Electronic Supplementary Information

Cathodized Copper Porphyrin Metal-Organic Frameworks Nanosheets for Selective Formate and Acetate Production from CO_2 Electroreduction

Jian-Xiang Wu, Shu-Zhen Hou, Xiang-Da Zhang, Ming Xu, Hua-Fei Yang, Pei-Sheng Cao and Zhi-Yuan Gu*

Jiangsu Key Laboratory of Biofunctional Materials, Jiangsu Collaborative Innovation Center of Biomedical Functional Materials, Jiangsu Key Laboratory of New Power Batteries, School of Chemistry and Materials Science, Nanjing Normal University, Nanjing, 210023, P. R. China

Email: guzhiyuan@njnu.edu.cn, Fax/Phone: +86-25-85891952

Contents

Section S1. Chemicals

The following chemicals were used as received without further purification: copper (II) nitrate trihydrate, polyvinylpyrrolidone (M=40000), L-Ascorbic acid, sodium hydroxide, propionic acid, methyl p-formylbenzoate, ester, tetrahydrofuran, methanol, ethanol, hydrochloric acid copper (II) chloride dehydrate, 1-metilimidazole, ethyl bromide and $NaBF_4$ were purchased from Aladdin. Nafion D-521 dispersion (5 wt% in lower aliphatic alcohols and water) and Nafion 117 proton exchange membrane were purchased from Shanghai Hesen Electric Co. Ltd.. $Cu(NO_3)_2 \cdot 3H_2O$, $AgNO_3$, N,N-dimethylformamide (DMF) and acetonitrile (CH_3CN) were purchased from Aladdin. Fluorinedoped tin oxide (FTO) glass substrates (8 Ω/sq) were purchased from Dalian Qiseguang Solar Technology Development Co. Ltd.. All materials were used as obtained without further purification. 5,10,15,20-tetrakis (4-carboxyphenyl) porphyrin (H_2TCPP) and 1-Ethyl-3-methylimidazolium tetra-fluoroborate ($EMIMBF_4$) were prepared according to the published procedures. The ultrapure water (18.4 MΩ·cm) was prepared by an ELGA purification system (Veolia Water Solutions & Technologies, UK).

Section S2. Synthesis of Materials

Preparation method of MOF nanosheet

$Cu_2(CuTCPP)$ nanosheets were synthesized by using a solution reaction of $Cu(NO_3)_2 \cdot 3H_2O$ and H_2TCPP in N,N-diethylformamide (DMF). Typically, H_2TCPP (7.9 mg, 0.01 mmol), $Cu(NO_3)_2 \cdot 3H_2O$ (7.3 mg, 0.03 mmol), DMF 18 mL, were mixed in flask at room temperature. The mixture was kept at 85 ^oC for 24 hours with stirring, and then, the solid was collected by centrifugalize. After above processes, the purple nanosheets were obtained.[1, 2]

5,10,15,20-tetrakis (4-carboxyphenyl) porphyrin (H_2TCPP). To propionic acid (100 mL) in a 500-mL three necked flask pyrrole (3.0g, 0.043 mol) and methyl p-formylbenzoate (6.9 g, 0.042 mol) were added and refluxed for 12h. After the reaction mixture was cooled to room temperature, crystals were collected by filtration to afford purple crystals (TPP-COOMe). The obtained ester (0.75 g) was stirred in THF (25 mL) and MeOH (25 mL) mixed solvent, to which a solution of KOH (2.63 g, 46.95 mmol) in H_2O (25 mL) was introduced. This mixture was refluxed for 12 h. After cooling down to room temperature, the THF and MeOH were evaporated. Additional water was added to the resulting water phase and the mixture was heated until the solid was fully dissolved. Then the homogeneous solution was acidified with 1M HCl until no further precipitate was generated. The dark red was collected by filtration, washed with water and dried in vacuum overnight.[3]

[5,10,15,20-tetrakis(4-carboxyphenyl)porphyrinato]-Cu(II) (TCPP(Cu)). A solution of TPP-COOMe 0.854 g (1.0 mmol) and $CuCl_2 \cdot 2H_2O$ (2.2g, 12.8 mmol) in

100 mL of DMF was refluxed for 6 h. After the mixture was cooled to room temperature, 150 mL of H_2O was added. The resultant precipitate was filtered and washed with 50 mL of H_2O for two times. The obtained solid was dissolved in $CHCl_3$, followed by three times of washing with water. The organic layer was dried over anhydrous magnesium sulfate and evaporated to afford dark red crystals. The obtained ester (0.75 g) was stirred in THF (25 mL) and MeOH (25 mL) mixed solvent, to which a solution of KOH (2.63 g, 46.95 mmol) in H_2O (25 mL) was introduced. This mixture was refluxed for 12 h. After cooling down to room temperature, the THF and MeOH were evaporated. Additional water was added to the resulting water phase and the mixture was heated until the solid was fully dissolved. Then the homogeneous solution was acidified with 1M HCl until no further precipitate was generated. The dark red was collected by filtration, washed with water and dried in vacuum overnight.[3]

1-**Ethyl-3-methylimidazolium tetra-fluoroborate (EMIMBF$_4$).** 1-metilimidazole and ethyl bromide with mole ratio of 1: 1.2 was reacted in a flask at 70°C for 12 h. The impurities of raw product were washed and extracted by ethyl acetate and three times. The yellowish viscous liquid (EMIMBr) product was obtained after rotary evaporation at 65 °C for 6 h. The mixture of EMIMBr and $NaBF_4$ was stirred at 40 °C for 12 h. After the reaction, dichloromethane was added to extract the product EMIMBF$_4$. After the precipitated sodium bromide was separated by filtering the solution, the product EMIMBF$_4$ was obtained with rotary evaporation at 45 °C for 6 h

Copper electrode fabrication. FTO electrodes were dried after sequentially washing with 1M HCl and ethanol. The pretreated FTO electrodes with dimensions of 1×1 cm^2 were used as cathodes in a three electrode cell consisting of an anode (platinum sheet auxiliary electrode) and an Ag/AgCl reference electrode. 30 g/L of copper acetate and 20 g/L of sodium acetate mixed as an electrolyte at ambient temperature to synthesis copper onto FTO at -1.2 V versus Ag/AgCl for 200 s. Then, the Cu-FTO electrodes were obtained after washing with ultrapure water and drying under ambient conditions.[4]

Preparation of Cu_2O. 1 mL of $CuCl_2$ (0.1 M) and 0.1 g of PVP were dissolved into 40 mL of water. The solution was stirred for 5 min before the dropwise addition of 2.5 mL of NaOH (0.2 M). Then 2.5 mL of ascorbic acid (0.1 M) was dropwise added into the solution just 5 min after all NaOH was added. The mixture was continuously stirred for 5 min at room temperature, then the solid was recovered by centrifugation and washed with ethanol twice. At last, the Cu_2O nanoparticles were resuspended into 10 mL of ethanol (copper concentration: ca. 10 mM) for future investigation.[5]

Preparation of CuO. 1 mL of $CuCl_2$ (0.1 M) and 0.1 g of PVP were dissolved into 40 mL of water. The solution was stirred for 5 min before the dropwise addition of 2.5 mL of NaOH (0.2 M). The mixture was continuously stirred for 5 min at room temperature, then the solid was recovered by centrifugation and washed with ethanol twicend and dried in vacuum overnight.[5]

Section S3. Materials Characterization

X-ray diffraction (XRD) patterns were obtained from a Rigaku SmartLab 9 Kw instrument (Tokyo, Japan) D/MAX-2500 diffractometer with a Cu K_α radiation (1.54056 Å). Data was recorded from 5^o to 80^o. The scanning electron microscope (SEM) images were collected on a JSM-7600 scanning electron microscope (JEOL Ltd.). Transmission electron microscopy (TEM) images were recorded on a JEOL JEM-2100F transmission electron micro-scope operated at an accelerating voltage of 200 kV. Atomic force microscopy (AFM) measurements were per-formed with a PicoPlus in tapping mode (Agilent, US). X-ray photoelectron spectroscopy (XPS) were ESCALAB 250XI-AES (Thermo Fisher Scientific) equipped with Al K_α monochromator. Fourier transform infrared spectroscopy was obtained on Vertex 70 (Bruker, Germany).

Section S4. Electrochemical Study

To prepare the Cu_2(CuTCPP) nanosheets electrode, 0.5 mg Cu_2(CuTCPP) prepared above were suspended in 50 μL ethanol with 20 μL Nafion D-521 dispersion (5 wt%) to form a homogeneous ink assisted by ultrasound. Then, 110 μL of the ink was spread onto the FTO (1×1 cm^2) surface by a micropipette and then dried under room temperature. The loading of Cu_2(CuTCPP) catalyst was 0.5 mg/cm^2. Before experiment, all the auxiliary electrodes were sonicated in acetone for 10 min and then washed with water and ethanol, followed by drying. The electrochemical workstation (CHI 660E, Shanghai CH Instruments Co., China) was used in all the experiments of CO_2 reduction. Cyclic voltammetry (CV) and linear sweep voltammetry (LSV) measurements were carried out in a H-type cell with three-electrode configuration, which consisted of working electrode (Cu_2(CuTCPP) electrode), a platinum sheet auxiliary electrode, and an Ag/Ag^+ (0.01 M $AgNO_3$ in 0.1 M $EMIMBF_4$-MeCN) reference electrode. The electrolyte was bubbled with N_2 or CO_2 for at least 30 min to form N_2 or CO_2 saturated solution. The LSV and CV measurement in gas-saturated electrolyte was conducted in the potential range of 0.5 to -2.0 V vs. Ag/Ag^+ at a sweep rate of 50 mV/s. The electrolysis experiments were conducted at 25 °C in a typical H-type cell that was similar to that used in previous works. It consisted of a cathode (Cu_2(CuTCPP) electrode), an anode (platinum sheet auxiliary electrode), and an Ag/Ag^+ reference electrode. In the experiments, the cathode and anode compartments were separated through a

Nafion 117 proton exchange membrane. 1 M H_2O/CH_3CN solutions with 0.5 M $EMIMBF_4$ as an electrolyte at ambient temperature, which is a commonly used electrolyte. H^+ can be transferred from anode compartment to cathode compartment through Nafion 117 proton exchange membrane, which is the proton source. CO_2 was bubbled through the catholyte (15 mL/min) for 30 min before electrolysis.[6, 7]

Section S5. Product Analysis

The gaseous product of electrochemical experiments was collected using a gas cylinder and analyzed by gas chromatography (GC, SRI, 8610C), which was equipped with HID and thermal conductivity detector (TCD) using helium (99.999%) as the carrier gas, with 1 ml every time. Meanwhile the gas was seperated with MoleSieve 13X and Silica Gel inside of GC. The GC was equipped with a packed MolSieve 13X column and a packed Silica Gel column. Helium (99.999%) was used as the carrier gas. The column effluent (separated gas mixtures) was first passed through a TCD; it was then passed through a Helium Ionization Detector (HID). The liquid product was analyzed by ^{1}H NMR (Bruker Avance III 400 HD spectrometer) in DMSO-d_6 with TMS as an internal standard. Their faradic efficiency was calculated as follows:

$$\text{FE (\%)} = znF/Q \times 100\%, \qquad \text{(Equation 1)}$$

Where z is the number of electrons required to form a molecule of product, F is the Faraday constant (96500 C/mol), and Q is the total charge. All Faradaic efficiencies were calculated without any normalization.

Section S6. Calculation of Turnover Frequency

We integrated the anodic wave in the CV curve of $Cu_2(CuTCPP)$ under N_2 atmosphere (as depicted in Fig. S3), and then calculated the amount of quantity of electric charge: [8, 9]

$$Q = \frac{S}{v}$$

Where Q is the integrated charge of the anodic wave, S is the oxidation peak area of the cyclic voltammetry curve and v is the sweep speed.

The amount of surface active Cu by assuming a two-electron redox process:

$$n = \frac{Q}{F}$$

where n is the amount of surface active Cu on the working electrode, Q is the integrated charge of the anodic wave, and F is the Faraday constant.

The total amount of Cu was calculated as follows:

$$n_{tot} = \frac{m_{cat} W_{Cu}}{M_{Cu}}$$

where n_{tot} is the molar amount of Cu on the working electrode, m_{cat} is the mass of the hybrid electrocatalyst loaded on the working electrode, w_{Cu} is the weight fraction of Cu in the electrocatalyst determined, and M_{Cu} is the atomic weight of Cu.

Then, the surface fraction of electrochemically active Cu sites was determined as follows:

$$f = \frac{n}{n_{tot}}$$

Turnover frequency (TOF) is defined as the mole of reduction product generated per electrocatalytic active site per unit time. The equation below:

$$\mathrm{TOF} = \frac{(\mathrm{J}_{\mathrm{product}} / \mathrm{zF}) / \mathrm{n}_{\mathrm{tot}}}{\mathrm{f}} \times 3600$$

Where z is the number of electrons required to form a molecule of product, F is the Faraday constant (96500 C/mol), n_{tot} is the total amount of Cu on the working electrode and $J_{product}$ is the recorded current of product.

Section S7. Electrochemical CO_2 Reduction by Cu_2(CuTCPP)

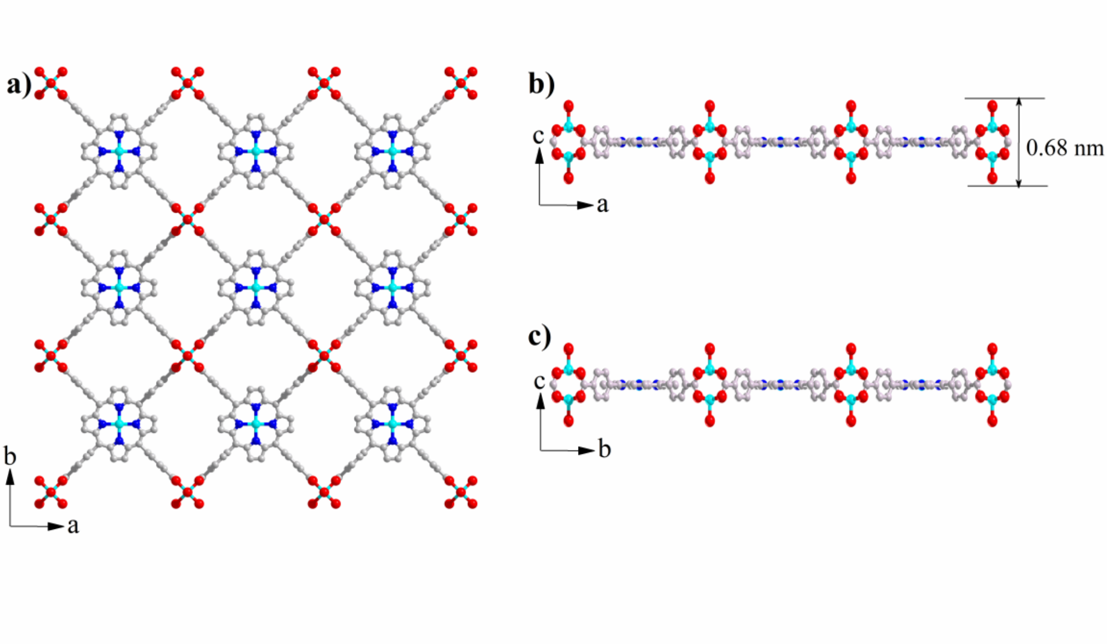

Fig. S1. Simulated crystal structure of Cu_2(CuTCPP) (a, b and c). Red is O, blue is N, grey is C and cyan is Cu.

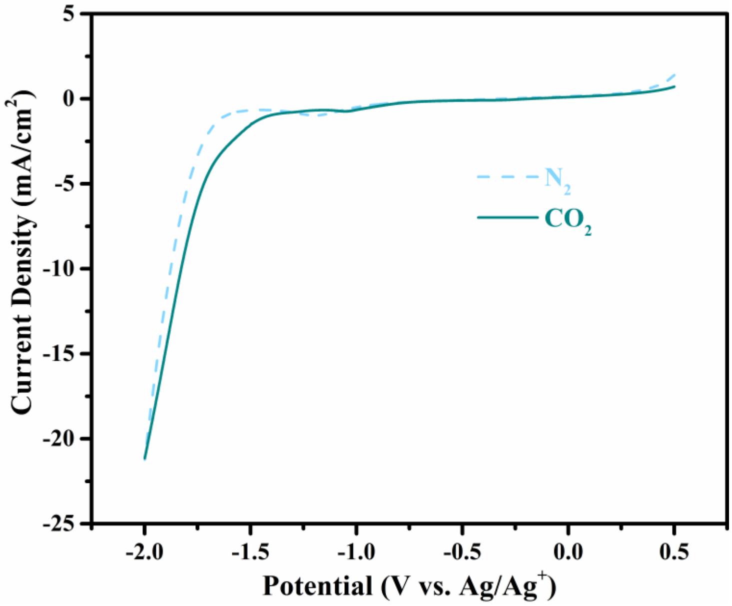

Fig. S2. Linear sweep voltammetry curves of Cu_2(CuTCPP) in N_2 - or CO_2 -saturated CH_3CN solutions with 1 M H_2O and 0.5 M $EMIMBF_4$.

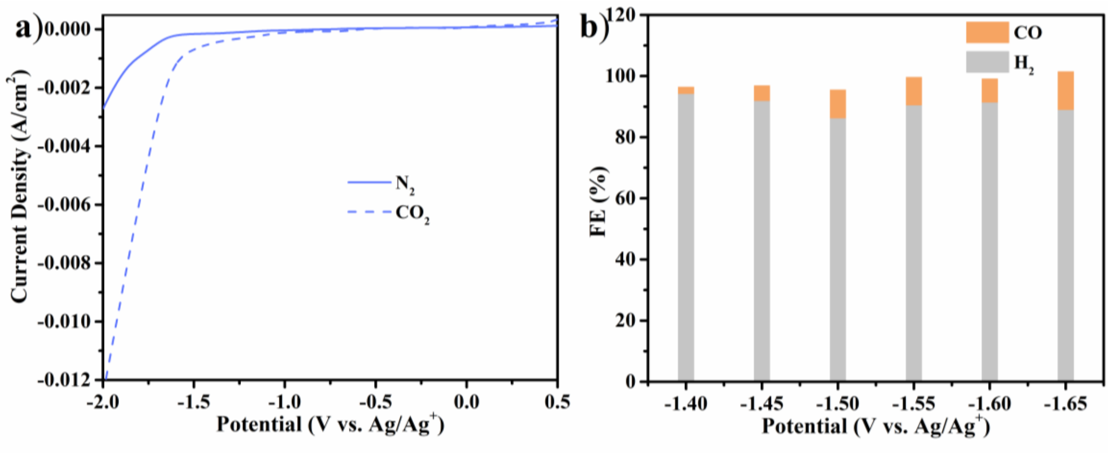

Fig. S3. Eletrochemical performance of pure FTO electrode. (a) LSV in N_2 - or CO_2 -saturated CH_3CN solutions with 1 M H_2O and 0.5 M $EMIMBF_4$; (b) Faradaic efficiency in CO_2 -saturated CH_3CN solutions with 1 M H_2O and 0.5 M $EMIMBF_4$.

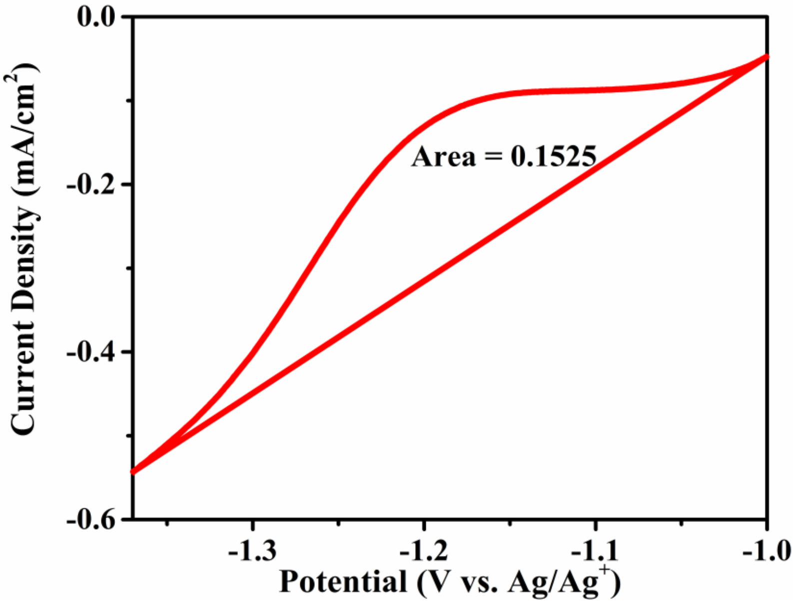

Fig. S4. Total charge integrated from the Cu^{2+}/Cu^0 cathodic wave. Using CV value at 50 mV/s, which was in N_2 -saturated CH_3CN solutions with 1 M H_2O and 0.5 M $EMIMBF_4$, we further estimated the percentage of surface Cu sites. The amount of surface active Cu is $n = \frac{Q}{F} = [0.1525\ (mA \cdot V/cm^2)\ /\ 0.05\ (V/s)]\ /\ 96500\ C/mol = 3.16 \times 10^{-8}\ mol/cm^2$.

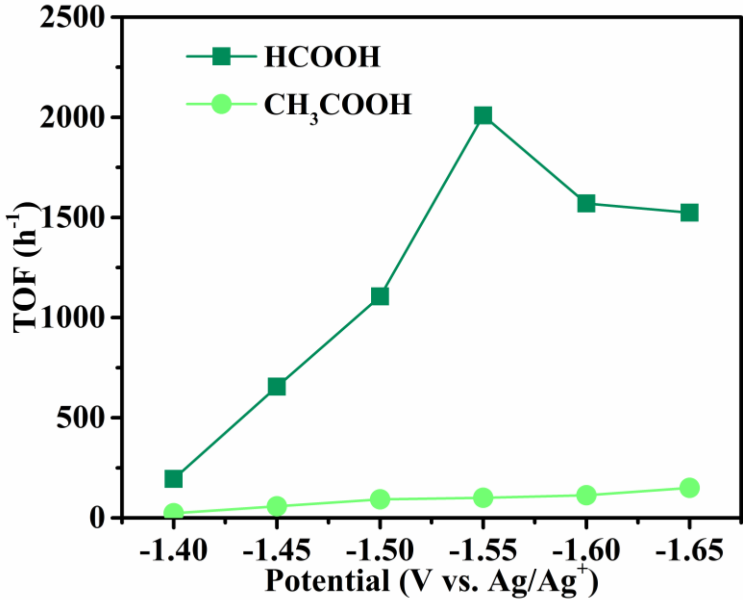

Fig. S5. TOF of formate and acetate by the pre-electrolyzed Cu_2(CuTCPP) nanosheets at different working potentials

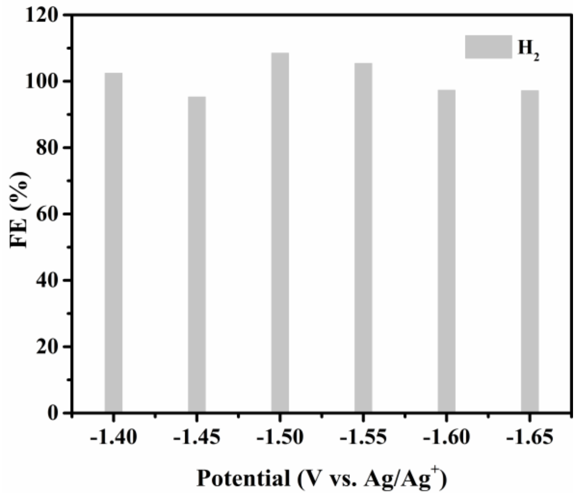

Fig. S6. Faradaic efficiencies of Cu_2(CuTCPP) in N_2 -saturated CH_3CN solutions with 1.0 M H_2O and 0.5 M $EMIMBF_4$.

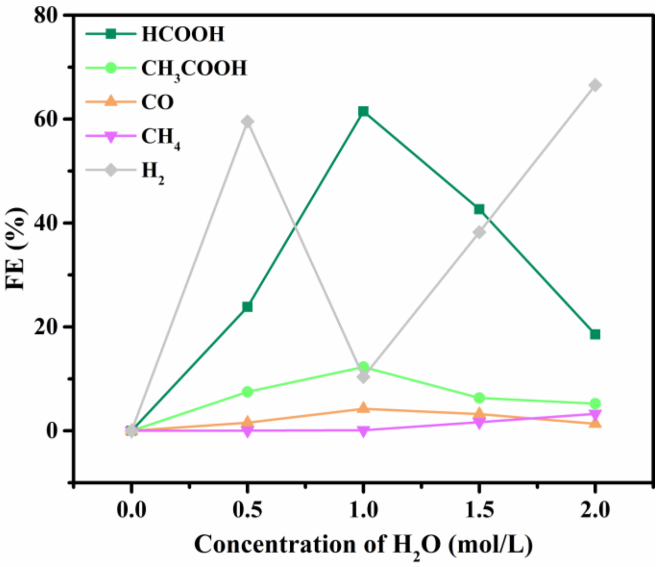

Fig. S7. The effect of H_2O concentration on FE in CH_3CN solutions with 0.5 M $EMIMBF_4$ at -1.55 V

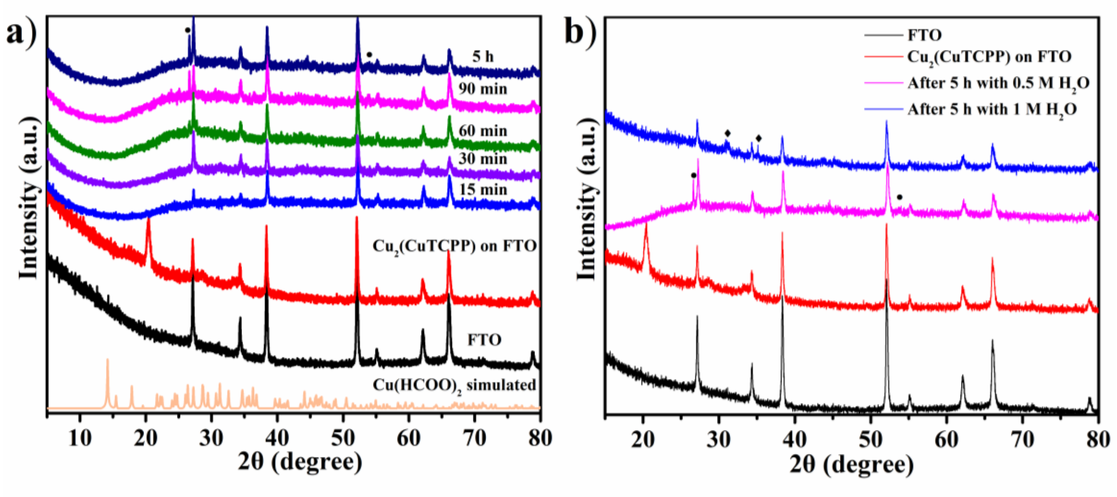

Fig. S8. XRD of Cu_2(CuTCPP) on FTO after electrolysis at different time in CO_2-saturated CH_3CN solutions with 0.5 M H_2O and 0.5 M $EMIMBF_4$ (● $Cu(HCOO)_2$; ◆ Cu_4O_3). The XRD results are significantly different from those obtained under 1.0 M H_2O condition (See Fig. 4a). After 5 h, only the intermediate $Cu(HCOO)_2$ was generated under the condition with 0.5 M water, while with 1.0 M water, the generation of the intermediate $Cu(HCOO)_2$ only took 30 min and would keep transformed to CuO, Cu_2O and Cu_4O_3. It seemed that the appropriate amount of water promoted the Cu_2(CuTCPP) cathodized procedure.

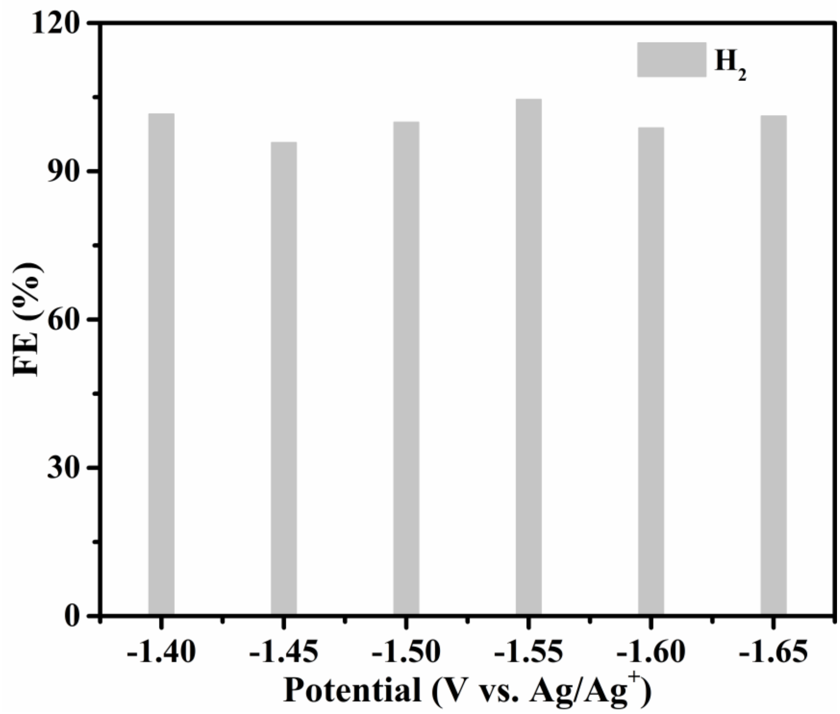

Fig. S9. Eletrochemical performance of Cu_2(CuTCPP) in CO -saturated CH_3CN solutions with 1 M H_2O and 0.5 M $EMIMBF_4$.

Section S8. Characterization of Other Cu Catalysts

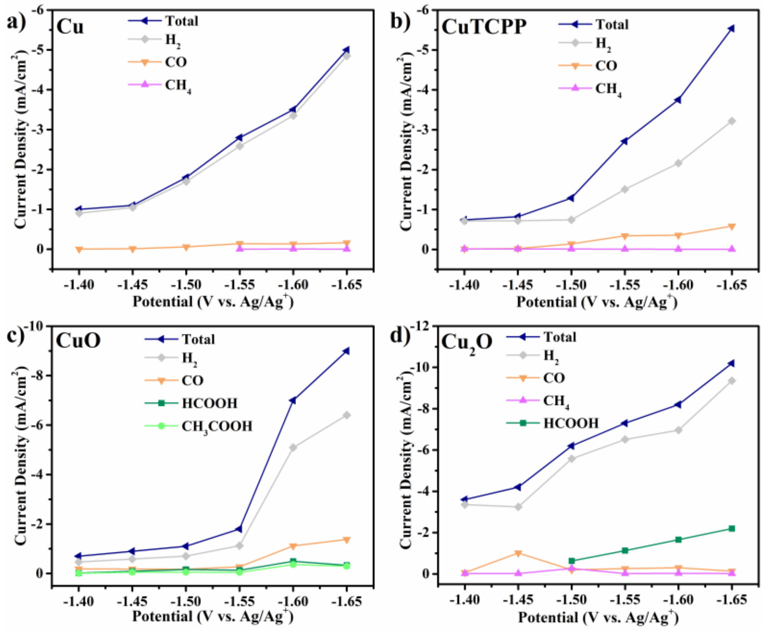

Fig. S10. Total and partial current densities of CO_2RR products for (a) Cu; (b) CuTCPP; (c) CuO; (d) Cu_2O catalysts.

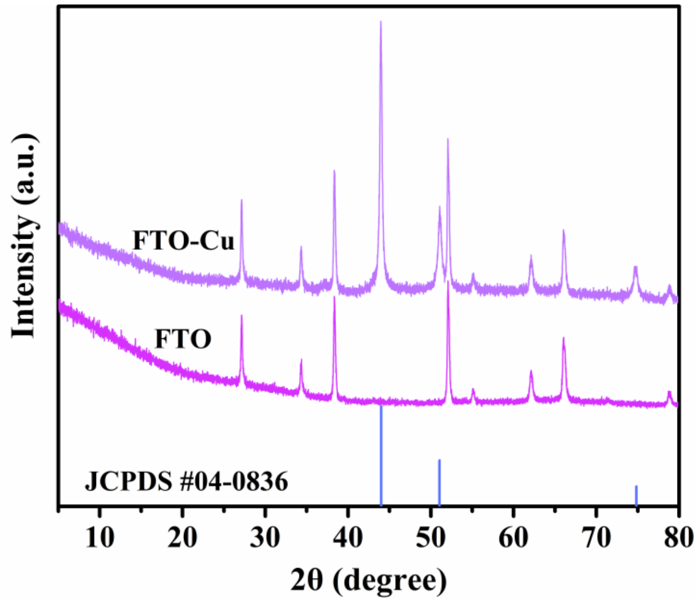

Fig. S11. XRD data of the as-synthesized Cu on FTO. All additional peaks match with JCPDS #04-0836.

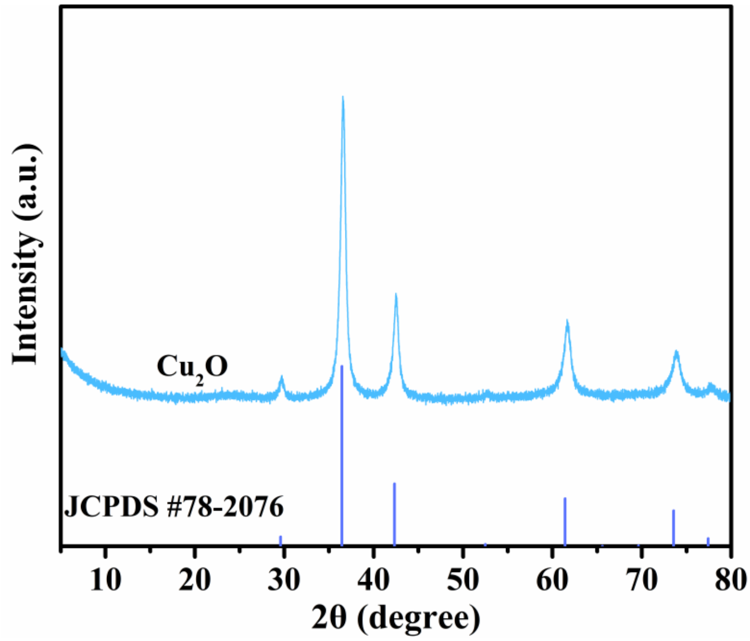

Fig. S12. XRD data of the as-synthesized Cu_2O. All peaks match with JCPDS #78-2076.

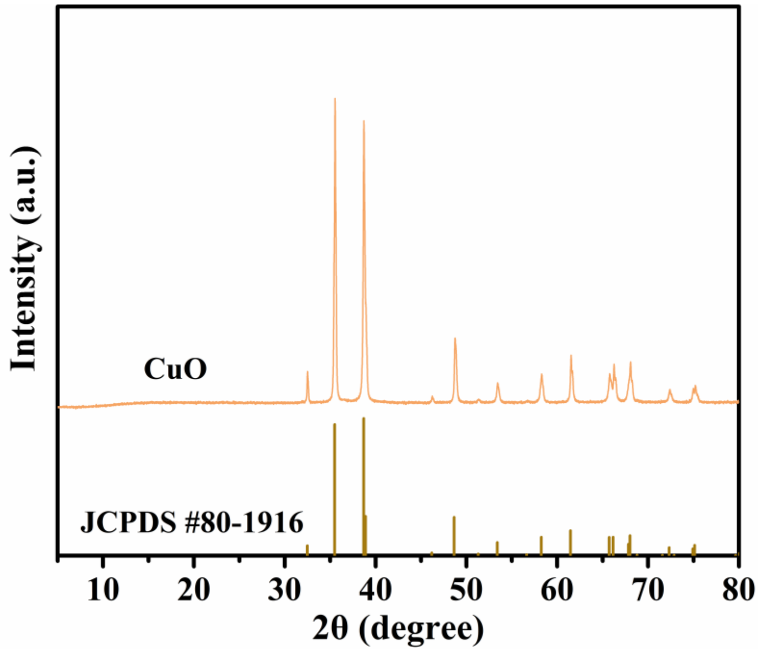

Fig. S13. XRD data of the as-synthesized CuO. All peaks match with JCPDS #80-1916.

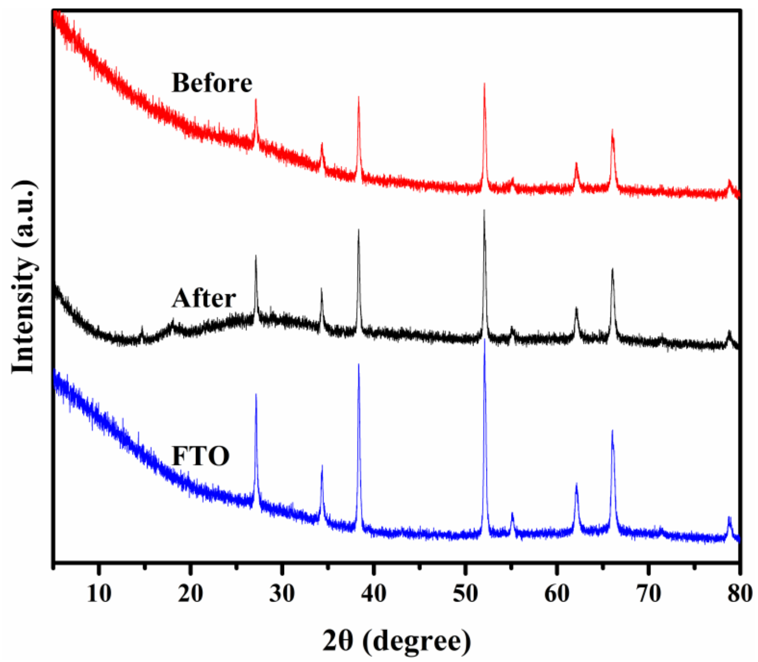

Fig. S14. XRD data of the as-synthesized CuTCPP before and after reaction.

Section S9. Cathodized Reconstruction of Cu_2(CuTCPP)

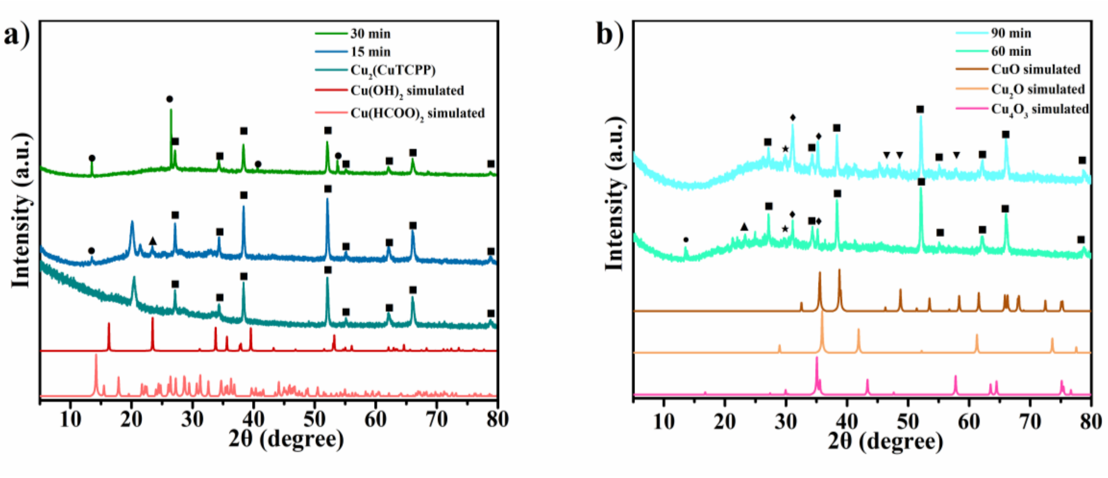

Fig. S15. XRD of Cu_2(CuTCPP) catalyst on FTO with different reaction time in CO_2-saturated CH_3CN solutions with 1 M H_2O and 0.5 M $EMIMBF_4$. a) 15 min and 30 min; b) 60 min and 90 min. Marked peaks with possible products, intermediates and FTO substrate as ● $Cu(HCOO)_2$; ◆ Cu_4O_3; ▲ $Cu(OH)_2$; ▼ CuO; ★ Cu_2O and ■ FTO.

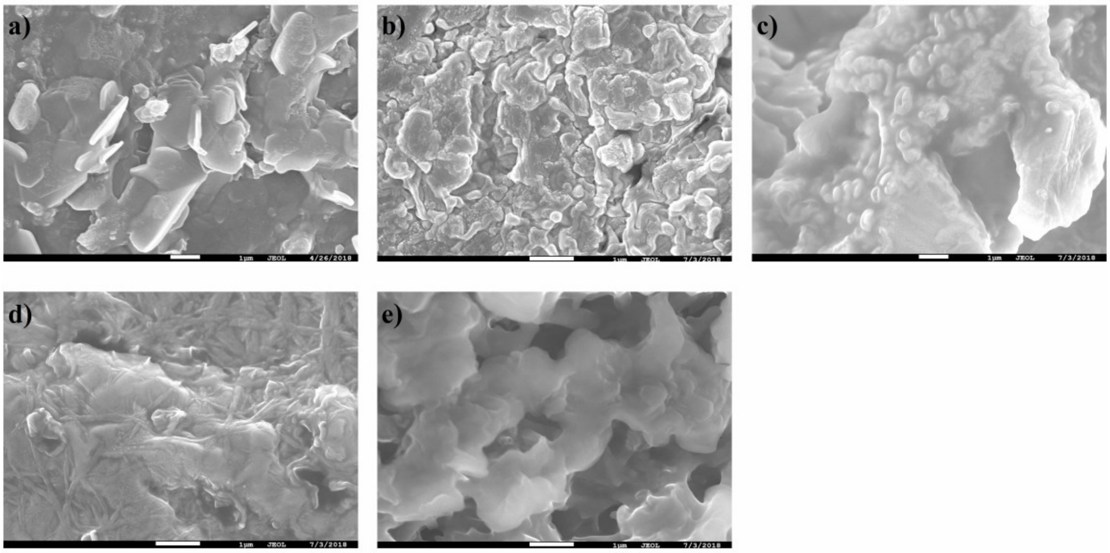

Fig. S16. SEM images of Cu_2(CuTCPP) on FTO after electrolysis at -1.55 V for different time (a) 0 min; (b) 15 min; (c) 30 min; (d) 60 min; (e) 90 min.

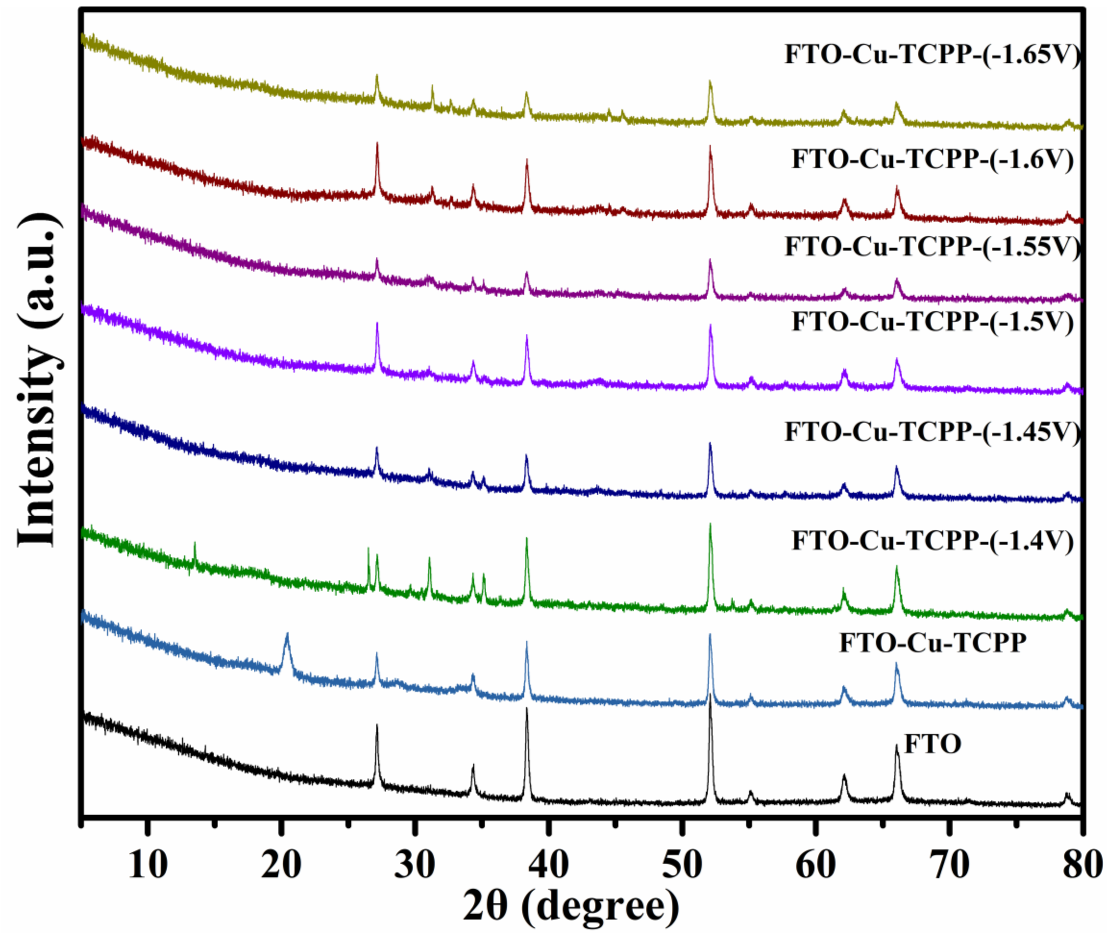

Fig. S17. XRD of Cu_2(CuTCPP) on FTO after electrolysis at different voltage in CO_2-saturated CH_3CN solutions with 1 M H_2O and 0.5 M $EMIMBF_4$

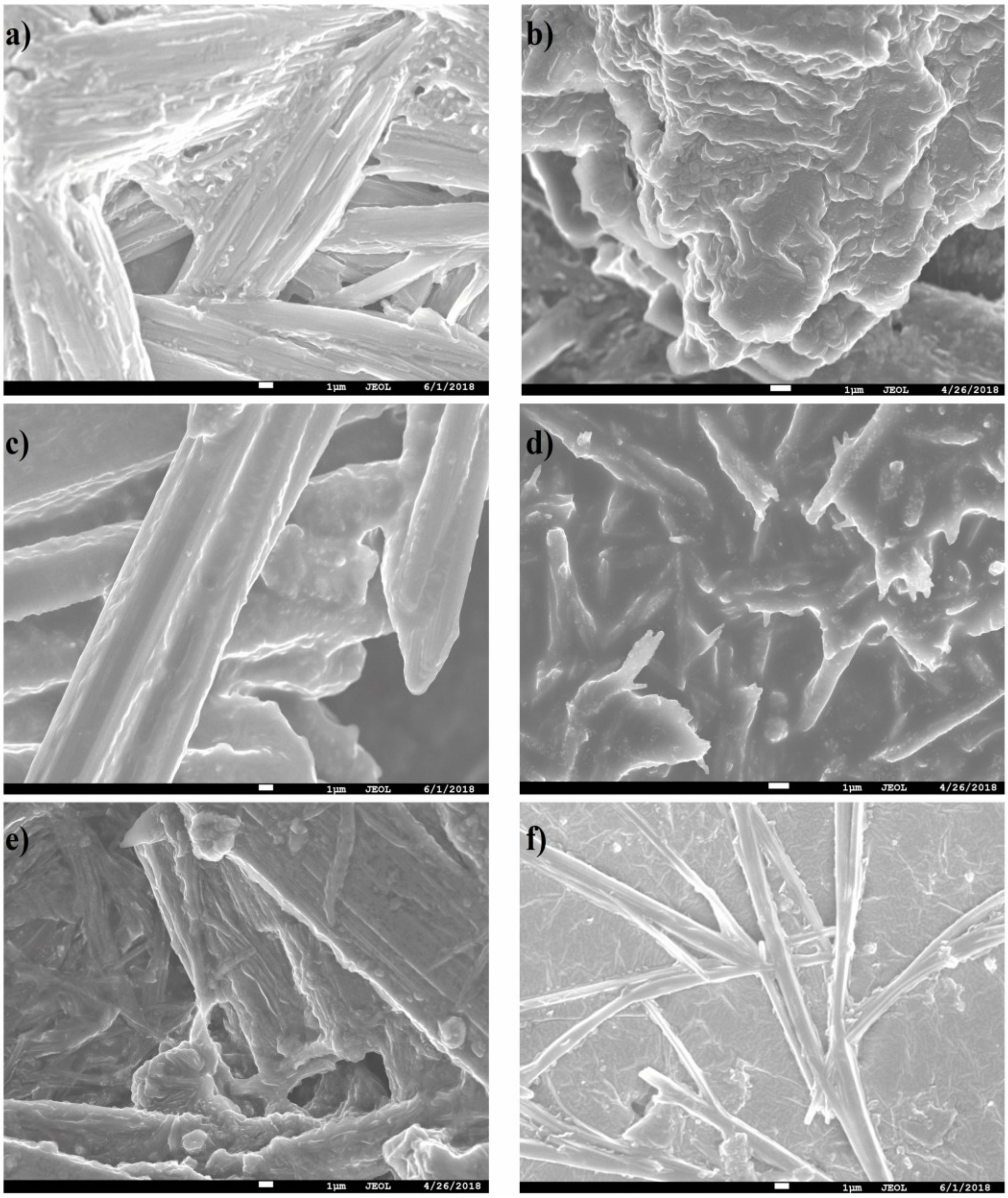

Fig. S18. SEM images of Cu_2(CuTCPP) on FTO after electrolysis at different voltage for 5 h (a) -1.45 V; (b)-1.45 V; (c) -1.50 V; (d) -1. 55 V; (e) -1.60 V; (f) -1.65 V.

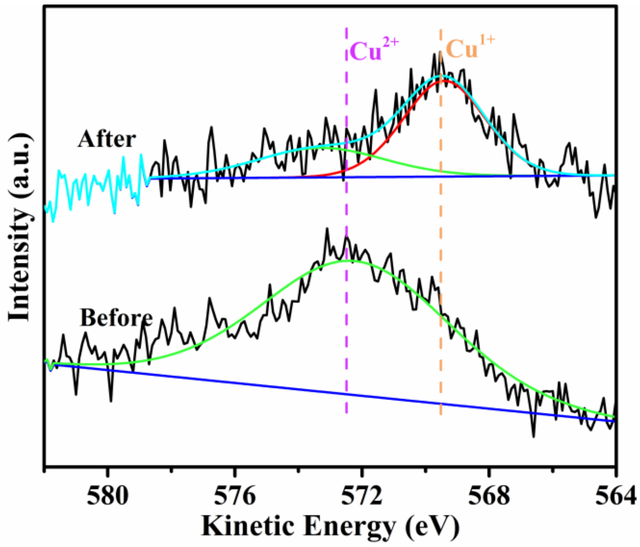

Fig. S19. The Auger spectra of as-synthesized Cu_2(CuTCPP) before and after reaction. The two overlapped peaks at 569.5 eV and 572.5 eV were ascribed to the Cu^+ and Cu^{2+}, respectively.[10]

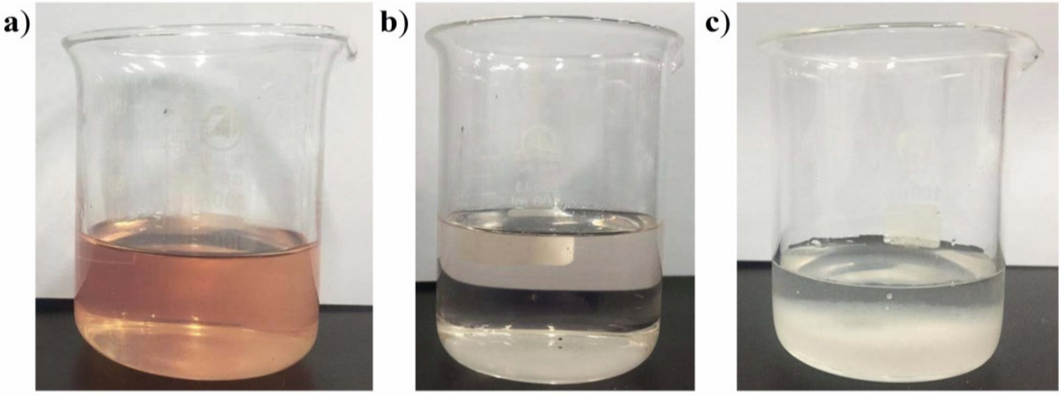

Fig. S20. (a) 40 mL pure electrolyte with 1 mg CuTCPP; (b) pure electrolyte with 0.1 mg CuTCPP; (c) the actual electrolyte after electrolysis with the precipitates of acetate and formate.

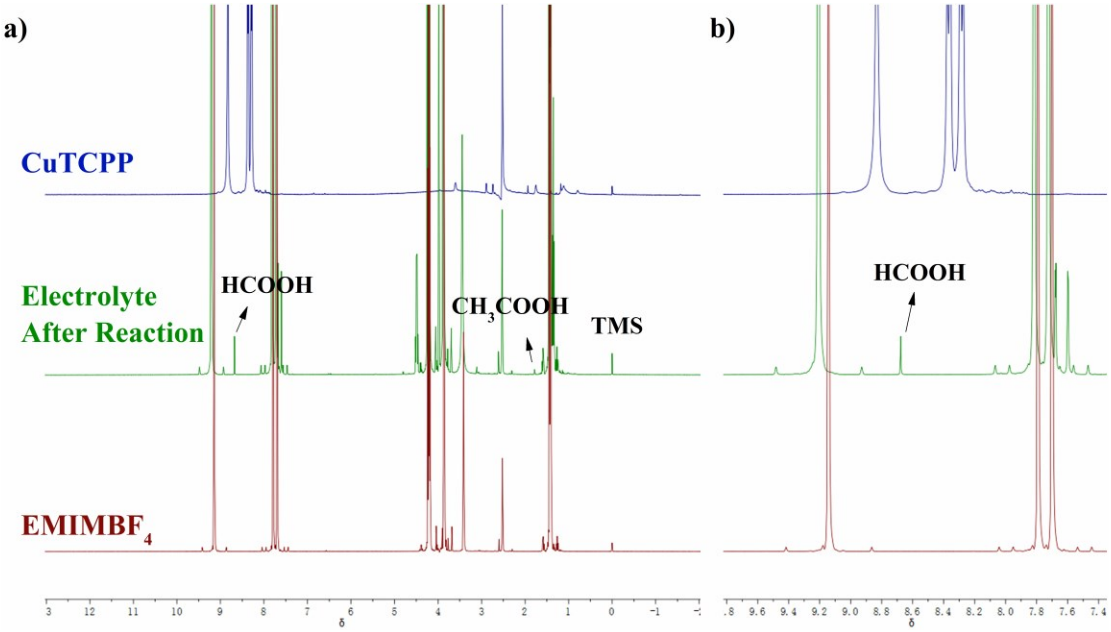

Fig. S21. (a) The NMR data and (b) enlarged spectra for CuTCPP ligand, EMIMBF$_4$ and electrolyte after reaction.

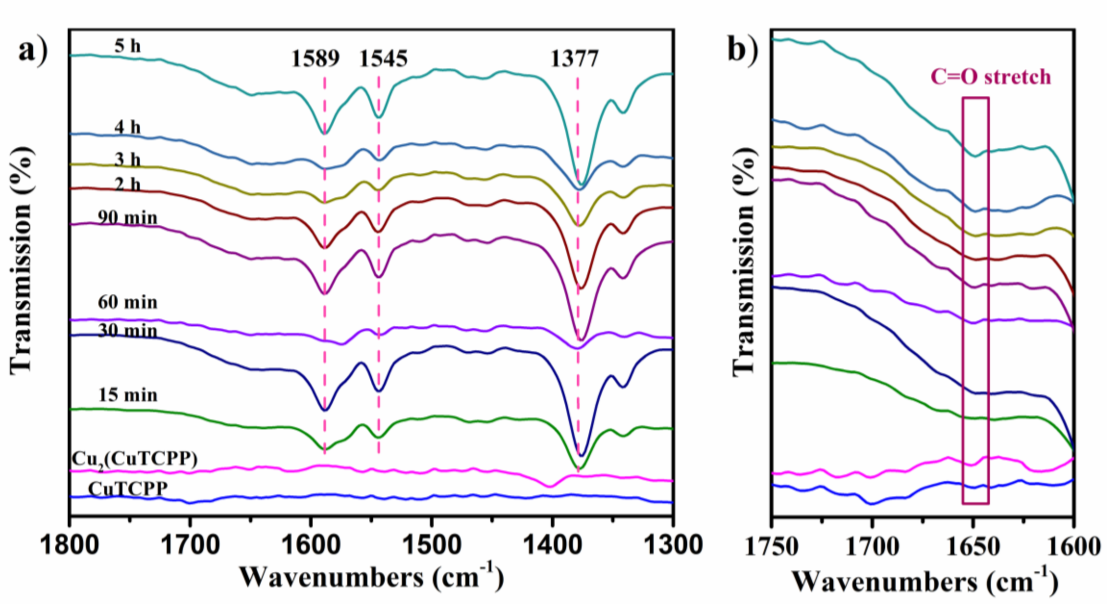

Fig. S22. The FT-IR spectra of catalysts before and after reduction at different time. The peaks at 1589, 1545 and 1377 cm^{-1} were the residual ionic liquid EMIMBF$_4$.[11]

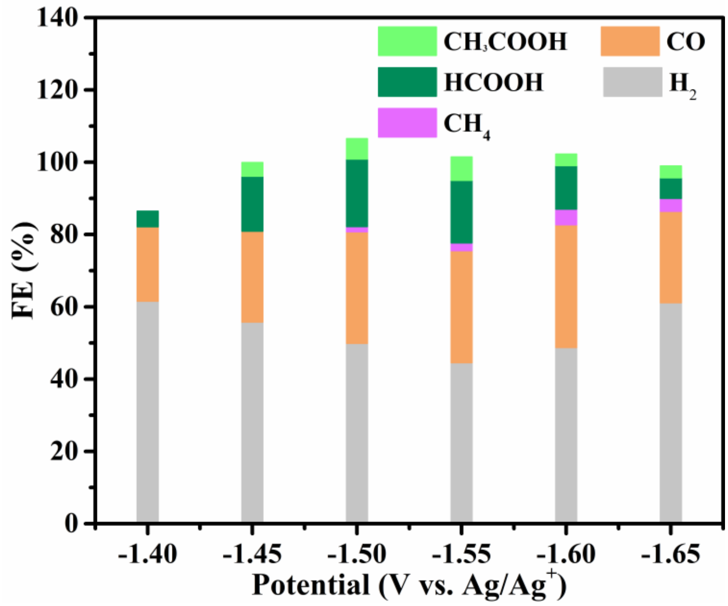

Fig. S23. Faradaic efficiencies of CuO/CuTCPP (molar ratio of 2:1) in CO_2 -saturated CH_3CN solutions with 1 M H_2O and 0.5 M $EMIMBF_4$ with different potentials.

Section S10. Standard Curve

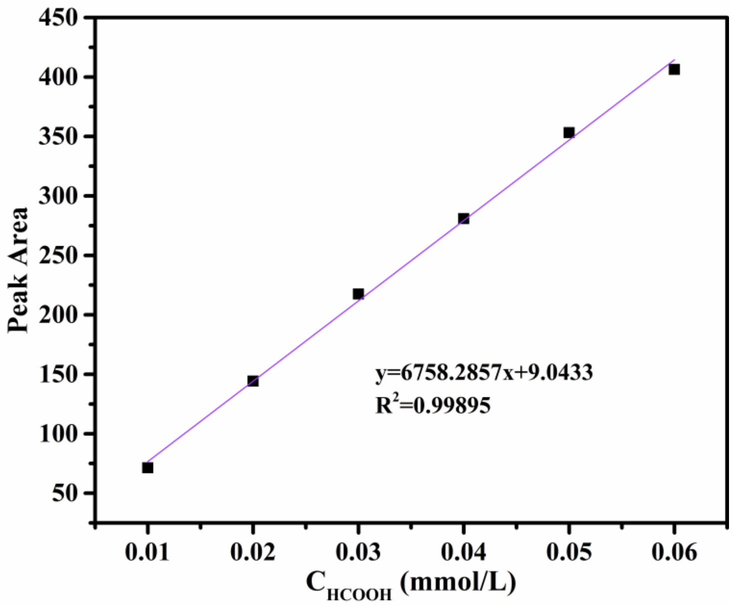

Fig. S24. Standard curve of HCOOH

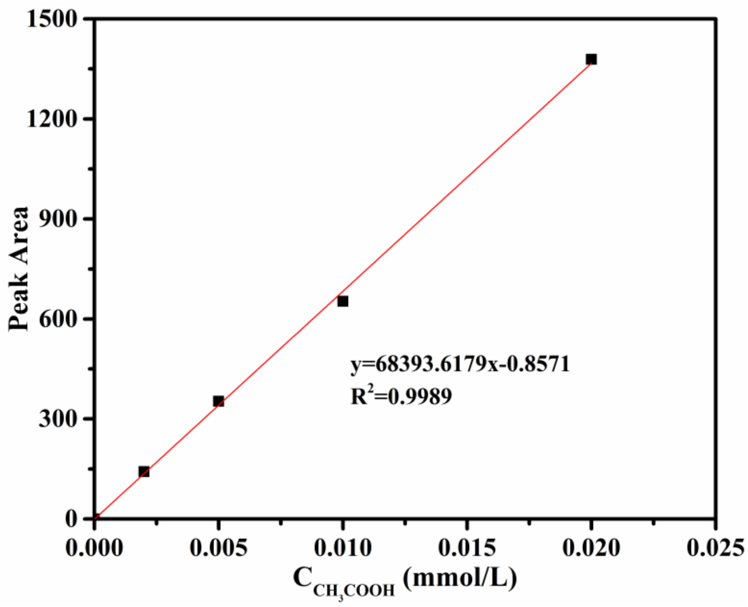

Fig. S25. Standard curve of CH_3COOH

Table S1. Product yield of different catalysts

Catalyst	H_2 (**μmol**)	CO (**μmol**)	CH_4 (**μmol**)	HCOOH (**μmol**)	CH_3COOH (**μmol**)
Cathodized Cu_2(CuTCPP)	44.6	55.2	0.139	312	19.2
Cu	215	11.6	0.0947	--	--
Cu_2O	607	21.4	0.369	105	--
CuO	105	25.2	--	12.3	1.05
CuTCPP	140	42.1	0.662	--	--

References

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