. Finally, the precipitate was collected and dried in a vacuum drying oven at 60 °C for overnight.

5,10,15,20-tetrakis(4-methoxycarbonylphenyl) porphyrin-X (X-TMCPP, X=Cu, Co or Ni)

Dissolve the TMCPP in 100 mL DMF and put it into 250 ml round bottom flask, then CuCl$_2$·2H$_2$O (1.416 mmol, 0.241 g) , CoCl$_2$·6H$_2$O (1.416 mmol, 0.337 g) or NiCl$_2$·6H$_2$O (1.416 mmol, 0.336 g) was added, stirred well and later refluxed for 6 h. After the solution was cooled to room temperature, about 100 mL H$_2$O was added to carry out suction filtration. During the suction filtration, the solid obtained was washed with water until the filtrate was clear. Finally, the washed solid was dried in a vacuum drying oven at 80 °C overnight to obtain X-TMCPP.

5,10,15,20-tetrakis(4-carboxyphenyl) porphyrin (TCPP)

Put TMCPP (500 mg) into the 250 mL round bottom flask with 40 mL THF and 40 mL MeOH, and 40 mL of water dissolved with 3 g KOH was added, then reflux the mixture solution at 90 °C for 6 h. After the solution cooling to room temperature, excess THF and MeOH were removed via a rotary evaporator, and unreacted TMCPP

was filtered out later. Adjust the pH value of the solution with HCl until there was no precipitation in the solution (pH ≈ 2), then suction filtration was carried out and washed with H_2O, finally the solid was dried in a vacuum drying oven at 80 °C overnight to obtain TCPP.

5,10,15,20-tetrakis(4-carboxyphenyl) porphyrin-X (X-TCPP, X=Cu, Co or Ni)

Put 500 mg CuTMCPP (CoTMCPP or NiTMCPP) into 250 mL round bottom flask with 40 mL THF and 40 mL MeOH, and 40 mL of water dissolved with 3 g KOH was added, then reflux the mixture solution at 90 °C for 6 h. After the solution cooling to room temperature, excess THF and MeOH were removed via a rotary evaporator, and unreacted CuTMCPP (CoTMCPP or NiTMCPP) was filtered out later. Adjust the pH value of the solution with HCl until there was no precipitation in the solution (pH ≈ 2), then suction filtration was carried out and washed with H_2O, finally the solid was dried in a vacuum drying oven at 80 °C overnight to obtain X-TCPP.

Photocatalytic H_2 evolution experiments

Under the ambient temperature, a 300 W Xe lamp equipped with a UV cut filter ($\lambda \geq 420$ nm) was used to carry out the photocatalytic hydrogen production experiment in a 100 mL optical reaction vessel. Usually, 10 mg sample reagent was dispersed in 17 mL deionized water, 3 mL triethanolamine (TEOA) was used as a sacrificial reagent and Eosin Y (EY) as a photosensitizer, then the suspension was bubbled with nitrogen for 15 min to remove air. A GC gas chromatograph (Beijing, GC 7920) equipped with a thermal conductivity detector and high-purity N_2 carrier gas was used to detect and analyze gas products. The cycle stability test was carried out under the duration for each cycle of 5 h. The AQE was measured through the equation below：

$$AQE\ (\%) = \frac{\frac{number\ of\ reacted\ electrons}{number\ of\ incident\ photons} \times 100\%}$$

$$= \frac{\frac{number\ of\ evolved\ H_2\ molecules\ \times\ 2}{number\ of\ incident\ photons} \times 100\%}$$

Electrochemical measurements

An electrochemical instrument with a three-electrode system was used to analyze electrochemical measurements. The working electrode was prepared as follows: added 50 μL of H_2O, 450 μL of ethanol, 10 μL of Nafion, reagent to the sample (1 mg) and ultrasonic dispersion for 30 min, and then transferred 100 μL of suspension to coat the ITO. The electrode was dried in air at room temperature. The reference electrode was calomel electrode and the counter electrode was platinum electrode. Electrochemical impedance spectroscopy (EIS) and transient photocurrent tests were conducted in Na_2SO_4 (0.2 M). A xenon lamp (300 W) was treated as the light irradiation for photocurrent test.

Characterization

The microstructure and morphology of Cu-PTM composites were characterized by X-ray powder diffraction (XRD) patterns (XPD-6100, Shimadzu, Japan), Fourier transform infrared (FT-IR) spectra (IRPrestige-21, Shimadzu, Japan), Atomic force microscope AFM (Dimension ICON, Brooklyn), Transmission electron microscope TEM (Talos F200 S, USA), X-ray photoelectron spectroscopy (XPS) (Thermo Scientific K-Alpha, USA), Brunauer-Emmett-Teller (BET) measurements (ASAP 2020, USA). Photocatalytic properties and mechanisms were investigated by UV-vis diffuse reflectance spectroscopy (UV-vis DRS) (UV-vis DRS, Shimadzu, Japan), Photoluminescence spectrum (PL spectrum) (F-7000, HITACHI, Japan and FLS1000,

Edinburgh instruments), Transient photocurrent response curve (PEC 1000), Electrochemical impedance spectroscopy (EIS) (PEC 1000), Linear sweep voltammetry (LSV) (PEC 1000), Electron spin-resonance spectroscopy (ESR) (Hitachi FA200).

Calculation Method of Differential Charge

We have employed the first-principles [1,2] to perform density functional theory (DFT) calculations within the generalized gradient approximation (GGA) using the Perdew-Burke-Ernzerhof (PBE) [3] formulation. We have chosen the projected augmented wave (PAW) potentials [4,5] to describe the ionic cores and take valence electrons into account using a plane wave basis set with a kinetic energy cutoff of 400eV. Partial occupancies of the Kohn−Sham orbitals were allowed using the Gaussian smearing method and a width of 0.05 eV. The electronic energy was considered self-consistent when the energy change was smaller than 10^{-5} eV. A geometry optimization was considered convergent when the energy change was smaller than 0.05 eV Å^{-1}. In our structure, the U correction is used for Ti atoms. The vacuum spacing in a direction perpendicular to the plane of the structure is 18 Å for the Cu-MOF surfaces. The Brillouin zone integration is performed using 2×2×1 Monkhorst-Pack k-point sampling for a structure. Finally, the adsorption energies(Eads) were calculated as Eads= Ead/sub -Ead -Esub, where Ead/sub, Ead, and Esub are the total energies of the optimized adsorbate/substrate system, the adsorbate in the structure, and the clean substrate, respectively. The free energy was calculated using the equation:

G=Eads+ZPE-TS

where G, Eads, ZPE and TS are the free energy, total energy from DFT calculations, zero-point energy and entropic contributions, respectively.

References

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2. Kresse, G.; Furthmüller, J. Efficient Iterative Schemes for Ab Initio Total-Energy Calculations Using a Plane-Wave Basis Set. Phys. Rev. B 1996, 54, 11169−11186.

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5. Blöchl, P. E. Projector Augmented-Wave Method. Phys. Rev. B 1994, 50, 17953−17979.
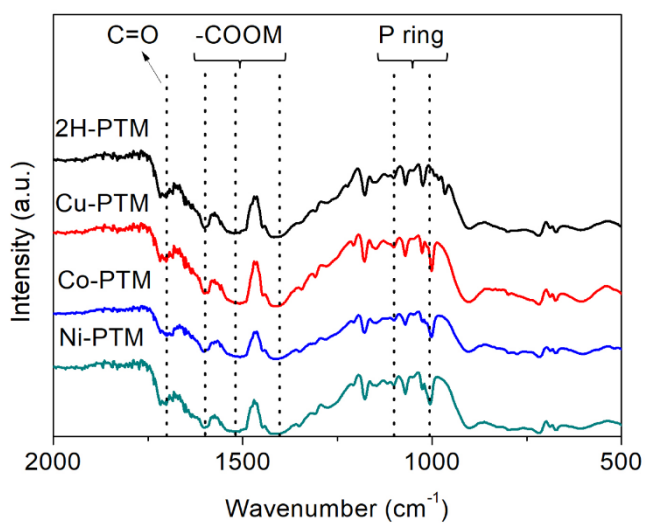
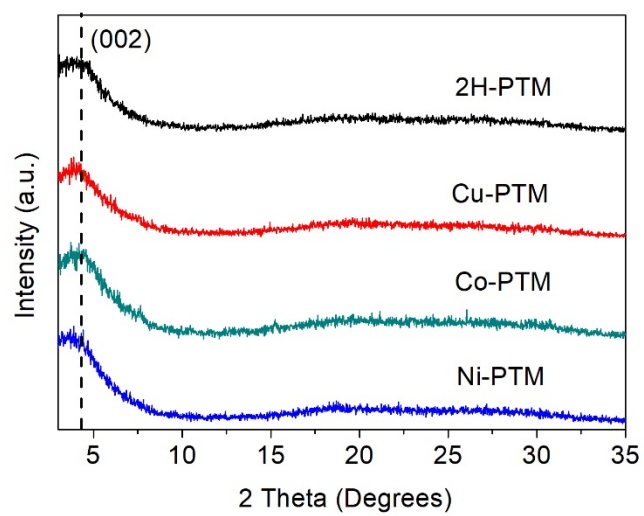**Fig. S1.** FTIR spectrums of 2H-PTM, Cu-PTM, Co-PTM and Ni-PTM.
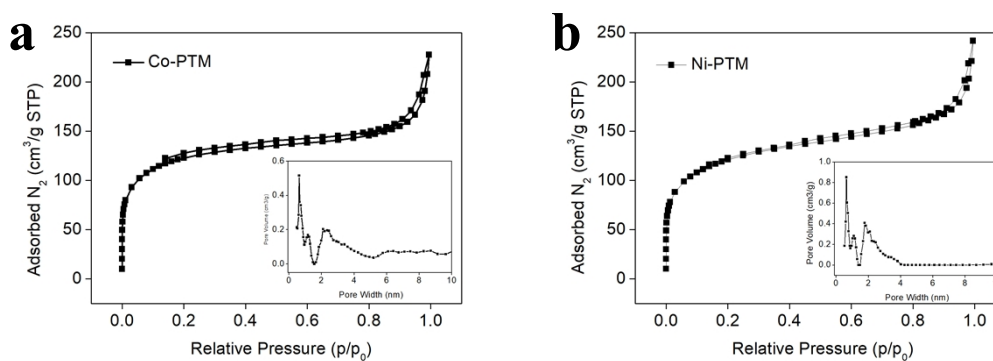
Fig. S2. N_2 adsorption isotherm of Co-PTM, Ni-PTM, the insert picture shows the pore size distribution curve.

Table S1. Structural parameters of different samples.

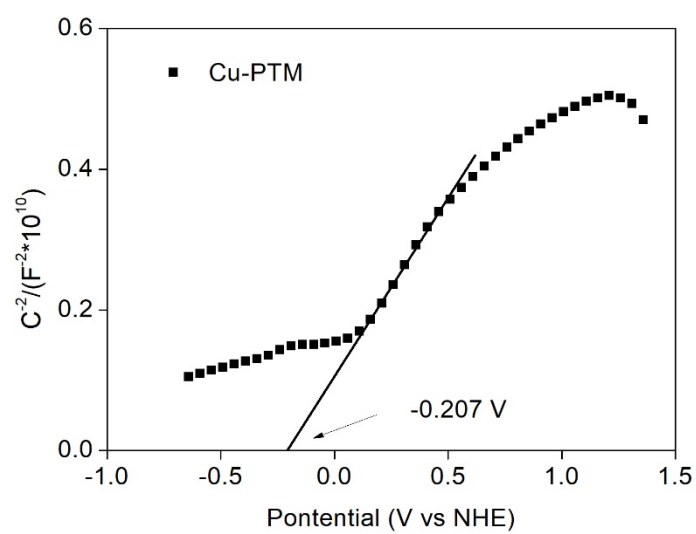| Sample	SBET ($m^2 \cdot g^{-1}$)	Total Pore Volume ($cm^3 \cdot g^{-1}$)	Pore Size (nm)
2H-PTM	331.7	0.268	6.7
Cu-PTM	449.2	0.278	7.7
Co-PTM	432.8	0.281	6.8
Ni-PTM	429.9	0.299	6.1

Fig. S3. XRD pattern of 2H-PTM and Cu-PTM, Co-PTM and Ni-PTM.
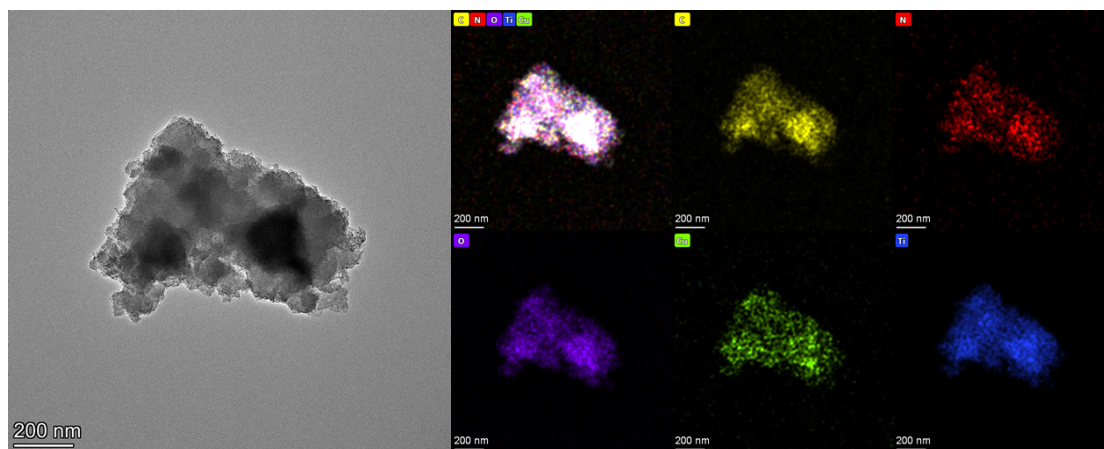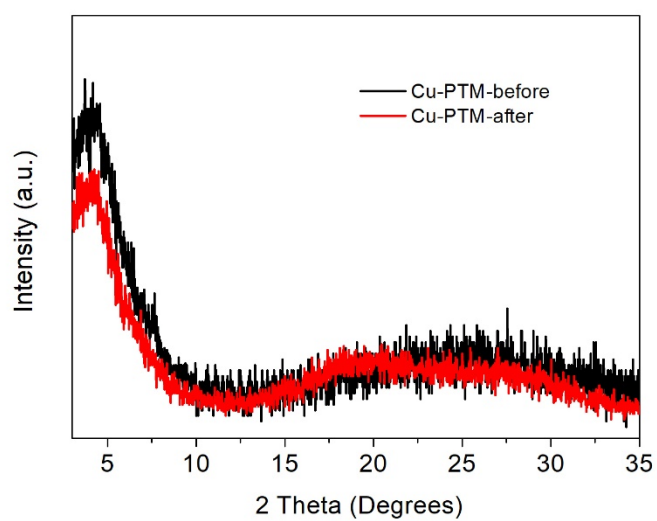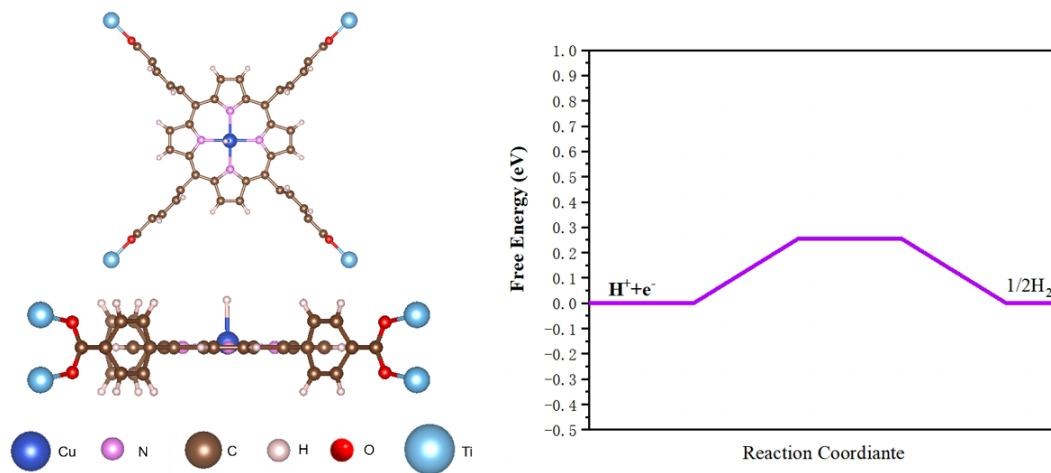

Fig. S4. TEM image mapping of Cu-PTM.

Fig. S5. Mott−Schottky plots of Cu-PTM in 0.5 M Na$_2$SO$_4$.

Fig. S6. XRD comparison of Cu-PTM before and after activity testing.

Fig. S7. Adsorption structure of H and free energy of H in the Cu-PTM structure.