Supporting Information for

Cupric Porphyrin Frameworks on Multi-junction Silicon Photocathode to Expedite the Kinetics of CO₂ Turnover

Zhihe Wei,^{1,2} Qiaoqiao Mu,¹ Ronglei Fan,² Yanhui Su,¹ Yongtao Lu,¹ Zhao Deng,¹ Mingrong Shen²*, Yang Peng¹*

¹Soochow Institute of Energy and Material Innovations, College of Energy, Soochow Municipal Laboratory for Lowe Carbon Technoliges and Industries, Soochow University, Suzhou 215006, China.

²School of Physical Science and Technology, Jiangsu Key Laboratory of Thin Films, Collaborative Innovation Center of Suzhou Nano Science and Technology, Soochow University, Suzhou 215006, China.

*Email: mrshen@suda.edu.cn, ypeng@suda.edu.cn

Experimental section

Materials

All the reagents, including methyl p-formylbenzoate, pyrrole, propionic acid, dichloromethane (CH₂Cl₂), methanol (CH₃OH), tetrahydrofuran (THF), hydrochloride (HCl), cupric acetate anhydrous (Cu(CH₃COO)₂), sodium hydroxide (NaOH), silver nitrate (AgNO₃), ammonium persulphate ((NH₄)₂S₂O₈), N,N-Dimethylformamide (DMF), tetrabutylammonium tetrafluoroborate (TBABF₄), acetonitrile (MeCN), absolute ethanol and tetrakis (4-carboxyphenyl) porphyrin (H₂TCPP) were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China), and used as received without further purification.

Preparation of TCPP(Cu)

The metalloporphyrin ligand TCPP(Cu) was synthesized following a previous report with some modifications.¹ Firstly, methyl p-formylbenzoate (6.53 g, 40 mmol) was dissolved in propionic acid (100 mL) in a 500 mL three necked flask. Pyrrole (2.68 g, 40 mmol) was then added dropwise, and the mixture was refluxed for 2 h. After the reaction mixture was cooled to room temperature, purple crystals (TPP-COOMe) were collected by suctionfiltration (~15% yield). Next, TPP-COOMe (0.5 g) and Cu(CH₃COO)₂ (2 g) were added into a mixed solvent of CH_2Cl_2 (100 mL) and CH_3OH (100 mL), followed by refluxing for 6 h. Then, the solvents of CH_2Cl_2 and CH_3OH were distilled and 150 mL of H_2O was introduced. The resultant precipitate was filtered and washed with 50 mL of H_2O twice. The obtained dark red solid was redissolved in $CHCl_3$ and washed three times with distilled water. The organic layer was then dried over anhydrous magnesium sulfate and evaporated to give crystals in almost 100% yield. The obtained ester was stirred in a mixed solvent of 50 mL THF/ 50 mL CH_3OH / 50 mL H_2O contain 0.75 g NaOH. This mixture was refluxed for 6 h, followed by heating to 100 °C unitl all THF and CH_3OH were evaporated. The mixture was acidified with 1 M HCl to pH = 4. The solid was collected by filtration and washed with water until the Cl^- ions in the filtrate was undetectable by AgNO₃. Finally, the solid was dried in vacuum for overnight and properly stored for further use.

Fabrication of SiT, SiTC and SiTCM and SiTCM(Cu)

The preparation of pyramidal n⁺-p Si wafers refers to our previous work.² The pyramidal n⁺-p Si wafers were cut into pieces of 1.2 cm × 1.2 cm with the surface oxides etched by 5 wt% HF. The etched wafer was immediately transferred to an atomic layer deposition (ALD) chamber for depositing the TiO₂ protective layer (denoted as SiT). A ~5 nm protective layer of TiO₂ was deposited on the n⁺-p Si wafer by using Tetra(dimethylamino) titanium (TDMAT) as the precursor. After TiO₂ deposition, a Cu overlayer of ~50 nm was further deposited by thermal evaporation at a deposition rate of 1 Å/s (denoted as SiTC). Next, the n⁺-p Si/TiO₂/Cu electrodes were immersed in an aqueous solution (5 mL) of NaOH (0.5 M) and (NH₄)₂S₂O₈ (0.125 M) for about 10 seconds at room temperature to grow a surface array of Cu(OH)₂, followed by thoroughly rinsing with ethanol and water, and drying under vacuum. The asobtained SiTC/Cu(OH)₂ electrodes were then immersed in 5 mL DMF solution of H₂TCPP/CU) (0.5 mg/mL), transforming the Cu(OH)₂ array into Cu-TCPP/Cu-TCPP(Cu) MOFs. Thereby, the samples with freebase and metalloporphyrins are denoted as SiTCM and SiTCM(Cu), respectively, which were further rinsed with DMF and ethanol, and dried under vacuum at 120 °C for overnight.

To fabricate the photocathodes, a Cu wire was electrically welded to the back edge of the silicon wafer primed with an Al backcoating. Epoxy (Loctite 9460, Hysol) was used to

encapsulate the electrode surrounding, exposing a central surface area of ~ 1 cm². The exact surface area exposed were calculated by the ImageJ software.

Characterization

Field emission scanning electron microscopy (FEI, Scios and FE-SEM, SU8010) and transmission electron microscopy (TEM, Tecnai G2 F20-S-TWIN) equipped with an energydispersive X-ray spectroscopy analyzer (EDS) were employed to inspect the morphology and microstructure of the samples. Attenuated total reflectance Fourier-transform infrared (ATR-IR) spectra were recorded on a Nicolet iS50 spectrometer. Ultraviolet-visible (UV-vis) spectrometer with an integrating sphere detector (SHIMADZU UV-2600) was employed to acquire the UV-vis diffuse reflectance spectroscopy (DRS). Raman spectra were acquired using a confocal laser Raman microscopy (Horiba Jobin Yvon, HR Evolution) and the excitation wavelength is 532 nm. The surface composition and valence states of the samples were analyzed using X-ray photoelectron spectroscopy (XPS, Thermo Fisher, Escalab 250Xi) with all binding energy values calibrated by C 1s = 284.8 eV. CO₂ adsorption were determined on Micromeritics ASAP 2460. ¹HNMR spectra were acquired by a DD2-600 NMR spectrometer (400 MHz, Agilent Technologies). Steady-state photoluminescence spectra (PL) were measured on a FLS1000 fluorescence spectrophotometer (Edinburgh Instruments, UK) and the excitation wavelength is 340 nm.

PEC CO₂RR Measurements

PEC CO₂ reduction was performed in CO₂-saturated 10:1 acetonitrile (MeCN):H₂O containing 0.1 M TBABF₄ solution in a conventional H-cell (separated by Nafion 115) under 25 °C and 1 bar, using a three-electrode configuration with the fabricated Si electrodes as the working electrodes, Ag/Ag⁺ as the reference electrode (with a ferrocene/ferrocenium (Fc/Fc⁺) couple as the internal potential reference), and a carbon rod as the counter electrode. During PEC measurements, the photocathodes were irradiated by a Xenon lamp source (Beijing Perfectlight Technology, PLS-SXE300+) equipped with an AM 1.5G and UV cut-off ($\lambda > 420$ nm) filter. The intensity of the light was adjusted to 100 mW cm⁻², as quantified by a Thorlabs power calibrator. High-purity CO₂ gas of 20 cm³ min⁻¹ was supplied to the gas chamber controlled by a digital mass flow controller (Horiba). An electrochemical workstation (CHI

660E, Shanghai Chenhua Instruments) was used to conduct the linear sweep voltammetries (LSV) curves and chronoamperometries. LSV curves were performed at a scan rate of 50 mV/s. As the Ag/Ag⁺ electrode is not a standard reference for a nonaqueous system, the recorded potentials vs. Ag/Ag⁺ were converted to the ones vs. Fc/Fc⁺ by the following equation: $E(vs. Fc/Fc^+) = E(vs. Ag/Ag^+) - E(Fc/Fc^+)$, where the Fc/Fc⁺ potential vs. Ag/Ag⁺ is measured as 0.19 V in acetonitrile.³ The reactor cell was connected to a gas chromatography (GC, FL9790 Plus, FULI INSTRUMENTS). H₂ were detected by TCD and CO was detected by FID. Electrochemical impedance spectra (EIS) were carried out at -2.5 V (vs. Fc/Fc⁺) under visible light irradiation and CO₂-saturation conditions in 10:1 (V/V) MeCN-H₂O containing 0.1 M TBABF₄ solution. Chopped light response experiments were performed at - 2.5 V (vs. Fc/Fc⁺) under visible light irradiation and CO₂-saturation conditions in the same electrolyte.

2nF

Q The faradaic efficiency (FE) of CO and H₂ was calculated by using the equation:

FE (%) =

where 2 is the number of electrons required for CO and H_2 products, n is the total amounts of products (moles), F represents the Faraday constant (96485 C mol⁻¹), and Q corresponds to the amount of cumulative charge during CO₂ reduction.

CV Measurements with Standalone MOF Powders

Electrochemical CV tests were carried out by loading the separately prepared MOF catalysts (Cu-TCPP/Cu-TCPP(Cu)) onto glassy carbon working electrodes in Ar/CO₂saturated MeCN-H₂O (10:1) electrolyte containing 0.1 M TBABF₄. To prepare the catalyst ink, 4 mg of the sample powder and 1mg of Ketjen Black were mixed with 50 µL Nafion solution (5%) in 1 mL ethanol by ultrasonic dispersion for 15 min. Next, 10 µL of the asprepared ink was drop-coated onto the glassy carbon electrode with a surface area of 0.197 cm⁻², ٥C followed by heating 50 until completely dried. at

Supplementary Figures



Fig. S1 SEM images of SiT.



Fig. S2 SEM images of the Cu coating on SiTC.



Fig. S3 SEM images of the surface Cu(OH)₂ arrays on SiTC.



Fig. S4 SEM images of SiTCM with different magnifications.



Fig. S5 ATR-IR spectra of TCPP(Cu) and H₂TCPP.



Fig. S6 Raman spectra of TCPP(Cu) and H₂TCPP.



Fig. S7 SEM images of different magnifications for (a1, a2) pristine SiTCM(Cu), and (b1, b2) SiTCM(Cu) immersed in 0.1 M TBABF₄/ MeCN:H₂O (10:1) for one week.



Fig. S8 ATR-IR spectra of the pristine and immersed SiTCM(Cu).



Fig. S9 The CO Faradaic efficiencies of SiTCM(Cu) in electrolyte solutions with different ratio of acetonitrile to water at - 2.5 V (vs. Fc/Fc⁺) under illumination.



Fig. S10 (a) Setup to measure the electrolyte temperature. (b) Change of the temperature with continuous

irradiation for a total of 3 hours.



Fig. S11 LSV curves of SiTCM and SiTCM(Cu) in dark and illuminated conditions.



Fig. S12 ¹HNMR of the electrolyte after the potentiostatic PEC CO₂RR by SiTCM(Cu).



Fig. S13 Chronoamperometric stability tests on SiTCM(Cu) at (a) -1.9 V and (b) -2.5 V vs. Fc/Fc⁺.



Fig. S14 ATR-IR spectra taken on the SiTCM(Cu) photocathodes before and after PEC CO₂RR at (a) -1.9 V and (b) -2.5 V vs. Fc/Fc^+ .



Fig. S15 SEM images of different magnifications taken on the SiTCM(Cu) photocathodes after PEC CO₂RR for (a1, a2) 0 s, (b1, b2) 1800 s, and (c1, c2) 3600 s at -2.5 V vs. Fc/Fc⁺.

Photocathode	Condition	Performance	Reference
SiTCM(Cu)	0.1 M TBABF₄ in MeCN:H₂O (10:1), 100 mW cm² (AM1.5G, λ > 420 nm)	87% CO at -10.2 mA cm ⁻²	This Work
n ⁺ -p Si/GaN/Pt-TiO ₂	0.5 M KHCO ₃ , 800 mW cm ⁻²	78% CO at ~-5 mA cm ⁻²	J. Am. Chem. Soc., 2018, 140 , 7869-7877.
n ⁺ -p-Si NW/Au ₃ Cu	0.1 M KHCO ₃ , 20 mW cm ⁻²	~60% CO at ~-4.5 mA cm ⁻²	Nano Lett., 2016, 16, 5675-5680.
p-Si/Ag	0.5 M KHCO ₃ , 50 mW cm ⁻²	60-90% CO at -9 mA cm ⁻²	J. Mater. Chem. A, 2018, 6, 21906-21912.
Si n-GaN -NPhN4-Ru(CP)2 ²⁺ - RuCt	0.05 M KHCO ₃ , 100 mW cm ⁻²	69% HCOO ⁻ at -1.1 mA cm ⁻²	Nat. Energy, 2019, 4 , 290-299.
p-Si/mesoTiO ₂ /CotpyP	$0.1M~TBABF_4$ in MeCN:H2O (3:2), 100 $$\rm mW~cm^{-2}$$	47.6% CO, 12.8% HCOO ⁻ , ~-0.1 mA cm ⁻²	Nat. Catal., 2019, 2, 354-365.
NiO Si-poly(Ru ^{II})-poly(Re ^I)	0.05 M KHCO ₃ , 100 mW cm ⁻²	65% CO at ~0.015 mA $\rm cm^{-2}$	ACS Energy Lett., 2019, 4 , 629- 636.
p-i-n a-Si/TiO ₃ /Au	0.1 M KHCO ₃ , 100 mW cm ⁻²	50%CO at -4.8 mA cm ⁻²	Energy Environ. Sci., 2019, 12 , 923.
Cu ₂ O/Al:ZnO/TiO ₂ / Re(bpy)(CO) ₃ Cl	0.1 M Bu ₄ NPF ₆ in MeCN, 1 sun	95% CO at ~-2.5 mA cm ⁻²	J. Am. Chem. Soc., 2016, 138 , 1938-1946.
p-Si/mesoTiO ₂ /CoPcP	0.5 M KHCO ₃ , 100 mW cm ⁻²	56% CO at -1.5 mA cm ⁻²	ACS Catal., 2021, 11, 1868-1876.
Cr ₂ O ₃ /N,Zn-Fe ₂ O ₃ /TiO ₂ / Ru(MeCN)CO ₂ C ₃ Py-P	0.1 M KHCO ₃ , 100 mW cm ⁻²	63% HCOOH, 30% CO at - 0.15 mA cm ⁻²	ACS Catal., 2018, 8, 1405-1416.
CIGS f-TiO ₂ Co-qPyH	0.1 M KHCO ₃ , NR	89% CO at -0.81 mA cm ⁻²	Nat. Commun., 2020, 11, 3499.
Cu ₃ (BTC) ₂ /Cu ₂ O/ITO	0.1 M TBAPF ₆ in MeCN	95% CO (dark) 0.83% STC efficiency at ~- 0.78 mA cm ⁻²	J. Am. Chem., Soc., 2019, 141 , 10924-10929.

Table S1 Performance comparison of various PEC CO₂RR systems engaging catalysts from recent literature.

* TBABF₄: tetrabutylammonium tetrafluoroborate; Bu₄NPF₆ and TBAPF₆: tetrabutylammonium hexafluorophosphate

** NR not reported

*** STC: solar-to-CO (100 mW·cm⁻² with an AM 1.5G filter)

 Table S2 Fitting results of EIS taken at -2.5 V vs. Fc/Fc⁺ under illumination in CO₂-saturated electrolyte for different photocathodes.

Photocathode	$R_s(\Omega)$	$R_1(\Omega)$	$R_2(\Omega)$
SiT	107.0	39.6	150.5
SiTC	106.5	27.8	100.2
SiTCM	106.1	16.0	63.8
SiTCM(Cu)	105.2	11.9	40.7

References

1 D. Feng, H. L. Jiang, Y. P. Chen, Z. Y. Gu, Z. Wei and H. C. Zhou, Inorg Chem, 2013, 52, 12661-

12667.

- 2 R. L. Fan,; G. P. Huang,; Y. J. Wang, Z. T. Mi and M. R. Shen, Appl. Catal. B, 2018, 237, 158-165.
- 3 X. Deng, R. Li, S. Wu, L. Wang, J. Hu, J. Ma, W. Jiang, N. Zhang, X. Zheng, C. Gao, L. Wang, Q. Zhang, J. Zhu and Y. Xiong, J. Am. Chem. Soc., 2019, 141, 10924-10929.